

**THE THERMAL DECOMPOSITION REACTIONS
OF SOME LANTHANIDE AND
URANIUM(IV) NITRATES**

by

CHRISTIENA ADRIANA STRYDOM

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PRETORIA

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To Hendrik and my Parents ...

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ABSTRACT

THE THERMAL DECOMPOSITION REACTIONS OF SOME LANTHANIDE AND URANIUM(IV) NITRATES

by

Christiena Adriana Strydom

Promoter: Prof. C.P.J. van Vuuren

Department of Chemistry, University of Pretoria

Degree: Ph.D

The thermal decomposition of some lanthanide nitrates was studied. Moving down the lanthanide series, an increasing number of reversible processes, occurring during the decomposition reactions, was observed. These temperature-dependent reversible processes could be phase transitions (only in the solid state) or minor structural changes in the lanthanide nitrates. All reversible processes are endothermic, except for the process at 349 °C for $\text{Ho}(\text{NO}_3)_3$. The reversible processes cause changes in the kinetics of the decomposition reactions.

The dehydrated lanthanide nitrates decompose to oxynitrates, except $\text{Ce}(\text{NO}_3)_3$, which decomposes directly to the oxide. The temperatures at which decomposition starts, and the reaction enthalpy values at a pressure of 5×10^3 kPa, were used as relative measures of the thermal stability. An increasing instability was found on moving down the lanthanide series. The enthalpy at atmospheric pressure showed an increase in value on moving down the lanthanide series, due to the increasing number of reversible processes occurring during the decomposition reactions. The pressure of $5 \times$

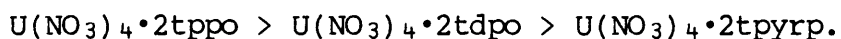
x

10^3 kPa seems to inhibit the reversible endothermic processes. The relationship between increasing ionic radii and reaction enthalpy at 5×10^3 kPa, seems to be of an exponential order.

The comparison of the experimental data to the nineteen different kinetic models, seems to have only empirical importance. This could be due to the sample preparation.

Decreasing ionic radii in the lanthanide series give rise to greater polarisation of the nitrate ions and therefore greater instability of the lanthanide nitrate.

The solid state chemistry of $U(NO_3)_4 \cdot 2L$ ($L = \text{tdpo}$, tppo and tpyrp) has been investigated. Taking into consideration the decomposition onset temperatures, the enthalpy values, the bond lengths in the molecules and the XPS data, an order of stability was established;



From crystal and molecular structure data, it seems that tppo is the strongest electron donor ligand, followed by tdpo and then tpyrp . The stronger the electron donor properties of the ligand, the more stable is the uranium(IV) nitrate complex. Due to the stabilizing effect of the stronger donor ligand, the $U-O(NO_2)$ bonds are also stabilized and strengthened.

Activation energy and pre-exponential factor values determined from the nineteen kinetic models for solid state reactions do not seem to be comparable to one another. The values seem to be associated with a definite process, e.g. three-dimensional diffusion, in the solid state.

OPSOMMING**"THE THERMAL DECOMPOSITION REACTIONS OF SOME LANTHANIDE AND URANIUM(IV) NITRATES"**

deur

Christiena Adriana Strydom

Promotor: Prof. C.P.J. van Vuuren

Departement Chemie, Universiteit van Pretoria

Graad: Ph.D.

Die termiese ontbinding van verskeie lantaniednitrate is ondersoek. Gedurende die ontbindingsreaksies vind 'n toenemende aantal omkeerbare prosesse plaas, soos wat met die lantaniedreeks afbeweeg word. Hierdie temperatuur-afhanklike omkeerbare prosesse kan faseveranderinge (slegs in die vaste stof fase) of klein struktuurveranderinge van die lantaniednitrate wees. Al die omkeerbare prosesse is endotermies, behalwe die proses by 349°C vir $\text{Ho}(\text{NO}_3)_3$. Die omkeerbare prosesse veroorsaak veranderinge in die kinetiese meganismes van die ontbindingsreaksies.

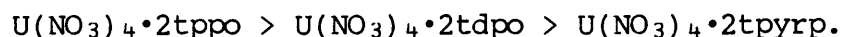
Die gedehidreerde lantaniednitrate ontbind na oksi-nitraatverbindinge, behalwe $\text{Ce}(\text{NO}_3)_3$, wat direk na die oksied ontbind. Die temperatuur waar ontbinding begin, en die reaksie-entalpiewaardes by 'n druk van 5×10^3 kPa is as relatiewe maatstawwe van die termiese stabiliteit gebruik. Soos wat deur die lantaniedreeks beweeg word, is 'n toenemende onstabiliteit opgemerk. Die entalpie by atmosferiese druk toon 'n toename as deur die reeks beweeg word, as gevolg van die toenemende aantal omkeerbare prosesse wat gedurende die ontbinding plaasvind. By 'n druk van 5×10^3 kPa blyk dit dat die

omkeerbare endotermiese prosesse nie plaasvind nie. Die verband tussen toenemende ioonstraal en reaksie-entalpie by 5×10^3 kPa blyk van 'n eksponensiële orde te wees.

Die verband tussen die eksperimentele data en die negentien verskillende kinetiese modelle blyk slegs van empiriese waarde te wees. Dit kan te wyte wees aan die monstervoorbereiding.

Afnemende ioonstrale in die lantaniedreeks veroorsaak groter polarisasie van die nitraatone en daardeur groter onstabiliteit van die lantaniednitrate.

Die vaste toestandchemie van $U(NO_3)_4 \cdot 2L$ ($L = \text{tdpo}$, tppo en tpyrp) is ondersoek. As die ontbindingsaanvangstemperature, die entalpie-waardes, die bindingslengtes in die molekules en die XPS-data in ag geneem word, kan 'n stabiliteitsvolgorde afgelei word;



Uit kristal- en molekulêre struktuurdata blyk dit dat tppo die sterkste elektronskenkerligand is, gevolg deur tdpo en dan tpyrp . Hoe sterker die elektronskenkereienskap van die ligand, hoe stabiel is die uraan(IV) nitraatkompleks. As gevolg van die stabiliserende uitwerking van die sterker elektronskenkerligand, is die $U-O(NO_2)$ bindings self ook meer gestabiliseer en versterk.

Aktiveringsenergie en pre-eksponensiële faktor waardes, bereken met behulp van die negentien kinetiese modelle vir vaste toestandreaksies, blyk nie met mekaar vergelykbaar te wees nie. Die waardes blyk met 'n definitiewe proses, soos driedimensionele diffusie, in die vaste toestand, geassosieer te wees.

ABBREVIATIONS

tdpo : tris(dimethyl amino) phosphine oxide

tppo : triphenyl phosphine oxide

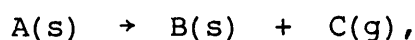
tpyrp : tripyrrolidino phosphine oxide

CHAPTER 1

INTRODUCTION

1.1 Thermal decomposition reactions of solids

The term "thermal decomposition of solids" signifies the breakdown of one or more constituents of the reactants into simpler atomic groupings upon heating. The thermal decomposition of solids involves the destruction of the stabilizing forces of the crystal lattice of a solid reactant, resulting both in chemical reactions and physical reorganizations. In recent years, a more restricted meaning of the definition [1] has become acceptable and is specifically applied to those processes in which bond redistribution yields a solid residue of a different chemical composition from that of the reactant. The thermal decomposition of a solid is therefore represented by



where A is the reactant and B and C are the product or products in either a solid state or a gaseous state [1]. Reactions of this nature are most easily studied quantitatively using the techniques of thermal analysis, i.e., thermogravimetry (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC).

An internationally accepted definition of thermogravimetry (TG) is the technique whereby the weight of a substance, in an environment heated or cooled at a controlled rate, is recorded as a function of time or temperature [2]. The

development and ready availability of reliable and accurate electronic microbalances in thermogravimetry have led to their wide application in kinetic studies of the decomposition of solids [3].

Two alternative methods are used in kinetic investigations of the thermal decomposition of solids: in one, yield-time measurements are made while the reactant is maintained at a known constant temperature [4] while, in the second method, the sample is subjected to a controlled rising temperature [5]. Measurements using both techniques have been widely and variously exploited in the determination of the thermal stability and kinetic characteristics of substances.

In the TG curve of a single non-isothermal reaction, there are two characteristic temperatures; the initial temperature T_i and the final temperature T_f . T_i is defined as "the lowest temperature where the cumulative weight change reaches a magnitude that a particular thermobalance can detect", and T_f "the temperature where the cumulative weight change first reaches its maximum value" [1]. Although T_i has no fundamental significance, it can still be a useful characteristic of a TG curve. It can be used as a relative measure of the thermal stability of a substance, provided that the conditions are well-specified and constant throughout the investigation. Factors that may influence the T_i value are the heating rate, sample mass, pre-treatment of the sample, type of atmosphere used in the thermogravimetric analyser (e.g. N_2 , Ar) and the flow rate of the gases employed in a dynamic atmosphere.

The thermal decomposition of a solid is sometimes associated with physical transformations, such as melting, sublimation and recrystallization. The recrystallization of a solid may result in the production of a higher temperature lattice modification, which permits increased freedom of motion of one or more lattice constituents. Recrystallization may also result in the elimination of regions of local lattice distortion, e.g. dislocations, grain boundaries, etc., without change in chemical composition or, indeed, lattice configuration [6].

The reactivity and chemical properties of solids are strongly influenced by the relative immobility of the constituent ions or molecules in the lattice of the reactant phase. The reactivity of identical chemical groupings in a solid reactant may vary with their position in the solid, as the structure may contain imperfections. In regions of local distortion, the forces of lattice stabilization may be relatively diminished, with a consequent increase in the probability of reaction. This contrasts with the homogeneous behaviour of similar groups in the liquid or gaseous phase. In rate processes of solids it is often observed that there are localized regions or sites of preferred onset of reaction. Such initiation usually occurs at a surface, leading to the development of a zone of preferred chemical transformation, which thereafter progressively advances into adjoining volumes of unreacted material. This restricted zone of the solid is called the reaction interface [1].

The occurrence of reaction is usually regarded as being exclusively restricted to the reactant-product interface, at which local conditions markedly enhance the ease of the chemical transformation. The kinetic characteristics of the overall process are determined by the velocity of the advance of this interface into unchanged reactant and the variation of its effective area with time [1].

The process by which the reaction interface is initially established is nucleation. The interface is established at a limited number of points in the reactant, usually at a surface and possibly at an imperfection [7]. The initially generated germ nucleus develops into a growth nucleus, which increases in size through the advance of the reactant-product interface into the bulk of the solid.

The following general kinetic tenets have been used as a widely-accepted basis for the interpretation of the kinetic behaviour of the decomposition reactions of solids [1]:

- (i) The rate of reaction of a solid is proportional to the aggregate effective area of the reactant-product interface.
- (ii) The rate of interface advance is constant through an isotropic reactant under isothermal conditions.
- (iii) The temperature dependence of the rate coefficient obeys the Arrhenius equation.

These tenets are applicable only where the reactant undergoes no melting. If no melting occurs, the shape of the fraction decomposed (α) against time (t) curve for an isothermal reaction can be related to the geometry of formation and advance of the reaction interface [1].

1.2 Kinetic rate laws for the decomposition of solids

The number of potential nucleus-forming sites (N_0) and the number of molecules having an energy at least equal to the activation energy for nucleus formation, determines the rate at which nuclei are formed. The rate of nucleation can be determined by using one of the following equations [33,36]:

- A. $\frac{dN}{dt} = k_1 N_0 e^{-k_1 t}$;
- B. $\frac{dN}{dt} = k_1 N_0$;
- C. $N = N_0$ and
- D. $\frac{dN}{dt} = D \beta t^{\beta-1}$.

N represents the number of nuclei at time t . Equation A is called the exponential law and it results from a process of nucleation involving a single step. Equation B represents a linear law of nucleation and equation C, an instantaneous nucleation process. The power law (equation D) results from a process where several molecules are involved in the decomposition reaction. β can have the value 2 or 3. If successive decomposition of two molecules occurs, or one active intermediate forms a bimolecular combination with one of a constant number of sites, β assumes the value 2. $\beta = 3$ when three molecules are involved or when the decomposition occurs

via the bimolecular combination of two active intermediates [33,36].

The relationships between α (fraction decomposed) and t (time) are derived from the four equations that represent the rate of nucleation. Different postulates are proposed for the rate of growth of the nuclei [33]. The laws describing the decomposition rate in decomposition reactions are subdivided into three groups depending on the location of the maximum rate of decomposition, $(\frac{d\alpha}{dt})_{\max}$ [33]:

- (i) α against t relationships obeyed up to $(\frac{d\alpha}{dt})_{\max}$, and concerned with nuclei growth;
- (ii) α against t relationships obeyed on both sides of $(\frac{d\alpha}{dt})_{\max}$ and thus concerned with both nuclei growth and interference; and
- (iii) α against t relationships obeyed beyond $(\frac{d\alpha}{dt})_{\max}$, i.e. relationships concerned with either nuclei interference or a decreasing reaction interface.

The power law is represented by

$$\alpha = kt^n$$

and describes reactions up to the point where $\frac{d\alpha}{dt}$ is a maximum [33]. Mampel calculated a value of 4 for n in the initial period of decomposition in which the possibility of overlapping of the decomposition zones is taken into account [55]. The integer, n , is defined as $n = \beta + \lambda$, where β is the stage in nucleation, i.e. 2 or 3. According to the dimensions in which growth occurs, λ equals 1, 2 or 3.

The exponential law

$$\alpha = ke^{k't}$$

is also obeyed up to $(\frac{d\alpha}{dt})_{\max}$ [56]. The possibility of branching nuclei with no overlapping is taken into account. The appearance of fresh nuclei can be at either a constant or exponential rate, or it seems to be unimportant. The growth in length of the nuclei is assumed to be at a constant rate.

The decomposition mechanism describing the appearance of branching nuclei with interference between the nuclei during growth, was derived by Prout and Tompkins and is represented in two forms [57]:

$$(i) \quad \log \frac{\alpha}{1-\alpha} = kt + C; \quad \text{and}$$

$$(ii) \quad \log \frac{\alpha}{1-\alpha} = k \log t + C.$$

In this mechanism, the formation of nuclei appears to be unimportant, i.e. not rate-determining. If a uniform rate of branching occurs, equation (i) is valid. Equation (ii) is derived for a variation in the rate of branching with time.

Erofe'ev proposed equations describing isothermal solid decomposition with the general form

$$1-\alpha = e^{-kt^n} \quad [58].$$

For two-dimensional growth $n = 2$, for three-dimensional growth $n = 3$ and $n = 4$ can be interpreted as a two-stage nucleation. In the case of overlapping of growth nuclei with three-dimensional growth and initial random nucleation, Avrami deduced a similar equation with $n = 3$ [59].

A process for which the rate of decomposition continually decreases is described by Mampel's intermediate law with specific form

$$1-(1-\alpha)^{\frac{1}{3}} = \frac{v}{r} t,$$

where v is the velocity of interface advance and r the radius of the particles being decomposed [33]. A more general statement of this law is

$$1-(1-\alpha)^{\frac{1}{3}} = kt + b,$$

where $k = \frac{v}{r}$. This equation, representing the contracting sphere model, is deduced for a process of surface nucleation, growth over the surface and then the advance of the interface towards the centre of supposed spherical particles [60,61].

The above-mentioned equation becomes

$$1-(1-\alpha)^{\frac{1}{2}} = kt + b$$

when applied to two-dimensional growth and is called the contracting area model [33].

The first order decay law

$$1-\alpha = e^{-kt}$$

is a special case of the Erofe'ev equation with $n = 1$ [33]. This equation is valid at the end of the decomposition reaction and in the point $(\frac{d\alpha}{dt})_{\max}$. This law holds for a decomposition process dealing with relatively small particles [33].

In diffusion-controlled reactions a phase boundary is present and the rate of diffusion through the reacting material also influences the overall decomposition rate. The one-dimensio-

nal diffusion process or parabolic law is represented by

$$\alpha^2 = \frac{k}{x^2} t,$$

where $2x$ is the thickness of the reacting layer. This law is more commonly given as

$$\alpha = k_1 t^{1/2} [33].$$

The decomposition rate of a two-dimensional diffusion-controlled reaction is given by

$$(1-\alpha)\ln(1-\alpha) + \alpha = \frac{k}{r^2} t [62].$$

r represents the radius of the cylinder of reactant material formed as result of the two-dimensional diffusion process.

The Jander equation,

$$(1-(1-\alpha)^{1/3})^2 = \frac{k}{r^2} t,$$

is a contracting cube equation of a three-dimensional diffusion process and is a representation of the reaction of a particle as a sphere [63]. A more detailed treatment by Ginstling and Brounshtein takes the form

$$\left(1 - \frac{2}{3}\alpha\right) - (1-\alpha)^{2/3} = \frac{k}{r^2} t [64].$$

1.3 Kinetic parameters

By analogy with the application of the Arrhenius equation,

$$k = A \exp(-E/RT),$$

to homogeneous reactions in the liquid and gas phases, the coefficients A and E are referred to as the reaction frequency factor, and the activation energy of a reaction, respectively.

As there is no discrete activated state in the solid state,

activation energy values need to be evaluated critically before conclusions regarding the stability of the solid reactants can be drawn from them [8]. A homogeneously distributed activated state cannot be described in solid state reactions, as the solid state reactions develop through the nucleation effect, described earlier. The constant interactions through vibrations provide a means of distributing any increasing energy of an atom to its neighbours. The energy in any small region will thus have a narrow distribution. The lack of a statistically defined distribution rules out the use of the Arrhenius parameters as in liquid and gaseous phase reactions.

The activation energy value (E) is usually expressed as an energy quantity per mole ($\text{kJ}\cdot\text{mol}^{-1}$), since the measured slope of the Arrhenius plot ($\ln k$ vs T^{-1}) is divided by the gas constant, R ($R = 8,314 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$). There is a difficulty in assigning a meaning to the term "mole" in solid state reactions. If, however, $\Delta H \approx E$ and an independently measured ΔH value is available, and the ΔH value refers to the enthalpy of the reaction for a mole of reactant, then an estimation of the "mole of activated complex" can be made. The Arrhenius plots, however, can be used as indications of the relationship between the rate constants and the temperature values.

For the initial stages of the reaction ($\alpha < 0,1$), the relationship between the rate constants, k , and reaction time, t , can also be given as;

$$\frac{d\alpha}{dt} = kt,$$

with α the fraction decomposed [1]. Using these k values at various temperatures and applying them to the Arrhenius equation, an activation energy value for the nucleation process of a reaction can be obtained.

1.4 X-ray Photoelectron Spectroscopy

XPS, also known as ESCA (electron spectroscopy for chemical analysis), is based on the photoelectric effect, in which photons incident on a specimen are absorbed and electrons are emitted [20]. The binding energy of an electron relative to the vacuum level is the energy required to remove the electron to infinity with zero kinetic energy. The measured kinetic energy of the emitted electron is thus equal to the X-ray photon energy minus the binding energy of the state from which the electron was emitted. Measurement of the kinetic energy of the emitted electrons will thus, in principle, directly yield the binding energies of the occupied states. In practice, binding energies in XPS are measured relative to the Fermi level, rather than the vacuum level. In this case, the kinetic energy of the emitted electron is equal to the X-ray photon energy minus the sum of the binding energy relative to the Fermi level and the work function of the spectrometer.

The binding energy relative to the Fermi energy is given by

$$E_{B,F} = h\nu - E_k - \phi,$$

with ϕ the work function, E_k the kinetic energy of the photoelectron ejected from its energy level, and $h\nu$ the X-ray energy [53].

Each element has a set of energy levels (corresponding to atomic and molecular orbitals) with binding energies characteristic of that element. In a photoelectron intensity vs. binding energy plot, a set of peaks will be observed which corresponds to the energy levels of each element in the specimen being irradiated. The binding energy is actually a measure of the potential around the atoms of interest. The same atom in different chemical environments will have a different potential depending on the valence charge distribution. Binding to more electronegative atoms will result in charge transfer to the more electronegative atoms from the atom of interest, decreasing the valence charge density and thus increasing the binding energy. Differences in binding energies which are due to differences in the chemical environment are termed chemical shifts. Changes in the valence charge distribution can also arise from structural differences, which may result in observable binding energy shifts [50,51]. Chemical shift varies with bonding to more electronegative atoms or groups of atoms, even though the formal oxidation state may not change [52].

Several factors can influence the binding energy value. The observed binding energy is reduced relative to the actual binding energy by the recoil energy, which depends on the ratio of the electron mass to the mass of the ion left behind. It is expected to be a negligibly small effect in solids with large nuclear masses [53]. A more important effect is final state relaxation. When a photoelectron is emitted from an inner shell, the outer shells react to the

change in potential by relaxing toward the positively charged hole which is created. The lowering of the final state energy in this way occurs on a time scale ($\sim 10^{-15}$ s) comparable to that of the photoemission, and results in a transfer of additional kinetic energy to the photoelectron, and thus an apparent lowering of the binding energy [53]. It is assumed, however, that final state relaxation energies do not contribute to observed chemical shifts, though they certainly affect the absolute binding energies [53].

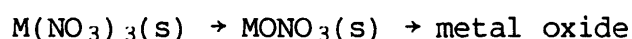
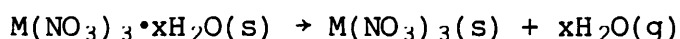
As already mentioned, the binding energy is a measure of the potential around the atom of interest. The valence electrons can be approximated as a charged spherical shell, resulting in a constant potential inside. A change in the valence charge will cause a change in the binding energy which is the same for all core electrons. A change in the chemical environment will result in a redistribution of the valence electronic charge, changing the potential and thus the binding energy. It has been verified experimentally that the various core levels in a given atom will exhibit the same chemical shift as a result of changes in the chemical environment [54].

A change in the potential due to valence charge redistribution can occur as a result of a change in the charge of the valence shell, or a change in the effective radius of the valence shell. That is, charge transfer can also accompany structural changes [53].

1.5 Thermal decomposition of lanthanide nitrates

The chemistry of the lanthanides is predominantly ionic and is determined primarily by the size of the Ln^{3+} ion [9]. The lanthanide contraction may contribute to the stability of the lanthanide nitrates, by destabilization of the NO_3^- groups. On moving down the lanthanide nitrate series, the charge density on the lanthanide ions increases, due to the lanthanide contraction, thus more strongly attracting the electrons in the nitrate groups. This fact may increase the instability of the NO_3^- groups and therefore the groups may be more easily decomposable.

Wendlandt [10] has shown that the rare earth nitrates, with the exception of cerium and samarium, decompose according to the general reaction



Anhydrous cerium nitrate decomposes directly to yield CeO_2 . Patil and co-workers [11] observed that for the hydrated rare earth nitrates the formation of the anhydrous nitrate was a definite stage in the thermal decomposition reactions.

The thermal decomposition of the lanthanide nitrates has been investigated to some extent [11,12,13]. Values for apparent activation energies for the decomposition of $\text{Nd}(\text{NO}_3)_3$, $\text{Dy}(\text{NO}_3)_3$ and $\text{Yb}(\text{NO}_3)_3$ were calculated as $33 \text{ kJ} \cdot \text{mol}^{-1}$, $23 \text{ kJ} \cdot \text{mol}^{-1}$ and $46 \text{ kJ} \cdot \text{mol}^{-1}$ respectively [11]. These values were calculated from the rate constants measured at only two

temperatures. No other kinetic results of the thermal decomposition of the lanthanide nitrates were found in the literature.

1.6 Thermal decomposition of the actinide nitrates

Nitrate complexes of uranium(IV) were only recently prepared and characterized [14], the main reason for this being the instability of tetranitrate uranium(IV). In his book Chernyaev [15] discussed the thermal decomposition of various uranium(IV) compounds. The discussions are however qualitative, concerning the characterization of the intermediates. The compound $\text{U}(\text{NO}_3)_4$ decomposes spontaneously, yielding the uranyl compound $\text{UO}_2(\text{NO}_3)_2$. The complex compounds of uranium(IV) are much more stable, e.g. $\text{Cs}_2\text{U}(\text{NO}_3)_6$ and $(\text{Et}_4\text{N})_2\text{U}(\text{NO}_3)_6$ [16].

Tetranitrate uranium(IV) can be stabilized and isolated from non-aqueous organic solvents as the neutral complex $\text{U}(\text{NO}_3)_4 \cdot 2\text{L}$, where L is a neutral donor ligand, such as *tdpo* (tris(dimethylamino)phosphine oxide), *tppo* (triphenyl phosphine oxide) and *tpyrp* (trispyrrolidino phosphine oxide) [17].

Kinetic information on the thermal decomposition of $\text{U}(\text{NO}_3)_4 \cdot 2\text{tpyrp}$ was found in the literature [19]. The thermal stability seems to be different for each complex isolated. Various factors, physical (crystal energy), as well as chemical, are responsible for this observed tendency [1]. The

donor properties (Lewis basicity) of the ligand has to be one of the more important chemical factors in determining the stability of the complexes. Physical factors such as imperfections in the crystal lattice and phase transitions are of importance during the decomposition reactions, especially at higher temperatures [1].

Crystal structure determinations of uranium nitrate complexes were mainly concerned with the structures of uranyl nitrate compounds [18]. No structure determination of any uranium(IV) nitrate complex could be found in the literature, which may be due to the instability of the uranium(IV) nitrates in X-rays. It was, however, necessary to obtain structural data for some uranium nitrate complexes in order to explain their thermal behaviour.

Studies of the X-ray photo-electron spectra (XPS) of uranium compounds recently became a useful tool in obtaining information about their valence electronic structure [21] and their binding energies. No XPS spectra of uranium nitrate complexes could be found in the literature.

1.7 Aims of this study

The aims of this study were twofold: Firstly; to obtain a critical evaluation of the kinetic behaviour of the dehydrated lanthanide nitrates. As starting materials $\text{La}(\text{NO}_3)_3$, $\text{Ce}(\text{NO}_3)_3$, $\text{Pr}(\text{NO}_3)_3$, $\text{Nd}(\text{NO}_3)_3$, $\text{Eu}(\text{NO}_3)_3$, $\text{Gd}(\text{NO}_3)_3$, $\text{Ho}(\text{NO}_3)_3$ and $\text{Er}(\text{NO}_3)_3$ were used. These nitrates, with the exception

of $\text{Ce}(\text{NO}_3)_3$, decompose to yield the oxynitrate, i.e. $\text{LnO}(\text{NO}_3)$, as a stable intermediate [10]. Overlapping chemical reactions, which may give rise to a misinterpretation of the kinetics [22] are therefore eliminated.

The second aim of this study concerns the thermal stability of some lanthanide and actinide nitrates. The aim is to link the observed stabilities to physical and chemical factors such as the ionic sizes of the metal ions, Lewis basicity of neutral donor ligands and binding energy values in the compounds.

To achieve these aims, the techniques of thermal analysis (TG, DTA and DSC) were used extensively. In addition, crystal structure determinations, crystal energy approximations and X-ray photoelectron spectroscopy measurements were used.

CHAPTER 2

EXPERIMENTAL

The thermal characteristics of the solid state reactions of some lanthanide nitrates and some uranium(IV) nitrate complexes were investigated by means of thermogravimetry (TG), differential scanning calorimetry (DSC), pressure DSC, X-ray powder diffraction and isothermal thermogravimetric techniques and X-ray photoelectron spectroscopy.

2.1 Thermal studies

2.1.1 Thermogravimetric analysis

A Stanton Redcroft STA 780 simultaneous thermal analyser was used to collect thermogravimetric data. The STA consists of an electronic microbalance connected to a microprocessor-based control unit and a Pt-Pt/13% Rh thermocouple system. Experiments were carried out in a nitrogen atmosphere, where the nitrogen passed through the system at a flow rate of $40 \text{ cm}^3 \cdot \text{min}^{-1}$. Platinum sample pans (volume 135 mm^3 , diameter 6 mm) were used as sample holders and reference containers. Temperature calibration of the equipment was achieved by using the ICTA (International Confederation for Thermal Analysis) recommended DTA temperature standards, GM 758, GM 759 and GM 760. Self-heating of the samples was reduced to a minimum by using small sample masses (8–16 mg).

2.1.1.1 Dynamic studies

In order to compare the thermal stability of the lanthanide nitrates, the conditions for the determination of the latter were kept constant. The heating rate was kept constant at $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$. Only by keeping this heating rate constant, was it possible to compare the different temperatures at which decomposition started, as relative values. A change in the heating rate can lead to highly different temperature values for the start of decomposition [23]. Along with the TG curves, the DTG and DSC curves recorded together with the TG curves, were used to determine the decomposition onset temperatures.

2.1.1.2 Isothermal studies

Isothermal studies were carried out in the 70°C to 500°C temperature range, depending on the thermal stability of each nitrate, as will be discussed later. Data were collected at a variety of temperatures and repeated for reproducibility.

2.1.2 DSC and pressure DSC studies

A Du Pont 910 differential scanning calorimeter and high pressure cell, controlled by a 1090 Thermal Analyser, was used for the DSC studies. Peak integration and subsequent enthalpy calculations were performed by using the Du Pont Partial Area Integration data analysis computer program, version 1.0. The melting of pure indium metal

($\Delta H = 28,4 \text{ J} \cdot \text{g}^{-1}$) and pure zinc metal ($\Delta H = 102,0 \text{ J} \cdot \text{g}^{-1}$) was used as a reference.

Samples of 10 mg to 15 mg were heated and cooled in platinum containers. Nitrogen (flowrate = $\pm 40 \text{ cm}^3 \cdot \text{min}^{-1}$), as well as pressurised nitrogen ($5 \times 10^3 \text{ kPa}$), was used as a reaction atmosphere.

2.2 Sample preparation

The method of preparation of the solid reactant, and the pre-treatment it receives prior to reaction, may profoundly influence its reactivity [1]. Nucleation is often controlled by the area and the imperfection of available surfaces, as well as the sizes and shapes of the constituent particles of a powder. The latter exerts an obvious control over the rates and geometry of interface development [1]. For these reasons the crystals were ground to a fine powder before use.

2.2.1 Lanthanide nitrates

The different hydrated lanthanide nitrates were obtained from Fluka. The anhydrous lanthanide nitrates were prepared by heating the hydrated nitrates at a rate of $5 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ to maximum temperatures. Table 2.1 refers to the different nitrates and the temperatures at which constant mass in the thermobalance was attained.

Table 2.1 Formation temperatures for dehydrated lanthanide nitrates

Lanthanide nitrate	Temperature(°C)
La(NO ₃) ₃	300
Ce(NO ₃) ₃	210
Pr(NO ₃) ₃	350
Nd(NO ₃) ₃	360
Eu(NO ₃) ₃	300
Gd(NO ₃) ₃	230
Ho(NO ₃) ₃	220
Er(NO ₃) ₃	210

2.2.2 Uranium(IV) nitrate complexes

2.2.2.1 U(NO₃)₄•2tdpo

A solution of 0,41 g of tris(dimethylamino)phosphine oxide in 5 cm³ acetone was added to a solution of 1,0 g Cs₂U(NO₃)₆ in 5 cm³ acetone. The mixture was cooled in ice, stirred for 10 minutes and filtered. Petroleum ether (5 cm³) was added to the filtrate and the filtrate was left to crystallize at 0 °C. The crystals were dried in vacuum. The crystals were used within three days of preparation. Uranium(IV) analysis yields 28,3% (calculated value: 28,20%).

2.2.2.2 $\text{U}(\text{NO}_3)_4 \cdot 2\text{tppo}$

A solution of 1,0 g of triphenyl phosphine oxide in 10 cm^3 CH_2Cl_2 was added to 1,70 g $\text{Cs}_2\text{U}(\text{NO}_3)_6$ in 5 cm^3 acetone. The mixture was cooled in ice, stirred for 10 minutes and filtered. Acetonitrile (7 cm^3) and petroleum ether (10 cm^3) were added to the filtrate and the filtrate was left to crystallize at 0°C . The crystals were filtered, washed with petroleum ether and dried in vacuum. Uranium(IV) analysis yields 22,6% (calculated value: 22,80%).

2.2.2.3 $\text{U}(\text{NO}_3)_4 \cdot 2\text{tpyrp}$

This complex was prepared as described in the literature [19]. A solution of 1,0 g of trispyrrolidino phosphine oxide in 10 cm^3 CH_2Cl_2 was added to a solution of 1,70 g $\text{Cs}_2\text{U}(\text{NO}_3)_6$ in 3 cm^3 acetone. The mixture was cooled in ice, stirred for 5 minutes and filtered. Seven cm^3 acetonitrile was added to the filtrate and this was left to crystallize at 0°C . The crystals were filtered, washed with petroleum ether and dried in vacuum. Uranium(IV) analysis yielded 23,8% (calculated value: 23,79%).

2.2.2.4 $\text{Cs}_2\text{U}(\text{NO}_3)_6$

0,75 g $\text{Na}_2\text{S}_2\text{O}_4$ was added to a solution of 1 g $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in 50 cm^3 of a $2 \text{ mol} \cdot \text{dm}^{-3}$ HNO_3 solution.

The mixture was stirred for 18 hours and then filtered. The filtrate and a second solution of 1,553 g CsNO_3 in 50 cm^3 $\text{HNO}_3(\text{conc.})$ were cooled in ice. The HNO_3 was treated with sulfamic acid prior to use. The Cesium-nitrate solution was added to the filtrate and stirred for 15 minutes. 300 cm^3 $\text{HNO}_3(\text{conc.})$ was added to the mixture and it was again stirred for 15 minutes. The crystals were filtered, washed with acetone and petroleum ether, and dried in vacuum.

2.2.2.5 $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{tdpo}$

A solution of 0,5 g tdpo in approximately 10 cm^3 acetone was added to a solution of 1,0 g $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in approximately 20 cm^3 acetone. The mixture was cooled in ice, stirred for 10 minutes and left to crystallize at 0 °C. The crystals were filtered, washed with ethyl acetate and dried in vacuum.

2.2.2.6 $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{tppo}$

A solution of 0,6 g tppo in approximately 10 cm^3 CH_2Cl_2 was added to a solution of 0,5 g $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in approximately 20 cm^3 acetone. The mixture was cooled in ice, stirred for 10 minutes and left to crystallize at 0 °C. The crystals were filtered, washed with petroleum ether and dried in vacuum.

2.2.2.7 $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{tpyrp}$

A solution of 0,5 g tpyrp in approximately 10 cm³ CH₂Cl₂ was added to a solution of 1 g UO₂(NO₃)₂·6H₂O in approximately 20 cm³ acetone. The mixture was cooled in ice, stirred for 10 minutes and left to crystallize at 0 °C. The crystals were filtered, washed with petroleum ether and dried in vacuum.

2.2.2.8 Uranium(IV) analysis

Uranium was precipitated with an aqueous solution of ammonia. The hydroxide precipitate was dissolved in diluted hydrochloric acid and the solution was titrated to uranium(VI) with dichromate [65]. The purity of the compounds was confirmed by mass losses observed on the thermobalance.

2.3 X-ray powder diffraction

X-ray and electron diffraction measurements have been mostly used to characterize the phases present in any reactant mixture, and provide a means of identifying solid reactants, intermediates and products.

X-ray analysis was carried out on the uranium(IV) nitrate complexes. The X-ray powder diffraction patterns were obtained by using a Seifert MZ IV diffractometer with CuK_α radiation at room temperature and for U(NO₃)₄·2tdpo also at 89 °C.

2.4 X-ray Photoelectron Spectroscopy

The XPS measurements were performed on a VG ESCALAB MK II. A hemispherical electron analyser fitted with multiple channel-trons was used for photoelectron detection. The instrument was used in constant analyser energy mode (CAE) with a fixed passed energy of 50 eV. The X-ray source uses a 15 Kev, 300 W electron beam incident on either a Mg or Al anode to produce non-monochromatic K_{α} X-rays. The X-rays illuminate a spot, approximately 1,5 mm in diameter, on the sample. The Mg K_{α} X-rays have an energy of 1253,6 eV and the Al K_{α} X-rays have an energy of 1486,6 eV. The spectrometer is equipped with an Argon ion sputtering gun for sample cleaning. Notwithstanding the fact that the samples were cooled to liquid nitrogen temperature to minimize X-ray radiation heat-induced effects, sample decompositions were observed. As an alternative a 25 W electron beam was used. The Mg K_{α} X-rays source was not turned in, towards the sample, leaving a distance of 25 mm between source and sample. A reduced count rate resulted. At this low radiation, however, data could be acquired for hours, without significant changes in sample composition.

During measurements of complete spectra, the scanned energy was stepped in 0,05 eV increments and data were acquired for 50 ms at each increment. An average of 30 scans was used. Data acquisition was under control of an IBM AT computer. The software includes a curve fitting routine and non-linear background subtraction to aid in the analysis of chemical

shifts of measured peaks. Data were corrected for any charging.

2.5 Molecular structures of uranium complexes

X-ray crystal structure determinations of $\text{U}(\text{NO}_3)_4 \cdot 2\text{L}$ ($\text{L} = \text{tppo}$, tdpo and tpyrp) and $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{L}$ ($\text{L} = \text{tdpo}$ and tppo) were done at the NCNL at the CSIR on an Enraf Nonius CAD4 diffractometer with graphite-monochromated $\text{Mo-K}\alpha$ radiation $\lambda = 0,71069 \text{ \AA}$, ω - 2θ scans. The intensity data were corrected for Loretz-polarization and for absorption [24]. The structures were determined by the conventional Patterson, Fourier and least-squares refinement techniques, using the program SHELX with hydrogen atoms in calculated positions (C-H bond length $1,08 \text{ \AA}$, H-C-H angle $109,4^\circ$) [25]. The non-hydrogen atoms were refined anisotropically. Scattering factors for the neutral atoms were taken from 'International Tables for X-ray Crystallography' (1974).

Crystals were obtained from the slow evaporation of methylene chloride solutions in a petroleum ether atmosphere.

2.6 Data Processing of kinetic studies

The rate equations which have found application in kinetic studies of solid state decomposition reactions are given in table 2.2 [1].

The purpose of the solid state kinetic studies is to obtain

Table 2.2 The kinetic rate laws for solid state reactions

$f(\alpha)$ equation	Rate law
$kt = \alpha$	Power law with $n = 1$
$kt = \alpha^{0,25}$	Power law with $n = 4$
$kt = \alpha^{0,33}$	Power law with $n = 3$
$kt = \alpha^{0,5}$	Power law with $n = 2$
$kt = \alpha^2$	Power law with $n = \frac{1}{2}$
$kt = 1-(1-\alpha)^{0,5}$	Contracting area
$kt = 1-(1-\alpha)^{0,33}$	Contracting volume
$kt = (1-\alpha)\ln(1-\alpha)+\alpha$	Two-dimensional diffusion
$kt = (1-0,67\alpha)-(1-\alpha)^{0,67}$	Three-dimensional diffusion
$kt = (1-(1-\alpha)^{0,33})^2$	Jander
$kt = -\ln(1-\alpha)$	Avrami-Erofe'ev with $n = 1$
$kt = (-\ln(1-\alpha))^{0,67}$	Avrami-Erofe'ev with $n = \frac{3}{2}$
$kt = (-\ln(1-\alpha))^{0,5}$	Avrami-Erofe'ev with $n = 2$
$kt = (-\ln(1-\alpha))^{0,33}$	Avrami-Erofe'ev with $n = 3$
$kt = (-\ln(1-\alpha))^{0,25}$	Avrami-Erofe'ev with $n = 4$
$kt = \ln\left(\frac{\alpha}{1-\alpha}\right)$	Prout-Tompkins
$kt = \frac{1}{1-\alpha} - 1$	Second order
$kt = \ln \alpha$	Exponential law
$kt = \left(\frac{1}{1-\alpha}\right)^{0,5} - 1$	Third order

information concerning the reaction mechanism, through comparison of a series of measured α -time values and the theoretical functions (table 2.2). The $f(\alpha)$ equations have been derived from models based on the geometry of interface initiation and advance and/or diffusion processes occurring in the solid. The problem may be regarded as the identification of the functional relationship between the fraction decomposed (α) and time (t), $f(\alpha)=kt$, where k is the conventional rate coefficient.

The experimental (α , time) values were fitted to these $f(\alpha)=kt$ equations to obtain the equation which provided the most accurate fit to the experimental data. The linearity of the plots of $f(\alpha)$ values against time at a constant temperature was taken as a criterion for identification of the rate equation. A computer program was used to determine the correlation coefficient and slope of the different $f(\alpha)=kt$ equations for each of the sets of experimental data. The correlation coefficient is defined by

$$r = \frac{n \sum (xy) - (\sum x)(\sum y)}{((n \sum x^2 - (\sum x)^2)(n \sum y^2 - (\sum y)^2))^{0.5}}$$

with x the time values, y the α values and n the number of (x,y) values. In addition to the correlation coefficient values visual observations of the plots of the $f(\alpha)$ equations were made.

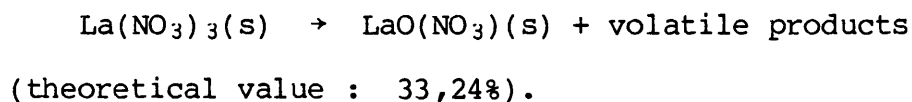
CHAPTER 3

RESULTS OF THE STUDY ON THE THERMAL DECOMPOSITION REACTIONS OF SOME LANTHANIDE NITRATES

3.1 Lanthanum(III) nitrate

The TG curve of the thermal decomposition of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ at a heating rate of $5\text{ }^\circ\text{C} \cdot \text{min}^{-1}$ is shown in figure 3.1. The curve indicates that, using this heating rate, $\text{La}(\text{NO}_3)_3$ starts to decompose to $\text{LaO}(\text{NO}_3)$ at $375\text{ }^\circ\text{C}$.

Using the heating rate of $5\text{ }^\circ\text{C} \cdot \text{min}^{-1}$ the result shows that it is difficult to separate the overlapping decomposition reactions of $\text{La}(\text{NO}_3)_3$ and $\text{LaO}(\text{NO}_3)$ in the temperature range of $410\text{ }^\circ\text{C}$ to $430\text{ }^\circ\text{C}$. To avoid decomposition of the oxynitrate, all the isothermal measurements were done at temperatures below $410\text{ }^\circ\text{C}$. Average mass losses of 32,9% were observed for the reaction,



Isothermal mass loss curves were recorded at temperatures between $360\text{ }^\circ\text{C}$ and $410\text{ }^\circ\text{C}$. Isothermal decomposition curves of $\text{La}(\text{NO}_3)_3$ are given in figure 3.2, at the indicated temperatures. The rate data for $\text{La}(\text{NO}_3)_3$ fitted the contracting area equation, $f(\alpha) = 1 - (1 - \alpha)^{1/2} = kt$, best, as is represented in figure 3.3. The correlation coefficients for all other $f(\alpha)$ functions were lower at all the experimental

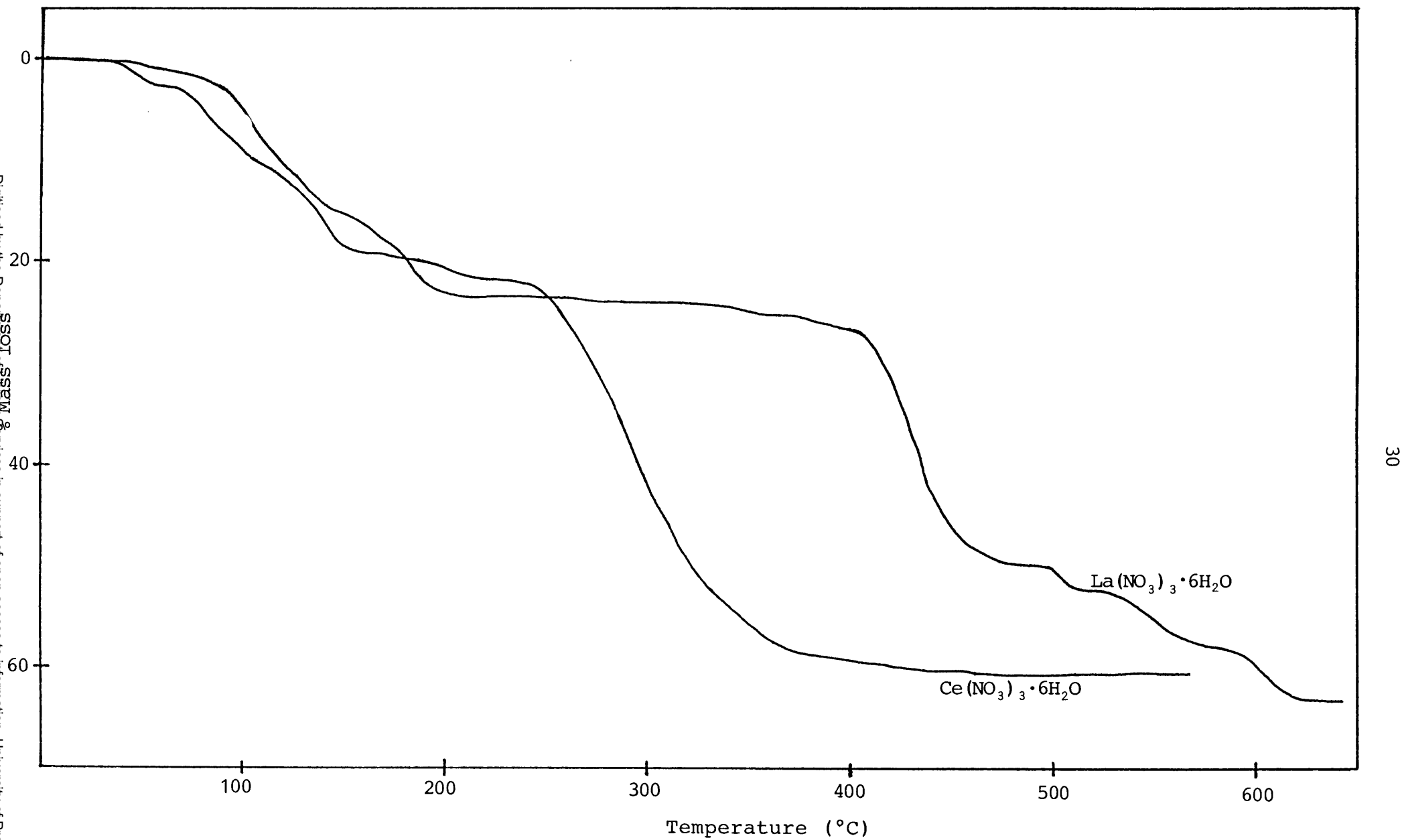


Figure 3.1. TG curves of the thermal decomposition of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$

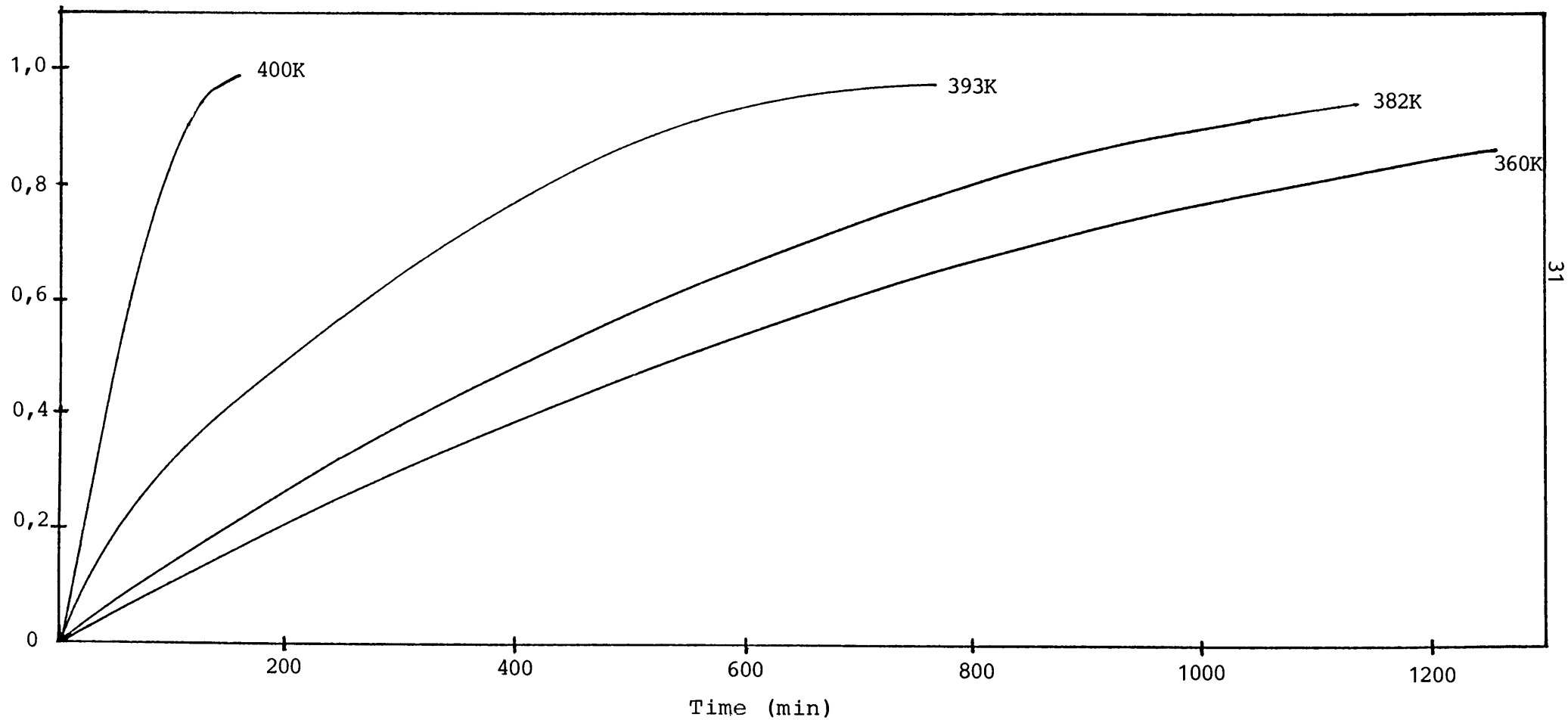


Figure 3.2. Isothermal decomposition curves of $\text{La}(\text{NO}_3)_3$

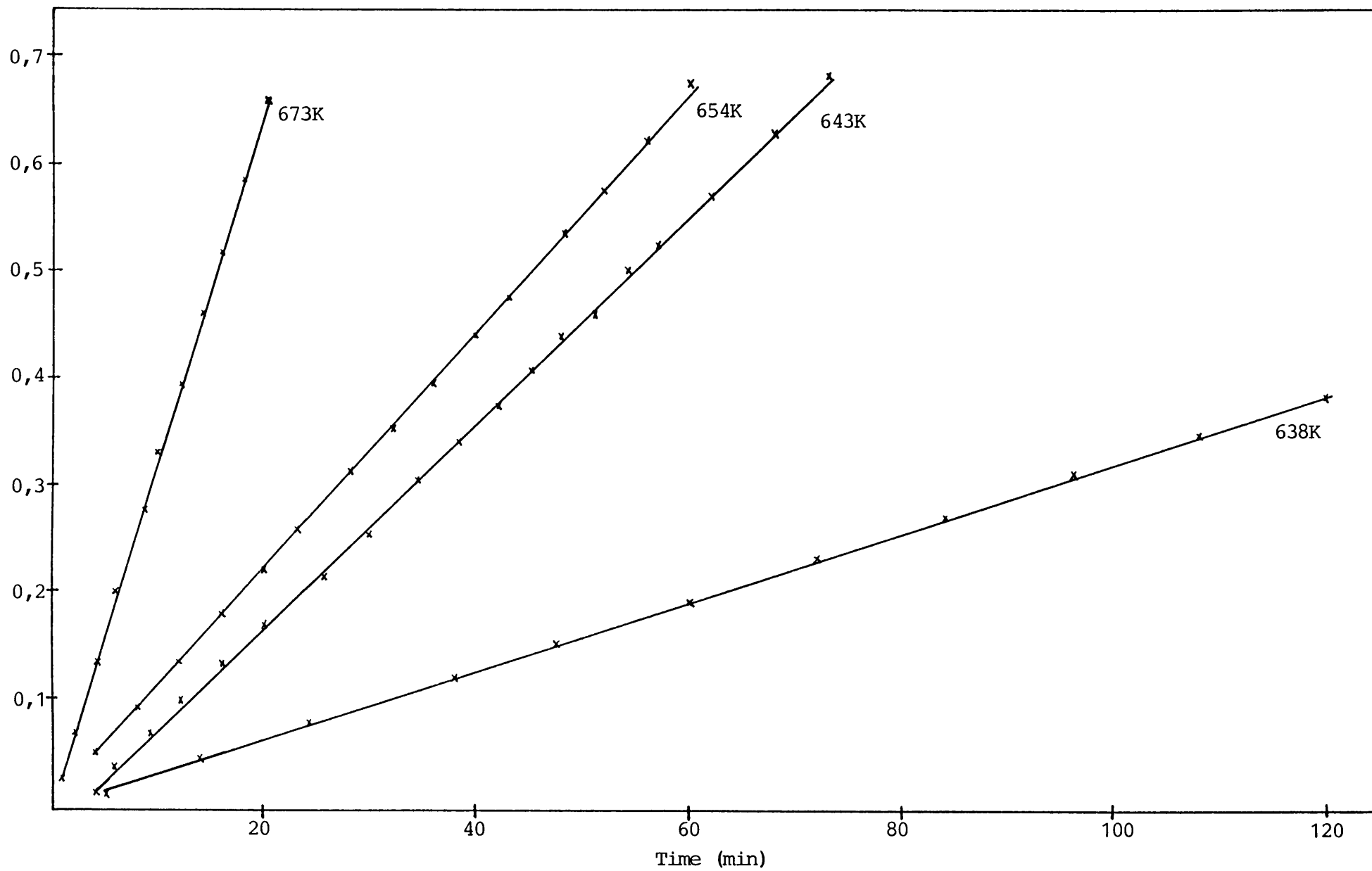


Figure 3.3. Rate data of the thermal decomposition of $\text{La}(\text{NO}_3)_3$ fitted to the contracting area equation

temperatures (see paragraph 4.2.1.1.)

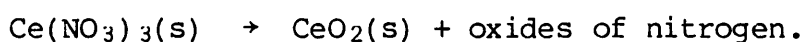
The Arrhenius parameters for the reaction were calculated from the rate constant values (figure 3.4) and were found to be $226,8 \text{ kJ}\cdot\text{mol}^{-1}$ $\text{La}(\text{NO}_3)_3$ for the activation energy and $35,5$ for the $\ln(A/\text{min}^{-1})$ value.

The DSC curve of the thermal decomposition of $\text{La}(\text{NO}_3)_3$ shows a shoulder that starts at approximately 410°C (figure 3.5). This shoulder is due to the start of the decomposition of $\text{LaO}(\text{NO}_3)$. Using the Du Pont Partial Area Integration program, the average enthalpy for the decomposition of $\text{La}(\text{NO}_3)_3$ to $\text{LaO}(\text{NO}_3)$ was estimated as $123,4 \text{ kJ}\cdot\text{mol}^{-1}$ $\text{La}(\text{NO}_3)_3$. No reversible process was observed on cooling samples from 410°C to 360°C .

3.2 Cerium(III) nitrate

The observed TG curve of $\text{Ce}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$ is represented in figure 3.1 and it indicates that $\text{Ce}(\text{NO}_3)_3$ is only stable over a limited temperature range, i.e. 210°C to 220°C . Even so, it was still possible to prepare the anhydrous material as described in the experimental section.

The decomposition of $\text{Ce}(\text{NO}_3)_3$ as reflected by a mass loss observed over the temperature range of 230°C to 360°C , is considered to be a redox reaction written overall as



An average mass loss of $47,6\%$ was observed (theoretical value : $47,20\%$). No oxynitrate could be detected.

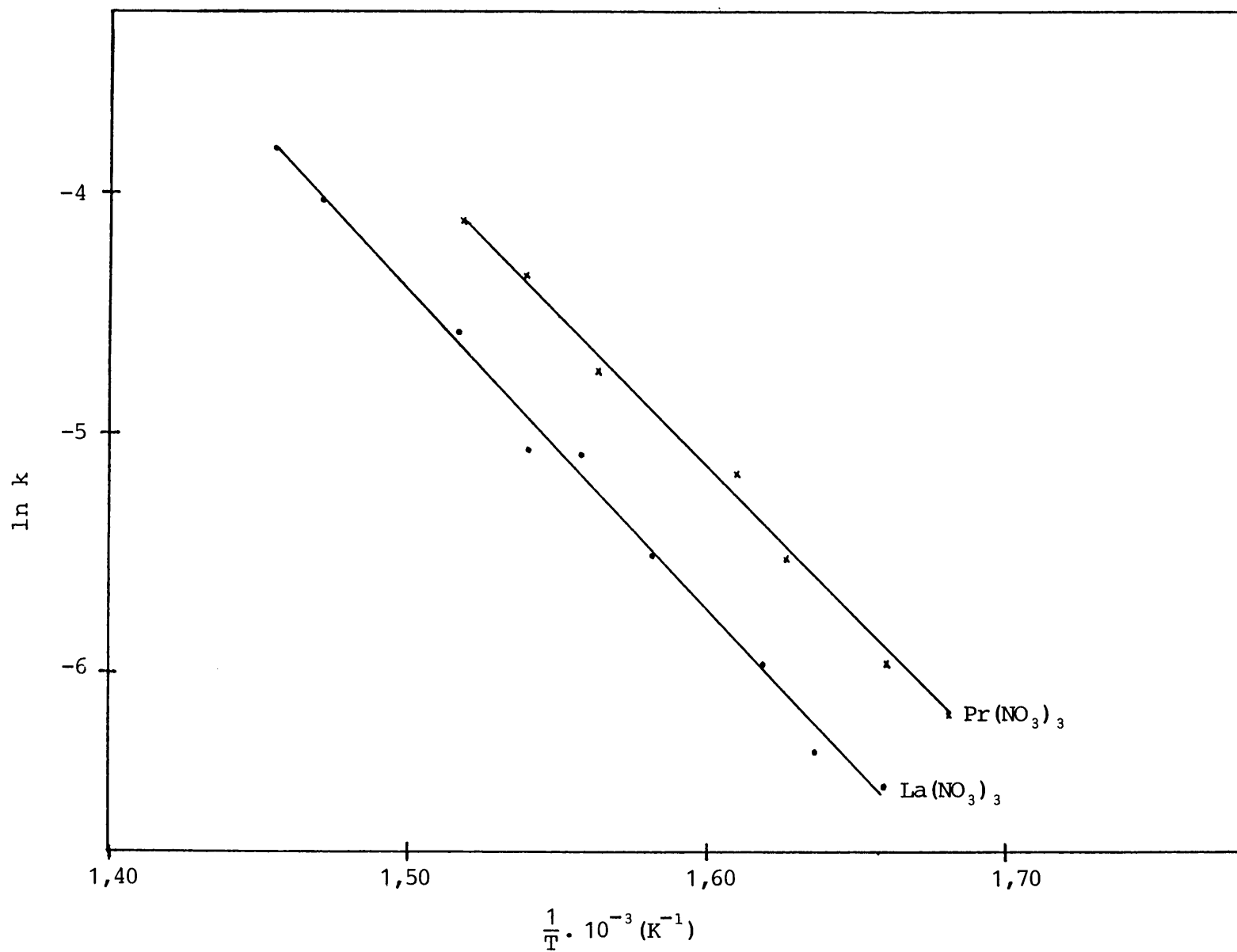


Figure 3.4. Arrhenius plots for the thermal decomposition of $La(NO_3)_3$ and $Pr(NO_3)_3$

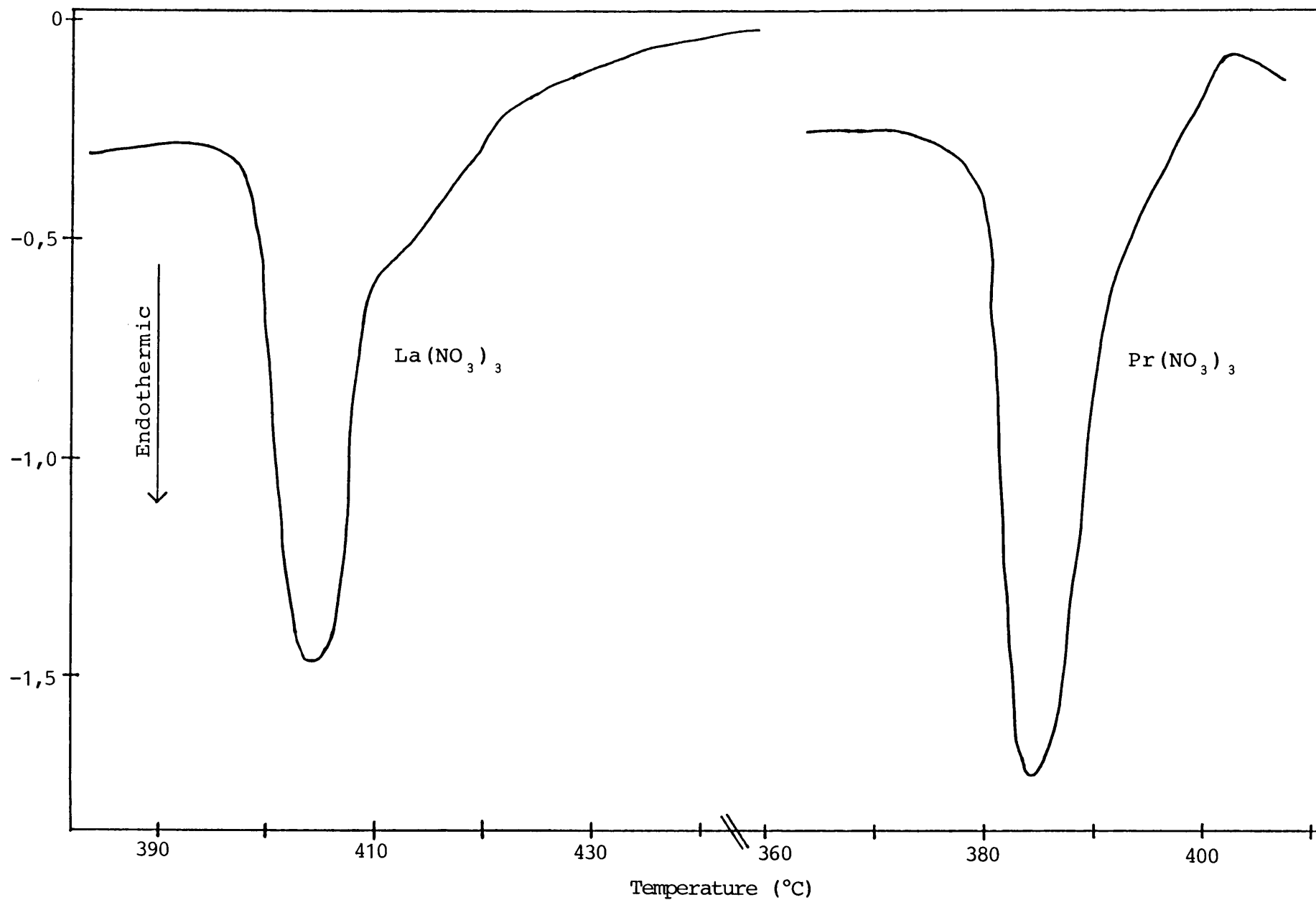


Figure 3.5. DSC curves of the thermal decomposition of $\text{La}(\text{NO}_3)_3$ and $\text{Pr}(\text{NO}_3)_3$

Isothermal mass loss curves at temperatures between 230 °C and 360 °C were recorded and the data fitted to the different $f(\alpha)$ equations. The kinetic data fitted the equation for a second order solid state reaction,

$$f(\alpha) = \frac{1}{1-\alpha} - 1 = kt,$$
 best at all the experimental temperatures (see paragraph 4.2.1.2). Figure 3.6 represents some of the rate data fitted to the second order solid state reaction equation. The Arrhenius parameters for the reaction were calculated from the rate constant values and found to be $E_a = 104,0 \text{ kJ}\cdot\text{mol}^{-1}$ and $\ln(A/\text{min}^{-1}) = 21,7$ (figure 3.7).

The enthalpy of the reaction was estimated as $111,1 \text{ kJ}\cdot\text{mol}^{-1}$ $\text{Ce}(\text{NO}_3)_3$ and was found to be pressure-independent up to the maximum experimental pressure of $5 \times 10^3 \text{ kPa}$. The symmetrical shape of the DSC peak suggests that the decomposition reaction is not accompanied by any other changes (figure 3.8).

3.3 Praseodymium(III) nitrate

Using a heating rate of $5 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$, the TG curve of $\text{Pr}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ indicates that $\text{Pr}(\text{NO}_3)_3$ starts to decompose at 365 °C (figure 3.9). $\text{PrO}(\text{NO}_3)$ starts to decompose to praseodymiumoxide at 430 °C. $\text{PrO}(\text{NO}_3)$ is stable over a very limited temperature range, i.e. 425 °C to 430 °C.

The theoretical mass loss for the reaction

$$\text{Pr}(\text{NO}_3)_3(\text{s}) \rightarrow \text{PrONO}_3(\text{s}) + \text{volatile products, amounts to } 33,04\%.$$
 An average mass loss of 32,7% was observed for the reaction.

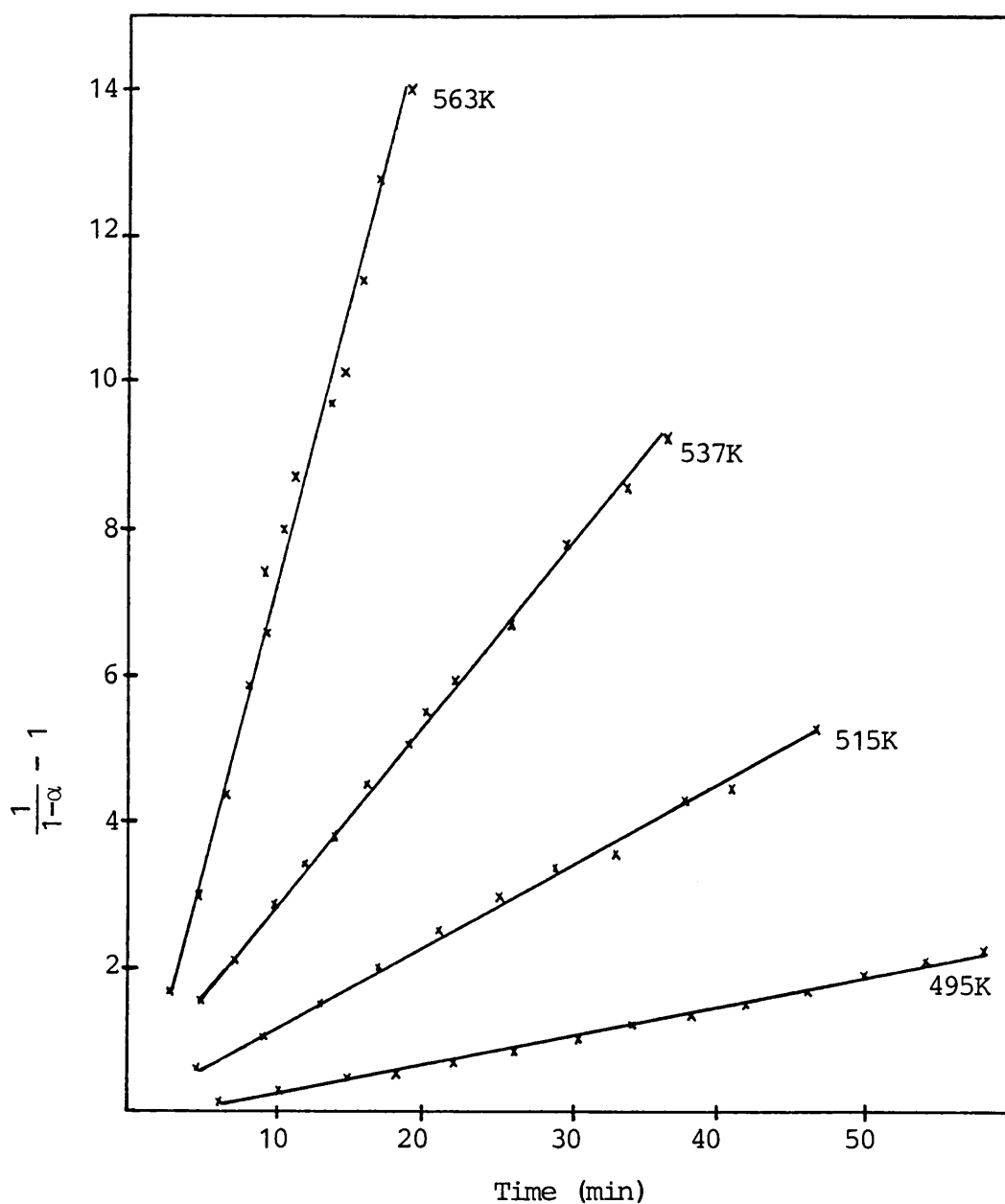


Figure 3.6. Rate data of the thermal decomposition of $\text{Ce}(\text{NO}_3)_3$ fitted to the second order solid state reaction equation

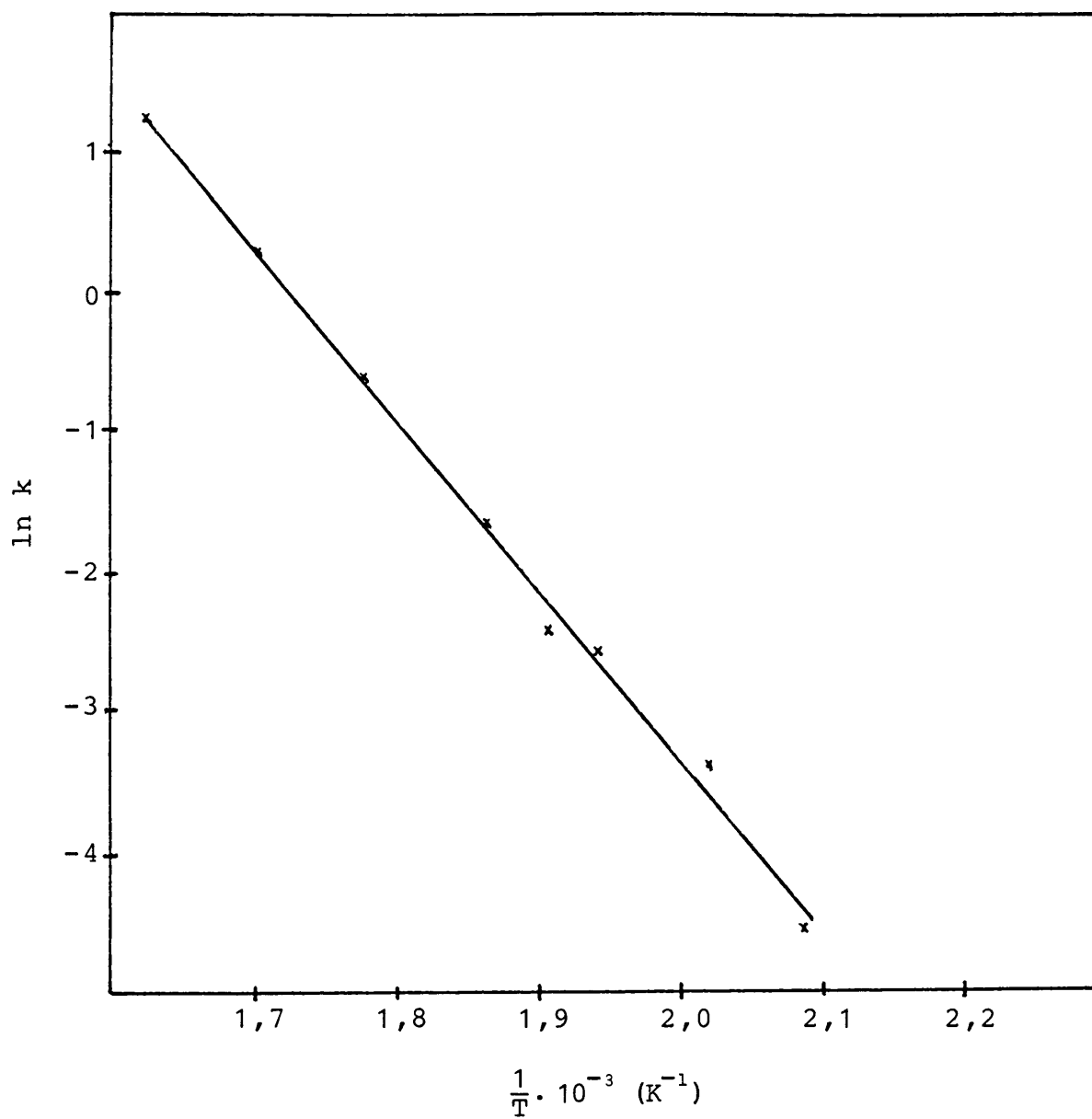


Figure 3.7. Arrhenius plot for the thermal decomposition of $\text{Ce}(\text{NO}_3)_3$

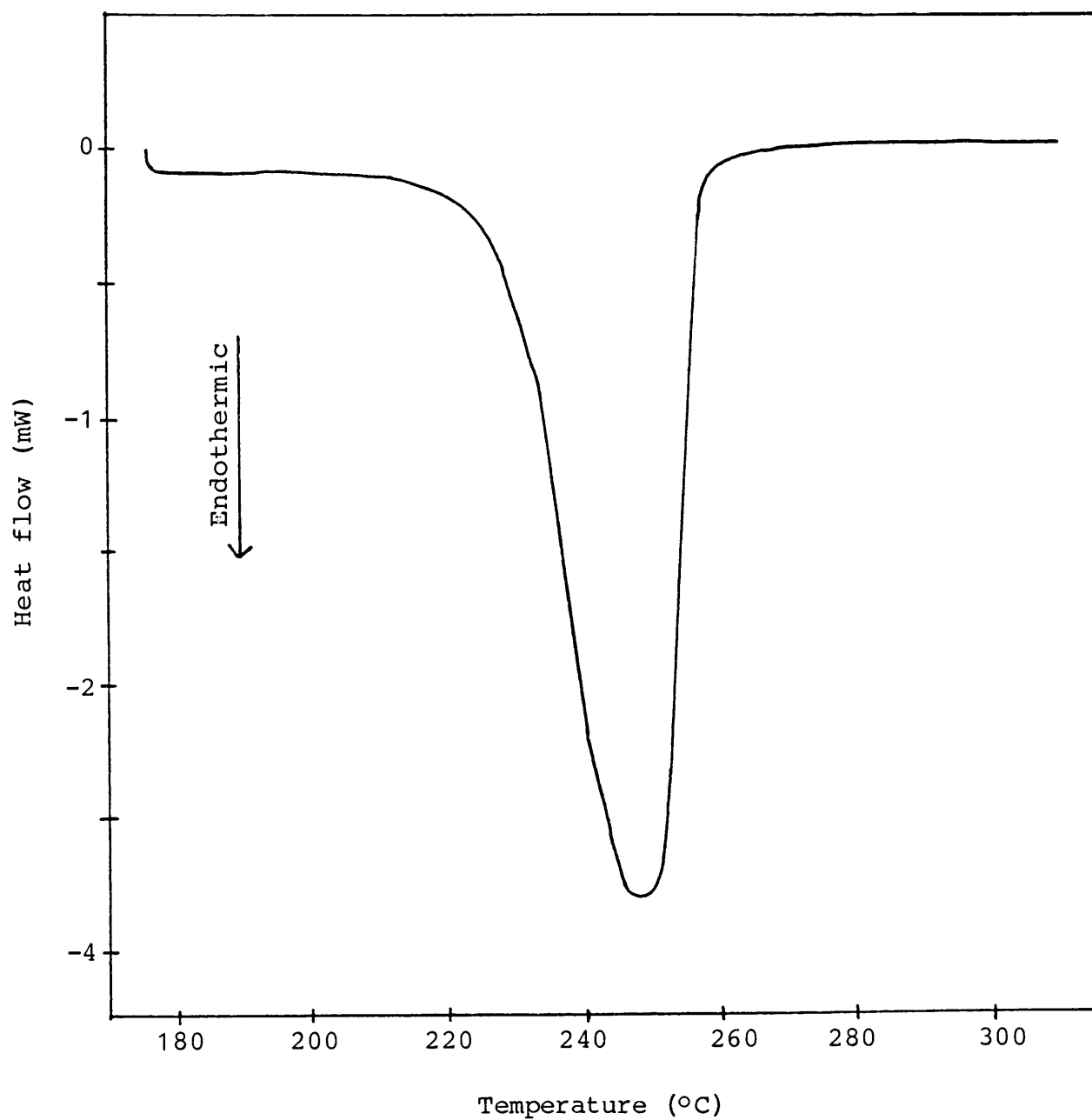


Figure 3.8. DSC curve of the thermal decomposition of $\text{Ce}(\text{NO}_3)_3$

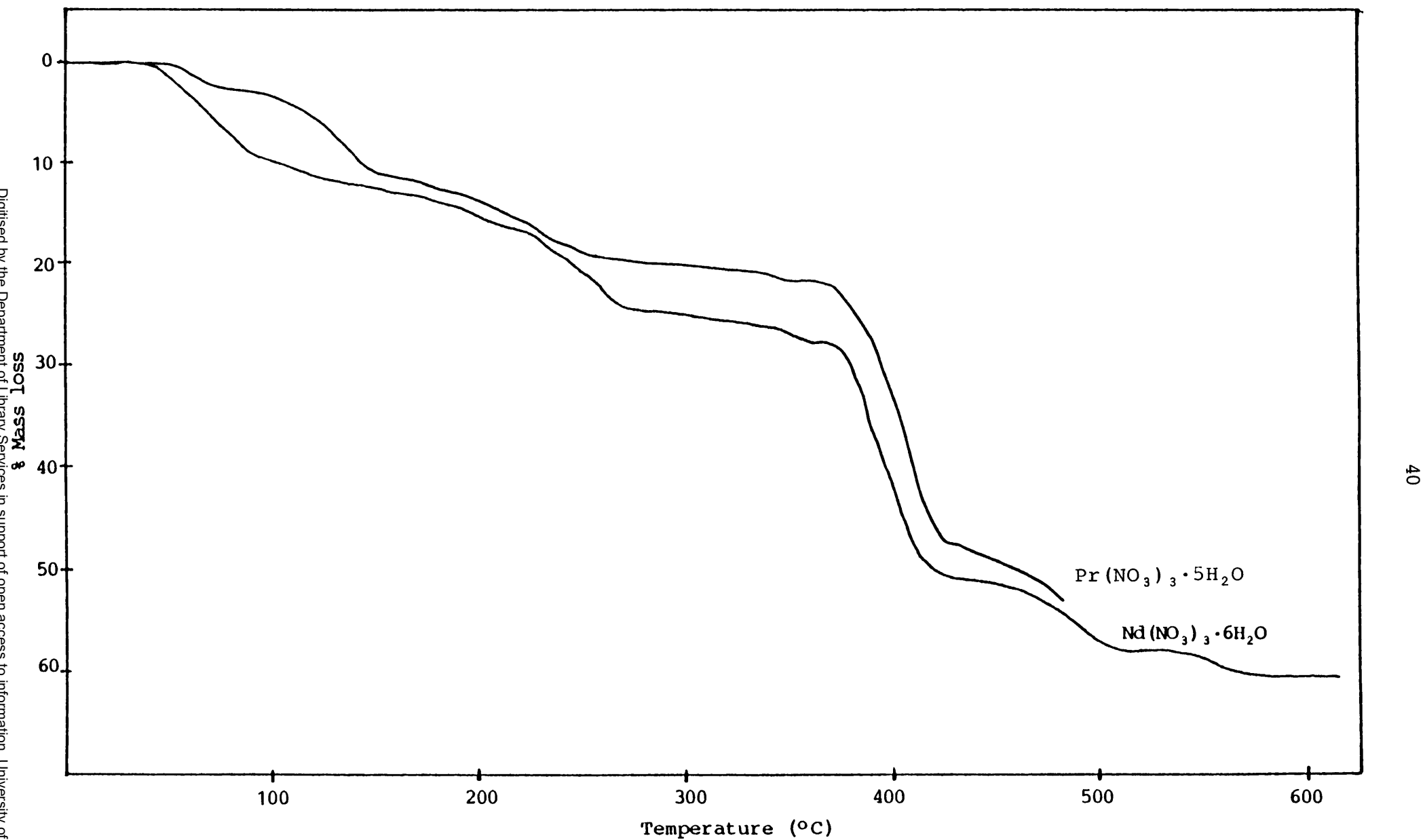


Figure 3.9. TG curves of the thermal decomposition of $\text{Pr}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and $\text{Nd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$

Since $\text{PrO}(\text{NO}_3)$ starts to decompose at 430°C , when using a heating rate of $5^\circ\text{C}\cdot\text{min}^{-1}$, isothermal mass loss curves were recorded at temperatures below 400°C , where no decomposition of $\text{PrO}(\text{NO}_3)$ was observed. Isothermal mass loss data was collected at different temperatures starting at 350°C .

The contracting volume equation, $f(\alpha)=1-(1-\alpha)^{1/3}=kt$, describes the decomposition kinetics of $\text{Pr}(\text{NO}_3)_3$ best, as an average correlation coefficient value of 0,994 was observed for the plots of $f(\alpha_i)$ against time. The correlation coefficient values for all other $f(\alpha)$ functions at all the experimental temperatures were lower than 0,994 (see paragraph 4.2.1.3).

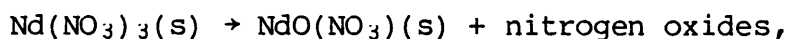
Using the Arrhenius equation, the activation energy parameters were calculated from the rate constant values (figure 3.4). The activation energy was found to be $206,8 \text{ kJ}\cdot\text{mol}^{-1}$ $\text{Pr}(\text{NO}_3)_3$ and $\ln(A/\text{min}^{-1})$ to be 32,3.

The DSC curve of the thermal decomposition of $\text{Pr}(\text{NO}_3)_3$ is given in figure 3.5. The enthalpy of the reaction was calculated as $102,6 \text{ kJ}\cdot\text{mol}^{-1}$ $\text{Pr}(\text{NO}_3)_3$. No reversible processes were observed on cooling the sample from 400°C to 350°C . No change in the reaction enthalpy value occurred when using a pressure of $5\times 10^3 \text{ kPa}$.

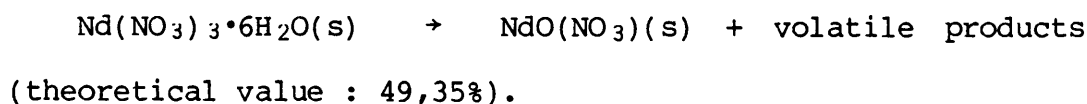
3.4 Neodymium(III) nitrate

The TG curve of $\text{Nd}(\text{NO}_3)_3\cdot 6\text{H}_2\text{O}$, using a heating rate of $5^\circ\text{C}\cdot\text{min}^{-1}$, indicates that $\text{Nd}(\text{NO}_3)_3$ starts to decompose at

360 °C (figure 3.9). The reaction



occurs in the temperature range of 360 °C to 430 °C. A mass loss of 48,5% was observed for the reaction,



The rate data, acquired from the isothermal decomposition curves at temperatures between 350 °C and 420 °C, fit the Ginstling-Brounshtein equation, $f(\alpha) = 1 - \frac{2\alpha}{3} - (1-\alpha)^{\frac{2}{3}} = kt$, best, as is shown in figure 3.10 (see paragraph 4.2.2.1). The rate constants estimated from the slopes of the $f(\alpha)$ curves, were found to be temperature dependent below 390 °C and much less so above 390 °C. This tendency is illustrated in an Arrhenius plot, which was used to calculate the Arrhenius parameters (figure 3.11). The activation energy value below 390 °C was calculated to be 805,0 kJ·mol⁻¹ Nd(NO₃)₃ and ln(A/min⁻¹) to be 161,5. Above 390 °C the values are, $E_a = 165,4 \text{ kJ} \cdot \text{mol}^{-1} \text{Nd}(\text{NO}_3)_3$ and $\ln(A/\text{min}^{-1}) = 26,1$. The value of the activation energy reported by Rao [6] was 33 kJ·mol⁻¹ Nd(NO₃)₃, but was only calculated for measurements at temperatures above 390 °C. Measurements by Rao were carried out at two temperatures only.

The DSC curve of the decomposition of Nd(NO₃)₃ suggested that the decomposition is not a straightforward process (figure 3.12). The peak maximum is at 377 °C with a shoulder at 400 °C. On cooling a sample from 400 °C, two exothermic peaks were observed at 390 °C and 335 °C. The exothermic peak at 335 °C was associated with the endotherm at 320 °C in

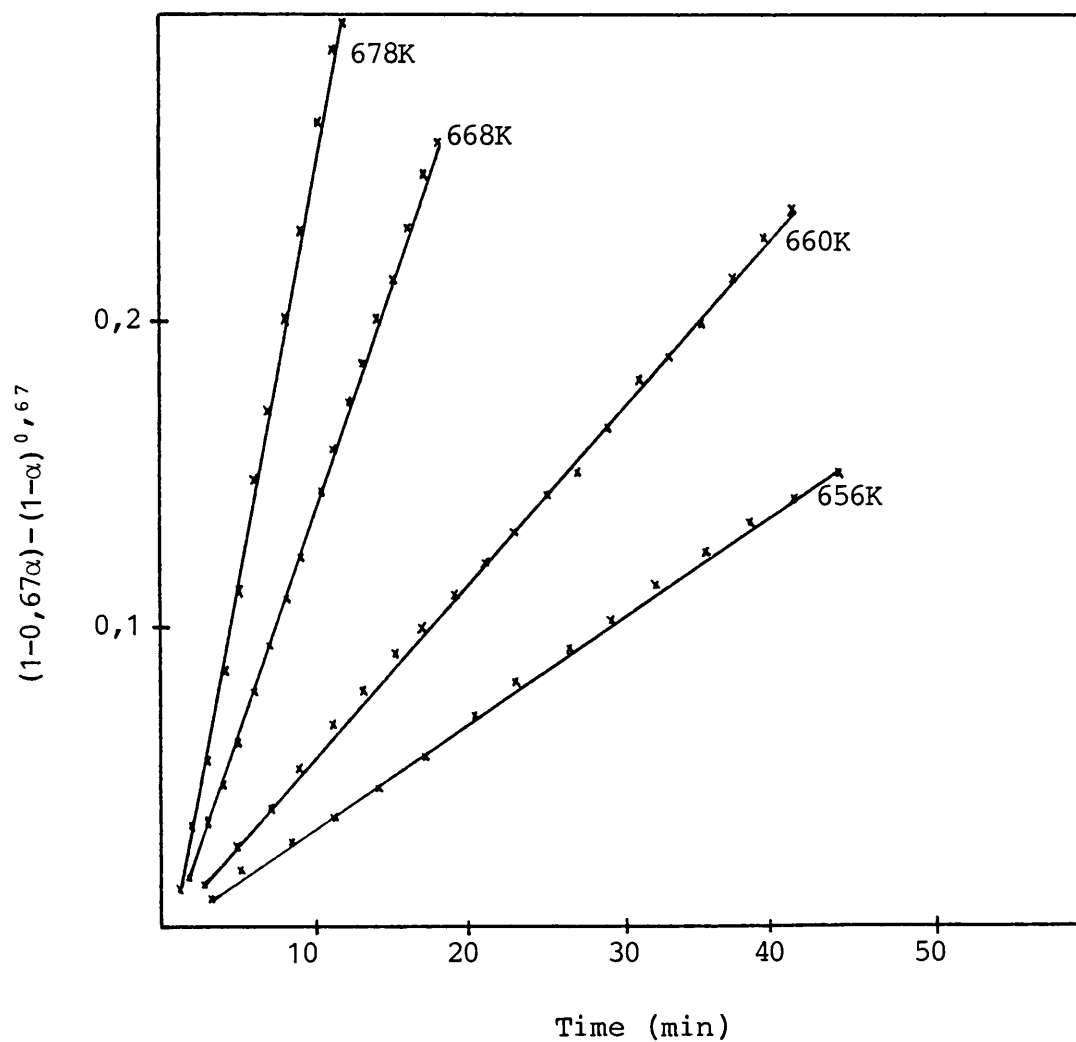
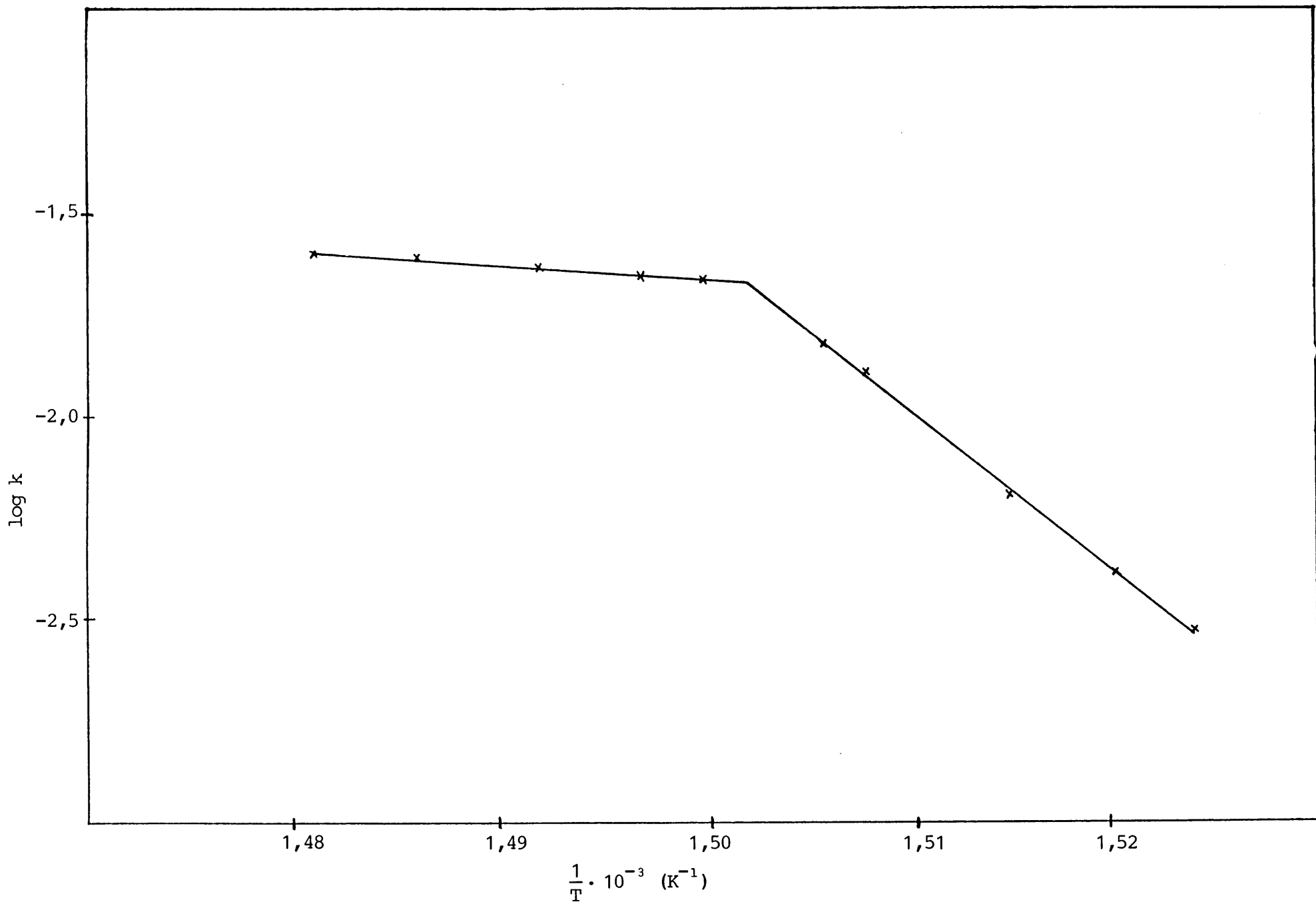


Figure 3.10. Rate data of the thermal decomposition of $\text{Nd}(\text{NO}_3)_3$ fitted to the Ginstling-Brounshtein equation



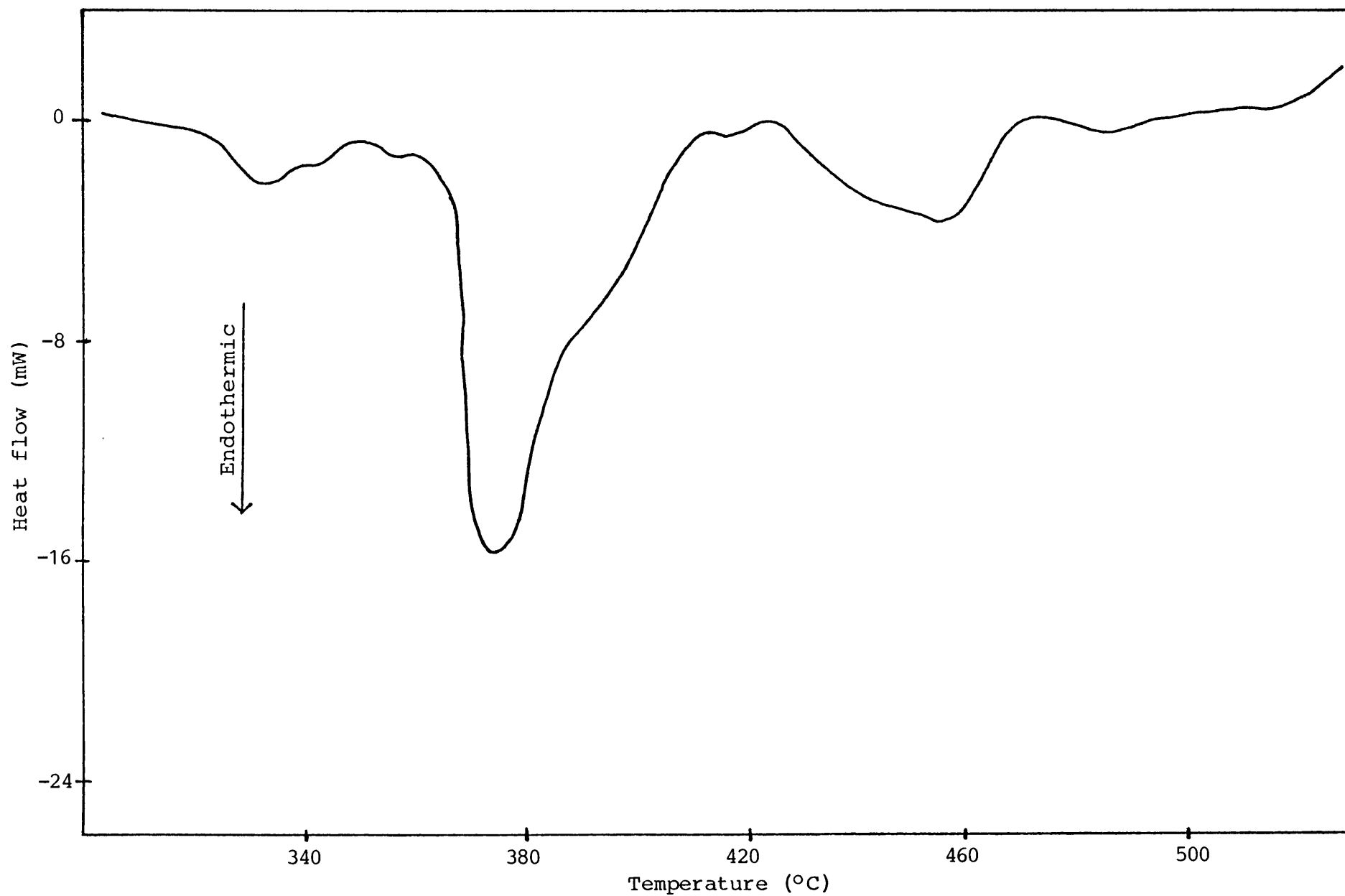
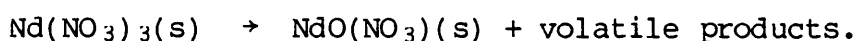


Figure 3.12. DSC curve of the thermal decomposition of $\text{Nd}(\text{NO}_3)_3$ at atmospheric pressure

the heating curve. The peak at 390 °C suggested that a temperature-dependent reversible process occurs together with the decomposition reaction.

The total enthalpy of the decomposition reaction of $\text{Nd}(\text{NO}_3)_3$ was calculated as $109,6 \text{ kJ} \cdot \text{mol}^{-1} \text{ Nd}(\text{NO}_3)_3$. This value contains contributions from the reversible transition at 390 °C and the decomposition reaction



The DSC curve of the decomposition of $\text{Nd}(\text{NO}_3)_3$ at a pressure of $5 \times 10^3 \text{ kPa}$ is given in figure 3.13. The shape of the curve at this higher pressure differs from the curve at atmospheric pressure. The shoulder observed at 400 °C, disappeared at this higher pressure and the peak maximum shifted to a higher temperature, at 442 °C. The enthalpy of the decomposition reaction at $5 \times 10^3 \text{ kPa}$ was estimated as $98,4 \text{ kJ} \cdot \text{mol}^{-1} \text{ Nd}(\text{NO}_3)_3$. The higher pressure seems to inhibit the reversible process occurring at 390 °C and therefore the lower enthalpy value was observed. The reversible process at 390 °C also seems to be responsible for the change in the temperature dependence of the rate constants at atmospheric pressure.

3.5 Europium(III) nitrate

The TG curve of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ at a heating rate of $5 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ indicates that $\text{Eu}(\text{NO}_3)_3$ starts to decompose at 320 °C (figure 3.14). The decomposition to $\text{EuO}(\text{NO}_3)$ is completed at 405 °C.

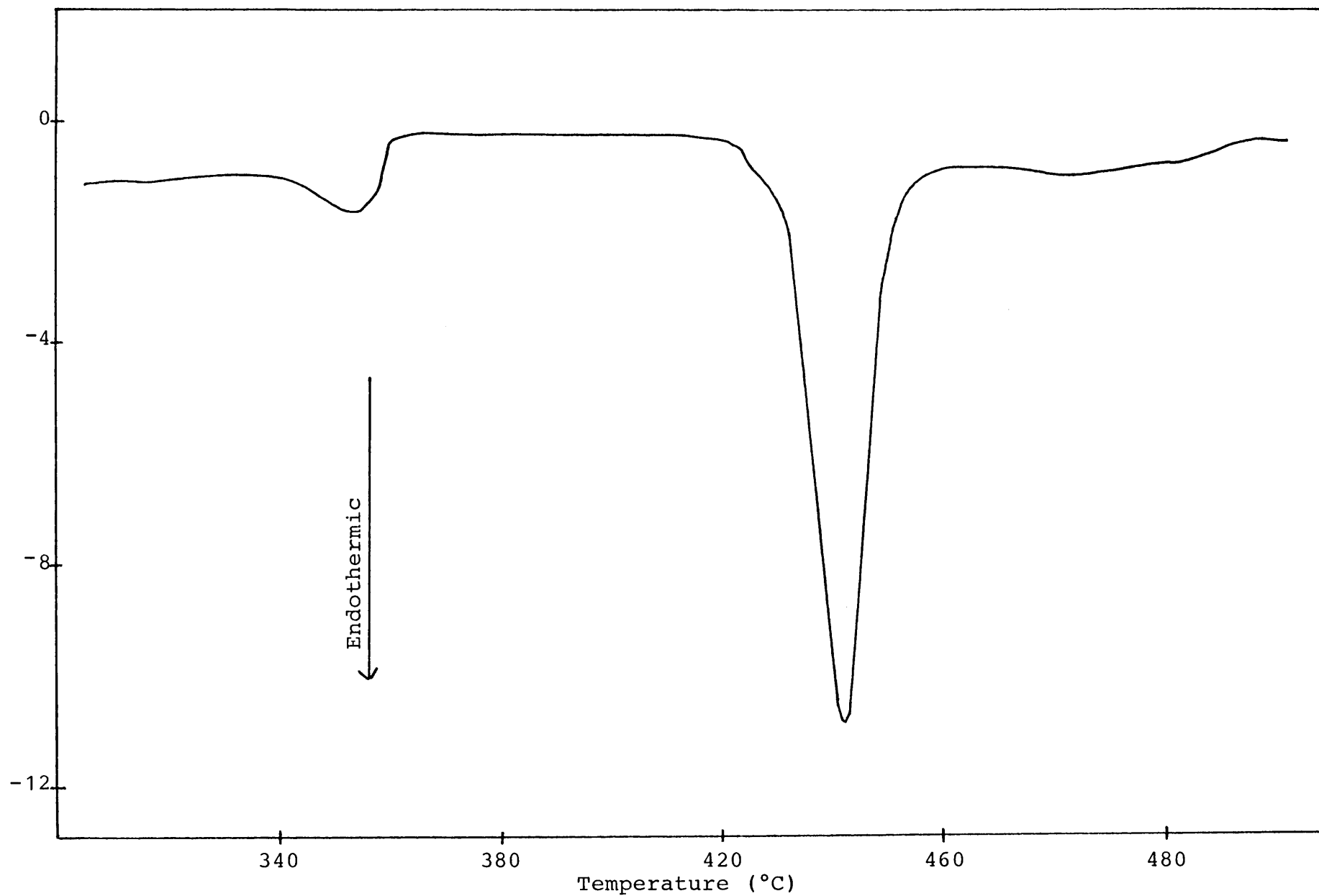


Figure 3.13. DSC curve of the thermal decomposition of $\text{Nd}(\text{NO}_3)_3$ at a pressure of 5×10^3 kPa

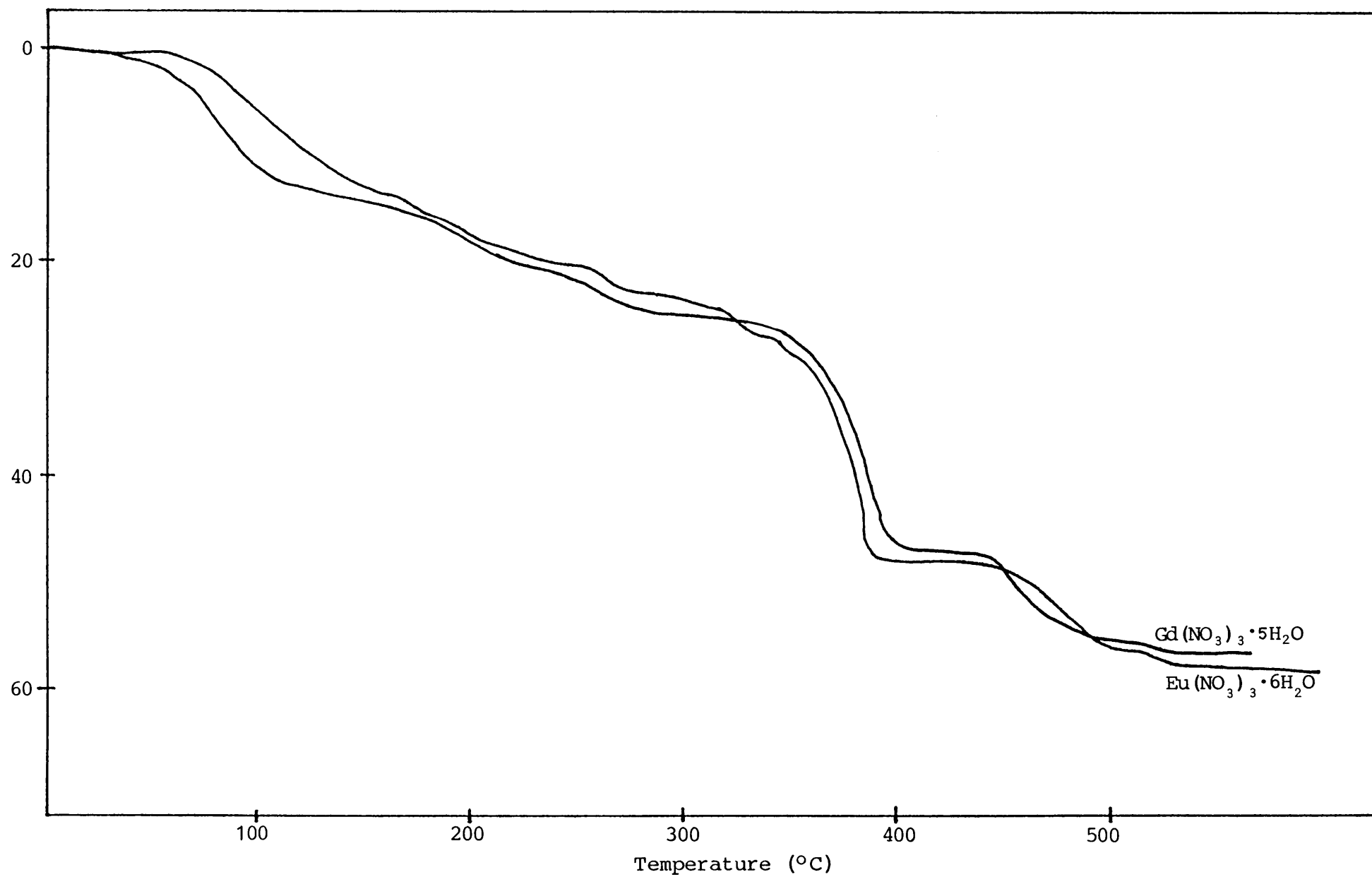
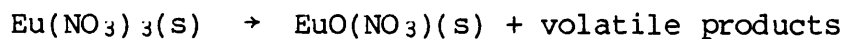


Figure 3.14. TG curves of the thermal decomposition of $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Gd}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$

The oxynitrate starts to decompose at 425 °C, thus no interference with the reaction studied was observed.

An average mass loss of 31,0% was observed for the reaction,



(theoretical value : 31,96%).

Isothermal mass loss curves were recorded at selected temperatures between 310 °C and 400 °C. The rate data fit the Avrami-Erofe'ev equation best, with $n = \frac{3}{2}$, $f(\alpha) = (-\ln(1-\alpha))^{\frac{2}{3}}$ = kt (figure 3.15). The correlation coefficient values for all other $f(\alpha)$ functions at all the experimental temperatures were lower than the value for the Avrami-Erofe'ev equation ($n = \frac{3}{2}$) (see also paragraph 4.2.2.2).

The Arrhenius plot for the decomposition of $\text{Eu}(\text{NO}_3)_3$ shows two straight lines (figure 3.16). In the temperature range of 355 °C to 400 °C, the activation energy was calculated as 139,9 kJ·mol⁻¹ and $\ln(A/\text{min}^{-1})$ as 24,3. Below 350 °C the activation energy amounts to 189,6 kJ·mol⁻¹ and the $\ln(A/\text{min}^{-1})$ value to 32,3.

The DSC curve of the thermal decomposition of $\text{Eu}(\text{NO}_3)_3$ shows a shoulder, starting at 350 °C (figure 3.17). The enthalpy for the overall decomposition reaction of $\text{Eu}(\text{NO}_3)_3$ to $\text{EuO}(\text{NO}_3)$ is calculated as 119,6 kJ·mol⁻¹ $\text{Eu}(\text{NO}_3)_3$. On cooling a sample from 365 °C an exothermic peak is observed at 347 °C. The change in the activation energy value at 350 °C seems to be due to this reversible process, that

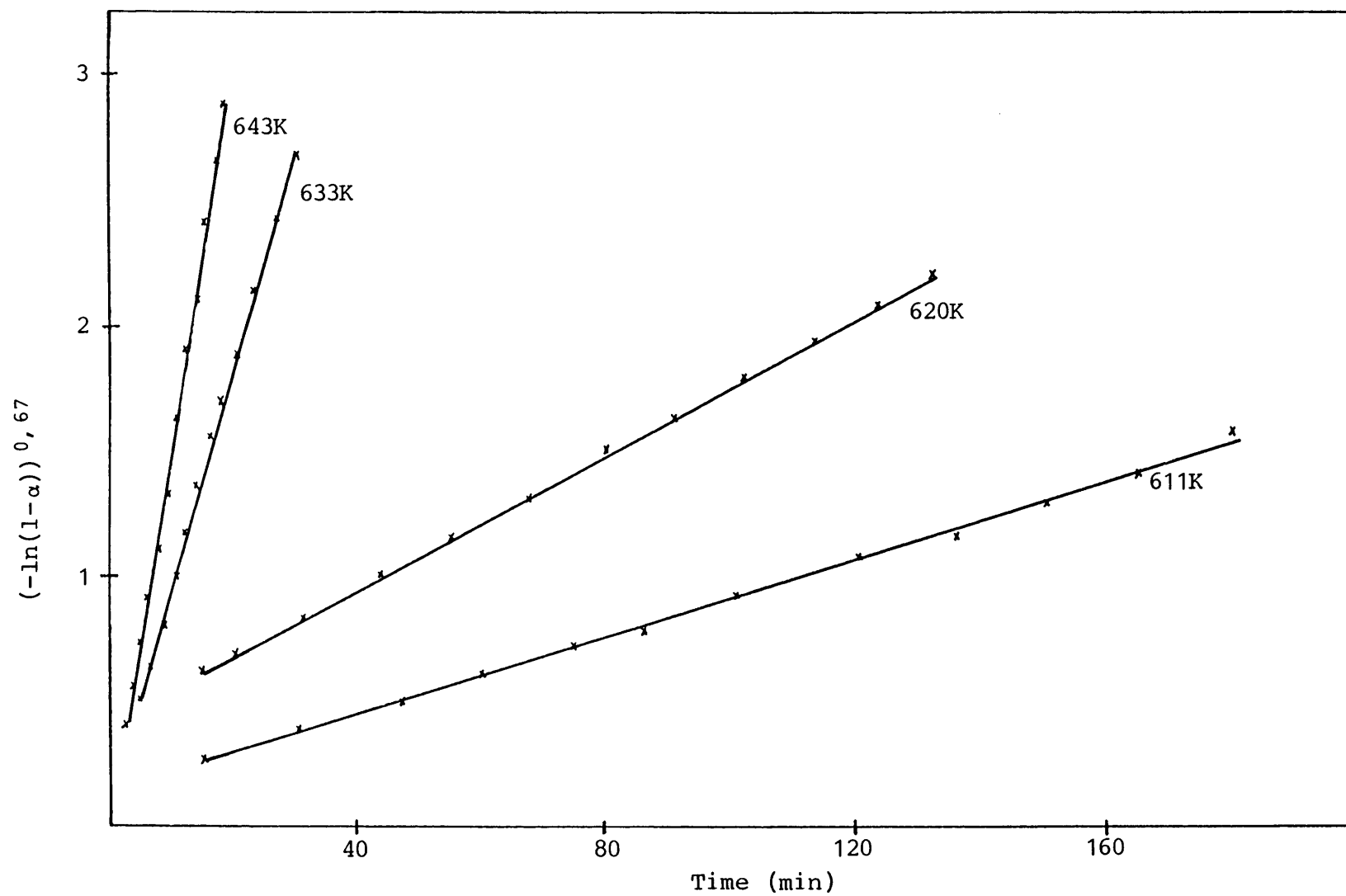


Figure 3.15. Rate data of the thermal decomposition of $\text{Eu}(\text{NO}_3)_3$ fitted to the Avrami-Erofe'ev equation ($n = \frac{3}{2}$)

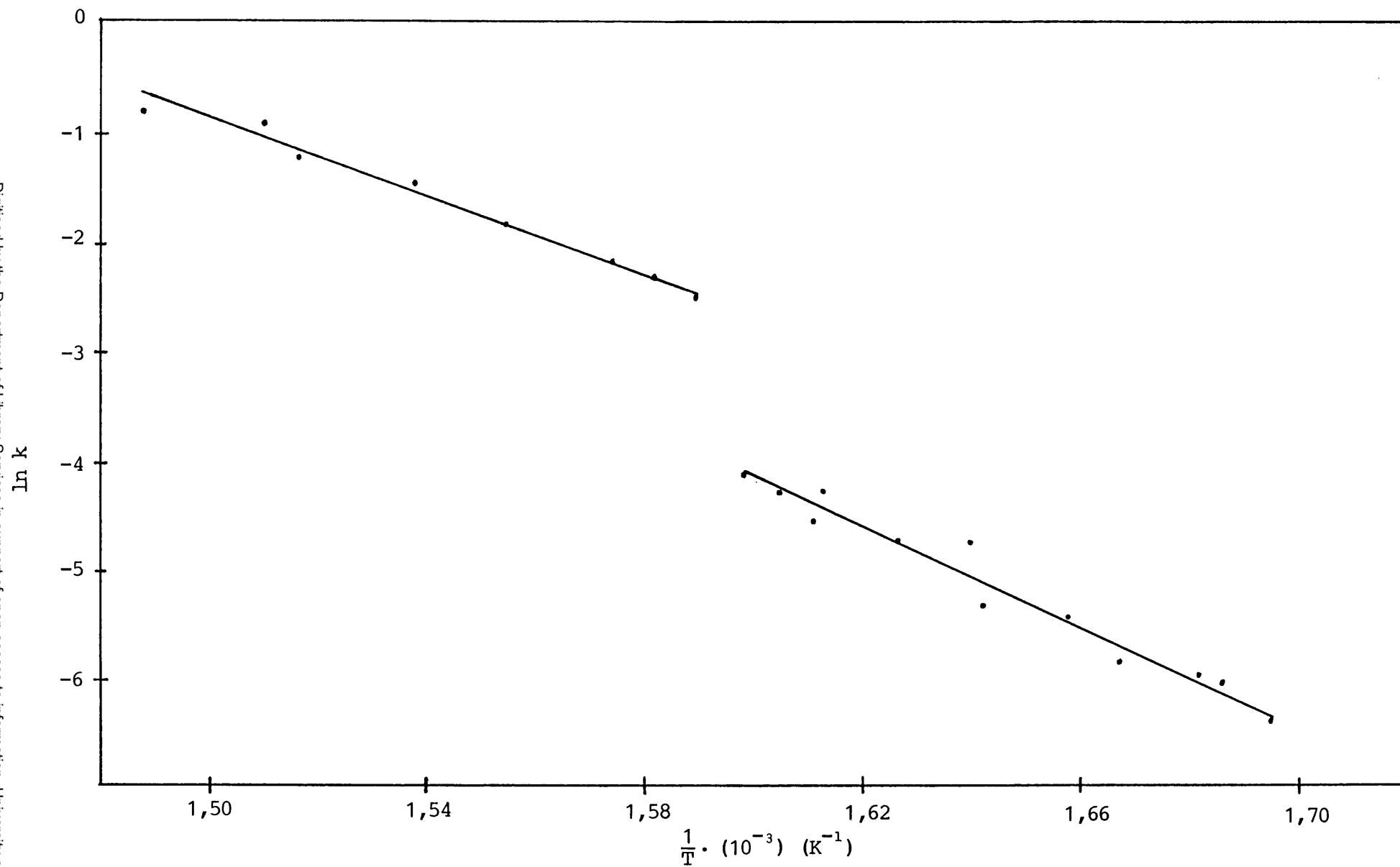


Figure 3.16. The Arrhenius plot for the thermal decomposition of $\text{Eu}(\text{NO}_3)_3$

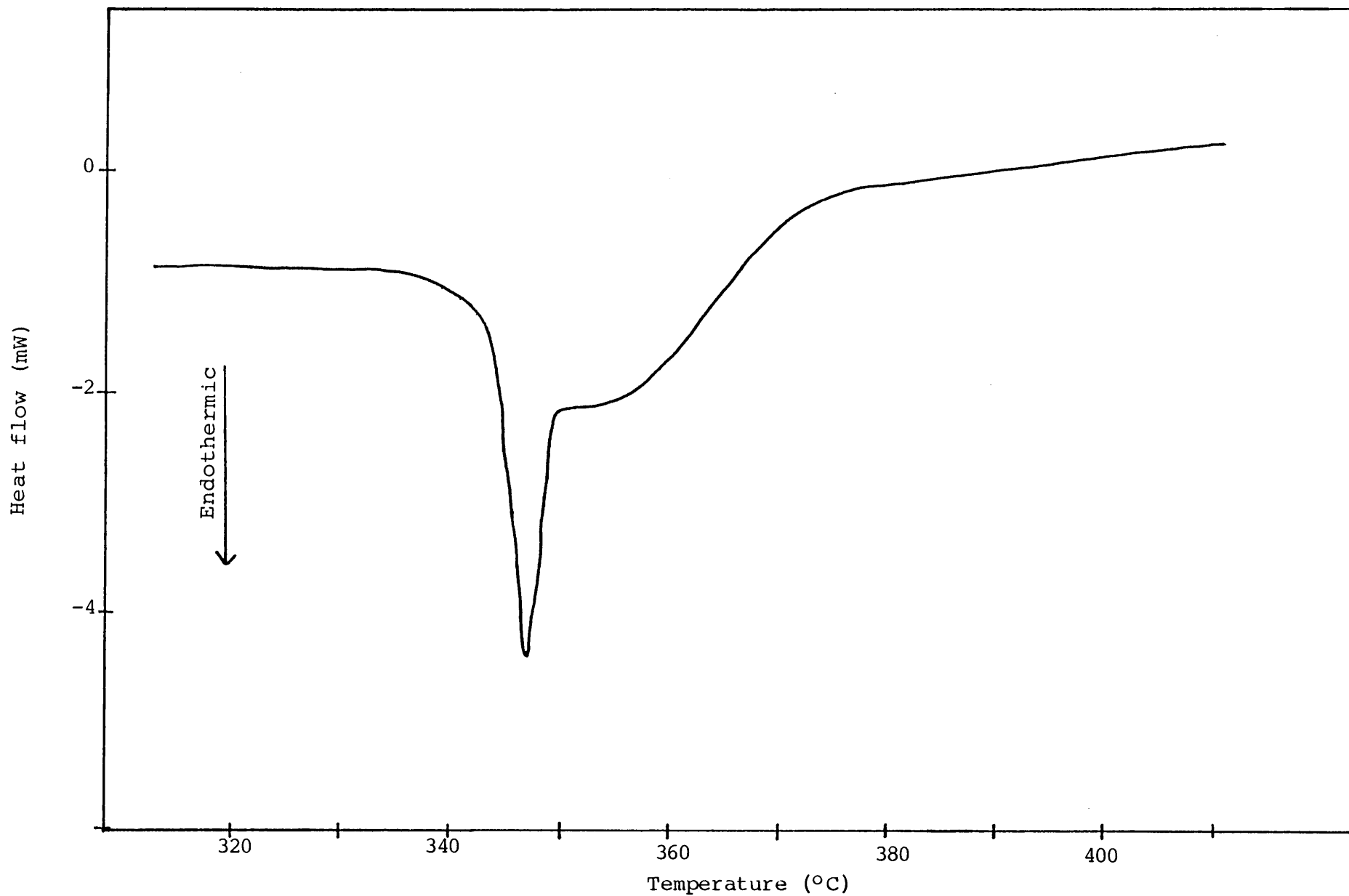


Figure 3.17. The DSC curve of the thermal decomposition of $\text{Eu}(\text{NO}_3)_3$ to $\text{EuO}(\text{NO}_3)_3$ at atmospheric pressure

occurs during the decomposition of $\text{Eu}(\text{NO}_3)_3$.

The DSC curve of the decomposition of $\text{Eu}(\text{NO}_3)_3$ at a pressure of 5×10^3 kPa is given in figure 3.18. The shoulder observed at 350°C under atmospheric pressure, disappeared at this higher temperature. The enthalpy of the reaction at 5×10^3 kPa was estimated as $96,8 \text{ kJ} \cdot \text{mol}^{-1}$ $\text{Eu}(\text{NO}_3)_3$. The higher pressure seems to inhibit the reversible process occurring at 350°C and therefore the lower enthalpy value was observed.

3.6 Gadolinium(III) nitrate

Using a heating rate of $5^\circ\text{C} \cdot \text{min}^{-1}$, $\text{Gd}(\text{NO}_3)_3$ starts to decompose to $\text{GdO}(\text{NO}_3)$ at 275°C (figure 3.14). The decomposition to $\text{GdO}(\text{NO}_3)$ is completed at 400°C when using this heating rate. The oxynitrate starts to decompose at 420°C , thus no interference with the reaction studied was observed.

For the solid state thermal decomposition reaction,

$\text{Gd}(\text{NO}_3)_3(\text{s}) \rightarrow \text{GdO}(\text{NO}_3)(\text{s}) + \text{volatile products}$, an average mass loss of 30,5% was observed (theoretical value : 31,47%).

Isothermal mass loss curves were recorded at selected temperatures between 270°C and 410°C . No single $f(\alpha)$ equation fits the rate data at all the temperatures. It was observed that in the temperature range of 270°C to 315°C the Avrami-Erofe'ev equation, with $n = 2$, $f(\alpha) = (-\ln(1-\alpha))^{0,5} = kt$,

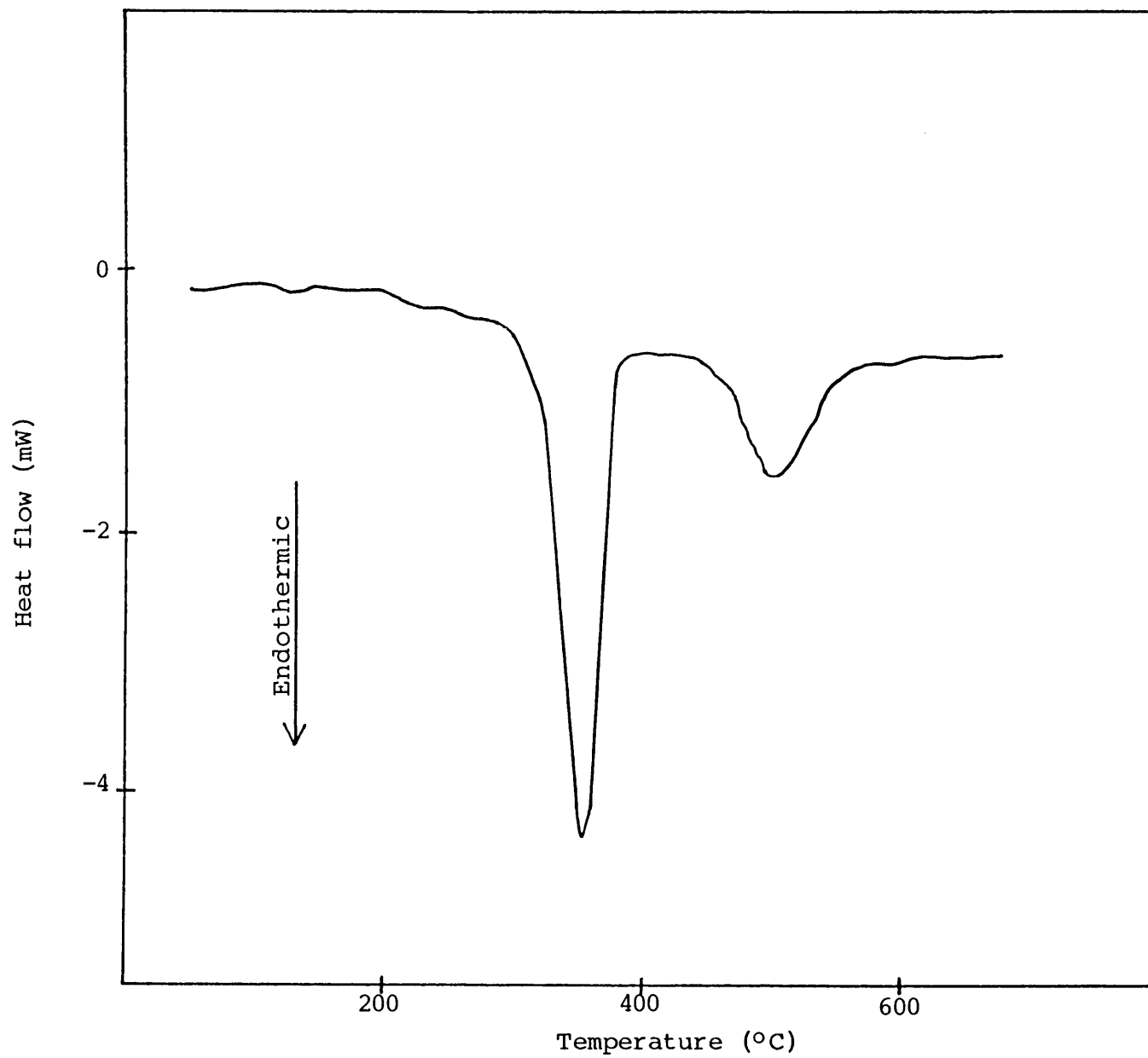


Figure 3.18. DSC curve of the thermal decomposition of $\text{Eu}(\text{NO}_3)_3$ at a pressure of 5×10^3 kPa

gave the best fit ($\alpha = 0,02$ to $\alpha = 0,98$). In the temperature range of 320 °C to 385 °C, the Avrami-Erofe'ev equation with $n = \frac{3}{2}$, $f(\alpha) = (-\ln(1-\alpha))^{\frac{2}{3}} = kt$, fits best and in the range of 390 °C to 410 °C, the Prout-Tompkins equation, $f(\alpha) = \ln \frac{\alpha}{1-\alpha} = kt$, best describes the reaction kinetics (figure 3.19) (see also paragraph 4.2.3.1).

The Arrhenius plot for the thermal decomposition of $\text{Gd}(\text{NO}_3)_3$ shows three straight lines (figure 3.20). The activation energy was calculated to be 82,7 $\text{kJ}\cdot\text{mol}^{-1}$ $\text{Gd}(\text{NO}_3)_3$ and $\ln(A/\text{min}^{-1})$ 10,9 in the temperature range of 270 °C to 315 °C. In the range of 320 °C to 385 °C the activation energy amounts to 243,2 $\text{kJ}\cdot\text{mol}^{-1}$ $\text{Gd}(\text{NO}_3)_3$ and $\ln(A/\text{min}^{-1})$ to 43,2. The activation energy in the temperature range of 390 °C to 410 °C is 99,5 $\text{kJ}\cdot\text{mol}^{-1}$ and $\ln(A/\text{min}^{-1}) = 17,8$.

Using a heating rate of 5 °C $\cdot\text{min}^{-1}$, the DSC curve for the thermal decomposition of $\text{Gd}(\text{NO}_3)_3$ shows two peaks, a small peak with a maximum at 317 °C and a bigger peak with a maximum at 368 °C (figure 3.21). The enthalpy of the overall decomposition reaction of $\text{Gd}(\text{NO}_3)_3$ to $\text{GdO}(\text{NO}_3)$ is estimated as 138,1 $\text{kJ}\cdot\text{mol}^{-1}$ $\text{Gd}(\text{NO}_3)_3$. The enthalpy of the process at 317 °C is calculated to be 8,9 $\text{kJ}\cdot\text{mol}^{-1}$ $\text{Gd}(\text{NO}_3)_3$. On cooling a sample from 400 °C, two exothermic peaks were observed, one at 387 °C and the other at 315 °C. These two peaks were associated with reversible processes, occurring during the decomposition reaction. These two reversible processes seem to be the reason for the change in the relationship between the rate constant, k , and temperature, as is shown on the

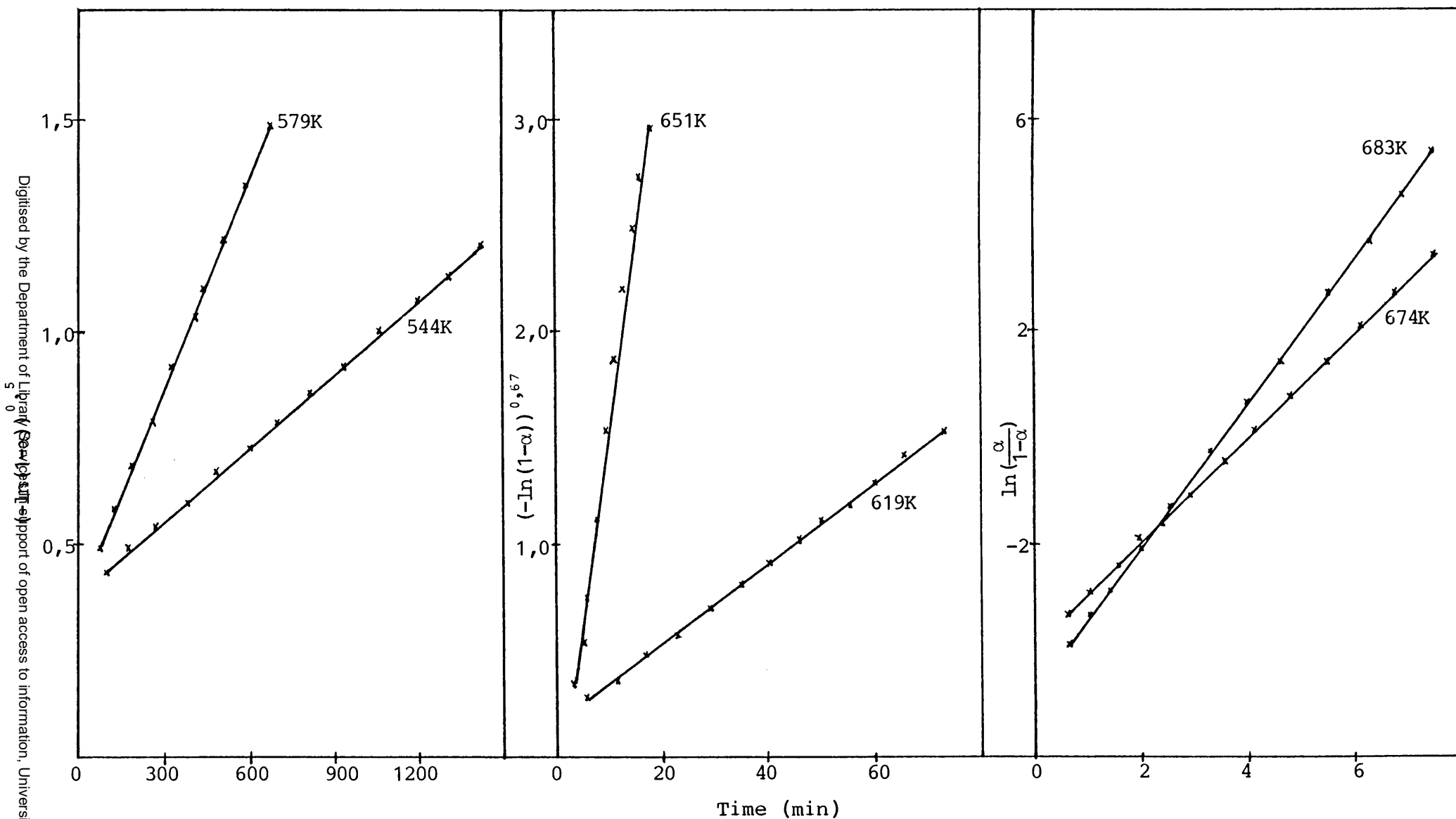


Figure 3.19. Rate data of the thermal decomposition of $Gd(NO_3)_3$ fitted to the Avrami-Erofe'ev equation with $n = 2$ (270-315 °C), the Avrami-Erofe'ev equation with $n = \frac{3}{2}$ (320-385 °C) and the Prout-Tompkins equation (390-410 °C)

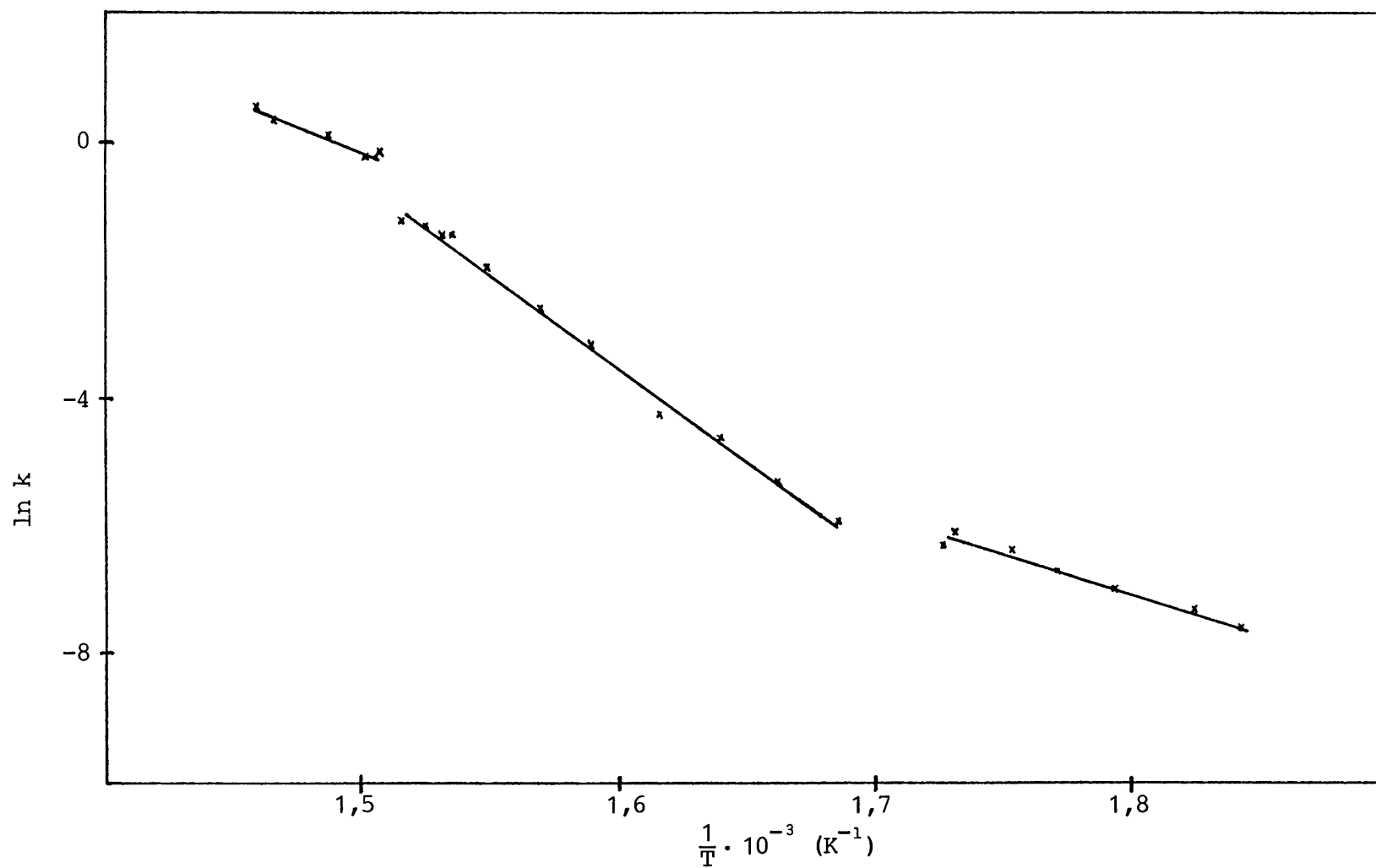


Figure 3.20. Arrhenius plot for the thermal decomposition of $\text{Gd}(\text{NO}_3)_3$

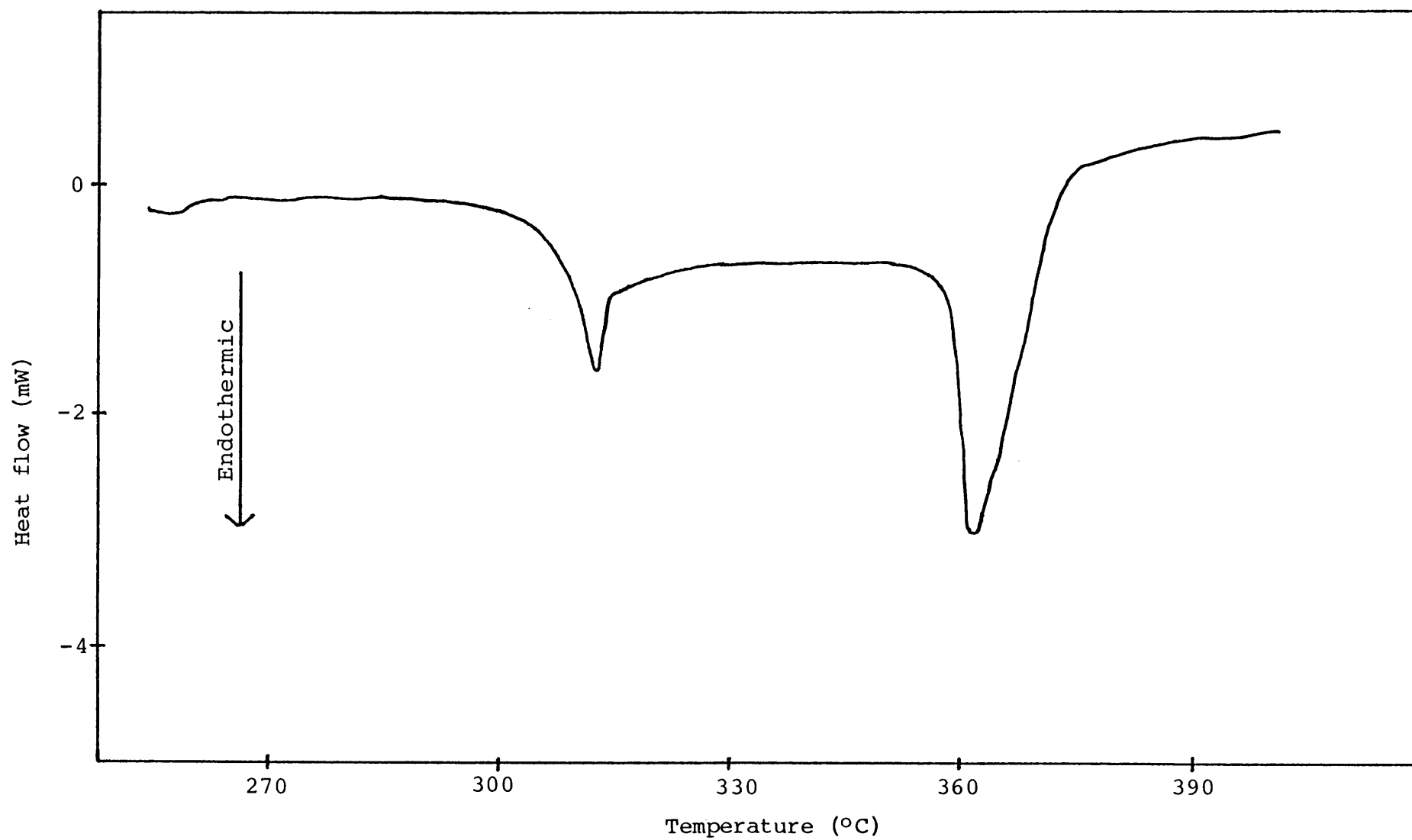


Figure 3.21. DSC curve of the thermal decomposition of $\text{Gd}(\text{NO}_3)_3$ to $\text{GdO}(\text{NO}_3)$

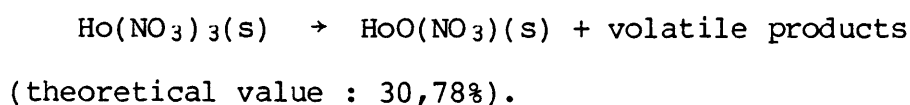
Arrhenius plot (figure 3.20). These processes also change the reaction mechanism of the decomposition reaction at these two temperatures.

The DSC curve for the thermal decomposition of $\text{Gd}(\text{NO}_3)_3$ at a pressure of 5×10^3 kPa shows three peaks (figure 3.22). Two very small peaks ($\Delta H < 2 \text{ kJ} \cdot \text{mol}^{-1}$) appeared at 308°C and 322°C , and a peak with a maximum at 365°C . The small peaks seems to be due to some reversible processes. The enthalpy of the reaction at this pressure was calculated as $95,2 \text{ kJ} \cdot \text{mol}^{-1} \text{ Gd}(\text{NO}_3)_3$.

3.7 Holmium(III) nitrate

As is shown on the TG curve of the thermal decomposition of $\text{Ho}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, the dehydrated nitrate starts to decompose at 250°C when using a heating rate of $5^\circ\text{C} \cdot \text{min}^{-1}$ (figure 3.23). The decomposition to the oxynitrate is completed at 395°C . The oxynitrate starts to decompose at 428°C , and no interference with the reaction studied was observed.

An experimental value of 31,5% was observed for the mass loss during the thermal decomposition reaction,



Isothermal mass loss curves were recorded at selected temperatures between 260°C and 375°C . It was observed that in

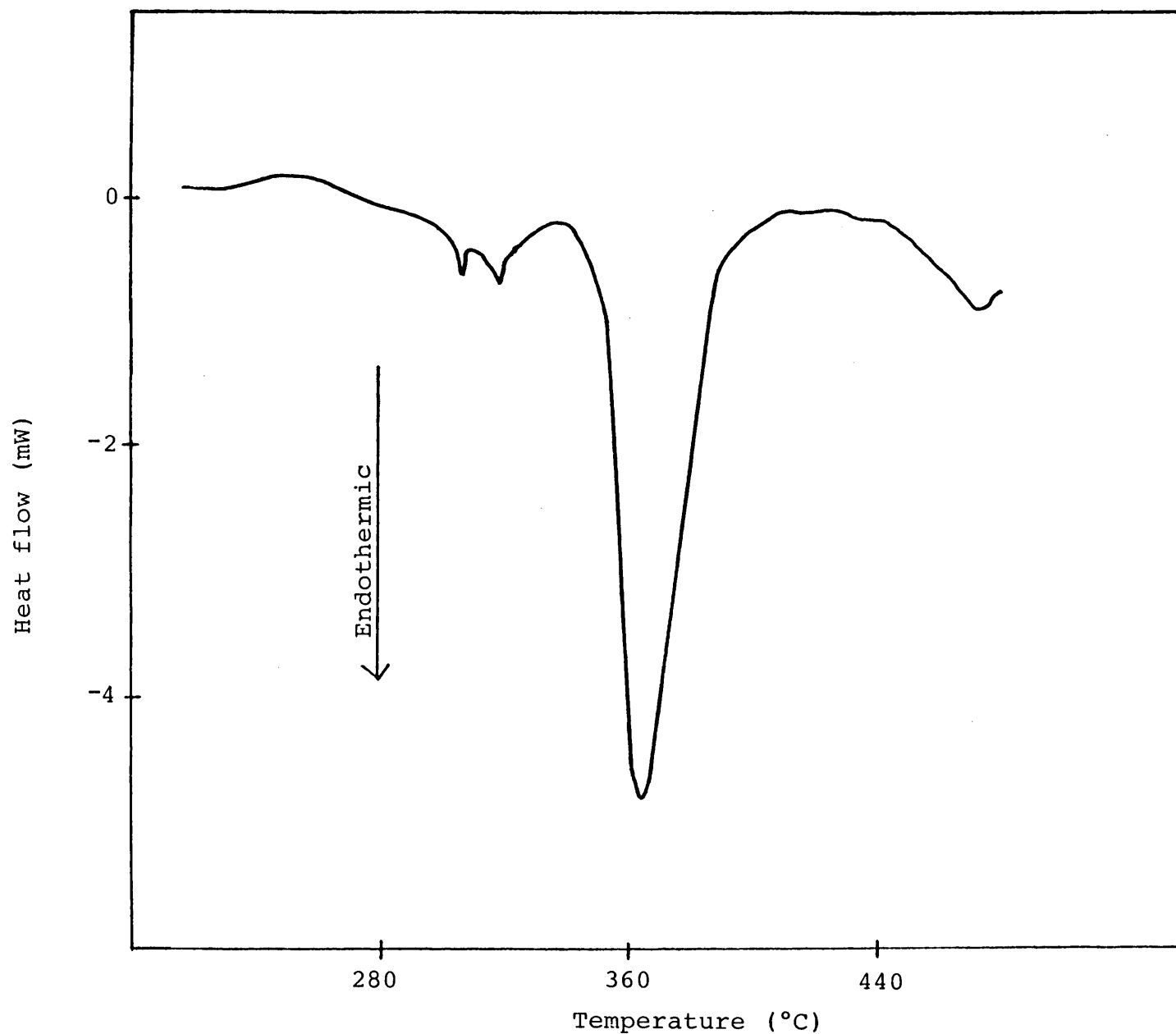


Figure 3.22. DSC curve of the thermal decomposition of $\text{Gd}(\text{NO}_3)_3$ at a pressure of 5×10^3 kPa

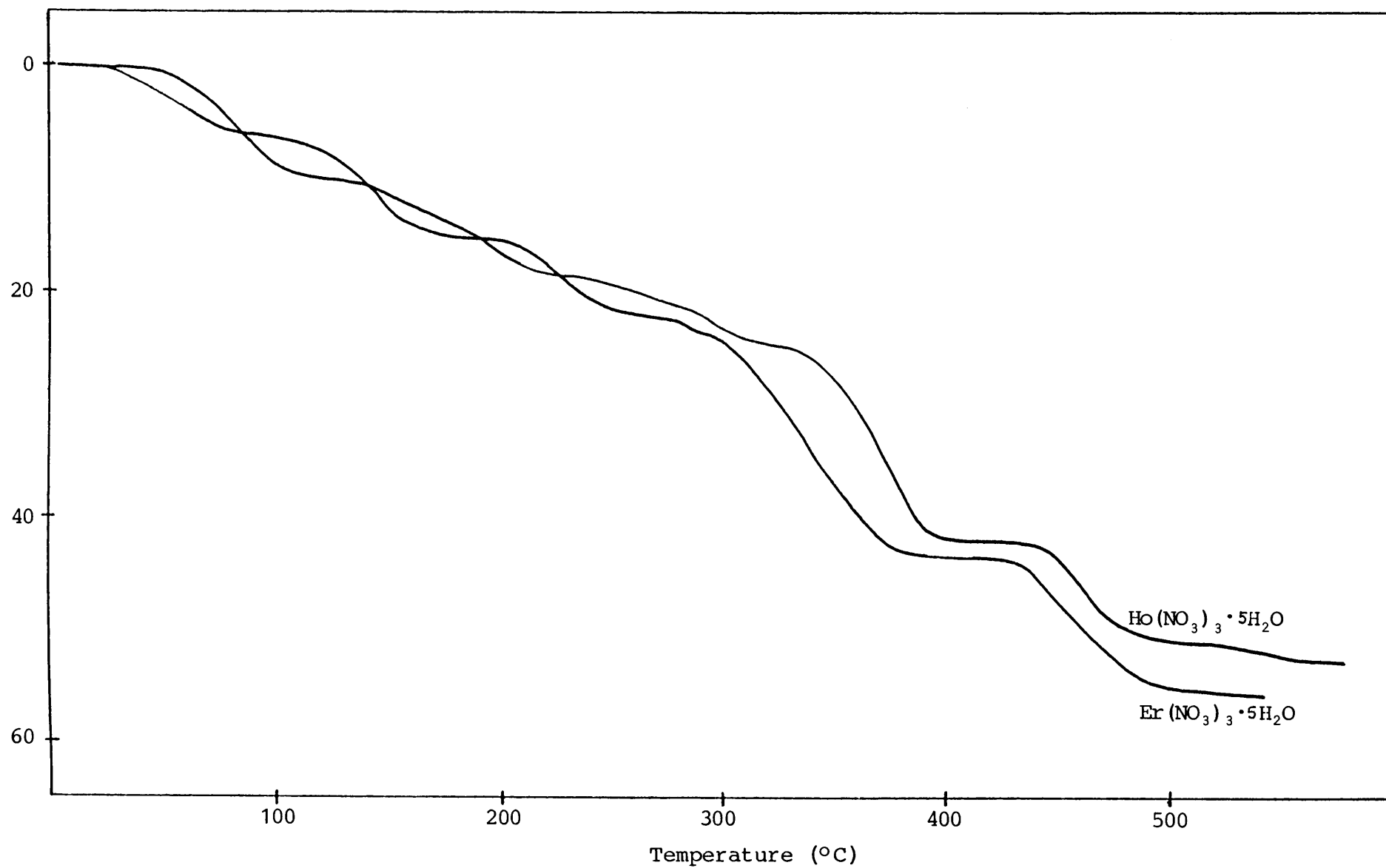


Figure 3.23. TG curve of the thermal decomposition of $\text{Ho}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$

different temperature ranges, different $f(\alpha)$ equations show the best fit. (Table 3.1) (see also paragraph 4.2.3.2).

Table 3.1 Kinetic data for the thermal decomposition reaction of $\text{Ho}(\text{NO}_3)_3$.

Temperature range ($^{\circ}\text{C}$)	Equation	Mathematical form	Activation Energy $\text{kJ}\cdot\text{mol}^{-1}$	$\ln(A/\text{min}^{-1})$
260–285	Avrami-Erofe'ev, $n=1$	$f(\alpha) = -\ln(1-\alpha) = kt$	96,2	15,6
290–305	Avrami-Erofe'ev, $n=\frac{3}{2}$	$f(\alpha) = (-\ln(1-\alpha))^{\frac{2}{3}} = kt$	229,2	43,3
310–330	Contracting volume	$f(\alpha) = 1 - (1-\alpha)^{\frac{1}{3}} = kt$	36,3	2,6
335–345	Avrami-Erofe'ev, $n=\frac{3}{2}$	$f(\alpha) = (-\ln(1-\alpha))^{\frac{2}{3}} = kt$	480,2	91,2
350–375	Avrami-Erofe'ev, $n=2$	$f(\alpha) = (-\ln(1-\alpha))^{\frac{1}{2}} = kt$	102,6	17,8

The Arrhenius plot for the thermal decomposition of $\text{Ho}(\text{NO}_3)_3$ shows five straight lines (figure 3.24). The activation energy values and the $\ln(A/\text{min}^{-1})$ values associated with each straight line, are given in table 3.1.

The DSC curve for the thermal decomposition of $\text{Ho}(\text{NO}_3)_3$ shows a broad peak, consisting of multiple overlapping peaks, suggesting multiple overlapping processes (figure 3.25). The total enthalpy of the decomposition of $\text{Ho}(\text{NO}_3)_3$ to $\text{HoO}(\text{NO}_3)$ and the reversible processes at atmospheric pressure were calculated as $119,9 \text{ kJ}\cdot\text{mol}^{-1}$ $\text{Ho}(\text{NO}_3)_3$. On cooling samples from 300°C , 315°C , 340°C and 360°C , exothermic peaks at

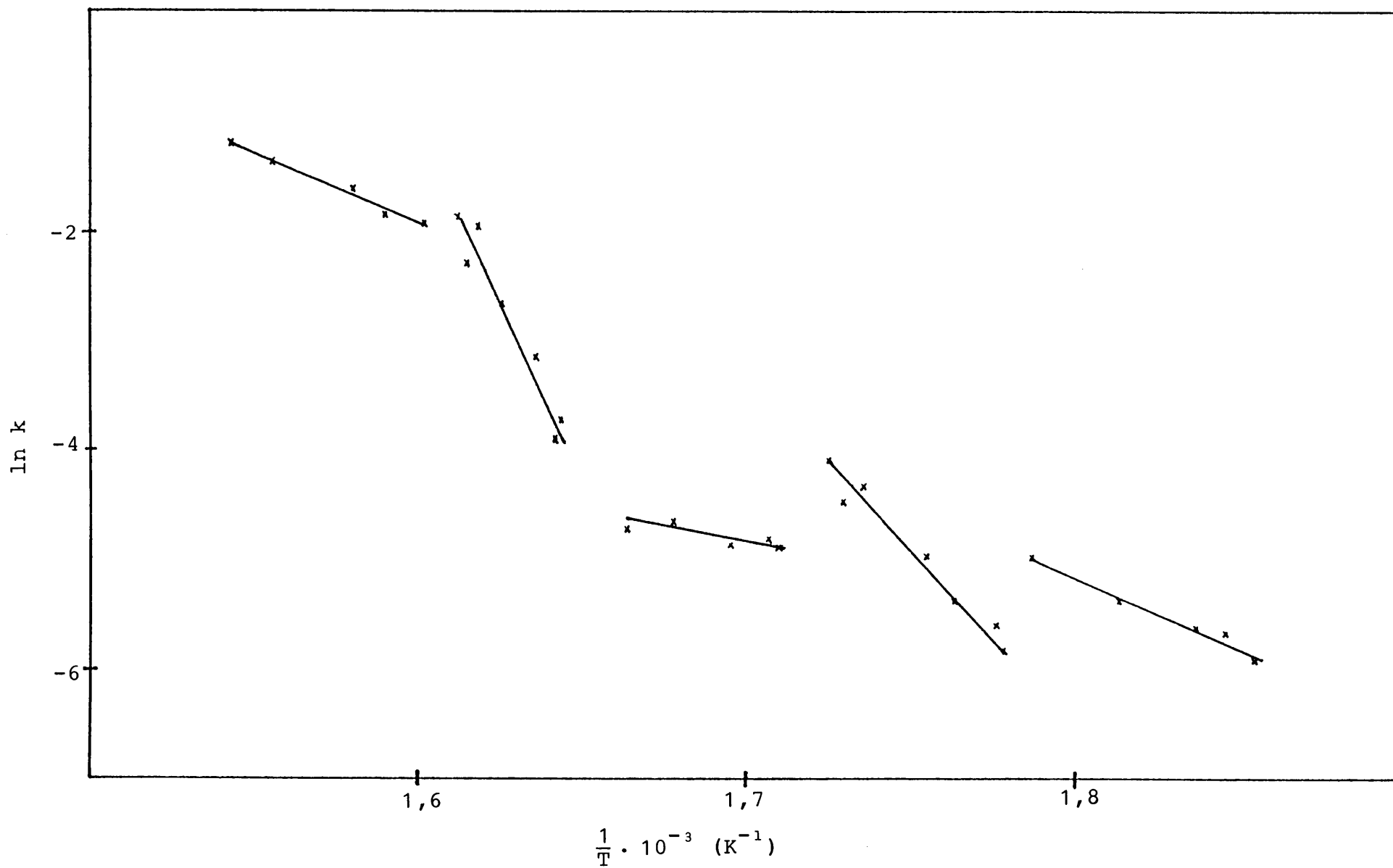


Figure 3.24. Arrhenius plot for the thermal decomposition of $\text{Ho}(\text{NO}_3)_3$

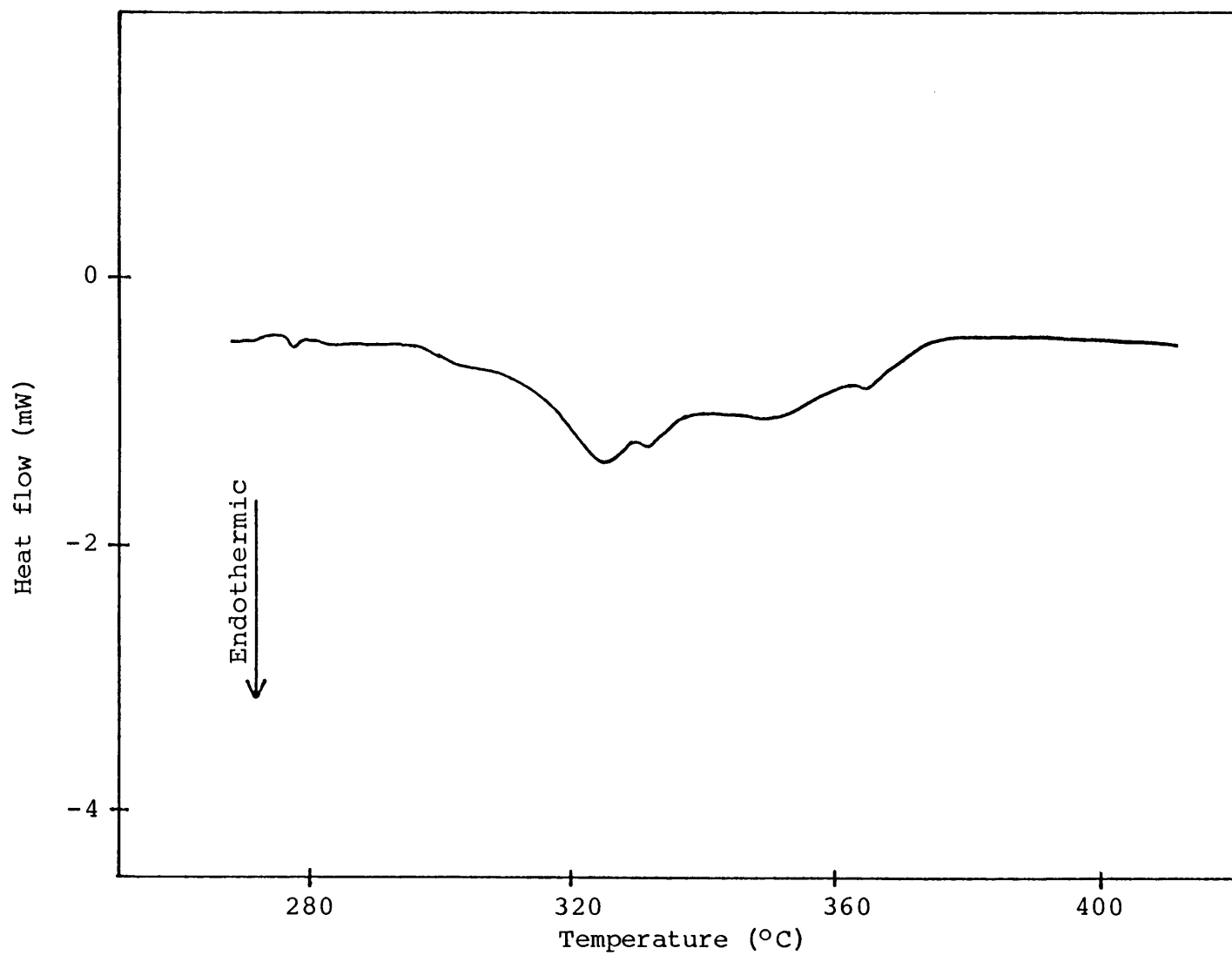


Figure 3.25. DSC curve of the thermal decomposition of $\text{Ho}(\text{NO}_3)_3$

285 °C, 305 °C and 328 °C and an endothermic peak at 345 °C were observed. These four observed reversible processes seem to be responsible for the change in the relationship between the rate constant value and temperature, as is shown in the Arrhenius plot (figure 3.24). These processes also result in a change in the reaction kinetic mechanism at 288 °C, 309 °C, 331 °C and 349 °C.

The DSC curve of the thermal decomposition of $\text{Ho}(\text{NO}_3)_3$ at a pressure of 5×10^3 kPa shows two distinct peaks with maximum values at 341 °C and 384 °C (figure 3.26). Although under atmospheric pressure the oxynitrate starts to decompose above 400 °C, it seems that the second peak is due to the oxynitrate decomposition, probably as a result of a solid state phase of the oxynitrate that enhanced the decomposition reaction. The enthalpy of the decomposition of Holmium-nitrate to its oxynitrate at the pressure of 5×10^3 kPa is calculated to be $60,6 \text{ kJ} \cdot \text{mol}^{-1}$. The higher pressure seems to inhibit the endothermic reversible processes occurring during the decomposition reaction. The enthalpy of the second reaction (decomposition of the oxynitrate) at the pressure of 5×10^3 kPa was calculated to be $67,6 \text{ kJ} \cdot \text{mol}^{-1} \text{ HoO}(\text{NO}_3)$.

3.8 Erbium(III) nitrate

The TG curve of the thermal decomposition of $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ indicates that the decomposition of the dehydrated nitrate starts at 230 °C and is completed at 370 °C, when using a heating rate of $5 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$ (figure 3.23). The oxynitrate

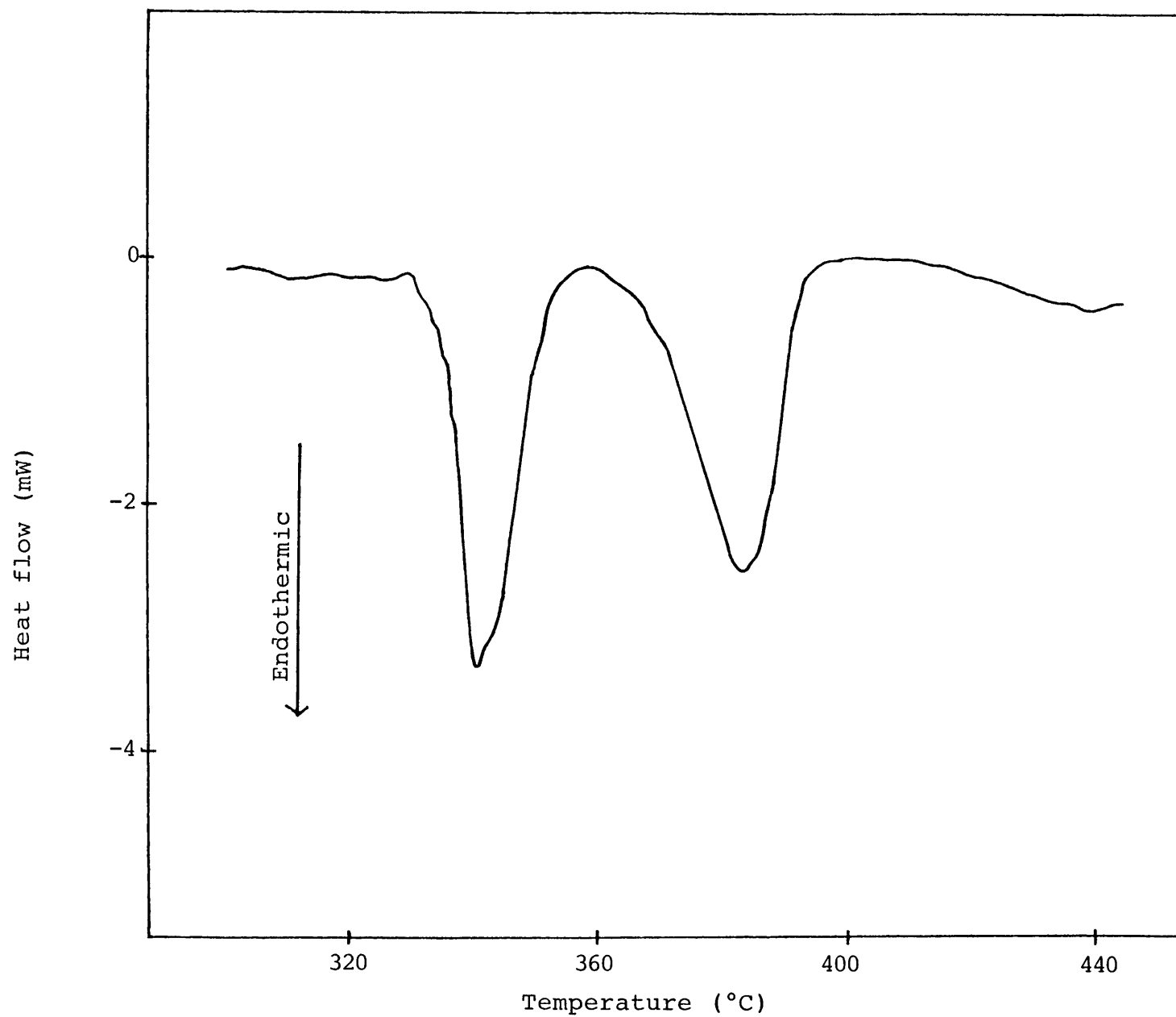
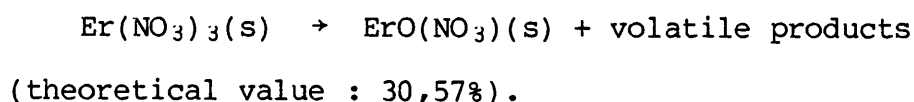


Figure 3.26. DSC curve of the thermal decomposition of $\text{Ho}(\text{NO}_3)_3$ at a pressure of 5×10^3 kPa

starts to decompose at 400 °C, and no interference with the reaction studied, was observed.

A value of 31,0% was observed for the mass loss percentage during the reaction,



Isothermal mass loss curves were recorded at selected temperatures between 250 °C and 370 °C. It was observed that different $f(\alpha)$ equations showed the best fit for the different temperature ranges, as is shown in table 3.2 (see also paragraph 4.2.3.3).

Table 3.2 Kinetic data for the thermal decomposition reaction of $\text{Er}(\text{NO}_3)_3$.

Temperature range (°C)	Equation	Mathematical form	Activation Energy kJ·mol	$\ln(A/\text{min}^{-1})$
250-260	Avrami-Erofe'ev, $n=2$	$f(\alpha) = (-\ln(1-\alpha))^{\frac{1}{2}} = kt$	84,2	12,1
263-278	Avrami-Erofe'ev, $n=1$	$f(\alpha) = -\ln(1-\alpha) = kt$	124,9	22,2
280-290	Avrami-Erofe'ev, $n=4$	$f(\alpha) = (-\ln(1-\alpha))^{\frac{1}{4}} = kt$	486,0	98,3
292-345	Avrami-Erofe'ev, $n=\frac{3}{2}$	$f(\alpha) = (-\ln(1-\alpha))^{\frac{2}{3}} = kt$	155,6	28,5
350-370	Avrami-Erofe'ev, $n=3$	$f(\alpha) = (-\ln(1-\alpha))^{\frac{1}{3}} = kt$	63,2	10,2

The Arrhenius plot for the thermal decomposition of $\text{Er}(\text{NO}_3)_3$ shows five straight lines (figure 3.27). The activation energy values and the $\ln(A/\text{min}^{-1})$ values, associated with each straight line, are given in table 3.2.

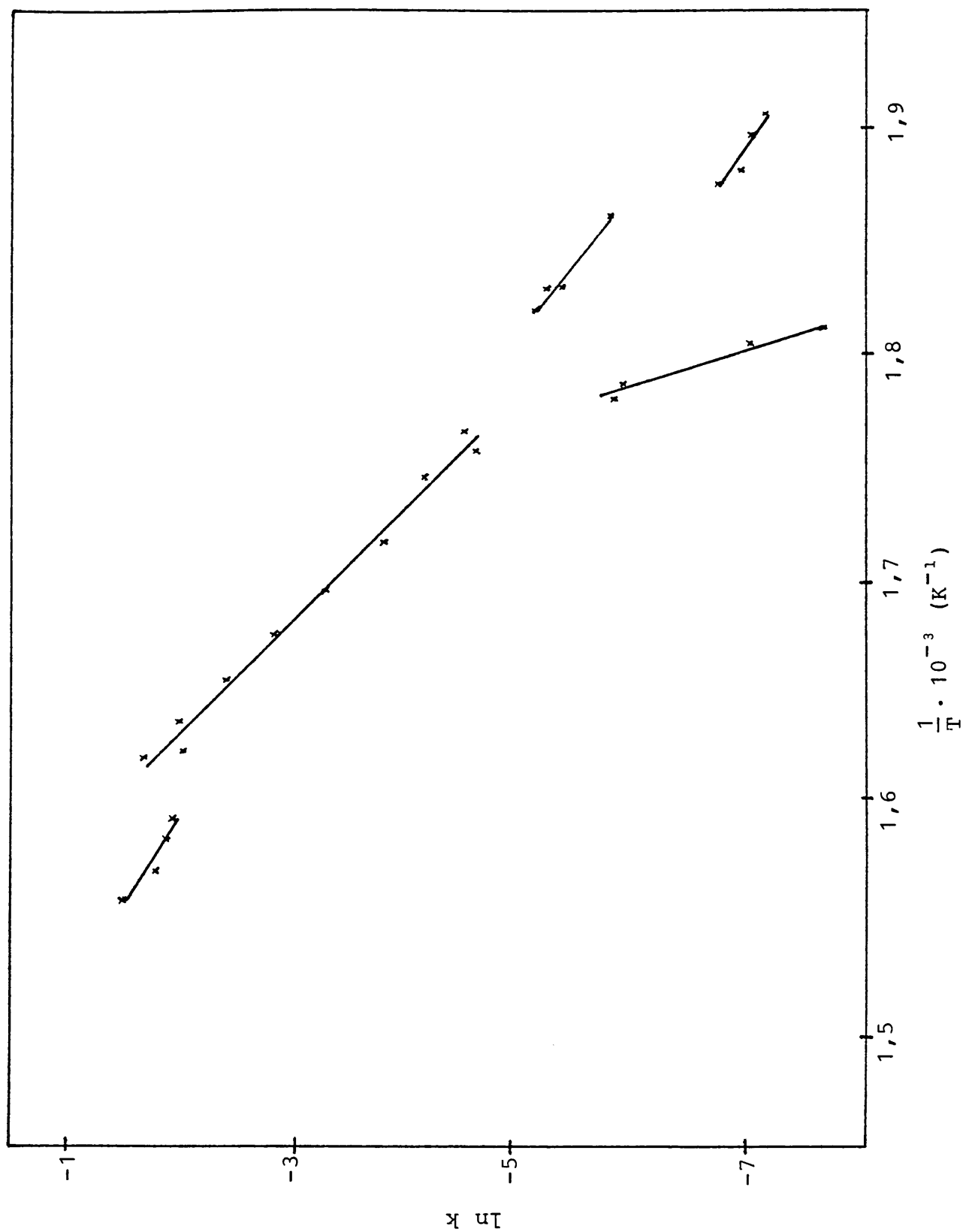


Figure 3.27. Arrhenius plot for the thermal decomposition of $\text{Fe}(\text{NO}_3)_3$.

The DSC curve for the thermal decomposition of $\text{Er}(\text{NO}_3)_3$ shows a broad peak with a maximum at approximately 320°C (figure 3.28), suggesting overlapping processes. The enthalpy for the overall decomposition reaction of $\text{Er}(\text{NO}_3)_3$ to $\text{ErO}(\text{NO}_3)$ amounts to $197,2 \text{ kJ}\cdot\text{mol}^{-1}$. On cooling samples from 270°C , 285°C , 300°C and 360°C , exothermic peaks at 259°C , 275°C , 288°C and 345°C were observed. These four reversible processes seem to be responsible for the change in the rate constant - temperature relationship, as is shown in figure 3.27. These processes seem also to change the reaction kinetic mechanism of the decomposition reaction at 262°C , 278°C , 290°C and 350°C .

The DSC curve of the thermal decomposition of $\text{Er}(\text{NO}_3)_3$ at a pressure of $5 \times 10^3 \text{ kPa}$ shows three peaks with maxima at 318°C , 344°C and 381°C . The first two peaks are small with enthalpy values of $2,3 \text{ kJ}\cdot\text{mol}^{-1} \text{ Er}(\text{NO}_3)_3$ and $8,4 \text{ kJ}\cdot\text{mol}^{-1} \text{ Er}(\text{NO}_3)_3$ respectively. The enthalpy for the decomposition of $\text{Er}(\text{NO}_3)_3$ to its oxynitrate at the pressure of $5 \times 10^3 \text{ kPa}$ is calculated to be $92,7 \text{ kJ}\cdot\text{mol}^{-1} \text{ Er}(\text{NO}_3)_3$. The higher pressure seems to inhibit at least some of the reversible processes, occurring during the decomposition reaction at atmospheric pressure. The decomposition peak is much sharper at this higher pressure than at atmospheric pressure (figures 3.28 and 3.29).

The two small peaks on the DSC curve at 318°C and 344°C seem to be due to some of the reversible processes, but as a result of their small size, it was difficult to obtain

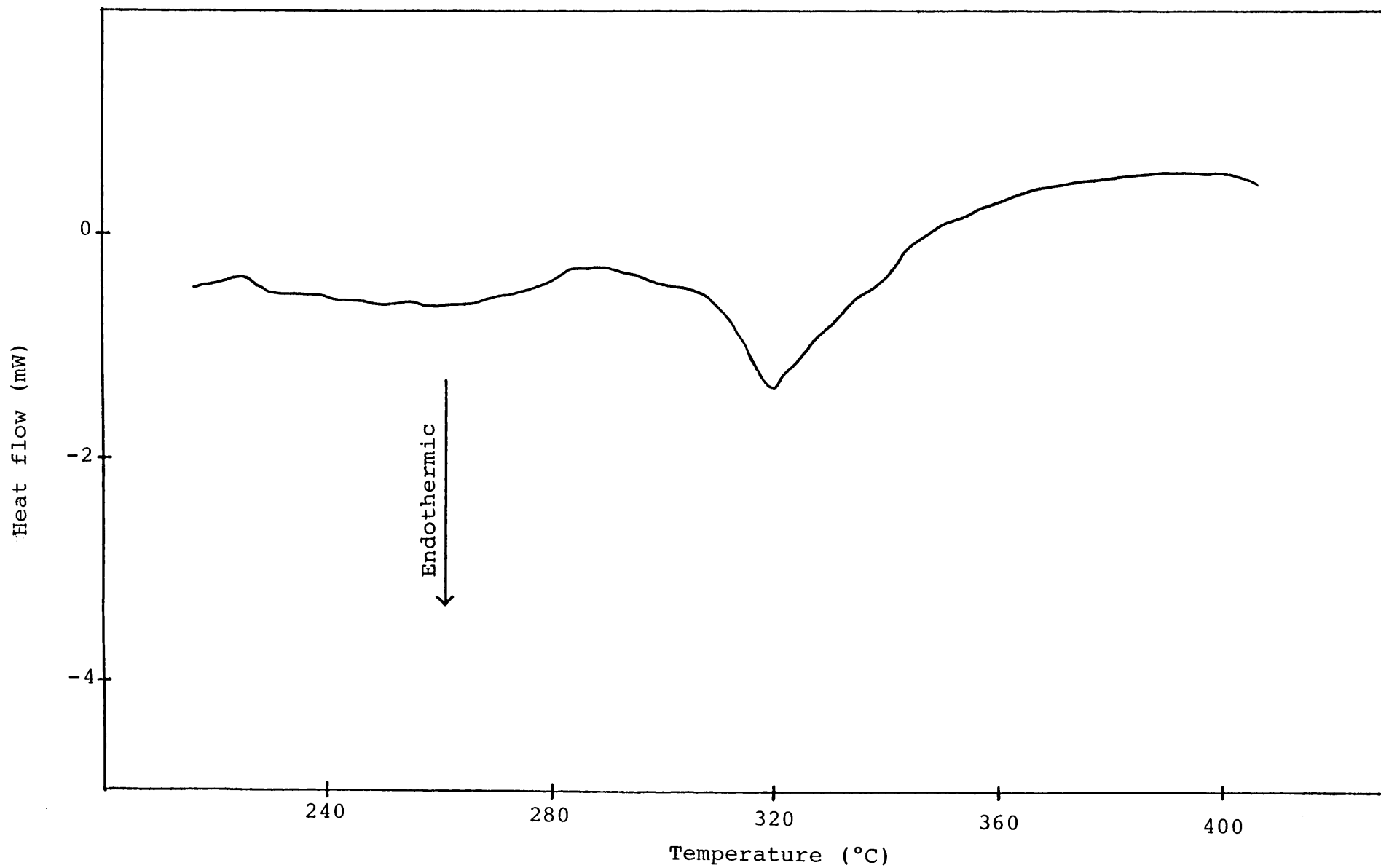


Figure 3.28. DSC curve of the thermal decomposition of $\text{Er}(\text{NO}_3)_3$

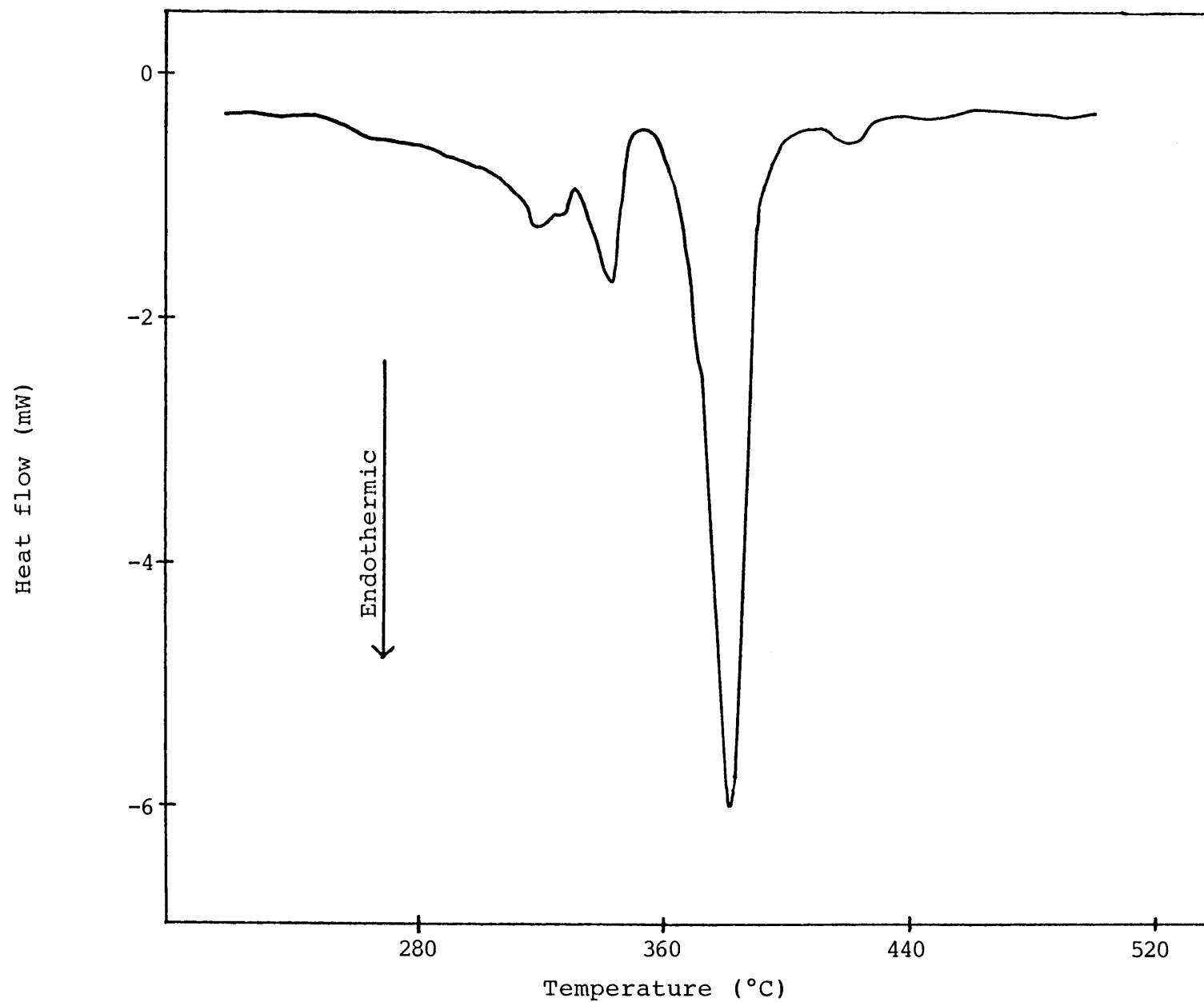


Figure 3.29. DSC curve of the thermal decomposition of $\text{Er}(\text{NO}_3)_3$ at a pressure of 5×10^3 kPa

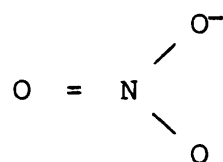
further data on them. On heating a sample to 360 °C at a pressure of 5×10^3 kPa, cooling it to 250 °C and reheating it to 360 °C, these two small peaks become even smaller. This observed tendency could be due to the fact that the reversible processes are not time independent, but require a certain period of time for them to react completely.

CHAPTER 4

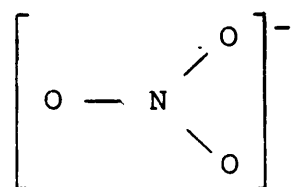
DISCUSSION OF THE RESULTS OF THE STUDIES ON SOME LANTHANIDE NITRATES

4.1 Possible decomposition mechanisms for the nitrate

When considering the nitrate group on its own, it is best written as consisting of one double covalent bond, one single covalent bond and a co-ordination covalent bond [28]:

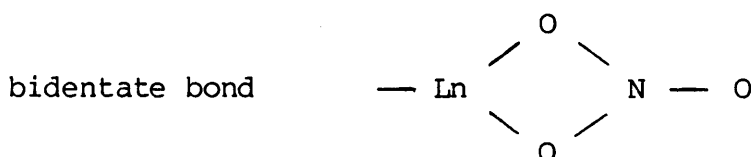
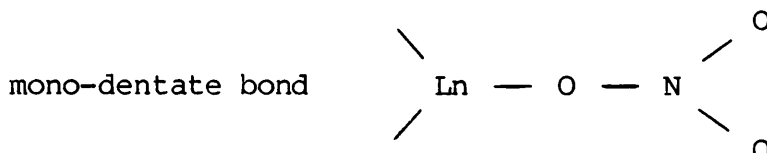


Despite this formalism all bonds in the nitrate ion are equivalent, as charges are delocalized over the whole ion. The nitrate ion is thus rather written as

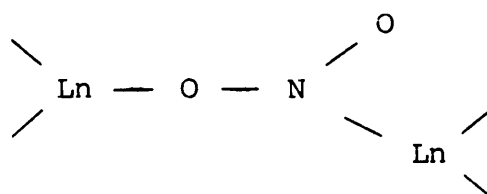


No structures for the anhydrous lanthanide nitrates could be found in the literature. In a study by Vratny and Honig [29], they concluded that praseodymium nitrate may exist in the bridged-nitrate structure, as was found for praseodymium nitrite [30].

Different co-ordination modes for the lanthanide-nitrate bond are possible. Regarding covalent bonds, a mono-dentate, a bidentate or a bridged nitrate-metal bond can exist. In an ionic molecule, the metal ion and nitrate ion will exist as different species.



bridged nitrate-metal bond



Due to the lanthanide contraction it is expected that the molecules at the beginning of the series will have a more ionic character, while those at the end of the series will have a more covalent character.

Considering first the covalent lanthanide nitrate molecules, the following possible mechanisms for decomposition are proposed. Decomposition will occur when a temperature is reached at which rupture of the metal-oxygen link is possible, or at which rupture of the nitrogen-oxygen bond occurs.

If the reaction proceeds by rupture of the N-O bond, this would be followed by rupture of a second Ln-O bond, or else the oxidation state of the lanthanide ion would have to be 4⁺ to accommodate the oxygen atom. If the reaction proceeds via rupture of Ln-O bonds only, the lanthanide ion would have to find an oxygen atom from the surrounding atmosphere. As all reactions proceed in an inert dynamic nitrogen atmosphere, it seems unlikely that this route could be followed.

Rupture of the N-O⁻ and Ln-O bonds result in the formation of NO₃⁻ ions and NO₂ molecules. Thus further decomposition of NO₃⁻ ions and possibly NO₂ molecules have to occur, that is, further rupture of N-O bonds. The nitrate ions decompose to oxygen and a variety of nitrogen oxides. The nitrogen oxides were found to be temperature-dependent and exist as the following molecules at the specified temperatures [1]:

- (i) N₂O₅ is unstable at > 25 °C and reacts to form N₂O₄ or N₂O₃.
- (ii) N₂O₄ dissociates ($\rightleftharpoons$ 2NO₂) with increasing temperature and at 127 °C the partial pressure of N₂O₄ is negligible.
- (iii) N₂O₃ is unstable at > 127 °C, decomposing to NO₂ and NO.
- (iv) NO₂ predominates in the equilibrium

$$\text{NO} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{NO}_2 \text{ up to } 227^\circ\text{C, but at higher temperatures both NO and NO}_2 \text{ are present.}$$

- (v) The rates of decomposition of NO_2 and of NO to N_2 and O_2 are negligible at temperatures $< 727^\circ\text{C}$.

Considering these probable compositions of product mixtures, it seems that during the decomposition of the lanthanide nitrates, both NO and NO_2 form at the experimental temperature.

If the lanthanide nitrates are considered to be totally ionic molecules, decomposition of these compounds has to proceed by overcoming the electrostatic forces between the lanthanide ion and the nitrate ion. The decomposition products are oxynitrate compounds, and it thus seems unlikely that a totally ionic character could exist for the lanthanide nitrates, as oxygen then has to be found from an inert and dynamic atmosphere.

Reactions in which a metal-oxygen link is ruptured depend critically on the size and charge of the metal ion [31]. As it seems that both Ln-O and N-O bonds have to be ruptured during the thermal decomposition of the lanthanide nitrates and considering the fact that the charge on the metal ion remains 3^+ during decomposition (with the exception of cerium), it is proposed that the size of the metal ion contributes to a large extent to the thermal stability of these compounds.

The decomposition of the lanthanide nitrates seems to be complex as it includes a large number of different reactions (rupture of a number of different bonds).

4.2 Kinetic studies

In endothermic solid decompositions, the energy of activation is normally approximately equal to the overall enthalpy change of the reaction if the reactants and products are both in their standard states [32]. As discussed in chapter 1, there are questions about the "per mole" part of the activation energy term. In homogeneous conditions, the order of reaction and the activation energy can be related to collisions between molecules [33]. Redfern defines E in the solid state reaction as the average excess energy a reactant molecule has to possess in order to react [34]. This energy can be obtained from the vibration of an atom or molecule in the lattice, which could, at a certain temperature, provide sufficient energy at a particular point for the reaction to start. This energy term is considered by many to be related to the rupture of chemical bonds [33]. The Arrhenius parameters, activation energy and the pre-exponential term, on the other hand, can be regarded as mathematical parameters describing the reaction and having empirical rather than theoretical significance.

The pre-exponential term in the Arrhenius equation is largely ignored, but it can be used to evaluate the validity of a kinetic model for a certain decomposition reaction. Placing the Polanyi-Wigner equation in the appropriate form of

$$\frac{\delta n}{s \tau_0} e^{-E/RT},$$

it can be directly applied to the motion of interfaces in

solid decompositions [35]. $\frac{n}{s}$ is the density per unit area of reactive molecules, δ_0 the period of one vibration, E the energy of activation and τ_0 the atomic diameter. This equation can only be applied to irreversible reactions and it can be considered as a form of the Arrhenius equation with a better description of the pre-exponential or frequency factor. If the entropy of activation is arbitrarily set to zero, then the frequency factor should be in the range of 10^{11} to 10^{14} [32]. For $\ln A$, these values are between 25 and 33. It was found however, that where the energy of activation exceeds the enthalpy, the frequency factor could range from a few to 22 orders of magnitude from the values of 10^{11} to 10^{14} [36].

Considering the empirical description of the decomposition kinetics of the lanthanide nitrates, (table 4.1), it seems that the data can be divided into three groups. The first group consists of the lanthanide nitrates for which only one kinetic equation was found to be valid during the entire decomposition reaction ($\text{La}(\text{NO}_3)_3$, $\text{Ce}(\text{NO}_3)_3$ and $\text{Pr}(\text{NO}_3)_3$). The second part includes the lanthanide nitrates for which a single reversible reaction causes a change in the activation energy value, but no change of kinetic model describing the decomposition was found ($\text{Nd}(\text{NO}_3)_3$ and $\text{Eu}(\text{NO}_3)_3$). $\text{Gd}(\text{NO}_3)_3$, $\text{Ho}(\text{NO}_3)_3$ and $\text{Er}(\text{NO}_3)_3$ form the last group for which different kinetic models describe the decompositions in different temperature ranges. The kinetic studies on the lanthanide nitrates will be discussed according to these three groups.

Table 4.1 The kinetic equations, with their Arrhenius energy parameters, that best fit in the different temperature ranges.

Lanthanide nitrate	Temperature range* (°C)	Kinetic equation	Activation energy (kJ·mol ⁻¹)	Pre-exponential factor ln(A/min ⁻¹)
La(NO ₃) ₃	360 - 410	$f(\alpha) = 1 - (1 - \alpha)^{1/2}$	226,8	35,5
Ce(NO ₃) ₃	230 - 360	$f(\alpha) = \frac{1}{1 - \alpha} - 1$	104,0	21,7
Pr(NO ₃) ₃	350 - 400	$f(\alpha) = 1 - (1 - \alpha)^{1/3}$	206,8	32,3
Nd(NO ₃) ₃	350 - 390	$f(\alpha) = 1 - \frac{2\alpha}{3} - (1 - \alpha)^{2/3}$	805,0	161,5
	395 - 420	$f(\alpha) = 1 - \frac{2\alpha}{3} - (1 - \alpha)^{2/3}$	165,4	26,1
Eu(NO ₃) ₃	310 - 350	$f(\alpha) = (-\ln(1 - \alpha))^{2/3}$	189,6	32,3
	355 - 400	$f(\alpha) = (-\ln(1 - \alpha))^{2/3}$	139,9	24,3
Gd(NO ₃) ₃	270 - 315	$f(\alpha) = (-\ln(1 - \alpha))^{1/2}$	82,7	10,9
	320 - 385	$f(\alpha) = (-\ln(1 - \alpha))^{2/3}$	243,2	43,2
	390 - 410	$f(\alpha) = \ln\left(\frac{\alpha}{1 - \alpha}\right)$	99,5	17,8
Ho(NO ₃) ₃	260 - 285	$f(\alpha) = -\ln(1 - \alpha)$	96,2	15,6
	290 - 305	$f(\alpha) = (-\ln(1 - \alpha))^{2/3}$	229,2	43,3
	310 - 330	$f(\alpha) = 1 - (1 - \alpha)^{1/3}$	36,3	2,6
	335 - 345	$f(\alpha) = (-\ln(1 - \alpha))^{2/3}$	480,2	91,2
	350 - 375	$f(\alpha) = (-\ln(1 - \alpha))^{1/2}$	102,6	17,8
Er(NO ₃) ₃	250 - 260	$f(\alpha) = (-\ln(1 - \alpha))^{1/2}$	84,2	12,1
	263 - 278	$f(\alpha) = -\ln(1 - \alpha)$	124,9	22,2
	280 - 290	$f(\alpha) = (-\ln(1 - \alpha))^{1/4}$	486,0	98,3
	292 - 345	$f(\alpha) = (-\ln(1 - \alpha))^{2/3}$	155,6	28,5
	350 - 370	$f(\alpha) = (-\ln(1 - \alpha))^{1/3}$	63,2	10,2

* The temperature range is the range for which the given kinetic equation is valid.

4.2.1 Group 1: $\text{La}(\text{NO}_3)_3$, $\text{Ce}(\text{NO}_3)_3$ and $\text{Pr}(\text{NO}_3)_3$

4.2.1.1 $\text{La}(\text{NO}_3)_3$

For the thermal decomposition of $\text{La}(\text{NO}_3)_3$ to $\text{LaO}(\text{NO}_3)$ the contracting area kinetic model ($kt = 1 - (1 - \alpha)^{\frac{1}{2}}$) showed the best average correlation coefficient value of 0,998. The next best fit was found to be for the contracting volume kinetic model ($kt = 1 - (1 - \alpha)^{\frac{1}{3}}$) with an average correlation coefficient value of 0,991. These values are close to one another and it becomes difficult to decide on a specific model.

Another method of determining which kinetic model best describes experimental data, is the reduced time plots developed by Sharp [37]. The kinetic relationship, $F(\alpha) = kt$, is altered so that the function $F(\alpha)$ becomes:

$$F(\alpha) = A \left(\frac{t}{t_{0,5}} \right),$$

where $t_{0,5}$ is the time for 50% reaction and A is a calculable constant depending on the form of $F(\alpha)$. For the contracting area equation the function $F(\alpha)$ becomes:

$$F(\alpha) = 0,2929 \frac{t}{t_{0,5}} \quad \text{and for the con-}$$

tracting volume equation it is derived as

$$F(\alpha) = 0,2063 \frac{t}{t_{0,5}} \quad [33].$$

Using tabulated values of $F(\alpha)$ for various steps of α , another table is constructed containing various values of $\frac{t}{t_{0,5}}$ against α values [33]. A master plot of these theoretical values is constructed on this reduced time scale. To establish which mechanism is being followed,

the master plot for the theoretical expressions is merely superimposed over the common reduced time plot obtained experimentally and through observation, the theoretical expression that fits the experimental data most closely, is selected. Theoretical values for the reduced time plots for the contracting area and contracting volume kinetic models are shown in figure 4.1, as well as the experimental data for this plot. According to this plot the contracting area kinetic model is the best fit for the kinetics of the decomposition of $\text{La}(\text{NO}_3)_3$, as is also suggested by the least square analysis.

A reason for the good fit of both the contracting area and contracting volume kinetic models could be the fact that the crystals were ground to a fine powder prior to heating. It is well-known that the preparation of a solid plays an extremely important role in the kinetics of its decomposition reactions [32].

Comparing the activation energy for the decomposition of $\text{La}(\text{NO}_3)_3$ ($226,8 \text{ kJ}\cdot\text{mol}^{-1}$) to the enthalpy value of $123,4 \text{ kJ}\cdot\text{mol}^{-1}$, it seems that the activation energy is a factor of two bigger than the enthalpy value. The "per mole" part of the activation energy value could thus actually be "per two moles" of the activated complex, giving a value of $113,4 \text{ kJ}$ for one mole.

The frequency factor determined for the thermal decomposition of $\text{La}(\text{NO}_3)_3$ ($\ln A = 35,5$) is approximately one

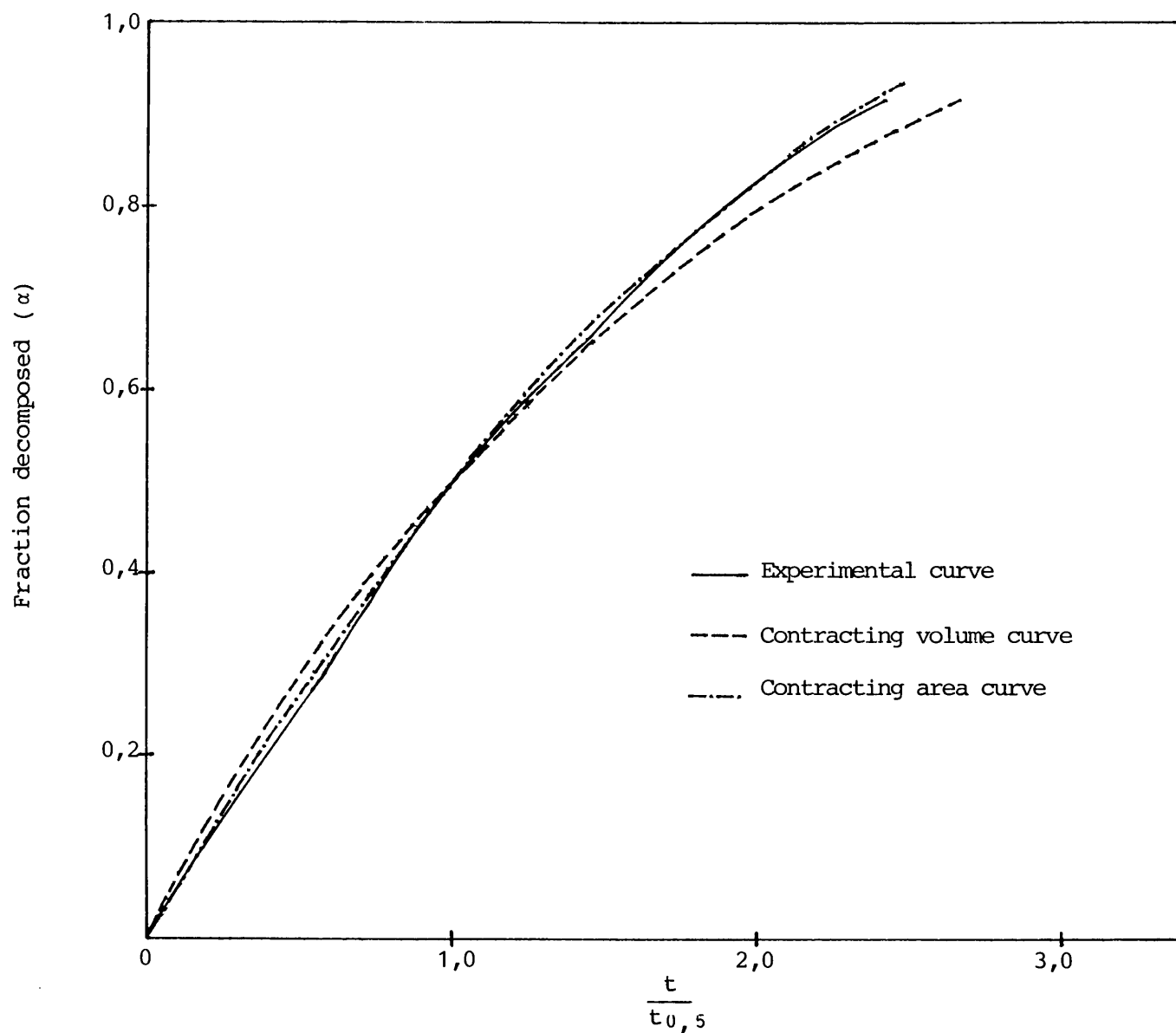


Figure 4.1 Reduced time plots for the thermal decomposition of $\text{La}(\text{NO}_3)_3$

order of magnitude bigger than 10^{14} . As the calculated activation energy value also exceeds the enthalpy value and the pre-exponential factor is only one order of magnitude too big, the value of the frequency factor was considered to be acceptable. This also implies that the chosen kinetic model (contracting area model) for this decomposition reaction, seems to be correct.

4.2.1.2 Ce(NO₃)₃

It is important to note that in contrast to the thermal decomposition of all the other lanthanide nitrates which were studied, ceriumnitrate undergoes an additional redox reaction together with the breaking of the N-O and Ln-O bonds as described earlier. Decomposition also proceeds to the oxide and not the oxynitrate. The cerium ion is oxidised from the 3+ to the 4+ oxidation state. Although this decomposition includes a redox reaction, the overall reaction still is endothermic, and not exothermic as was found for the decomposition of the uranium(IV)nitrates to the uranyl nitrates (see later).

The correlation coefficient value calculated for the decomposition data's fit to the second order kinetic model ($kt = \frac{1}{1-\alpha} - 1$) amounted to an average of 0,979. The third order kinetic model ($kt = (\frac{1}{1-\alpha})^{0,5} - 1$) showed the next best fit, but with an average correlation coefficient value of 0,833. This much lower correlation coefficient value implies that the second order kinetic model

certainly gives the best description of the kinetics of the thermal decomposition of $\text{Ce}(\text{NO}_3)_3$.

The activation energy for the thermal decomposition of $\text{Ce}(\text{NO}_3)_3$ ($111,1 \text{ kJ}\cdot\text{mol}^{-1}$) is approximately the same as the enthalpy value ($104,0 \text{ kJ}\cdot\text{mol}^{-1}$). The frequency factor ($\ln A = 21,7$), calculated for the second order kinetic model, is just lower than the lowest value ($\ln A = 25$) as proposed by Bradley [35]. The value was not considered to be low enough to contradict the chosen kinetic model.

4.2.1.3 $\text{Pr}(\text{NO}_3)_3$

Vratny and Honig postulated that the thermal decomposition of praseodymium nitrate proceeds via an intermediate nitrite structure [29]. Patil and co-workers later showed that this could not be possible and that decomposition proceeds directly to an oxynitrate structure [7]. According to the TG trace of the thermal decomposition of $\text{Pr}(\text{NO}_3)_3$ (figure 3.9) no intermediate nitrite structure is formed.

For the thermal decomposition of $\text{Pr}(\text{NO}_3)_3$, it was found that the contracting volume equation, $(kt = 1 - (1 - \alpha)^{\frac{1}{3}})$, describes the decomposition kinetics best, as an average correlation coefficient value of 0,994 was observed for the plots of $f(\alpha_i)$ against time. The next best fit is the contracting area kinetic model, $(kt = 1 - (1 - \alpha)^{\frac{1}{2}})$, with

an average correlation coefficient of 0,914, well below the value of 0,994 for the contracting volume equation.

An activation energy value of $206,8 \text{ kJ}\cdot\text{mol}^{-1}$ was calculated and found to be twice the enthalpy value ($102,6 \text{ kJ}\cdot\text{mol}^{-1}$). It seems that, as was the case for $\text{La}(\text{NO}_3)_3$, the "per mole" part of the activation energy value actually should be "per two moles" of the activated complex. The kinetic models that describe the decomposition kinetics of $\text{La}(\text{NO}_3)_3$ and $\text{Pr}(\text{NO}_3)_3$ are closely related to one other, i.e. the contracting area and contracting volume models.

The pre-exponential factor (32,3), calculated from the Arrhenius plot, for the thermal decomposition of $\text{Pr}(\text{NO}_3)_3$, is found to be in the range (25 - 33) of valid values proposed earlier.

4.2.2 Group 2: $\text{Nd}(\text{NO}_3)_3$ and $\text{Eu}(\text{NO}_3)_3$

4.2.2.1 $\text{Nd}(\text{NO}_3)_3$

The Ginstling-Brounshtein equation, $1 - \frac{2\alpha}{3} - (1-\alpha)^{\frac{2}{3}} = kt$, showed the best fit for the experimental decomposition data of $\text{Nd}(\text{NO}_3)_3$ with an average correlation coefficient value of 0,996. Three other functions, however, also seem to describe the experimental data. They are the contracting area equation ($kt = 1 - (1-\alpha)^{\frac{1}{3}}$), with an average correlation coefficient value of 0,995; the Avrami-

Erofe'ev equation, $kt = (-\ln(1-\alpha))^{0,67}$ (correlation coefficient = 0,991) and the two-dimensional diffusion equation, $kt = (1-\alpha)\ln(1-\alpha)+\alpha$ (correlation coefficient = 0,994). In figure 4.2 the reduced time plots for these four equations, as well as for two sets of experimental data values are given. From the plot it is clear that the Avrami-Erofe'ev equation certainly is not a good fit to the experimental data. In fact, it seems that none of these four equations really gives a description of the decomposition kinetics. It seems that all these equations could be mathematical means of describing a reaction which has empirical rather than theoretical significance.

The activation energy parameters and frequency factors, calculated from the three functions that showed the best fit to the experimental data, are given in table 4.2. Considering that experimental errors are involved, the activation energy and frequency factor values above

Table 4.2 Arrhenius parameters for the thermal decomposition of $\text{Nd}(\text{NO}_3)_3$.

Kinetic model	< 390 °C		> 390 °C	
	E (kJ·mol ⁻¹)	ln(A/min ⁻¹)	E (kJ·mol ⁻¹)	ln(A/min ⁻¹)
Ginstling-Brounshtein $kt = 1 - \frac{2}{3}\alpha - (1-\alpha)^{2/3}$	805,0	161,5	165,4	26,1
Contracting area $kt = 1 - (1-\alpha)^{1/3}$	892,2	158,6	161,8	26,0
Two-dimensional diffusion $kt = (1-\alpha)\ln(1-\alpha)+\alpha$	742,0	131,0	161,4	26,3

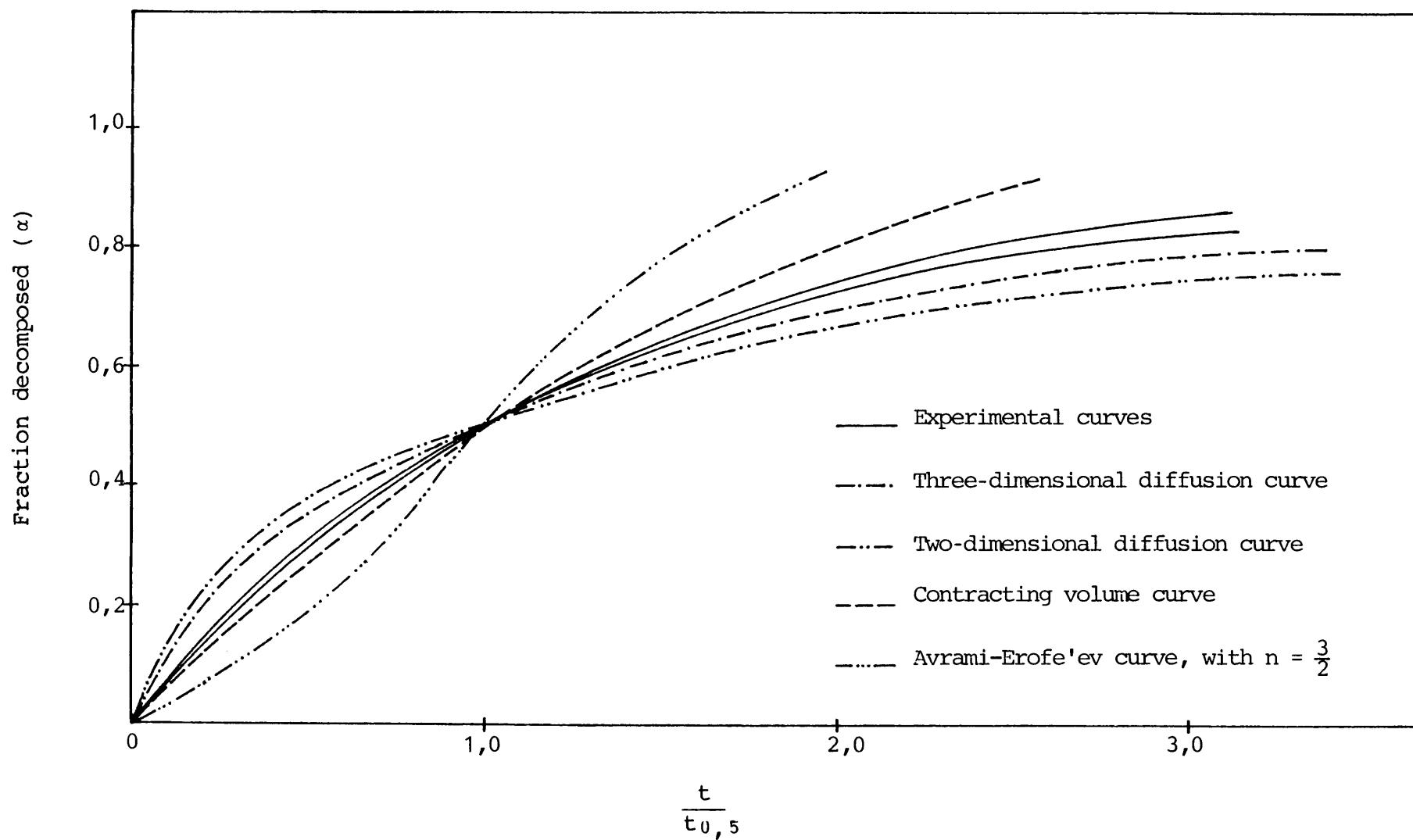


Figure 4.2 Reduced time plots for the thermal decomposition of $\text{Nd}(\text{NO}_3)_3$

390 °C are the same. Below 390 °C the same approximation can be made, as fewer experimental data values are available. Measurements in that temperature range also show a greater tendency towards experimental error, due to the long decomposition reactions (up to 50 hours). It seems that any mathematical equation, $F(\alpha) = kt$, that gives a linear description of the decomposition data, can be used to determine the activation energy and frequency factor values. These values seem to be independent of a kinetic model.

A comparison between the two activation energy values, calculated for the two temperature ranges, and the enthalpy value ($109,6 \text{ kJ}\cdot\text{mol}^{-1}$) is not possible. For a one-step nucleation reaction, that is the generation of a single molecule or atom of product that constitutes the establishment of a nucleus, the generalized equation

$$\frac{d\alpha}{dt} = kt \quad \text{can be applied [1].}$$

Assuming that all solid state decomposition reactions start with a nucleation process, it is possible to apply the given equation to the experimental data for which $\alpha < 0,1$. An activation energy value for this nucleation step can then be calculated from an Arrhenius plot. Applying this equation to the experimental decomposition data of $\text{Nd}(\text{NO}_3)_3$, a value of $221,6 \text{ kJ}\cdot\text{mol}^{-1}$ for the activation energy is observed. Again this activation energy value is approximately twice the enthalpy value ($109,6 \text{ kJ}\cdot\text{mol}^{-1}$) and the activation energy term could be "per two moles" of activated complex.

Using the method described in the previous paragraph, a frequency factor of $3,9 \times 10^{16}$ ($\ln A = 38,2$) is calculated. The frequency factors in table 4.2 at temperatures below 390°C are all extremely high, as are the activation energy values, thus the applicability of the kinetic models again is questioned. The frequency factors in table 4.2 at temperatures above 390°C are within the range of values given for valid frequency factor values ($\ln A = 25$ to 33).

4.2.2.2 Eu(NO₃)₃

The Avrami-Erofe'ev equation, with $n = \frac{3}{2}$, $kt = (-\ln(1-\alpha))^{\frac{2}{3}}$ with a correlation coefficient value of 0,993, showed the best fit to the experimental data. The Avrami-Erofe'ev equation, with $n = 1$, $kt = -\ln(1-\alpha)$, and the Avrami-Erofe'ev equation, with $n = 2$, $kt = (-\ln(1-\alpha))^{\frac{1}{2}}$, respectively, gave correlation coefficient values of 0,976 and 0,941. It seems therefore as though the experimental data conforms to the Avrami-Erofe'ev equation, with $n = \frac{3}{2}$.

Comparing the activation energy values in the two temperature ranges, with the experimentally determined enthalpy value, again proved to be difficult. Although the two values of $139,9 \text{ kJ}\cdot\text{mol}^{-1}$ below 400°C and $189,6 \text{ kJ}\cdot\text{mol}^{-1}$ above 400°C are of the same order of magnitude as the enthalpy ($119,6 \text{ kJ}\cdot\text{mol}^{-1}$), the method of determining activation energy for the nucleation process (paragraph 4.2.2.1) could give a better approximation of the real

value. From the rate constants calculated for the equation, $\frac{d\alpha}{dt} = kt$, an activation energy of $233,3 \text{ kJ}\cdot\text{mol}^{-1}$ is determined. This value is approximately twice the enthalpy value ($119,6 \text{ kJ}\cdot\text{mol}^{-1}$), which could again imply that two moles of activated complex are involved during the nucleation process.

The frequency factors calculated in the two temperature ranges, $\ln A = 24,3$ below 400°C and $\ln A = 32,3$ above 400°C , compare well with the proposed range of valid frequency factor values ($\ln A = 25$ to 33).

The thermal decomposition of $\text{Nd}(\text{NO}_3)_3$ and $\text{Eu}(\text{NO}_3)_3$ show the same trend, that is, a single mathematical equation describes the decomposition data over the whole decomposition temperature range. The single reversible process, (see later) that occurred during each decomposition, did not change this mathematical description, but only the gradient of the Arrhenius plot for each compound, resulting in different activation energy and frequency factor values.

4.2.3 Group 3: $\text{Gd}(\text{NO}_3)_3$, $\text{Ho}(\text{NO}_3)_3$ and $\text{Er}(\text{NO}_3)_3$

4.2.3.1 $\text{Gd}(\text{NO}_3)_3$

Table 4.3 summarizes the kinetic models which are applicable to the decomposition of $\text{Gd}(\text{NO}_3)_3$ in the different temperature ranges.

Table 4.3. Kinetic models describing the thermal decomposition of $Gd(NO_3)_3$

Temperature range ($^{\circ}C$)	Kinetic model	Correlation coefficient
270 - 315	Avrami-Erofe'ev ($n = 2$)	0,999
	Avrami-Erofe'ev ($n = 3$)	0,997
	Avrami-Erofe'ev ($n = \frac{3}{2}$)	0,995
	Avrami-Erofe'ev ($n = 4$)	0,995
320 - 385	Avrami-Erofe'ev ($n = \frac{3}{2}$)	0,996
	Avrami-Erofe'ev ($n = 2$)	0,993
	Avrami-Erofe'ev ($n = 3$)	0,983
	Avrami-Erofe'ev ($n = 4$)	0,981
390 - 410	Prout-Tompkins	0,996
	Avrami-Erofe'ev ($n = 4$)	0,993
	Avrami-Erofe'ev ($n = 2$)	0,991
	Avrami-Erofe'ev ($n = 3$)	0,990
	Avrami-Erofe'ev ($n = \frac{3}{2}$)	0,981

It proved difficult to decide on an equation which describes the decomposition data, as in all cases the average correlation coefficient values are very close to each other.

To evaluate the validity of the equations, the activation energy and frequency factor values for the Avrami-

Erofe'ev equation, with $n = 2$, were calculated in all temperature ranges and compared to the values determined from the equation that best fitted in the different temperature ranges. Table 4.4 gives a summary of these values. The Avrami-Erofe'ev equation, with $n = 2$, was chosen to determine the Arrhenius parameters in all temperature ranges, as it seemed to be a relatively good fit in all the ranges.

Table 4.4. Activation energy and frequency factors for the thermal decomposition of $Gd(NO_3)_3$

Temperature range ($^{\circ}C$)	Kinetic model	Activation energy ($kJ \cdot mol^{-1}$)	Frequency factor ($\ln(A/min^{-1})$)
270 - 315	Avrami-Erofe'ev ($n = 2$) (best fit)	82,7	10,9
320 - 385	Avrami-Erofe'ev ($n = \frac{3}{2}$) (best fit)	259,0	46,0
	Avrami-Erofe'ev ($n = 2$)	243,2	43,2
390 - 410	Prout-Tompkins (best fit)	104,2	17,3
	Avrami-Erofe'ev ($n = 2$)	99,5	17,8

Taking into consideration the error due to experimental measurements, the activation energy values and frequency factors are the same for the different kinetic models in the three temperature ranges. It seems that any $F(\alpha)$ equation, written in a linear form, $F(\alpha) = kt$, can be

used to calculate the activation energy and frequency factor for a reaction. These two Arrhenius parameters seem to be independent of the mathematical equation describing the reaction.

The method of determining activation energy from the nucleation step data, was again applied. The value of $59,7 \text{ kJ}\cdot\text{mol}^{-1}$ for activation energy is approximately half the enthalpy value of $95,2 \text{ kJ}\cdot\text{mol}^{-1}$. The "per mole" part of the activation energy term in this case, could be "per a half mole" of activated complex. Using this method a value of 7,7 was calculated for the frequency factor, $\ln A$. This frequency factor value is, compared to the proposed frequency factor range ($\ln A = 25 - 33$), far too low, as was the activation energy value. If the activation energy is corrected to one mole of activated complex, thus $119,4 \text{ kJ}\cdot\text{mol}^{-1}$, and this value is used to determine the pre-exponential factor, using the sets of experimental data values (k and T), an average frequency factor of 19,9 results. This value is also lower than the lower limit (25) for the proposed valid frequency factor values. It should, however, be borne in mind that this method of using the Arrhenius parameters, calculated from the nucleation step, gives only an approximation of these values.

4.2.3.2 Ho(NO₃)₃

The kinetic models, with their correlation coefficient values, which show the best fits in the different temperature ranges are given in table 4.5.

Table 4.5. Kinetic models that fit the decomposition data of $\text{Ho}(\text{NO}_3)_3$ best

Temperature range ($^{\circ}\text{C}$)	Kinetic model	Correlation coefficient
260 - 285	Avrami-Erofe'ev, $n = 1$	0,995
	Avrami-Erofe'ev, $n = \frac{3}{2}$	0,991
	Avrami-Erofe'ev, $n = 2$	0,990
290 - 305	Avrami-Erofe'ev, $n = \frac{3}{2}$	0,998
	Contracting volume	0,995
	Avrami-Erofe'ev, $n = 1$	0,993
310 - 330	Contracting volume	0,997
	Avrami-Erofe'ev, $n = 2$	0,994
	Avrami-Erofe'ev, $n = \frac{3}{2}$	0,994
	Avrami-Erofe'ev, $n = 1$	0,989
335 - 345	Avrami-Erofe'ev, $n = \frac{3}{2}$	0,993
	Avrami-Erofe'ev, $n = 2$	0,991
	Contracting volume	0,990
350 - 375	Avrami-Erofe'ev, $n = 2$	0,998
	Avrami-Erofe'ev, $n = \frac{3}{2}$	0,994
	Avrami-Erofe'ev, $n = 3$	0,993

All the correlation coefficient values are close to each other and it proved difficult to decide on a kinetic

model. Nevertheless it was found that the model that gave the best fit in a temperature range, showed the highest correlation coefficient values at all the experimental temperatures in that range.

To evaluate the validity of these kinetic models, the activation energies and pre-exponential factors were determined using the Avrami-Erofe'ev equation, with $n = 1$, for all the temperature ranges. These values are summarized in table 4.6.

Table 4.6. Arrhenius parameters for the thermal decomposition of $\text{Ho}(\text{NO}_3)_3$ using the Avrami-Erofe'ev ($n = 1$) equation

Temperature range ($^{\circ}\text{C}$)	Kinetic model	Activation energy ($\text{kJ}\cdot\text{mol}^{-1}$)	Frequency factor ($\ln(\text{A}/\text{min}^{-1})$)
260 - 285	Avrami-Erofe'ev, $n = 1$	96,2	15,6
290 - 305	Avrami-Erofe'ev, $n = 1$	269,3	52,1
	Avrami-Erofe'ev, $n = \frac{3}{2}$ (best fit)	229,2	43,3
310 - 330	Avrami-Erofe'ev, $n = 1$	32,0	3,4
	Contracting volume (best fit)	36,3	2,6
335 - 345	Avrami-Erofe'ev, $n = 1$	476,1	91,1
	Avrami-Erofe'ev, $n = \frac{3}{2}$ (best fit)	480,2	91,2
350 - 375	Avrami-Erofe'ev, $n = 1$	104,3	18,9
	Avrami-Erofe'ev, $n = 2$ (best fit)	102,6	17,8

From table 4.6 it is clear that the activation energy value and the pre-exponential factor are independent of the kinetic model, as the values are approximately the same for different models in a certain temperature range. It seems that the best approximation for these two values in a temperature range could be determined from any mathematical description, as long as it describes the decomposition data.

The nucleation activation energy, as described earlier, for the thermal decomposition of $\text{Ho}(\text{NO}_3)_3$, was calculated to be $57,7 \text{ kJ}\cdot\text{mol}^{-1}$ and the pre-exponential factor ($\ln A$) for the same step is 8,4. Comparing this activation energy with the enthalpy value of $119,9 \text{ kJ}\cdot\text{mol}^{-1}$, it seems that the activation energy again is smaller by a factor two. The "per mole" term of the activation energy could thus be "per a half mole" of activated complex. Correcting this term to one mole, a value of $115,4 \text{ kJ}\cdot\text{mol}^{-1}$ for the activation energy for the nucleation step was calculated.

Using the corrected value for the nucleation activation energy ($115,4 \text{ kJ}\cdot\text{mol}^{-1}$) and the experimental data values, a "corrected" $\ln A$ value of 20,3 was calculated. This higher value compares much better with the range of valid frequency factor values ($\ln A = 25$ to 33).

4.2.3.3 Er(NO₃)₃

The kinetic models with their correlation coefficient values, that best describe the thermal decomposition data of Er(NO₃)₃ are summarized in table 4.7.

Table 4.7. Kinetic models that best describe the thermal decomposition of Er(NO₃)₃

Temperature range (° C)	Kinetic model	Correlation coefficient
250 - 260	Avrami-Erofe'ev, $n = 2$	0,998
	Contracting volume	0,997
	Avrami-Erofe'ev, $n = \frac{3}{2}$	0,995
263 - 278	Avrami-Erofe'ev, $n = 1$	0,997
	Avrami-Erofe'ev, $n = 2$	0,991
	Contracting volume	0,989
280 - 290	Avrami-Erofe'ev, $n = 4$	0,997
	Contracting area	0,996
	Avrami-Erofe'ev, $n = 3$	0,994
292 - 345	Avrami-Erofe'ev, $n = \frac{3}{2}$	0,997
	Avrami-Erofe'ev, $n = 1$	0,995
	Avrami-Erofe'ev, $n = 2$	0,994
350 - 370	Avrami-Erofe'ev, $n = 3$	0,996
	Avrami-Erofe'ev, $n = 4$	0,994
	Avrami-Erofe'ev, $n = 1$	0,989

As was the case for $\text{Gd}(\text{NO}_3)_3$ and $\text{Ho}(\text{NO}_3)_3$, it proved difficult to decide on a kinetic model, as the correlation coefficient values for different models in the different temperature ranges are very close to one another. Although at some of the experimental temperatures, the next best correlation coefficient value is only 0,001 lower, the correlation coefficients for the model that showed an overall best fit, is the highest at all these experimental temperatures in the temperature range.

To evaluate the validity of the selection of a specific kinetic model to describe the decomposition kinetics, as was done for $\text{Gd}(\text{NO}_3)_3$ and $\text{Ho}(\text{NO}_3)_3$, an equation that showed a good fit over the entire decomposition temperature range, was selected to calculate the Arrhenius parameters in each of the temperature ranges. Table 4.8 gives a summary of the calculated values.

Taking experimental errors into consideration, it again seems that activation energies and the frequency factors are approximately the same for the different kinetic models.

The activation energy and pre-exponential factor were determined for the nucleation step of the decomposition reaction. The nucleation activation energy value of $49,9 \text{ kJ}\cdot\text{mol}^{-1}$ is approximately four times lower than the activation energy for the decomposition at atmospheric pressure ($197,2 \text{ kJ}\cdot\text{mol}^{-1}$) and twice as low as the decomposi-

Table 4.8. Arrhenius parameters for the thermal decomposition of $\text{Er}(\text{NO}_3)_3$

Temperature range ($^{\circ}\text{C}$)	Kinetic model	Activation energy ($\text{kJ}\cdot\text{mol}^{-1}$)	Frequency factor ($\ln(A/\text{min}^{-1})$)
250 - 260	Avrami-Erofe'ev, $n = 2$	84,2	12,1
263 - 278	Avrami-Erofe'ev, $n = 2$	131,4	24,6
	Avrami-Erofe'ev, $n = 1$ (best fit)	124,9	22,2
280 - 290	Avrami-Erofe'ev, $n = 2$	478,6	97,5
	Avrami-Erofe'ev, $n = 4$ (best fit)	486,0	98,3
292 - 345	Avrami-Erofe'ev, $n = 2$	157,9	28,1
	Avrami-Erofe'ev, $n = \frac{3}{2}$ (best fit)	155,6	28,5
350 - 370	Avrami-Erofe'ev, $n = 2$	48,5	7,8
	Avrami-Erofe'ev, $n = 3$ (best fit)	63,2	10,2

tion at a pressure of 5×10^3 kPa ($92,7 \text{ kJ}\cdot\text{mol}^{-1}$) (see later). Again, the activation energy seems to be lower by a factor two than the value for the decomposition reaction. The pre-exponential factor, determined by this method, gave a $\ln A$ value of 6,7. This value compared to the range of valid values ($\ln A = 25$ to 33) is far too

small. Using the Arrhenius equation, and correcting the activation energy to a value of $2 \times 49,9 = 99,8 \text{ kJ}\cdot\text{mol}^{-1}$, and using the experimental data values for k and T , a value of 16,0 for $\ln A$ was calculated. This value is still a few orders of magnitude smaller than the range of valid values.

4.2.4 Conclusion

The comparison of the experimental data to the nineteen different kinetic models (chapter 2), especially for decomposition reactions, with reversible processes occurring during the reactions, seems to have only empirical importance. Probably the best approximation of the activation energies and frequency factors could be made if a mathematical equation could be found exactly describing the decomposition data. It can thus be concluded that the 19 kinetic models proposed for solid state decomposition reactions, seem to be mathematical expressions describing decomposition data and not describing any mechanism for the thermal decomposition of the solids $\text{Ln}(\text{NO}_3)_3$, where $\text{Ln} = \text{La, Pr, Nd, Eu, Gd, Ho, Er}$.

A possible explanation for this observed behaviour of the lanthanide nitrates could be the sample preparation. Most solid state decompositions are governed by the movement of a reaction interface which determines the kinetics. The shape of the original particles largely determines the subsequent changing shape of the reaction interface and

hence the kinetics [31]. In powder compacts an additional factor is the spread of the reaction interface via the points of adhesion [42]. Another factor influencing the kinetics, is whether the product gases are removed as quickly as possible under vacuum conditions or at atmospheric pressure under specified conditions of flow [31]. The dehydration process in an inert atmosphere could produce an amorphous anhydrous material with a high surface area [31]. All these factors may contribute to the observed kinetic behaviour.

A further complicating factor in the interpretation of the kinetics is the observed reversible processes. These processes may be the reason for the observed changes in Arrhenius parameters, since the reversible processes occurred at the temperatures where the discontinuity in the Arrhenius plots was observed.

4.3 Reversible processes

The temperatures of the reversible processes, occurring during the thermal decomposition reactions of the studied lanthanide nitrates, are summarized in table 4.9. These reversible processes occur at the temperatures where changes in the Arrhenius parameters for the decomposition reactions were observed.

Moving down the lanthanide series, the number of reversible processes occurring during the decomposition reactions,

**Table 4.9 Temperatures where reversible processes occur
during the decomposition reactions of the
lanthanide nitrates**

Lanthanide nitrate	Reversible process temperatures (°C)
$\text{La}(\text{NO}_3)_3$	no reversible process
$\text{Ce}(\text{NO}_3)_3$	no reversible process
$\text{Pr}(\text{NO}_3)_3$	no reversible process
$\text{Nd}(\text{NO}_3)_3$	390
$\text{Eu}(\text{NO}_3)_3$	350
$\text{Gd}(\text{NO}_3)_3$	317 and 389
$\text{Ho}(\text{NO}_3)_3$	288, 309, 331 and 349
$\text{Er}(\text{NO}_3)_3$	262, 278, 290 and 350

increases. These temperature-dependent reversible processes could be phase transitions (only in the solid state) or minor structural changes in the lanthanide nitrates. No liquid state was observed during all the decomposition reactions. During the preparation of the anhydrous lanthanide nitrate, it is possible for the nitrate to dissolve to some extent in its crystal water. The hydrated lanthanide nitrates were all heated until an anhydrous solid lanthanide nitrate was formed.

The reversible processes are endothermic, except for the process at 349 °C for $\text{Ho}(\text{NO}_3)_3$. Although this result is unexpected, observations of exothermic reversible transitions

during decomposition of certain oxalates were recorded in the literature [38]. This exothermic process may indicate a low-temperature form which is metastable with respect to a higher temperature form, or it may represent an "amorphous" form changing to a crystalline phase. It proved difficult to determine the exact nature of this $\text{Ho}(\text{NO}_3)_3$ change, as the reversible process occurs during the decomposition of $\text{Ho}(\text{NO}_3)_3$.

Comparing the reaction enthalpy values at atmospheric pressure and at a pressure of 5×10^3 kPa, an approximation of the enthalpy values of the reversible processes could be made. For $\text{Nd}(\text{NO}_3)_3$ only one reversible process was observed during the decomposition reaction, with an approximate enthalpy value of $11,2 \text{ kJ} \cdot \text{mol}^{-1}$. The peak maximum on the DSC curve of the decomposition of $\text{Nd}(\text{NO}_3)_3$ at atmospheric pressure was at 377°C and that at 5×10^3 kPa at 442°C . When a sample of $\text{Nd}(\text{NO}_3)_3$ was heated to 400°C and then cooled, two exothermic peaks were found, one at 390°C and the other at 335°C . The exothermic peak at 335°C was associated with an endotherm at 320°C in the heating curve. This reversible process occurs just before the decomposition reaction. As $\text{Nd}(\text{NO}_3)_3$ was heated under 5×10^3 kPa from 300°C , it seems that at approximately 320°C this process did not occur, resulting in a different structure of $\text{Nd}(\text{NO}_3)_3$ at the beginning of the decomposition reaction in comparison to the reaction at atmospheric pressure. This structural or minor symmetry change can influence the decomposition reaction and causes the higher temperature for the peak maximum, if the

reactant at this higher pressure is in a more stable structural form than at atmospheric pressure.

The enthalpy value for the single reversible process occurring during the decomposition of $\text{Eu}(\text{NO}_3)_3$, is approximately $22,8 \text{ kJ}\cdot\text{mol}^{-1}$. The peak maximum of the DSC curve for the decomposition of $\text{Eu}(\text{NO}_3)_3$ at atmospheric pressure was at 347°C and at $5 \times 10^3 \text{ kPa}$ at 352°C . Taking experimental errors in consideration, no shift of the decomposition peak occurred, thus implying that both at atmospheric pressure and at $5 \times 10^3 \text{ kPa}$ the reactant was in the same structural state at the beginning of the decomposition. No reversible processes were observed just before the beginning of this decomposition reaction ($300 - 320^\circ\text{C}$).

The reversible process at 317°C , occurring during the thermal decomposition of $\text{Gd}(\text{NO}_3)_3$, was estimated to be $8,9 \text{ kJ}\cdot\text{mol}^{-1}$, thus leaving a value of $34,0 \text{ kJ}\cdot\text{mol}^{-1}$ for the reversible process at 389°C . (Enthalpy at atmospheric pressure - Enthalpy at $5 \times 10^3 \text{ kPa}$ - Enthalpy of reversible process at 317°C). The peak maximum of 368°C on the DSC curve at atmospheric pressure can be considered to be the same as the maximum of 365°C at a pressure of $5 \times 10^3 \text{ kPa}$.

It proved difficult to estimate values for the reversible processes occurring during the decomposition of $\text{Ho}(\text{NO}_3)_3$ and $\text{Er}(\text{NO}_3)_3$, as in both cases the DSC peak at atmospheric pressure consists of multiple overlapping peaks. Four reversible processes for each of these two compounds were also observed

and in the case of $\text{Ho}(\text{NO}_3)_3$ one of these was an exothermic process. The total enthalpy of the four reversible processes, occurring during the decomposition of $\text{Er}(\text{NO}_3)_3$ is approximately $104,5 \text{ kJ} \cdot \text{mol}^{-1}$.

The DSC curves for $\text{Ho}(\text{NO}_3)_3$ and $\text{Er}(\text{NO}_3)_3$ at $5 \times 10^3 \text{ kPa}$ show sharp well-defined peaks in comparison to the broad multiple peaks at atmospheric pressure. The peak maximum on the DSC curve for the decomposition of $\text{Ho}(\text{NO}_3)_3$ at atmospheric pressure was at 324°C . This temperature is slightly lower than the peak maximum of 340°C for the reaction at $5 \times 10^3 \text{ kPa}$. Again, it seems possible that the reactant, $\text{Ho}(\text{NO}_3)_3$ is in different structural states at the beginning of the reaction at the two pressures. For $\text{Er}(\text{NO}_3)_3$ a shift of approximately 61°C was observed for the peak maximum on the DSC curve at atmospheric pressure and at the pressure of $5 \times 10^3 \text{ kPa}$.

As these reversible processes occur during sample decomposition and are all temperature-dependent, it proved difficult to study them more closely. Following the decomposition reactions via an electronmicroscope can contribute to a better understanding of the reversible processes.

4.4 Thermal stability

In a study of the octahydrates of the sulphates of some lanthanides, it was found that the temperature for the removal of the first 4 or 6 molecules increases as the cation solvation-dipole interaction energy increases, that is as the

cation becomes smaller [39]. Negase stated that the thermal stability of an anhydrous complex decreases as the electron affinity of the central metal ion increases [40].

The relative stabilities of a few lanthanide oxalates were established to give the following sequence $Gd > Sm > Nd > La > Pr > Ce$ [41].

The temperature where decomposition starts, using a heating rate of $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$, was used as a relative measure of the thermal stability of the lanthanide nitrates. In table 4.10 the decomposition onset temperatures, the reaction enthalpy values at atmospheric pressure and the enthalpy values at a pressure of $5 \times 10^3\text{ kPa}$ are compared.

Table 4.10: Comparison of the decomposition onset temperatures and reaction enthalpy values of the lanthanide nitrates

Lanthanide nitrate	Decomposition onset temperature* ($^{\circ}\text{C}$)	Reaction enthalpy at atmospheric pressure ($\text{kJ}\cdot\text{mol}^{-1}$)	Reaction enthalpy at $5 \times 10^3\text{ kPa}$ ($\text{kJ}\cdot\text{mol}^{-1}$)	Radii [24] Å
$\text{La}(\text{NO}_3)_3$	375	123,4	123,4	1,14
$\text{Ce}(\text{NO}_3)_3$	230	111,1	111,1	1,07
$\text{Pr}(\text{NO}_3)_3$	365	102,6	102,6	1,06
$\text{Nd}(\text{NO}_3)_3$	360	109,6	98,4	1,04
$\text{Eu}(\text{NO}_3)_3$	320	119,6	96,8	0,98
$\text{Gd}(\text{NO}_3)_3$	275	138,1	95,2	0,97
$\text{Ho}(\text{NO}_3)_3$	250	119,9	60,6	0,91
$\text{Er}(\text{NO}_3)_3$	230	197,2	92,7	0,89

* The decomposition onset temperatures were determined from the TG curves, using a heating rate of $5\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$.

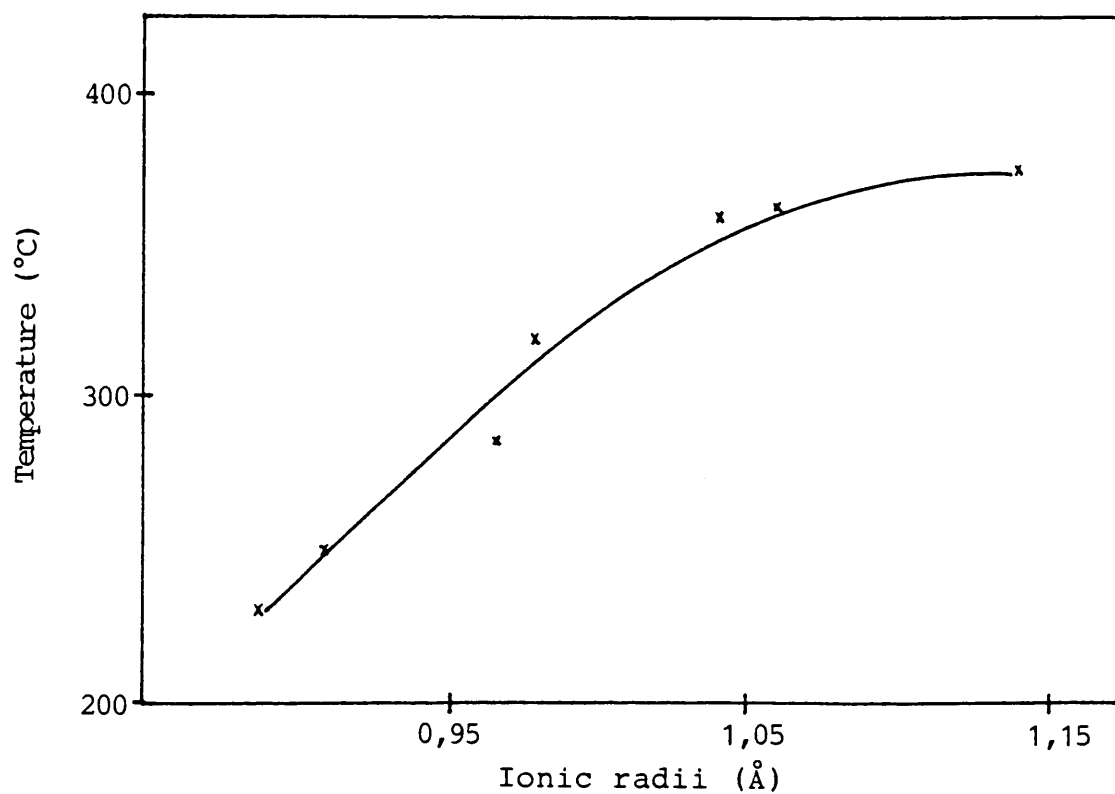


Figure 4.3. Correlation between the decomposition onset temperature and ionic radii

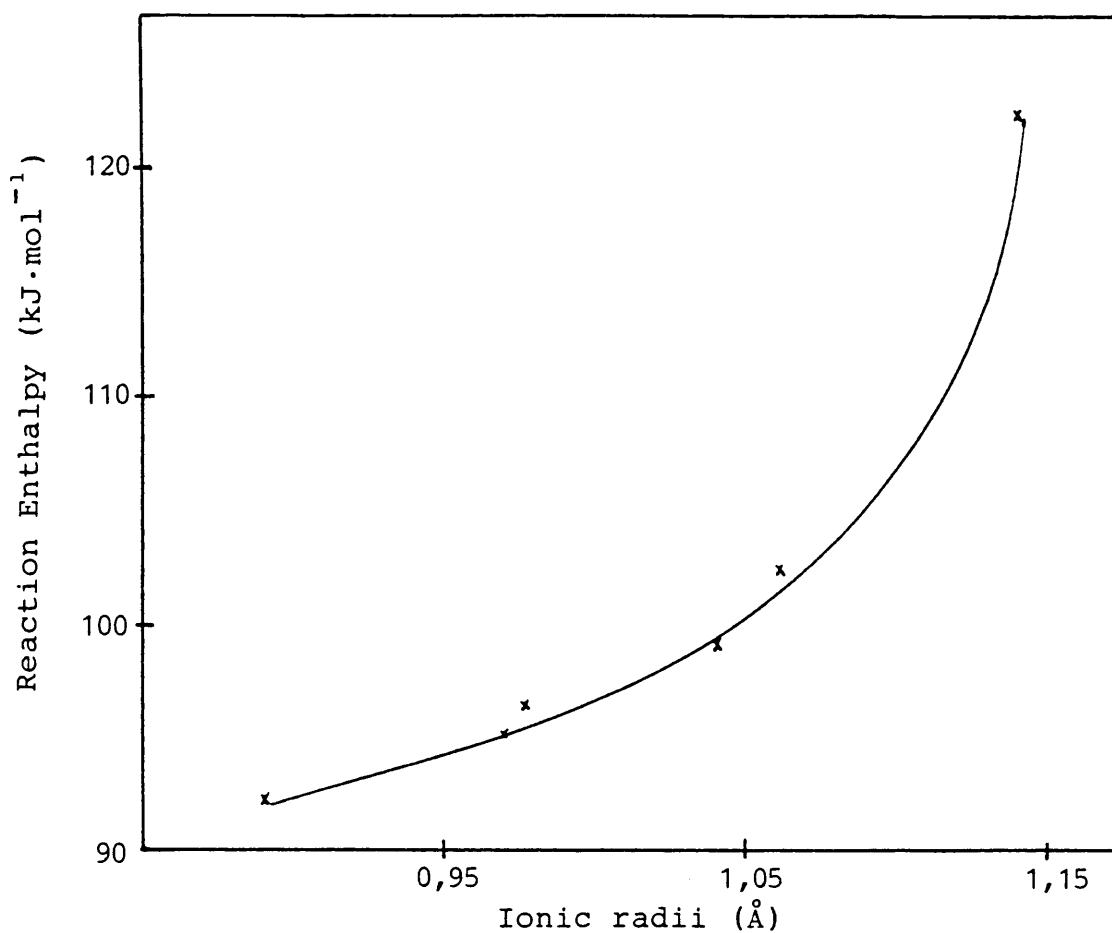


Figure 4.4. Correlation between the reaction enthalpy and ionic radii

When comparing the decomposition onset temperatures a definite increasing instability was found on moving down the lanthanide series (figure 4.3). The value for $\text{Ce}(\text{NO}_3)_3$ was excluded from the comparison, as a different chemical reaction results on heating $\text{Ce}(\text{NO}_3)_3$ [6]. $\text{Ce}(\text{NO}_3)_3$ decomposes directly to the oxide, while all the other nitrates decompose first to the oxynitrate and then to the oxide. The decomposition to the oxynitrate was confirmed to be a definite step in the decomposition of the lanthanide nitrate, with the exception of cerium [6].

The reaction enthalpy values at atmospheric pressure show an increase in value on moving down the lanthanide series. This must be due to the increasing number of reversible endothermic processes, occurring with the reactions (table 4.9). On moving down the lanthanide series, the reaction enthalpy values at a pressure of 5×10^3 kPa, show a decrease in value (figure 4.4). The relationship between increasing ionic radii and reaction enthalpy seems to be of an exponential order. The higher pressure seems to inhibit the reversible endothermic processes. The reaction enthalpy values at this higher pressure react in the same way as the decomposition onset temperatures. If the ease with which the reversible processes occur is used as an indication of the stability of the lanthanide nitrate crystals, then the increasing number of reversible processes on moving down the lanthanide series is also an indication of the increasing instability.

$\text{Ce}(\text{NO}_3)_3$ decomposes directly to the oxide, thus its enthalpy value cannot be compared with the others. During the decom-

position of $\text{Ho}(\text{NO}_3)_3$ an exothermic process is observed at 350°C . This results in a lower overall reaction enthalpy value. It seems that the exothermic process occurring during the decomposition of $\text{Ho}(\text{NO}_3)_3$ is not inhibited by the higher pressure, thus resulting in a lower enthalpy value at the high pressure than suspected.

Reactions in which a metal-oxygen link is ruptured, depend critically on the size and charge of the metal ion [31].

On moving down the lanthanide series, the decreasing ionic radii (table 4.10) give rise to greater polarisation of the nitrate ion and therefore greater instability of the lanthanide nitrate. The charge density on the lanthanide ions increases, resulting in a stronger attraction of the nitrates' electrons. This may increase the instability of the nitrate groups and therefore the groups are more easily decomposed.

CHAPTER 5

SOLID STATE CHEMISTRY OF URANIUM(IV) NITRATES

The solid state chemistry (thermal decomposition, crystal and molecular structures) was studied using techniques similar to the study of the lanthanide nitrates. Additional to these techniques, XPS, crystal and molecular data were also obtained.

5.1 Thermal studies

5.1.1 $U(NO_3)_4 \cdot 2tdpo$

The TG curve of the thermal decomposition of uranium(IV) nitrate bis(tris(dimethyl amino)phosphine oxide) is given in figure 5.1. The reaction,

$U(NO_3)_4 \cdot 2tdpo(s) \rightarrow UO_2(NO_3)_2 \cdot 2tdpo(s) + \text{oxides of nitrogen}$, starts at 98 °C and is completed at 156 °C, when using a heating rate of 5 °C·min⁻¹. The observed mass loss for the mentioned reaction was 11,2% (theoretical value : 10,9%).

The isothermal decomposition curves for $U(NO_3)_4 \cdot 2tdpo$ at some selected temperatures are given in figure 5.2. The rate data fit the equation for a first order solid state reaction, $f(\alpha) = -\ln(1-\alpha) = kt$, best at all the experimental temperatures (see also paragraph 6.1.1). The Arrhenius parameters were calculated from the slopes of the $f(\alpha)$ curves. An activation energy value of 127,0 kJ·mol⁻¹

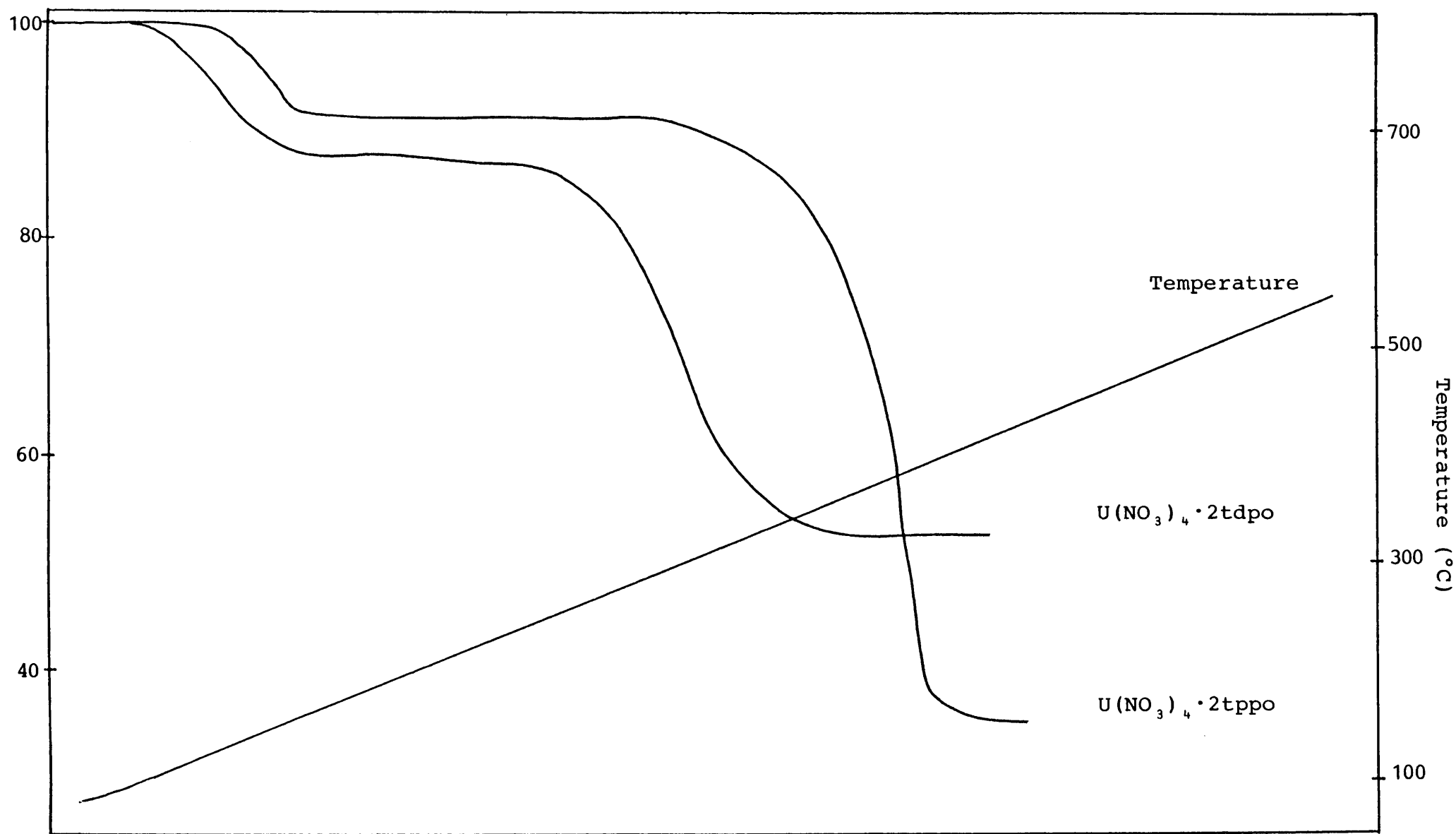


Figure 5.1. TG curves of the thermal decomposition of $\text{U}(\text{NO}_3)_4 \cdot 2\text{L}$ with $\text{L} = \text{tdpo}$ and tppo , using a heating rate of $5\text{ }^\circ\text{C} \cdot \text{min}^{-1}$

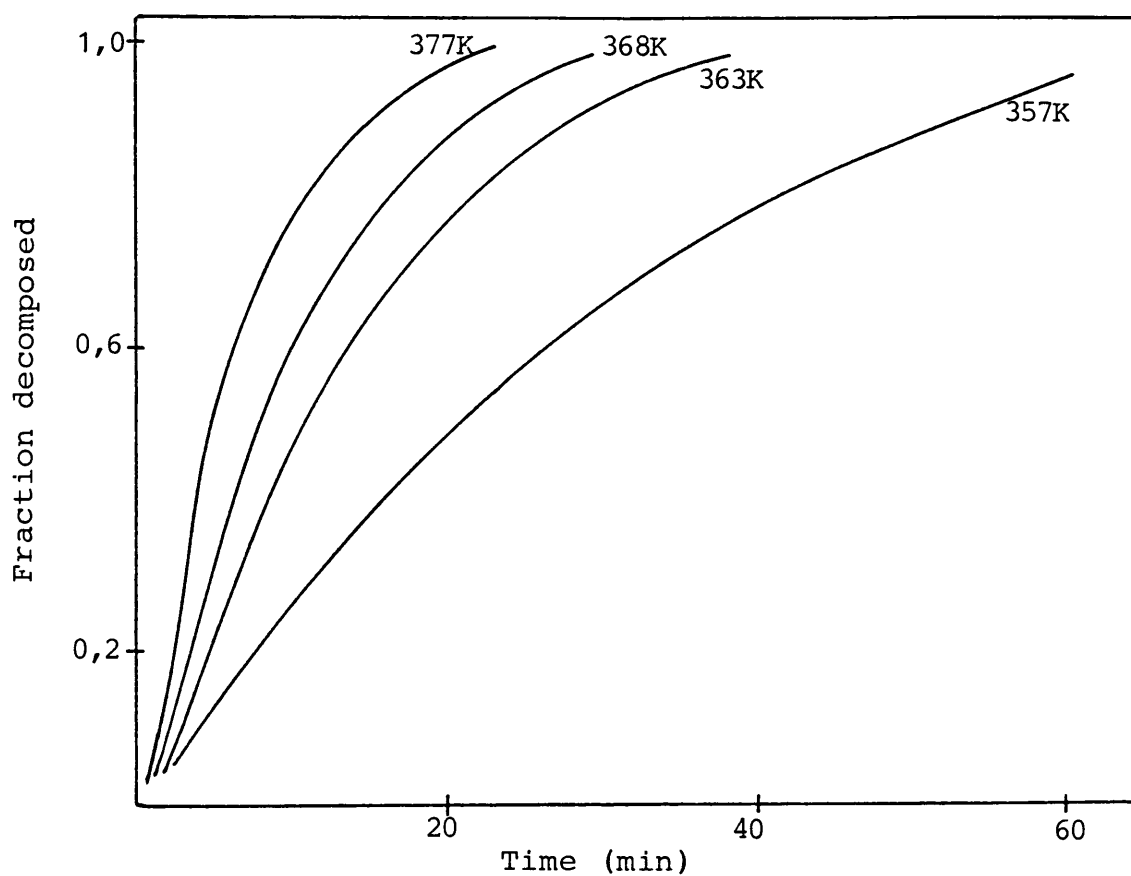


Figure 5.2. Isothermal decomposition curves of $U(NO_3)_4 \cdot 2tdpo$

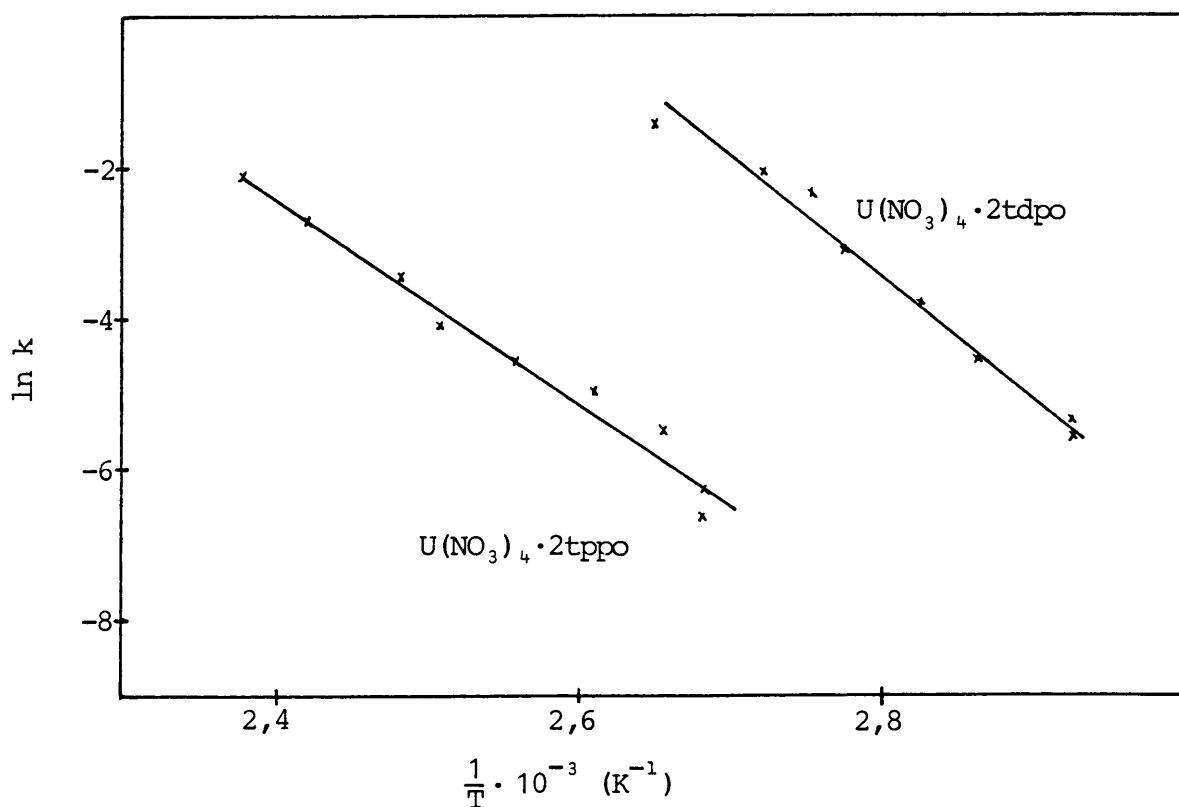


Figure 5.3. Arrhenius plots for the thermal decomposition of $U(NO_3)_4 \cdot 2L$ with $L = tdpo$ and $tppo$

$\text{U}(\text{NO}_3)_4 \cdot 2\text{tdpo}$ and a $\ln(A/\text{min}^{-1})$ value of 40,0 were determined from the Arrhenius plot (figure 5.3).

The DSC curve for the decomposition of $\text{U}(\text{NO}_3)_4 \cdot 2\text{tdpo}$ is given in figure 5.4. The curve shows an endothermic process at 78 °C, with an enthalpy value of 10,1 $\text{kJ} \cdot \text{mol}^{-1}$. The exothermic peak, associated with the reaction under study, gives an enthalpy value of -133,4 $\text{kJ} \cdot \text{mol}^{-1}$. On cooling a sample from 85 °C, a small exothermic peak is observed at 76 °C.

X-ray powder diffraction of $\text{U}(\text{NO}_3)_4 \cdot 2\text{tdpo}$ at room temperature and at 83 °C showed a small change in the diffractogram (figure 5.5). Instead of one peak at a 2θ value of 12,80° at room temperature, two peaks at 12,66° and 12,85° were observed at 83 °C. The X-ray powder diffraction data for $\text{U}(\text{NO}_3)_4 \cdot 2\text{tdpo}$ is given in table 5.1.

5.1.2 $\text{U}(\text{NO}_3)_4 \cdot 2\text{tppo}$

The TG curve of the thermal decomposition of uranium(IV) nitrate bis(triphenyl phosphine oxide) is given in figure 5.1. The reaction

$\text{U}(\text{NO}_3)_4 \cdot 2\text{tppo}(\text{s}) \rightarrow \text{UO}_2(\text{NO}_3)_2 \cdot 2\text{tppo}(\text{s}) + \text{oxides of nitrogen}$, starts at 130 °C and is completed at 162 °C, when using a heating rate of 5 °C $\cdot\text{min}^{-1}$. The average observed mass loss for the reaction was 8,6% (theoretical value : 8,80%).

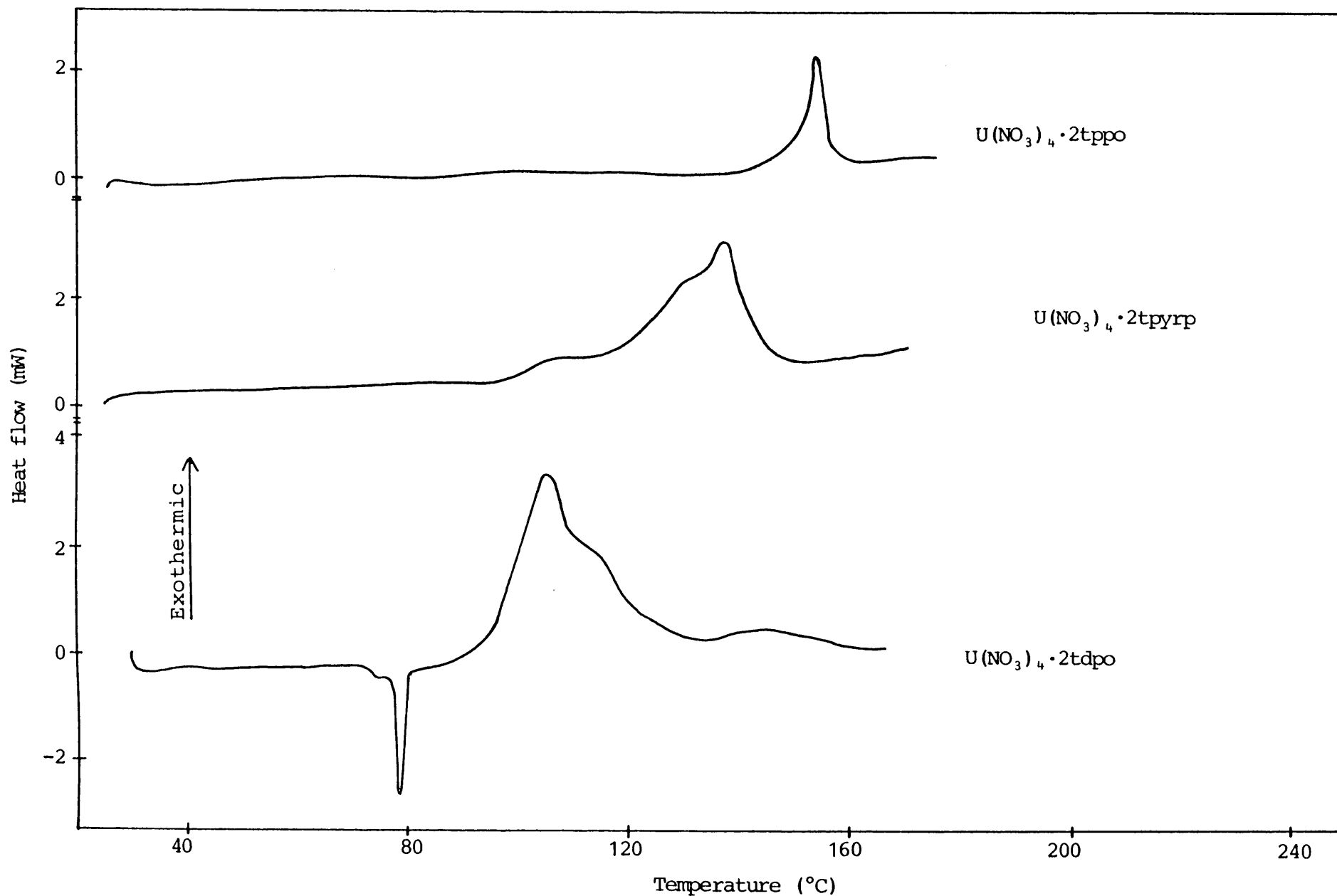


Figure 5.4. DSC curves of the thermal decomposition of $U(NO_3)_4 \cdot 2L$ ($L = tdpo, tppo$ and $tpyrp$)

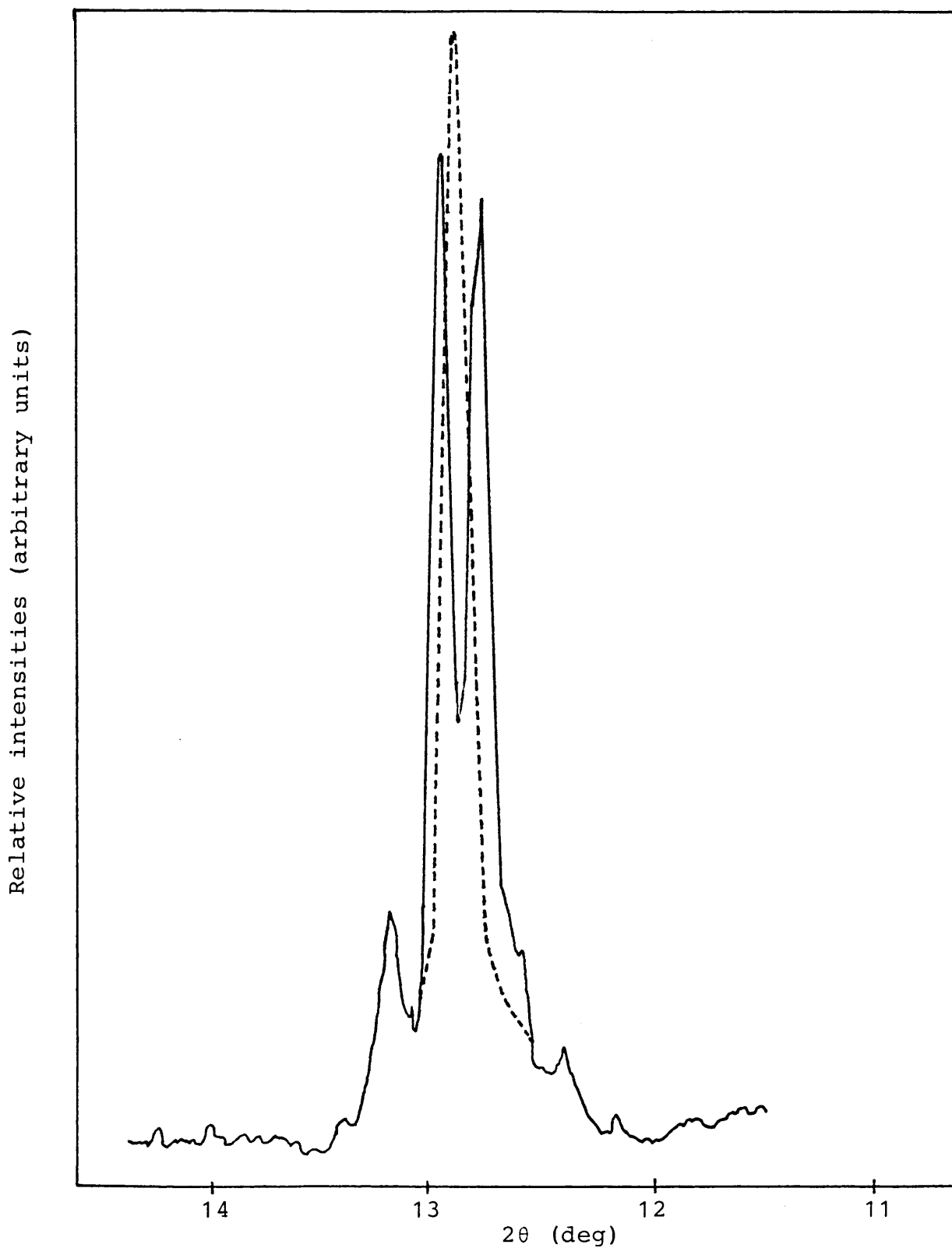


Figure 5.5. X-ray powder diffraction pattern for $\text{U}(\text{NO}_3)_4 \cdot 2\text{tdpo}$ at 25°C(---) and 83°C(—)

Table 5.1 X-ray powder diffraction data (Cu-K α) for the uranium(IV) nitrate complexes

U(NO ₃) ₄ •2tpyrp			U(NO ₃) ₄ •2tppo			U(NO ₃) ₄ •2tdpo		
2 θ /(deg)	d/(Å)	Rel I/(%)	2 θ /(deg)	d/(Å)	Rel I/(%)	2 θ /(deg)	d/(Å)	Rel I/(%)
21,35	4,1606	28,2	20,55	4,3361	48,8	20,80	4,2842	15,1
20,20	4,4047	42,6	19,70	4,5152	50,3	20,45	4,3510	21,6
18,40	4,8225	27,0	17,30	5,1650	53,2	17,35	5,1248	14,6
15,40	5,7269	51,7	16,05	5,5291	27,7	16,90	5,2420	19,0
12,05	7,4059	29,3	11,40	7,7934	100,0	13,20	6,7302	24,4
10,40	8,5139	100,0	10,70	8,2907	65,5	12,80	6,9352	100,0
9,70	9,0788	68,8	9,60	9,1675	81,7	11,40	7,8026	34,2
8,60	10,4570	69,3	8,10	10,9965	59,3	10,55	8,4048	50,5

Figure 5.6 represents some of the isothermal decomposition curves of $\text{U}(\text{NO}_3)_4 \cdot 2\text{tppo}$ at the indicated temperatures. The contracting area equation, $f(\alpha) = 1 - (1 - \alpha)^{\frac{1}{2}} = kt$, gave the best fit for the rate data at all the experimental temperatures (figure 5.7) (see also paragraph 6.1.2). Using the Arrhenius equation, a value of $109,4 \text{ kJ} \cdot \text{mol}^{-1}$ $\text{U}(\text{NO}_3)_4 \cdot 2\text{tppo}$ for the activation energy and a value of 30,0 for $\ln(A/\text{min}^{-1})$ was calculated (figure 5.3).

The DSC curve of the thermal decomposition of $\text{U}(\text{NO}_3)_4 \cdot 2\text{tppo}$ is given in figure 5.4. The curve shows an exothermic process, with an enthalpy value of $-24,1 \text{ kJ} \cdot \text{mol}^{-1}$ $\text{U}(\text{NO}_3)_4 \cdot 2\text{tppo}$. The X-ray powder diffraction data for $\text{U}(\text{NO}_3)_4 \cdot 2\text{tppo}$ are given in table 5.1.

5.1.3 $\text{U}(\text{NO}_3)_4 \cdot 2\text{tpyrp}$

Kinetics and stoichiometry of the thermal decomposition of $\text{U}(\text{NO}_3)_4 \cdot 2\text{tpyrp}$ were described previously [19]. The reaction enthalpy was reinvestigated using the same techniques as described for the other uranium(IV)nitrate complexes.

The DSC curve for the reaction,

$\text{U}(\text{NO}_3)_4 \cdot 2\text{tpyrp}(\text{s}) \rightarrow \text{UO}_2(\text{NO}_3)_2 \cdot 2\text{tpyrp}(\text{s}) + \text{oxides of nitrogen}$, is given in figure 5.4. The enthalpy for this reaction was estimated as $-165 \text{ kJ} \cdot \text{mol}^{-1}$ $\text{U}(\text{NO}_3)_4 \cdot 2\text{tpyrp}$. X-ray powder diffraction data for $\text{U}(\text{NO}_3)_4 \cdot 2\text{tpyrp}$ is given in table 5.1.

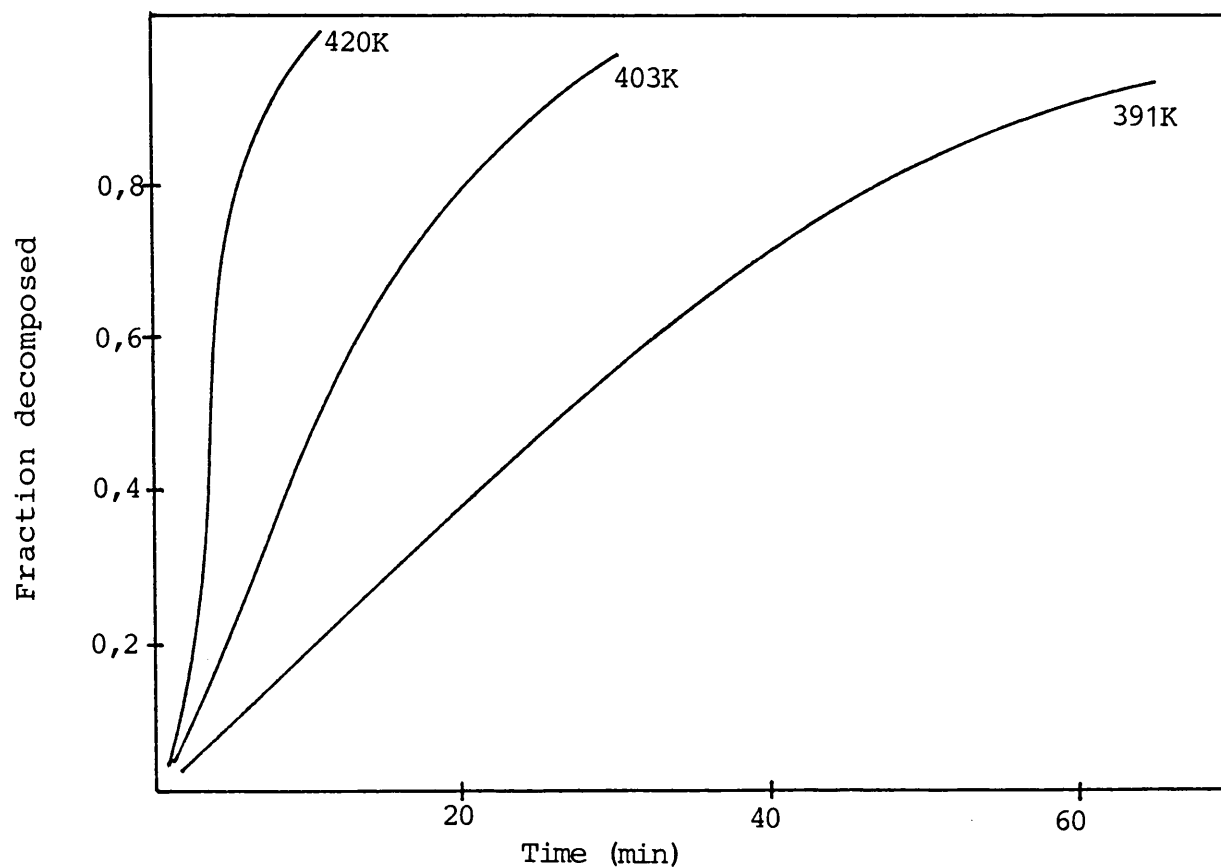


Figure 5.6. Isothermal decomposition curves of $\text{U}(\text{NO}_3)_4 \cdot 2\text{tppo}$

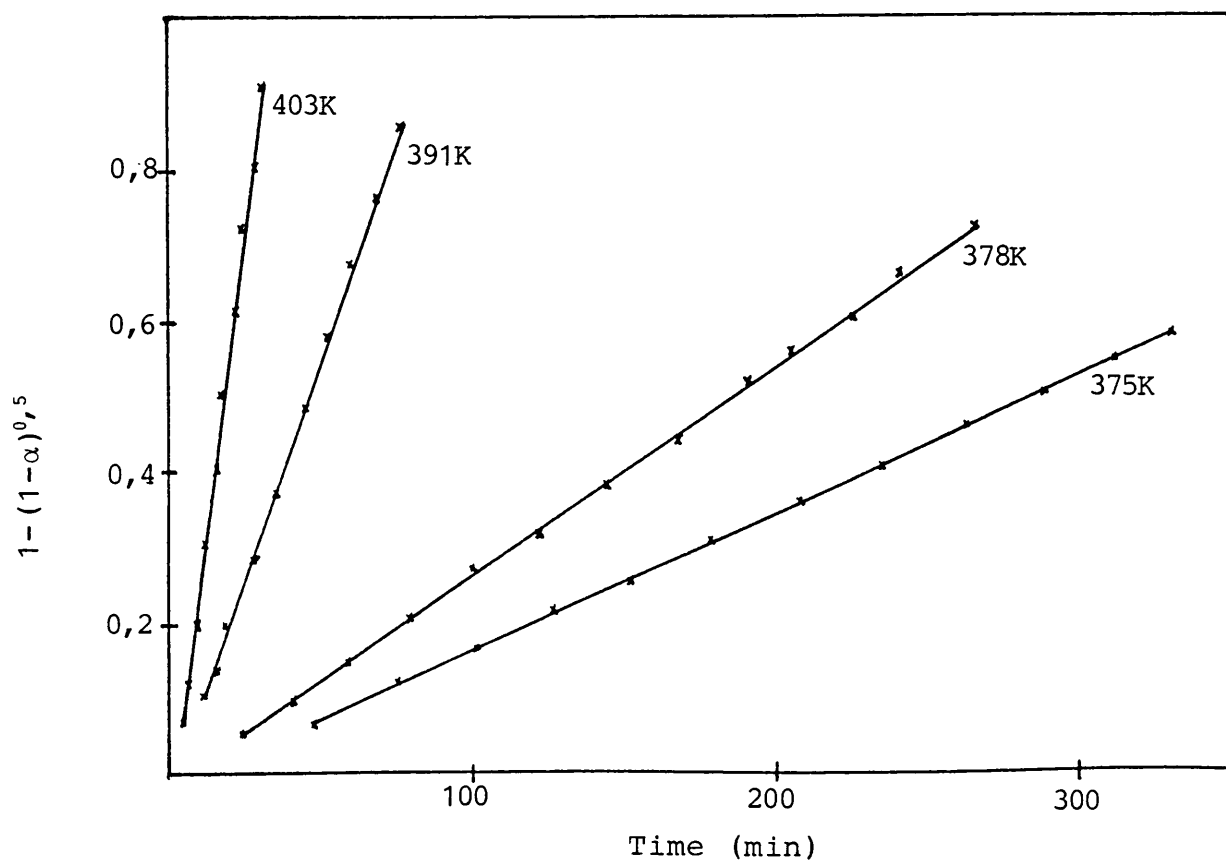


Figure 5.7. Rate data of the thermal decomposition of $\text{U}(\text{NO}_3)_4 \cdot 2\text{tppo}$ fitted to the contracting area equation

5.2 Crystal and Molecular Structures

The compounds $\text{U}(\text{NO}_3)_4 \cdot 2\text{L}$ and $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{L}$, with $\text{L} = \text{tdpo}$, tppo and tpyrp , have been characterized by means of X-ray structure analysis at the NCRL at the CSIR. The structures were determined using heavy atom methods and were refined by weighted least squares methods using SHELX [43].

5.2.1 $\text{U}(\text{NO}_3)_4 \cdot 2\text{tdpo}$

Crystal data : Molar mass = $844,5 \text{ g} \cdot \text{mol}^{-1}$

Triclinic structure

Space group : $P\bar{1}$

$a = 10,279(6) \text{ \AA}$

$b = 10,633(4) \text{ \AA}$

$c = 13,812(2) \text{ \AA}$

$\alpha = 89,45(2)^\circ$

$\beta = 88,70(2)^\circ$

$\gamma = 84,58(4)^\circ$

$U = 1502,38 \text{ \AA}^3$

$Z = 2$

$D_C = 1,548 \text{ g} \cdot \text{cm}^{-3}$

$\mu(\text{MoK}\alpha) = 52,8 \text{ cm}^{-1}$

Data were collected at $233 \pm 20 \text{ K}$. The diffraction data were refined by least squares methods to $R = 0,0817$ and $R_w = 0,0902$.

The structure was refined to the centro symmetric space group $P\bar{1}$. Refinement to the non-centro symmetric space

group P1 also showed approximately the same R-factor. The residual electron density of more than $3 \text{ e } \text{\AA}^{-3}$ is probably the result of the instability of the temperature at which data were collected. A variance of up to 40°C could have occurred. Nevertheless, the structural data proved to be good enough to be compared to the other structures.

The molecular structure of $\text{U}(\text{NO}_3)_4 \cdot 2\text{tdpo}$ is given in Figure 5.8. Some bond lengths ($\text{\AA}$) and angles ($^{\circ}$) in this molecule are given in table 5.2. A packing diagram is given in Figure 5.9.

Table 5.2 Bond lengths ($\text{\AA}$) and angles ($^{\circ}$) in $\text{U}(\text{NO}_3)_4 \cdot 2\text{tdpo}$

Bond	Length ($\text{\AA}$)	Angle	Degree ($^{\circ}$)
U - O(13)	2,226(10)	U - O(13) - P(2)	168,4(9)
O(13) - P(2)	1,514(12)	O(8) - N(3) - O(7)	113(2)
U - O(7)	2,539(14)	O(2) - N(1) - O(3)	117(2)
U - O(8)	2,485(14)	O(2) - U - O(3)	52,4(5)
U - O(3)	2,44(2)	O(13) - U - O(8)	119,9(5)
U - O(2)	2,46(2)	O(2) - U - O(8)	126,6(5)
N(3) - O(9)	1,19(3)	O(2) - U - O(7)	114,6(5)
N(1) - O(1)	1,22(3)		

5.2.2 $\text{U}(\text{NO}_3)_4 \cdot 2\text{tpo}$

Crystal data : Molar mass = $1042,7 \text{ g} \cdot \text{mol}^{-1}$

Monoclinic structure

Space group : $P2_1/n$

$a = 13,996(1) \text{ \AA}$

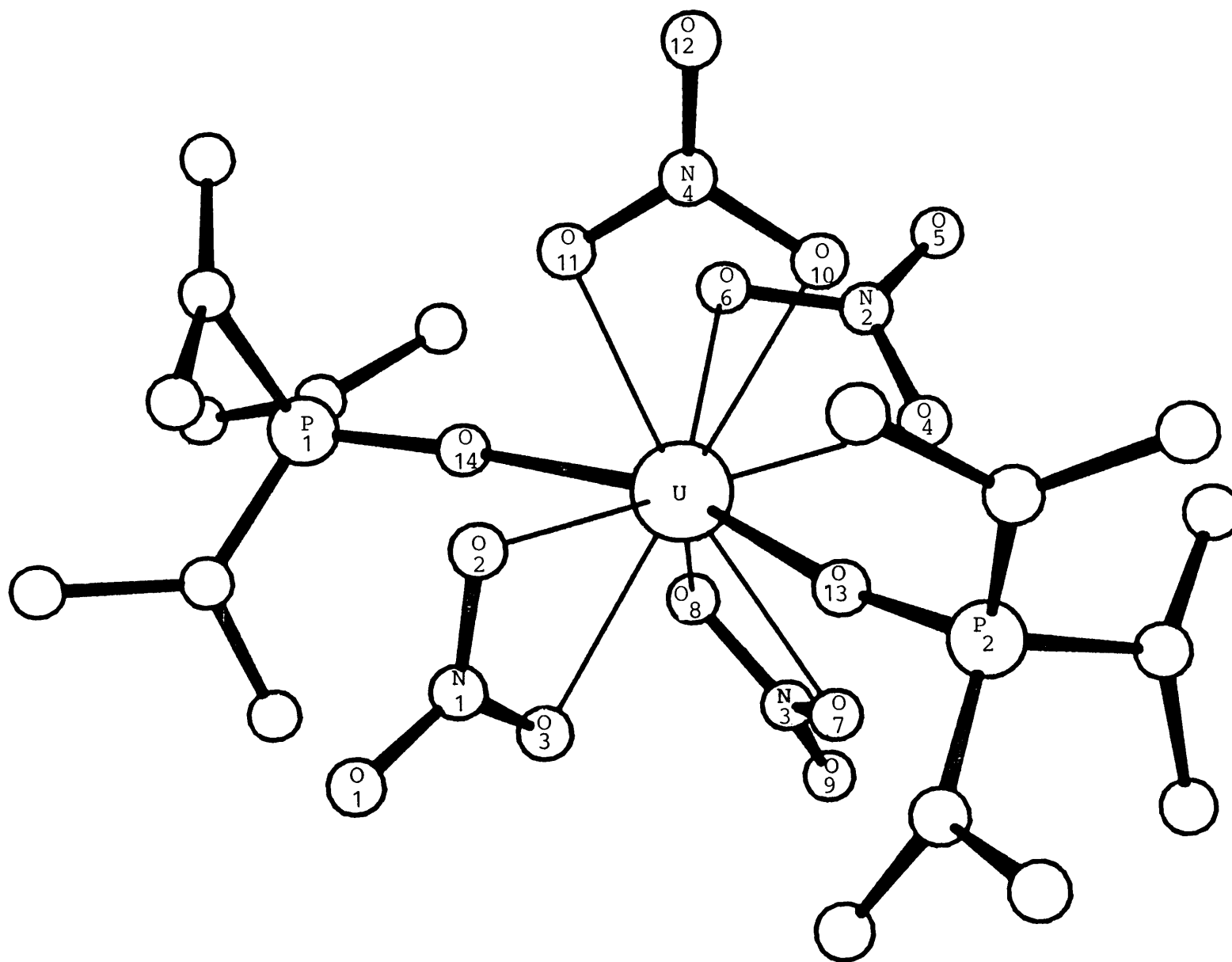


Figure 5.8 The molecular structure of $\text{U}(\text{NO}_3)_4 \cdot 2\text{tdpo}$

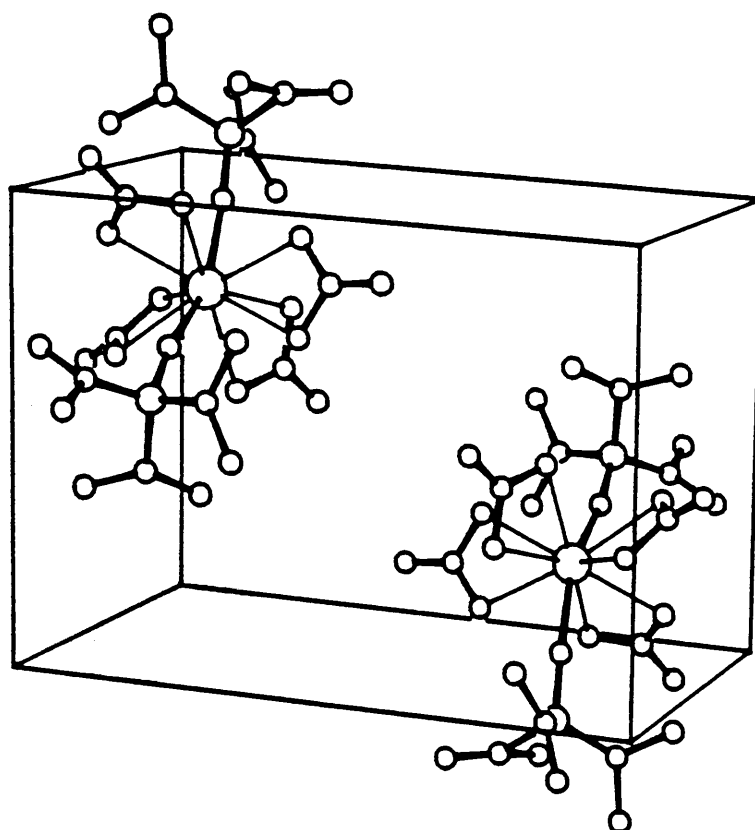
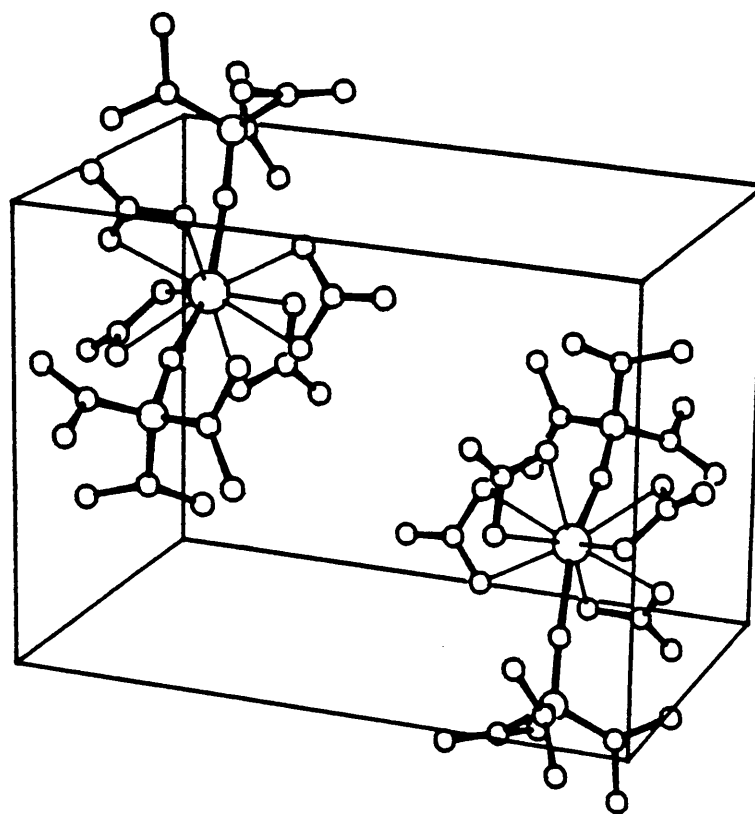


Figure 5.9 : Packing diagram of $\text{U}(\text{NO}_3)_4 \cdot 2\text{tdpo}$

$$b = 17,461(3) \text{ \AA}$$

$$c = 16,438(2) \text{ \AA}$$

$$\alpha = \gamma = 90^\circ$$

$$\beta = 91,13(1)^\circ$$

$$U = 4016,4 \text{ \AA}^3$$

$$Z = 4$$

$$D_C = 1,72 \text{ Mg} \cdot \text{cm}^{-3}$$

$$F(000) = 2096$$

$$\lambda = 0,71069 \text{ \AA}$$

$$\mu(\text{MoK}\alpha) = 3,99 \text{ mm}^{-1}$$

Data were collected at $295 \pm 1 \text{ K}$. The diffraction data were refined by least squares methods to $R = 0,096$ and $R_w = 0,053$ for 5969 reflections.

The molecular structure of $\text{U}(\text{NO}_3)_4 \cdot 2\text{tppo}$ is given in figure 5.10. Some bond lengths ($\text{\AA}$) and angles ($^\circ$) in this molecule are given in table 5.3. A packing diagram is given in figure 5.11.

5.2.3 $\text{U}(\text{NO}_3)_4 \cdot 2\text{tpyrp}$

Crystal data : Molar mass = $1000,7 \text{ g} \cdot \text{mol}^{-1}$

Tetragonal structure

Space group : $P4_12_12$

$$a = 10,607(11) \text{ \AA}$$

$$b = 10,607(11) \text{ \AA}$$

$$c = 33,497(4) \text{ \AA}$$

$$\alpha = \beta = \gamma = 90^\circ$$

$$U = 3768,7 \text{ \AA}^3$$

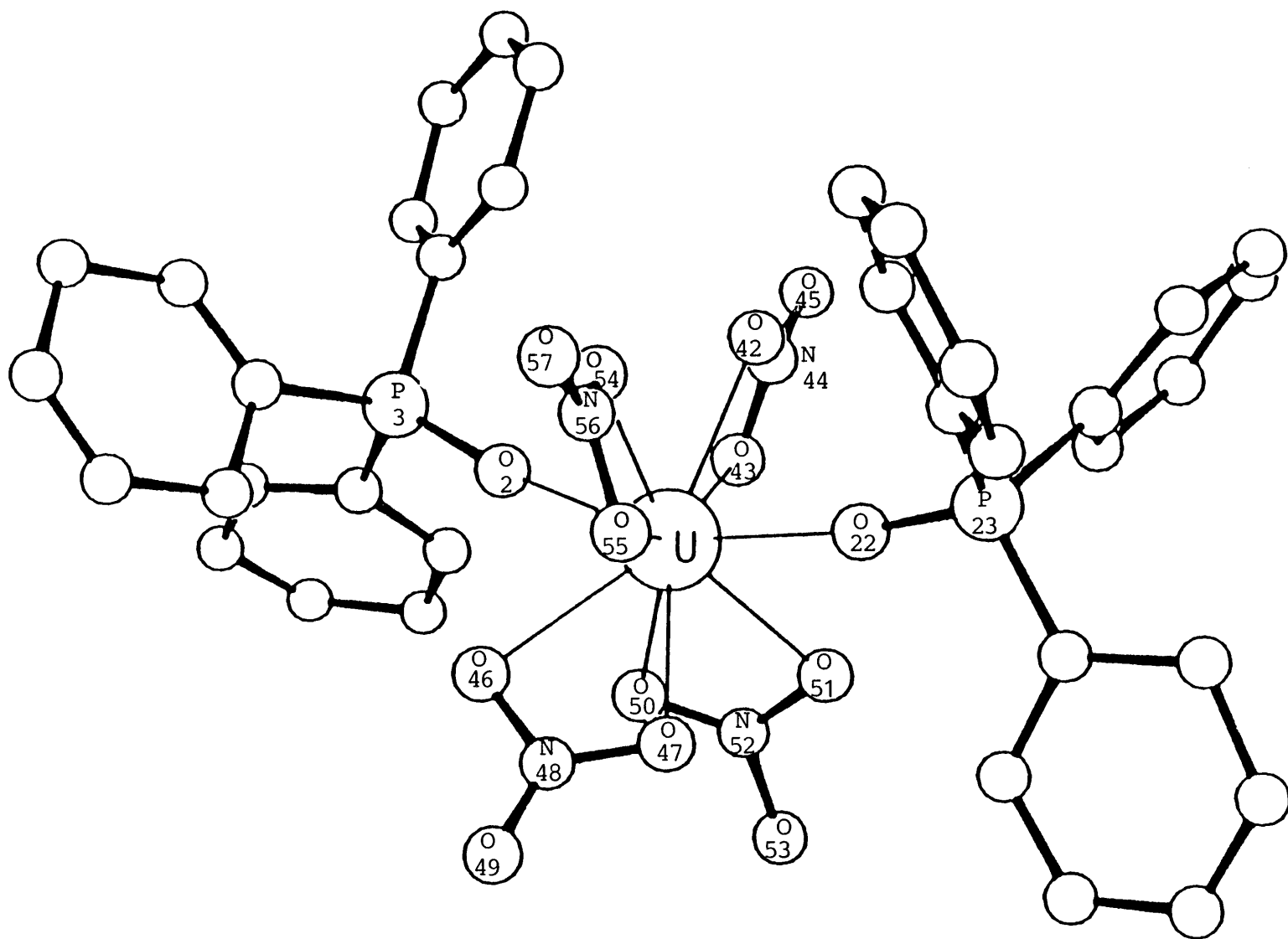


Figure 5.10 Molecular Structure of $\text{U}(\text{NO}_3)_4 \cdot 2\text{tppo}$

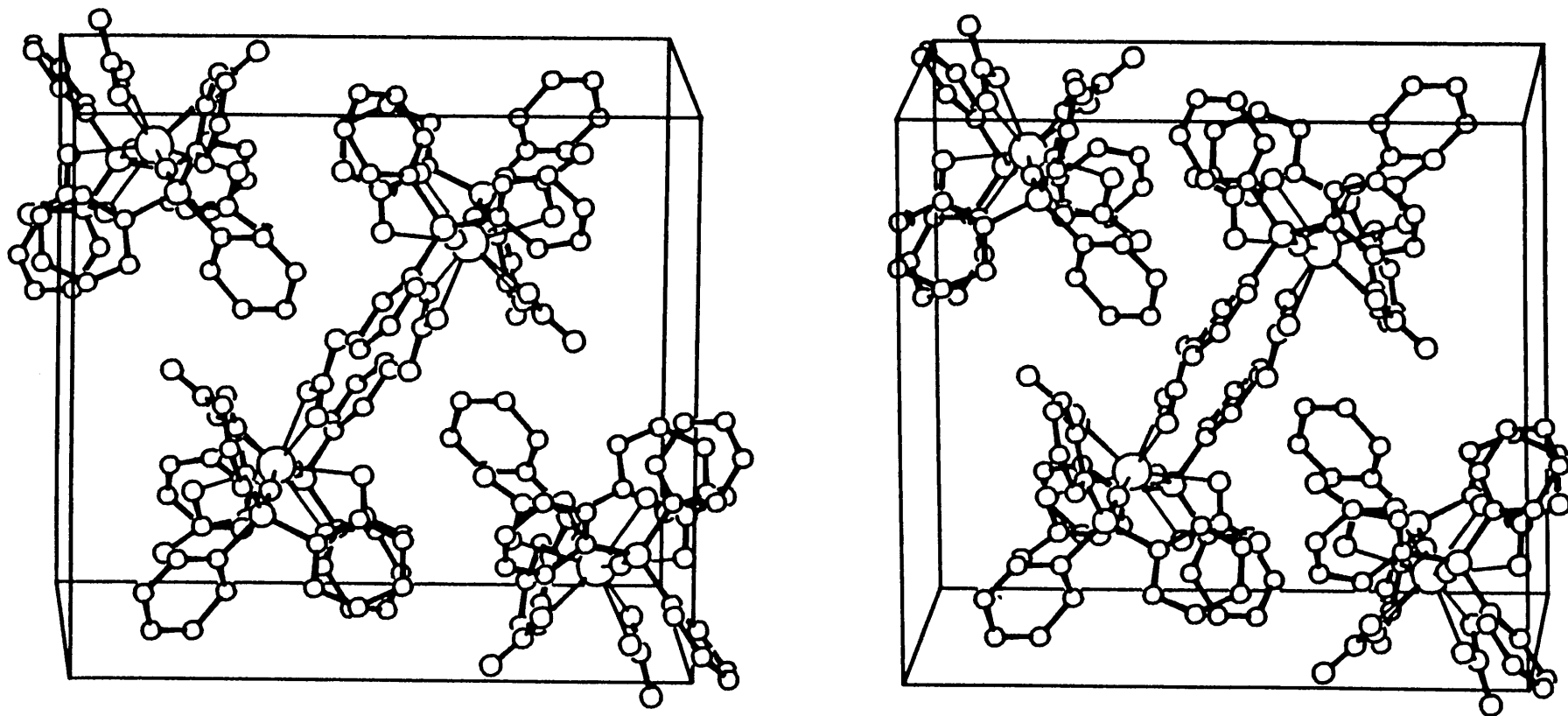


Figure 5.11 : Packing diagram of $\text{U}(\text{NO}_3)_4 \cdot 2\text{tppo}$

Table 5.3 Bond lengths (Å) and angles (°) in $U(NO_3)_4 \cdot 2tppo$

Bond		Length (Å)	Angle		Degree (°)
U	- O(2)	2,227(8)	O(2) - U - O(22)		157,6(3)
U	- O(22)	2,232(8)	U - O(2) - P(3)		171,3(5)
O(2)	- P(3)	1,554(9)	U - O(22) - P(23)		170,2(5)
O(22)	- P(23)	1,526(8)	O(42) - U - O(43)		48,7(4)
U	- O(42)	2,491(10)	O(50) - U - O(51)		52,0(4)
U	- O(43)	2,463(11)	O(46) - U - O(47)		50,1(3)
U	- O(46)	2,516(9)	O(54) - U - O(55)		50,2(5)
U	- O(47)	2,450(10)	O(42) - N(44) - O(43)		112,5(14)
U	- O(50)	2,381(11)	O(50) - N(52) - O(51)		112,9(14)
U	- O(51)	2,444(11)	O(46) - N(48) - O(47)		112,7(11)
U	- O(54)	2,251(14)	O(54) - N(56) - O(55)		110(2)
U	- O(55)	2,545(13)	O(2) - U - O(46)		71,9(3)
N(44)	- O(43)	1,23(2)	O(2) - U - O(42)		72,1(4)
N(44)	- O(42)	1,22(2)	O(2) - U - O(43)		84,0(3)
N(56)	- O(54)	1,23(3)	O(22) - U - O(42)		97,9(4)
N(56)	- O(55)	1,28(3)	O(22) - U - O(51)		67,0(3)
N(52)	- O(51)	1,35(2)	O(22) - U - O(55)		71,9(4)
N(52)	- O(50)	1,19(2)	O(46) - U - O(50)		69,5(4)
N(48)	- O(46)	1,27(2)	O(47) - U - O(50)		70,7(4)
N(48)	- O(47)	1,25(2)	O(43) - U - O(50)		122,5(4)

$$Z = 4$$

$$D_C = 1,76 \text{ Mg} \cdot \text{m}^{-3}$$

$$F(000) = 1984$$

$$\lambda = 0,71069 \text{ Å}$$

$$\mu(\text{MoK}\alpha) = 4,42 \text{ mm}^{-1}$$

Data were collected at $263 \pm 3 \text{ K}$. The diffraction data were refined by least squares methods to $R = 0,069$ and $R_w = 0,049$ for 1883 independent reflections.

The molecular structure of $\text{U}(\text{NO}_3)_4 \cdot 2\text{tpyrp}$ is given in figure 5.12. Some bond lengths ($\text{\AA}$) and angles ($^\circ$) in this molecule are given in table 5.4. A packing diagram is given in figure 5.13.

Table 5.4 Bond lengths ($\text{\AA}$) and bond angles ($^\circ$) in $\text{U}(\text{NO}_3)_4 \cdot 2\text{tpyrp}$

Bond	Length ($\text{\AA}$)	Angle	Degree ($^\circ$)
U - O(2)	2,241(10)	U - O(2) - P(3)	171,5(8)
O(2) - P(3)	1,479(11)	O(24) - U - O(25)	51,2(4)
U - O(22)	2,539(14)	O(20) - U - O(21)	50,5(5)
U - O(21)	2,49(2)	O(2) - U - O(20)	78,0(5)
U - O(24)	2,514(11)	O(2) - U - O(21)	79,6(4)
U - O(25)	2,509(12)	O(2) - U - O(25)	70,4(4)
N(19) - O(20)	1,21(3)	O(2) - U - O(24)	121,5(4)
N(19) - O(22)	1,17(3)	O(20) - U - O(24)	158,5(4)
U(19) - O(21)	1,27(2)	O(21) - U - O(25)	149,1(4)
N(23) - O(24)	1,29(2)	O(20) - N(19) - O(21)	120(2)
N(23) - O(26)	1,19(2)	O(24) - N(23) - O(25)	113(2)
N(23) - O(25)	1,32(2)	-	-

5.2.4 $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{tdpo}$

Crystal data : Molar mass = $748,41 \text{ g} \cdot \text{mol}^{-1}$

Tetragonal structure

Space group : $P4_12_12$

$a = 10,865(3) \text{ \AA}$

$b = 10,865(3) \text{ \AA}$

$c = 23,565(3) \text{ \AA}$

$\alpha = \beta = \gamma = 90^\circ$

$U = 2782(1) \text{ \AA}^3$

$Z = 4$

$D_C = 1,567 \text{ Mg} \cdot \text{m}^{-3}$

$F(000) = 1464$

$\mu(\text{MoK}\alpha) = 57,2 \text{ cm}^{-1}$

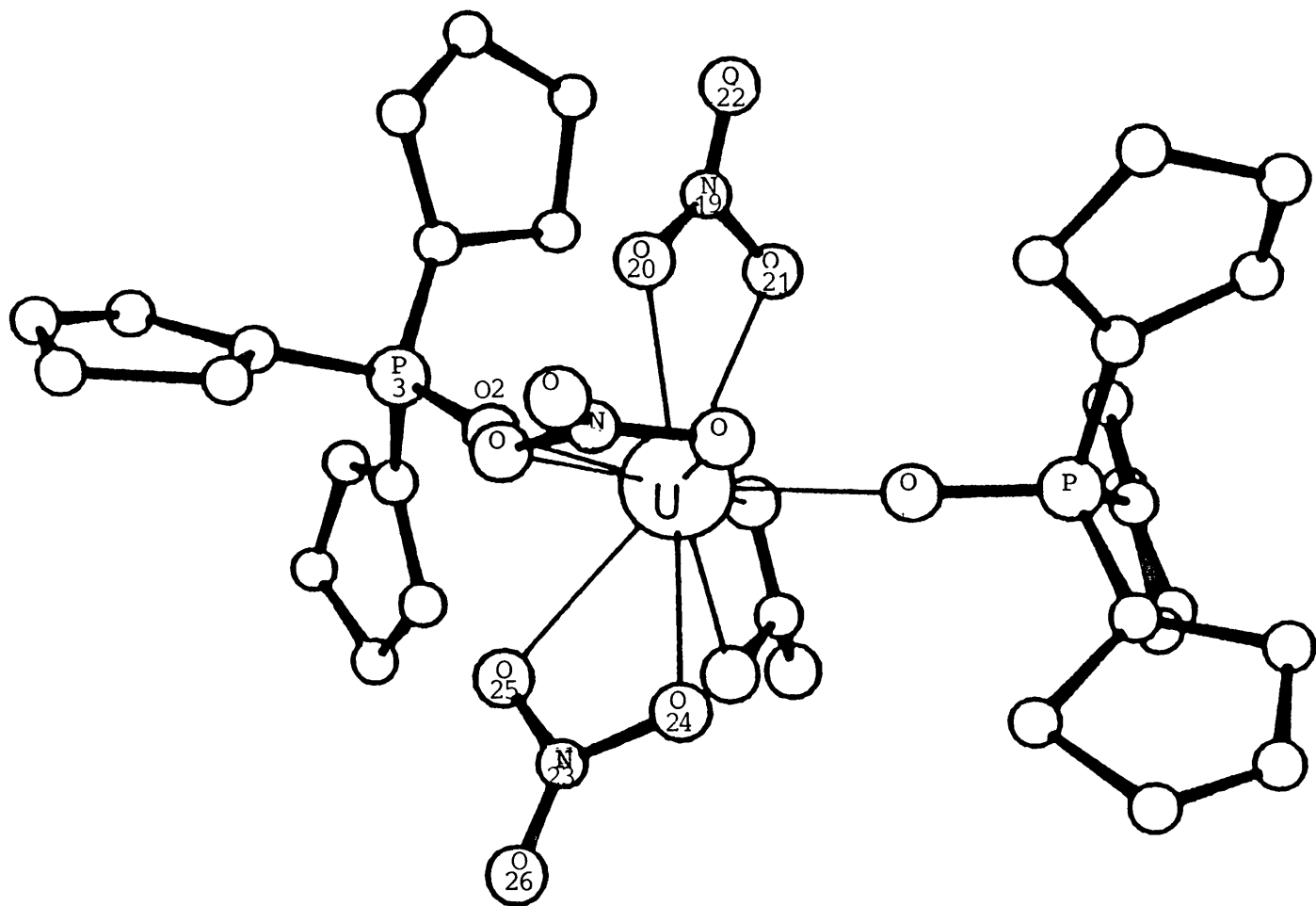


Figure 5.12 Molecular Structure of $U(NO_3)_4 \cdot 2tpyrp$

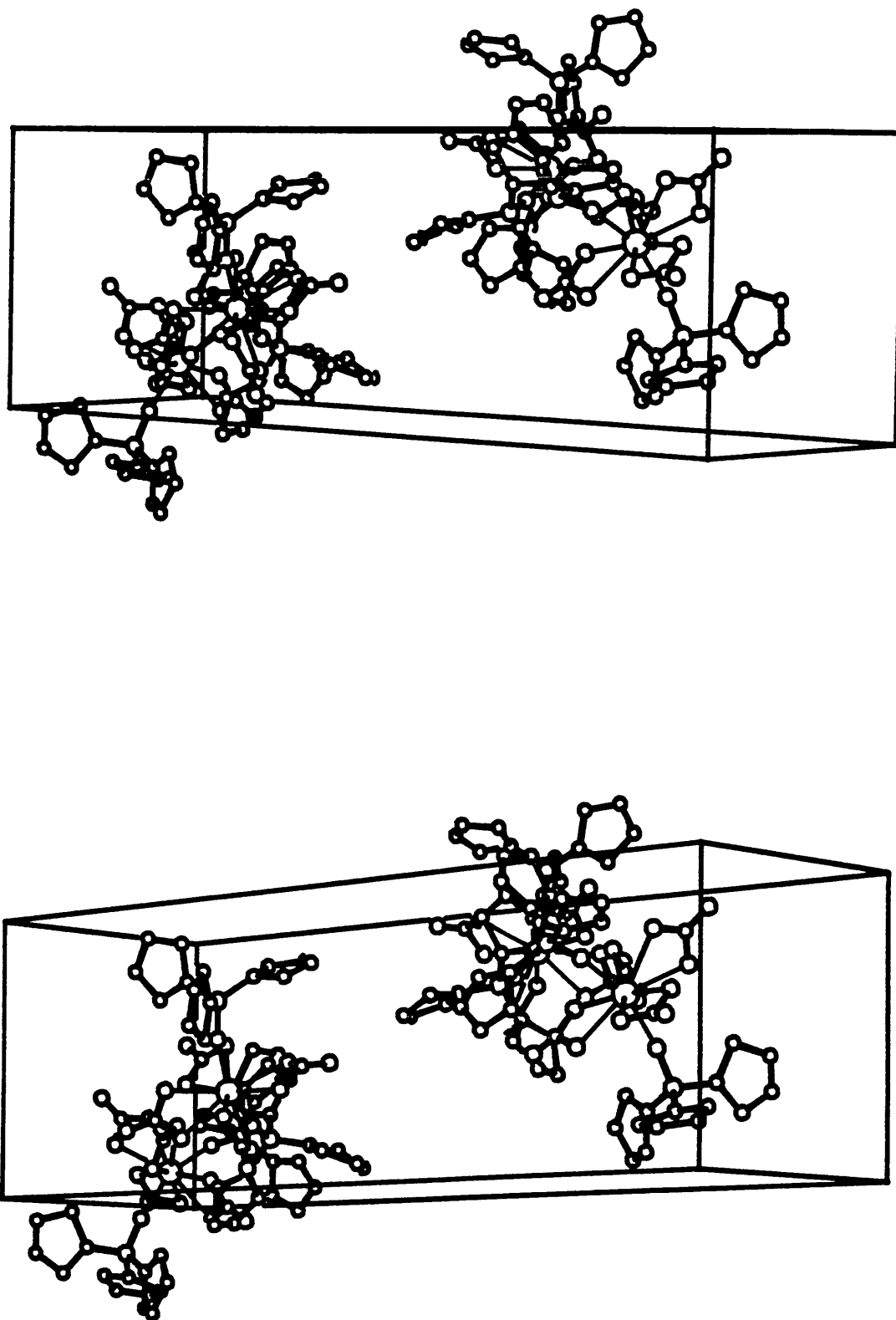


Figure 5.13 Packing diagram of $U(NO_3)_4 \cdot 2tpyrp$

Data were collected at 295 ± 3 K. The diffraction data were refined by least squares methods to $R = 0,061$ and $R_w = 0.037$ for 4547 reflections.

Figure 5.14 gives the molecular structure of $UO_2(NO_3)_2 \cdot 2tdpo$ and some bond lengths and angles are summarized in table 5.5. A packing diagram is given in figure 5.15.

Table 5.5 Bond lengths (Å) and angles (°) in $UO_2(NO_3)_2 \cdot 2tdpo$

Bond	Length (Å)	Angle	Degree (°)
U - O(2)	2,294(7)	U - O(3) - N(4)	92,1(11)
O(2) - P	1,502(7)	O(3) - N(4) - O(3)	125(2)
U - O(1)	1,755(6)	O(5) - N(5) - O(6)	119,4(11)
U - O(3)	2,556(10)	O(6) - U - O(6)	49,9(5)
U - O(6)	2,520(10)	O(1) - U - O(3)	86,8(5)
N(5) - O(5)	1,22(2)	O(3) - U - O(3)	50,7(4)
O(1) - U - O(2)	89,9(4)	O(3) - N(4) - O(4)	117,5(10)
O(2) - U - O(3)	116,3(3)	U - O(6) - N(5)	94,4(13)
O(2) - U - O(6)	64,2(3)	O(6) - N(5) - O(6)	121(2)
U - O(2) - P	179,3(6)		

5.2.5 $UO_2(NO_3)_2 \cdot 2tpo$

Crystal data : Molar mass = $950,7 \text{ g} \cdot \text{mol}^{-1}$

Monoclinic structure

Space group : $P2_1/c$

$a = 9,574(4)$

$b = 18,886(2)$

$c = 10,830(1)$

$\beta = 114,77(2)^\circ$

$V = 1778,10 \text{ Å}^3$

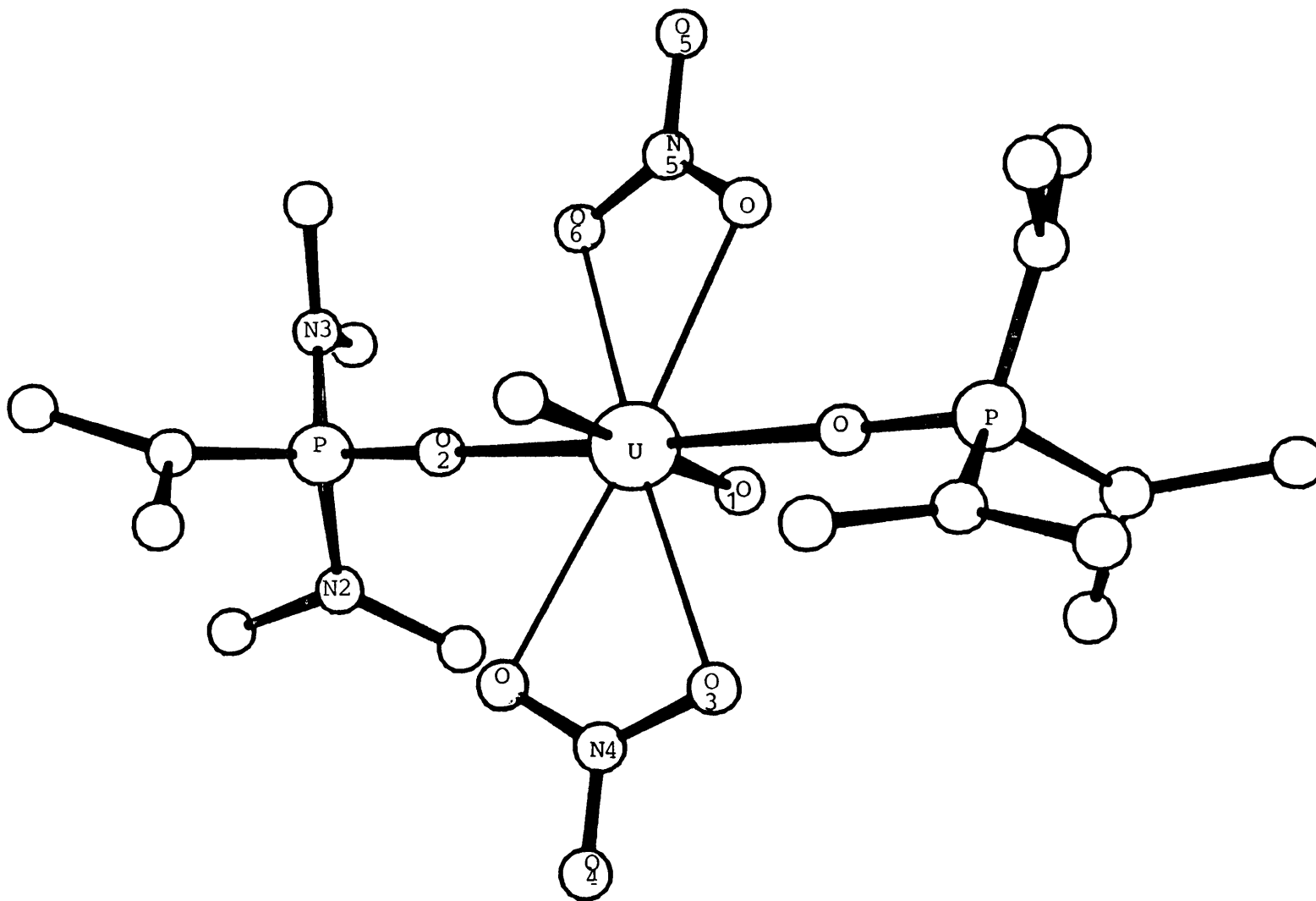


Figure 5.14 The molecular structure of $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{tdpo}$

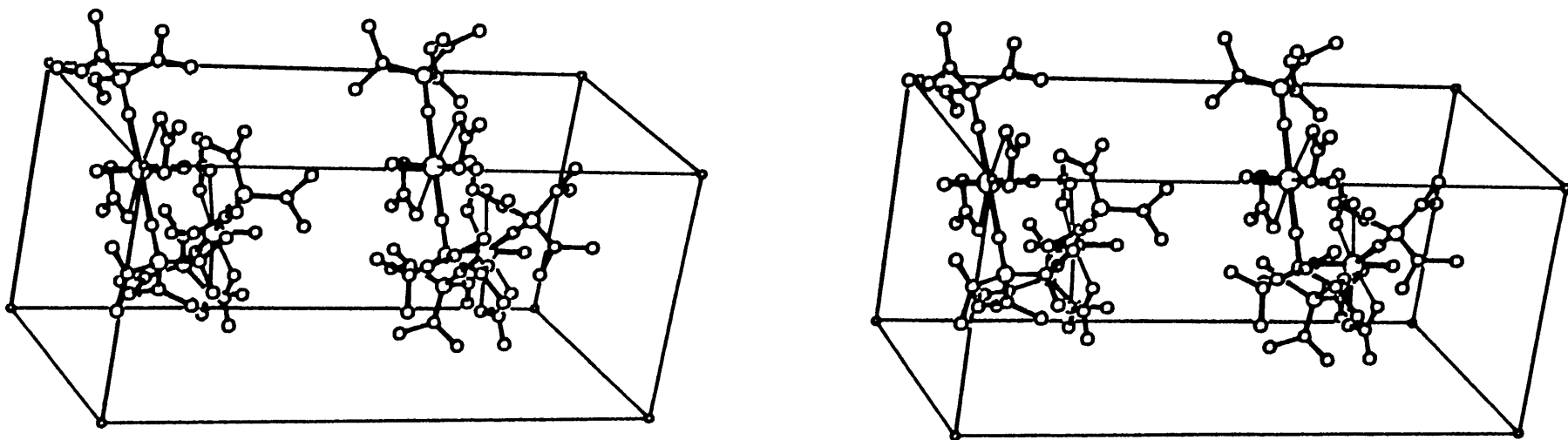


Figure 5.15 : Packing diagram of $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{tdpo}$

$$Z = 2$$

$$D_C = 1,776 \text{ g} \cdot \text{cm}^{-3}$$

$$F(000) = 923,9$$

$$\lambda = 0,7107 \text{ \AA}$$

$$\mu(\text{MoK}\alpha) = 4,482 \text{ mm}^{-1}$$

Data were collected at $295 \pm 3 \text{ K}$. The diffraction data were refined by least squares methods to $R = 0,045$ and $R_w = 0.037$ for 3002 independent reflections.

The molecular structure of $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{tppo}$ is given in figure 5.16 and table 5.6 summarizes some of the bond lengths. Figure 5.17 represents a packing diagram of the molecule.

Table 5.6 Bond lengths ($\text{\AA}$) in $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{tppo}$

Bond/Angle	Length ($\text{\AA}$)/Degree ($^\circ$)
U - O(2)	2,371(5)
O(2) - P	1,495(5)
U - O(1)	1,783(5)
U - O(4)	2,513(5)
U - O(3)	2,501(6)
N - O(5)	1,204(8)
U - O(2) - P	159,2(3)
O(4) - N - O(3)	113,8(7)
O(2) - U - O(1)	91,9(2)

5.2.6 $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{tpyrp}$

The structure of the compound $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{tpyrp}$ has been characterized by means of X-ray analysis at the University

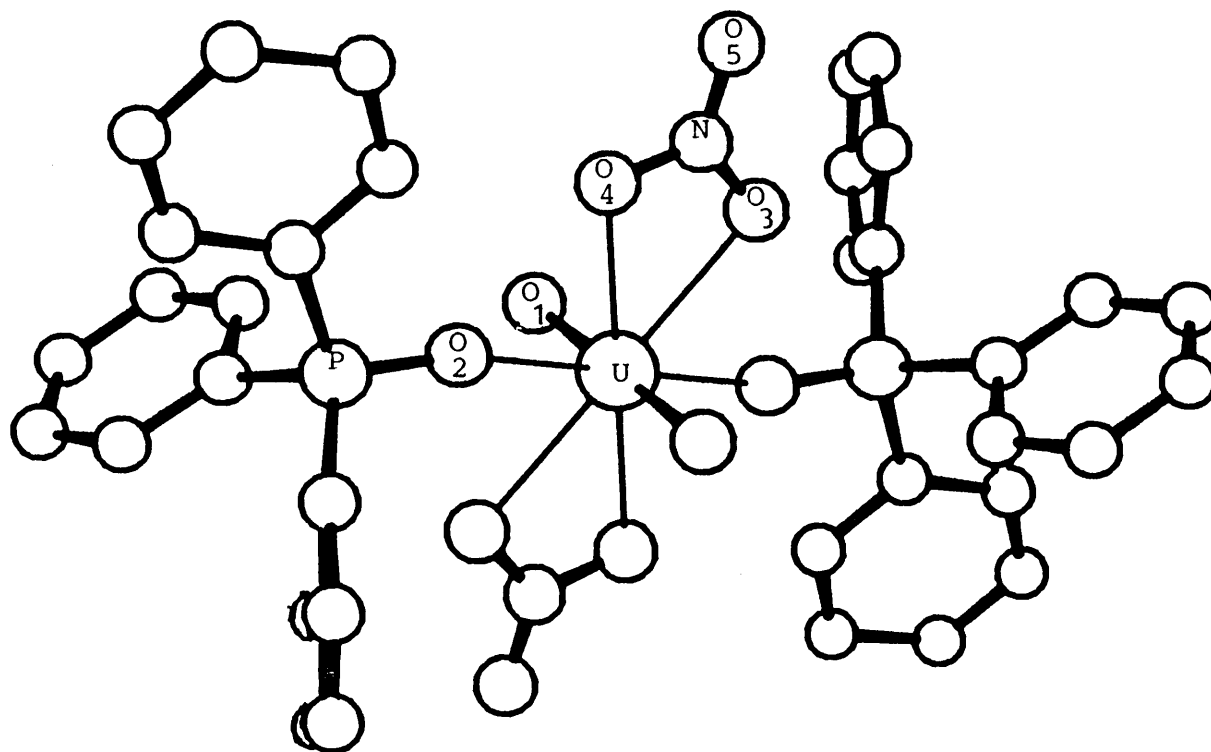


Figure 5.16 Molecular Structure of $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{tppo}$

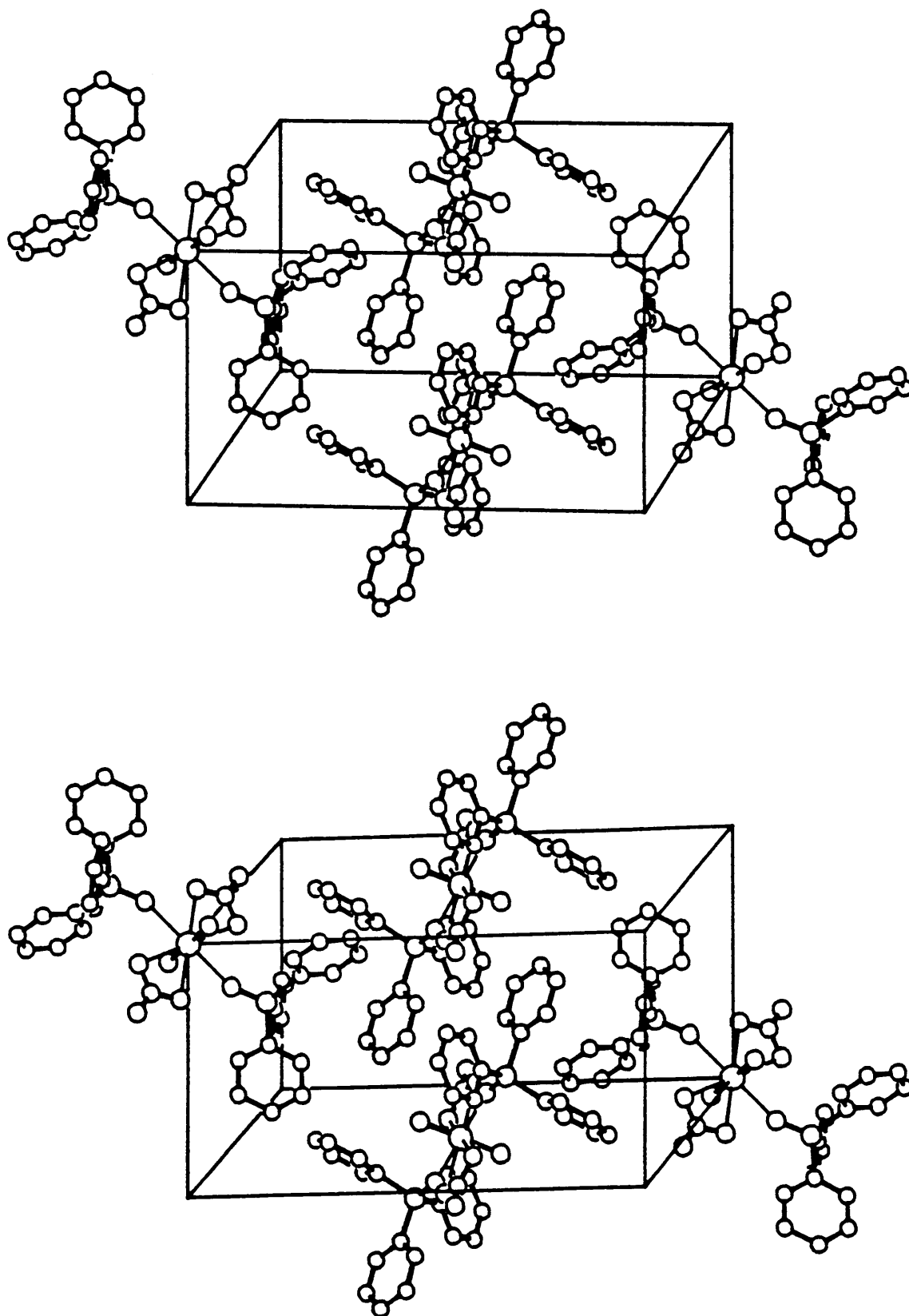


Figure 5.17 : Packing diagram of $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{tppo}$

of Port Elizabeth. The results received are summarized below.

Crystal data : Molar mass = 908,7 g·mol⁻¹

Triclinic structure

Space group : $P\bar{1}$

a = 10,10(1) Å

b = 14,12(1) Å

c = 8,66(1) Å

α = 123,9(1) Å

β = 65,3(1) Å

γ = 119,6(1) Å

The diffraction data were refined by least squares methods to $R = 0.029$ and $R_w = 0,026$ for 2390 independent reflections.

The molecular structure of $UO_2(NO_3)_2 \cdot 2tpyrp$ is given in figure 5.18 and table 5.7 summarizes some of the bond lengths and angles. A packing diagram is given in figure 5.19.

Table 5.7 Bond lengths (Å) and angles (°) in $UO_2(NO_3)_2 \cdot 2tpyrp$

Bond		Length (Å)	Angle	Degree (°)
U	- O(2)	2,341(3)	U - O(2) - P(3)	161,1(2)
O(2)	- P(3)	1,502(3)	O(19) - U - O(2)	90,7(1)
U	- O(19)	1,755(3)	O(21) - N(22) - O(20)	114,5(5)
U	- O(20)	2,570(4)	O(19) - U - O(21)	92,4(2)
U	- O(21)	2,554(4)	O(2) - U - O(20)	115,0(1)
N(22)	- O(23)	1,208(6)	O(2) - U - O(21)	66,4(1)
			O(21) - U - O(20)	48,8(1)

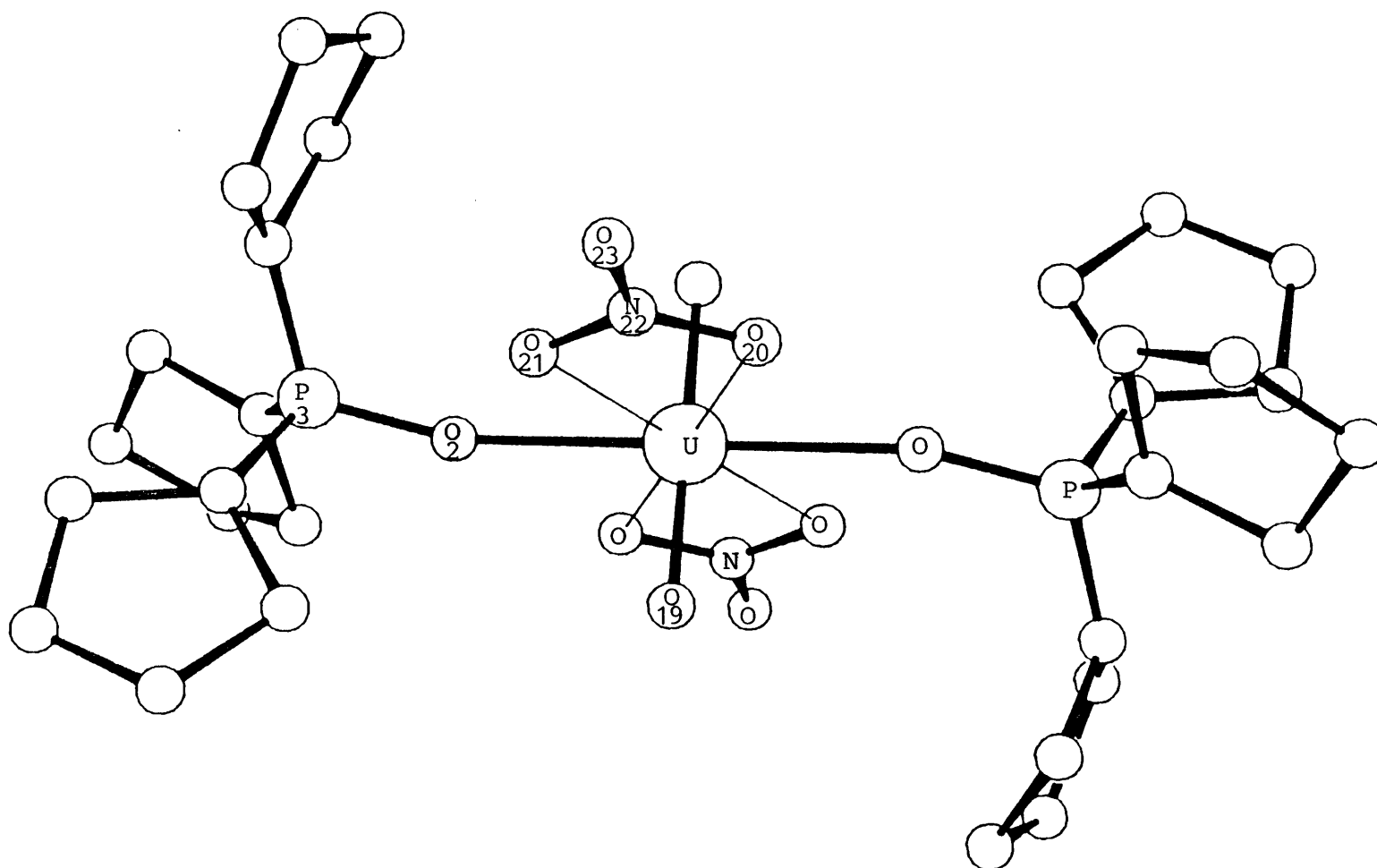


Figure 5.18 Molecular Structure of $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{tpyrp}$

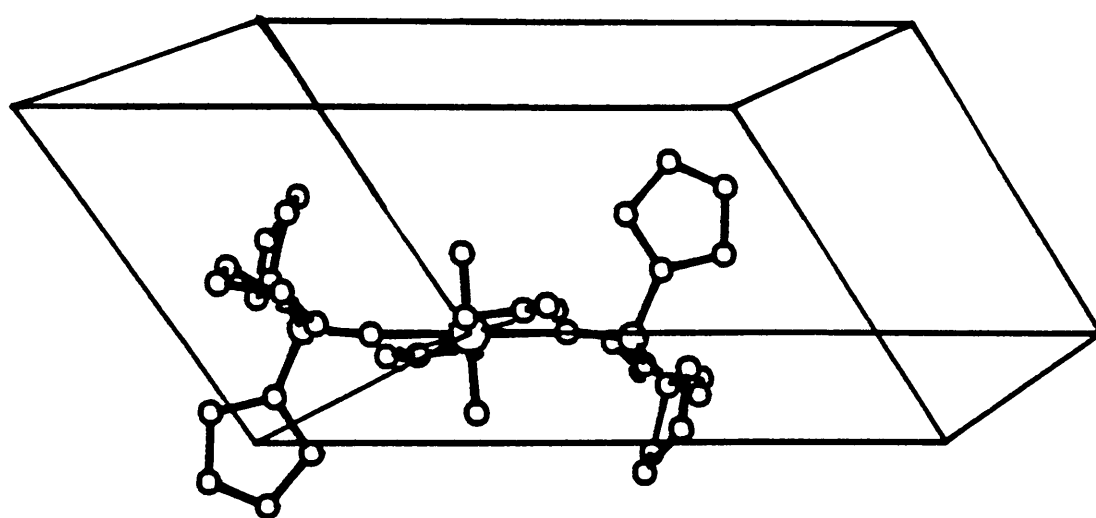
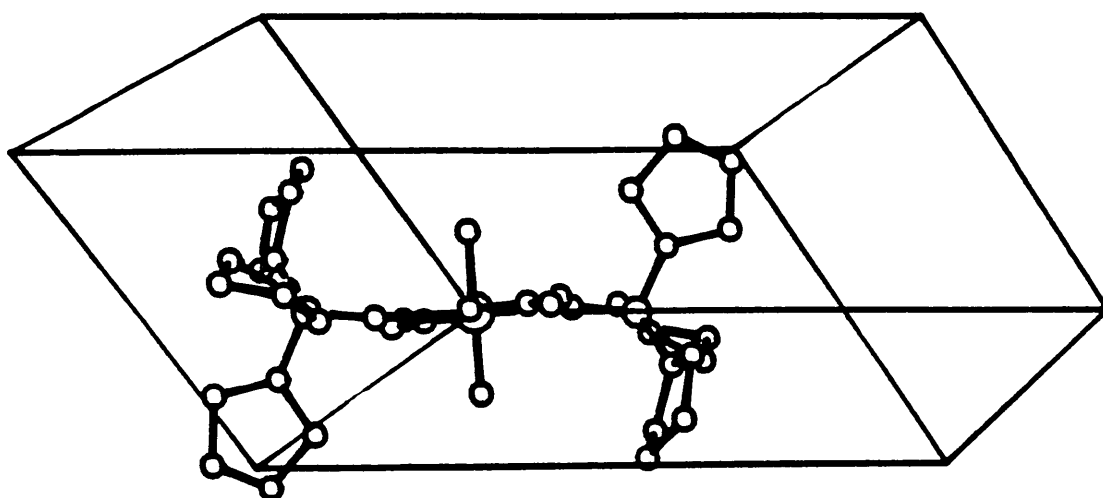


Figure 5.19 Packing diagram of $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{tpyrp}$

5.3 XPS Data

Table 5.8 summarizes peak maximum binding energies for the compounds $U(NO_3)_4 \cdot 2L$ and $UO_2(NO_3)_4 \cdot 2L$, with $L = tppo, tdpo$ and $tpyrp$. The values for the ligands, $tppo$ and $tdpo$, are also tabulated. $Tdpo$ was absorbed in carbon before analysis, as it is a liquid at the experimental pressure and temperature.

Uranium metal was etched with $HNO_3(\text{conc})$ and then sputtered with Argon atoms prior to analysis, to prepare a clean surface. Nevertheless, $O1s$ peaks were still observed, as oxygen was adsorbed from the atmosphere (table 5.8).

Figure 5.20 shows the valence band in uranium metal, and $U(NO_3)_4 \cdot 2L$ ($L = tppo, tdpo$ and $tpyrp$). Also in this graph are C 2p, O 2p, O 2s and possibly N 2p peaks. Figure 5.21 shows the same binding energy region as the previous figure for the compounds $UO_2(NO_3)_2 \cdot 2L$ ($L = tppo, tdpo$ and $tpyrp$.) Table 5.9 summarizes valence shell peak maxima. Binding energy values in this region are reported only to one decimal position, as overlapping peaks lead to bigger uncertainties in the determination of the peak maxima.

Figure 5.22 and 5.23 show respectively the $U4f_{7/2}$ and N 1s peaks for the uranium nitrate compounds studied.

The P 2p peaks are shown in figures 5.24 and 5.25. Figures 5.26 and 5.27 show the positions of the C 1s peaks in the various compounds and figures 5.28 and 5.29 the positions of the O 1s peaks.

Figure 5.30 show the P 2p peak in the compounds tppo and tdpo, where tdpo was absorbed in carbon. Figure 5.31 show the low binding energy orbitals in the two ligands tppo and tdpo. Unless otherwise stated, the binding energy values are quoted to an estimated accuracy of $\pm 0,01\text{eV}$.

Table 5.8 XPS Data for core levels

Compound	Binding energy peak maxima (eV)						
	U4f _{7/2}	U4f _{5/2}	NO ₃ ⁻ N 1s	Ligand N 1s	O 1s	C 1s	P 2p
Uranium metal	377,45	388,30	-	-	530,70	285,85	-
tppo	-	-	-	-	532,90	286,85	134,40
tdpo	-	-	-	400,00	533,00	291,65	134,50
U(NO ₃) ₄ •2tpyrp	384,75	395,65	410,45	403,00	536,10	288,50	137,30
U(NO ₃) ₄ •2tdpo	385,85	397,40	411,50	404,20	538,05	290,65	138,75
U(NO ₃) ₄ •2tppo	384,80	395,65	410,80	-	536,35	288,15	136,45
UO ₂ (NO ₃) ₂ •2tpyrp	387,85	398,35	412,20	404,20	537,65	290,40	138,05
UO ₂ (NO ₃) ₂ •2tdpo	387,75	398,80	412,50	404,70	537,85	291,05	138,75
UO ₂ (NO ₃) ₂ •2tppo	385,90	396,75	409,90	-	536,10	288,25	136,15

Table 5.9 XPS Data for valence shell

Compound	Binding energy valence shell peak maxima (eV)			
	U5f	U6p _{1/2}	U6p _{3/2}	O2s _{1/2}
Uranium metal	0,95	26,9	17,1	-
tppo	-	-	-	22,5
tdpo	-	-	-	(20,0)
U(NO ₃) ₄ •2tpyrp	6,4	28,5	17,5	22,6
U(NO ₃) ₄ •2tdpo	6,4	29,3	(19,5)	21,3
U(NO ₃) ₄ •2tppo	6,4	29,5	17,7	23,0
UO ₂ (NO ₃) ₂ •2tpyrp	-	30,1	(19,6)	24,8
UO ₂ (NO ₃) ₂ •2tdpo	-	30,0	(20,7)	22,5
UO ₂ (NO ₃) ₂ •2tppo	-	30,0	(18,3)	24,2

Parentheses denote less certain data.

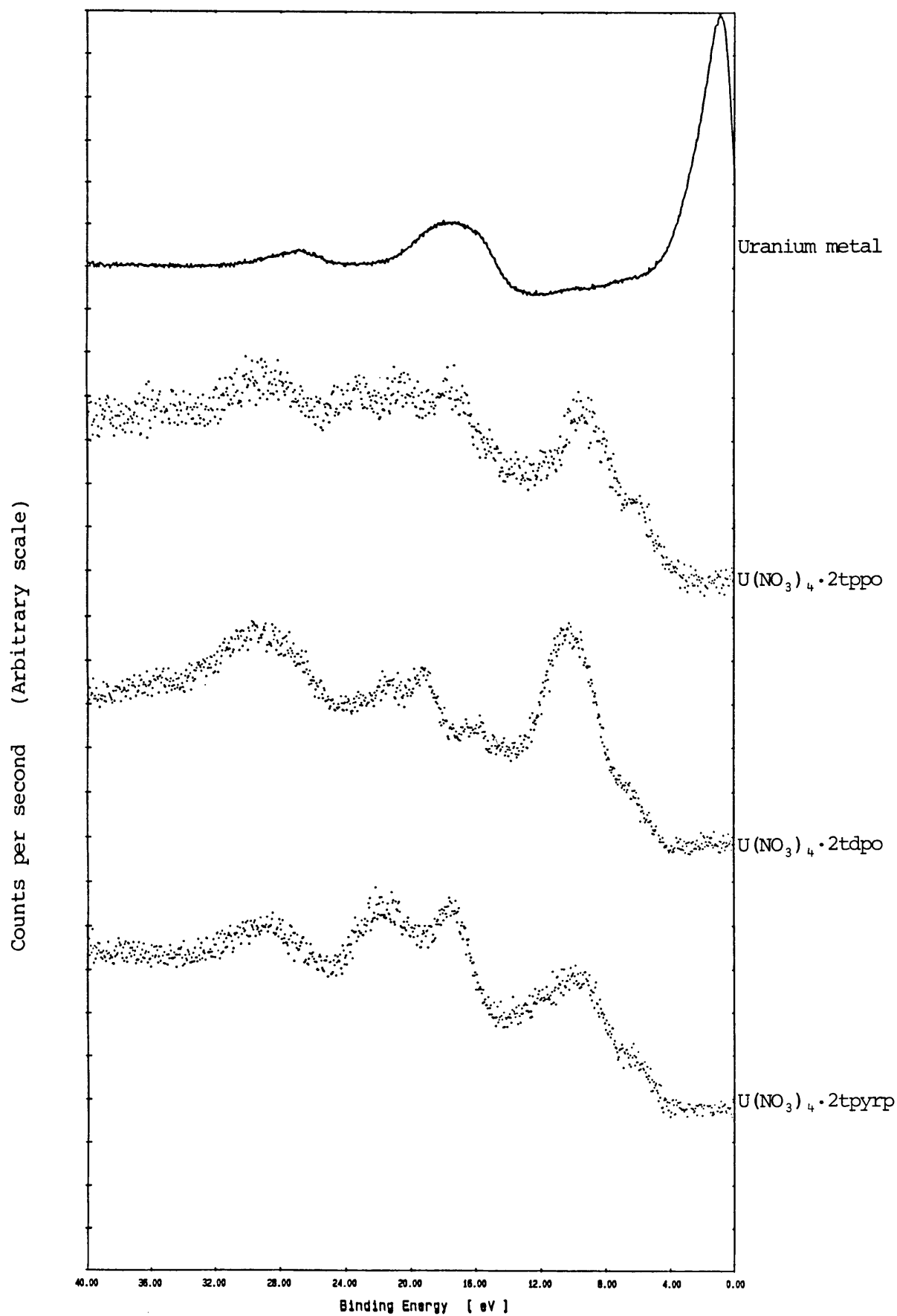


Figure 5.20 Valence band XPS data for uranium(IV) complexes

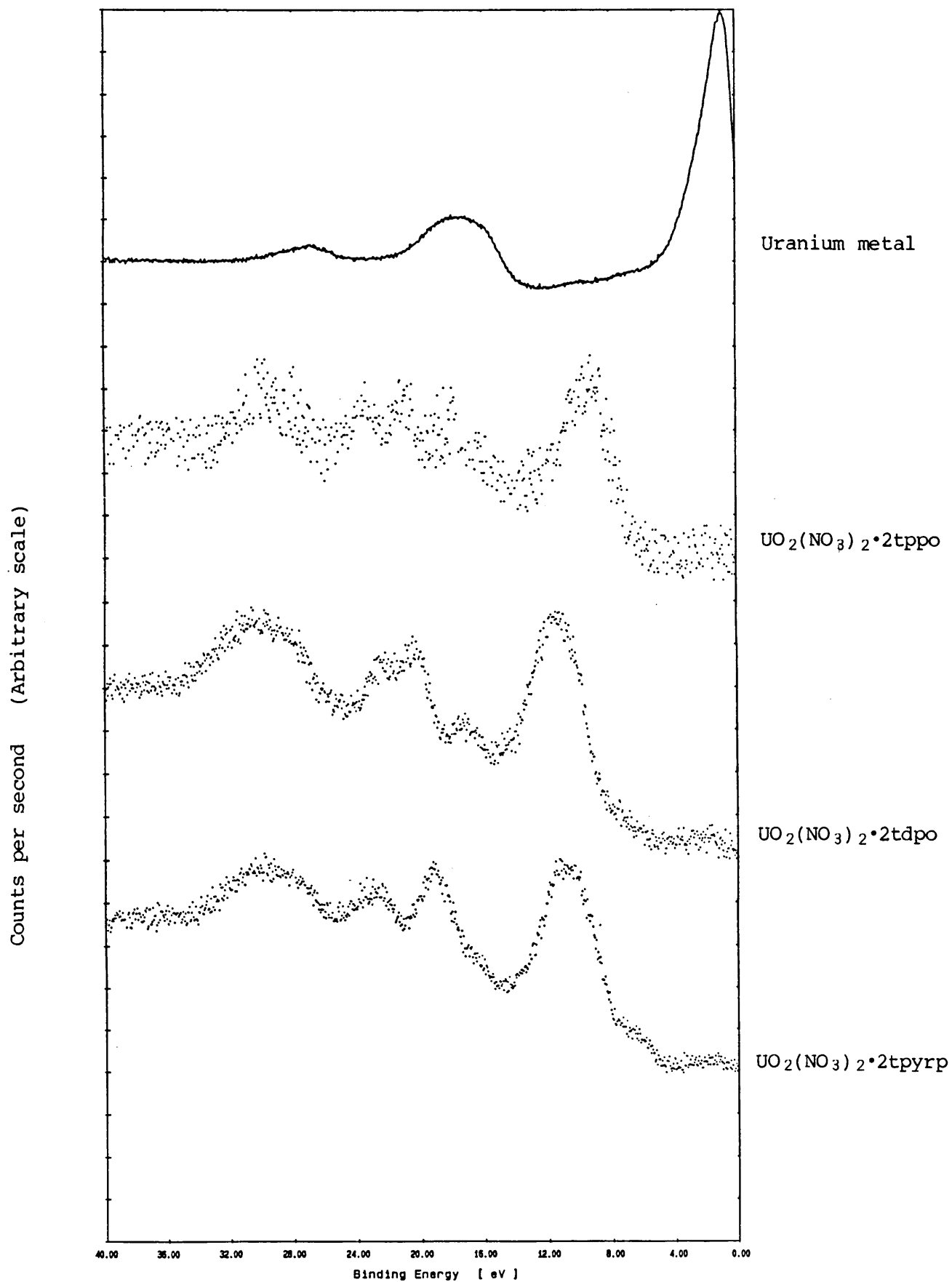


Figure 5.21 Valence band XPS data for uranium(VI) oxynitrate complexes

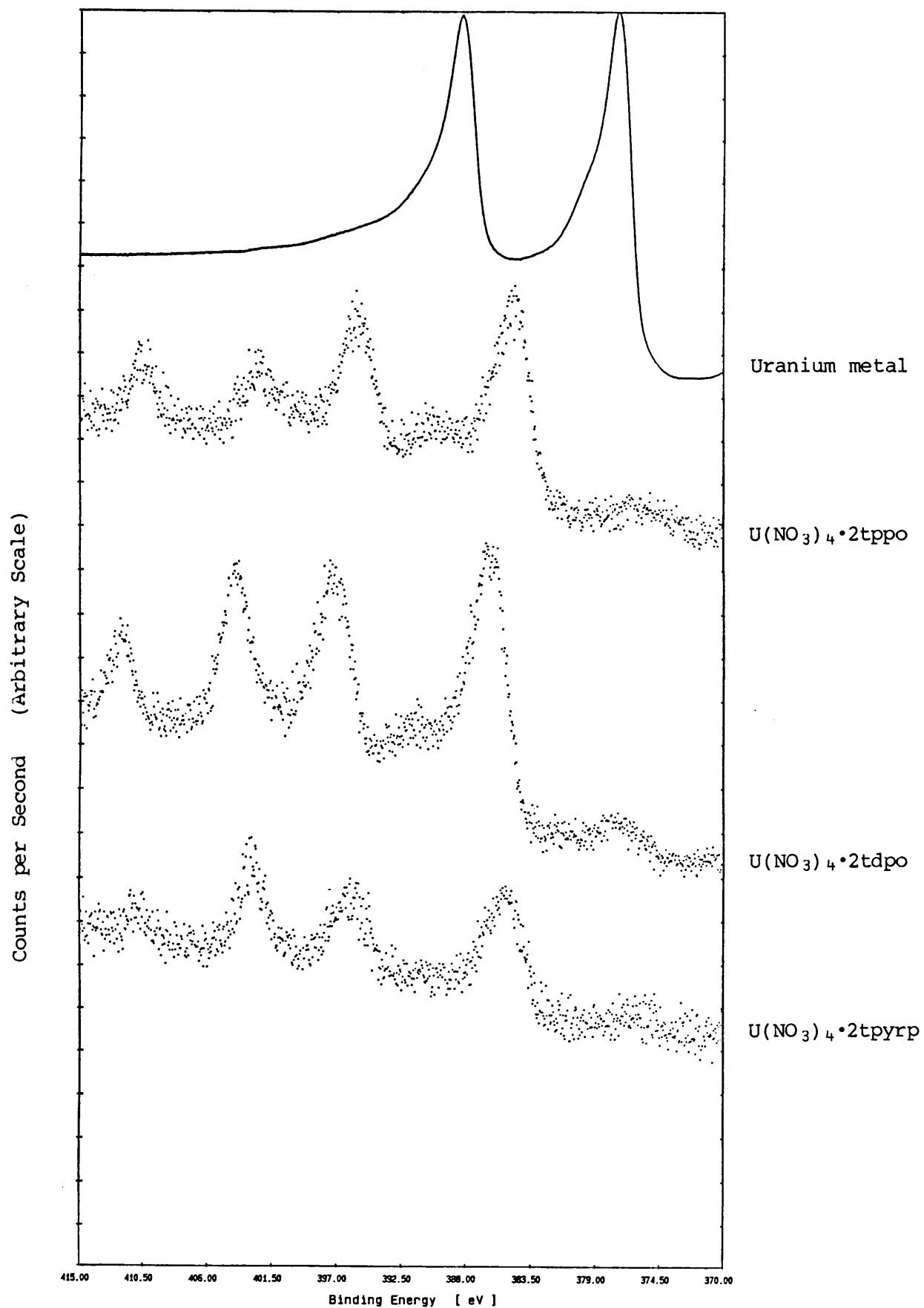


Figure 5.22 U4f and N1s XPS peaks for uranium(IV) complexes

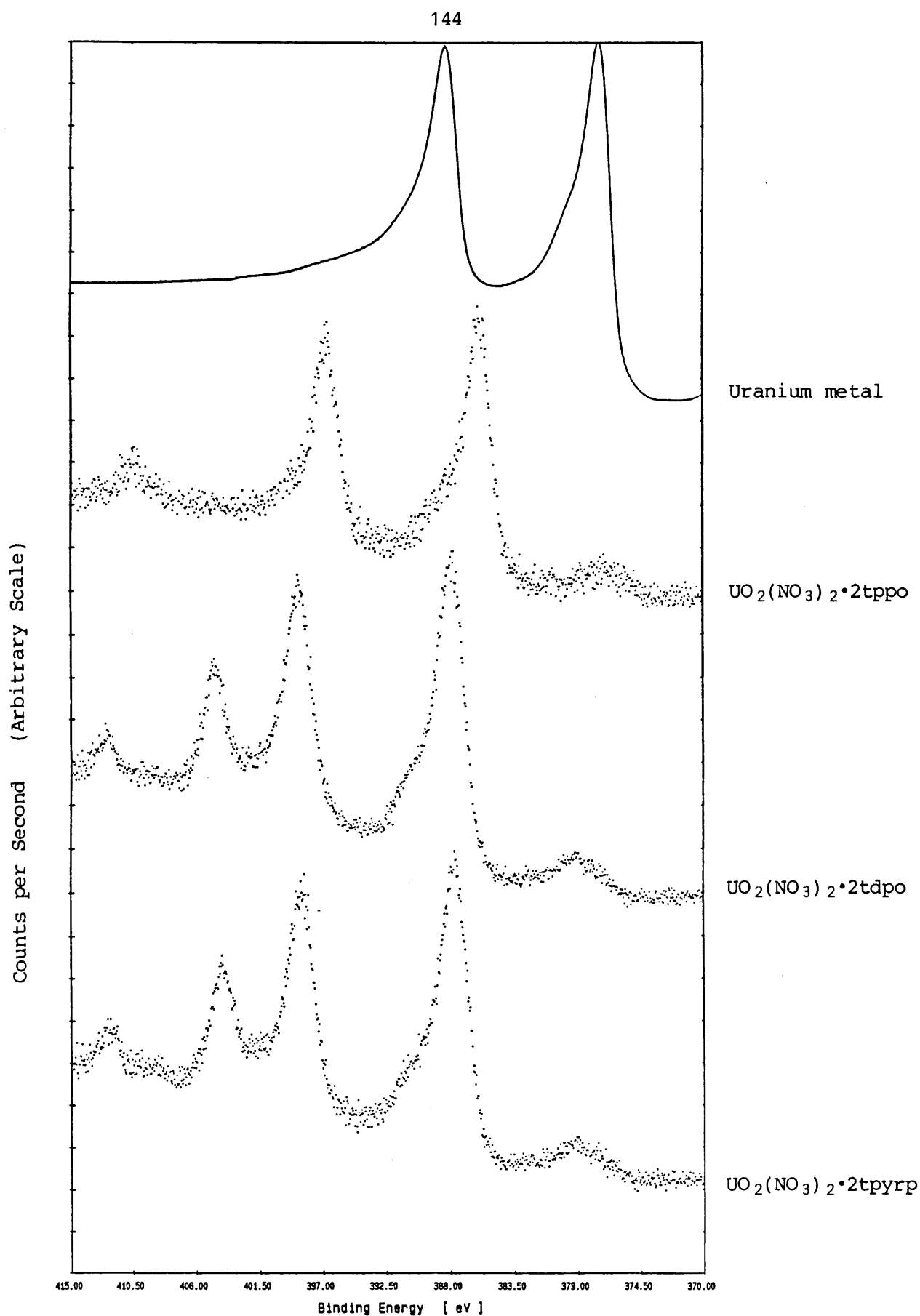


Figure 5.23 U4f and N1s XPS peaks for uranium(VI) complexes

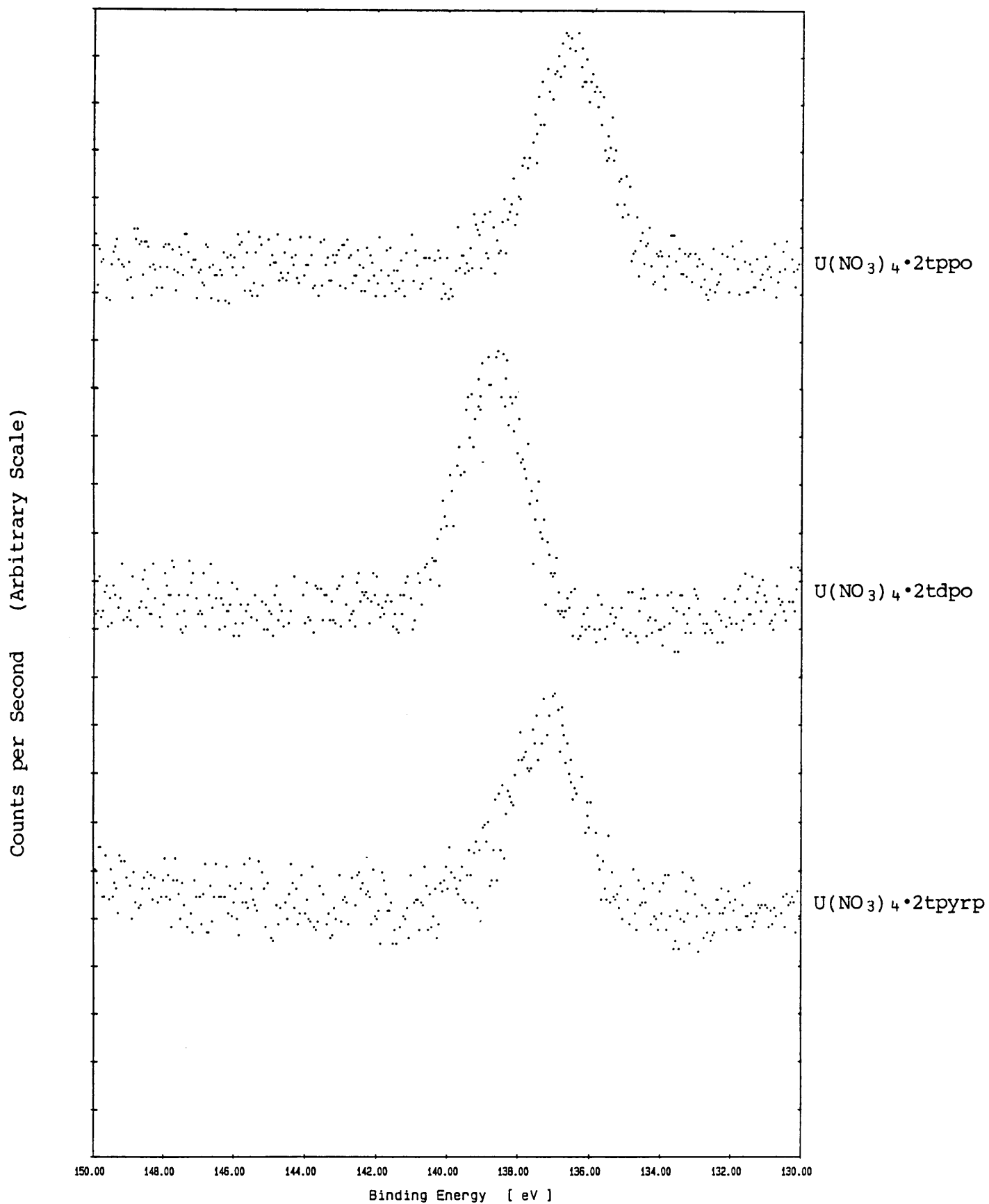


Figure 5.24 P2p XPS peaks for uranium(IV) complexes

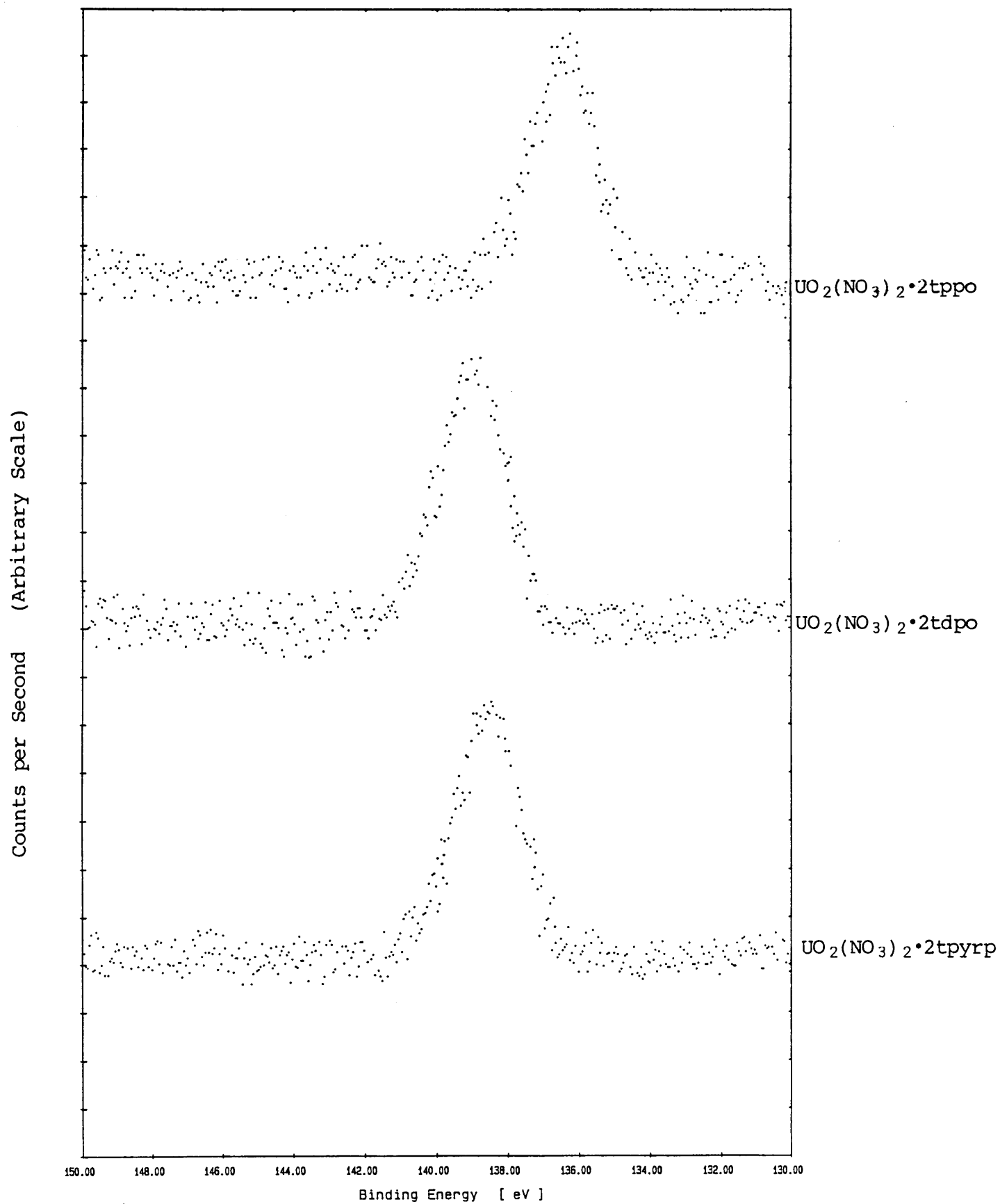


Figure 5.25 P2p XPS peaks for uranium(VI) complexes

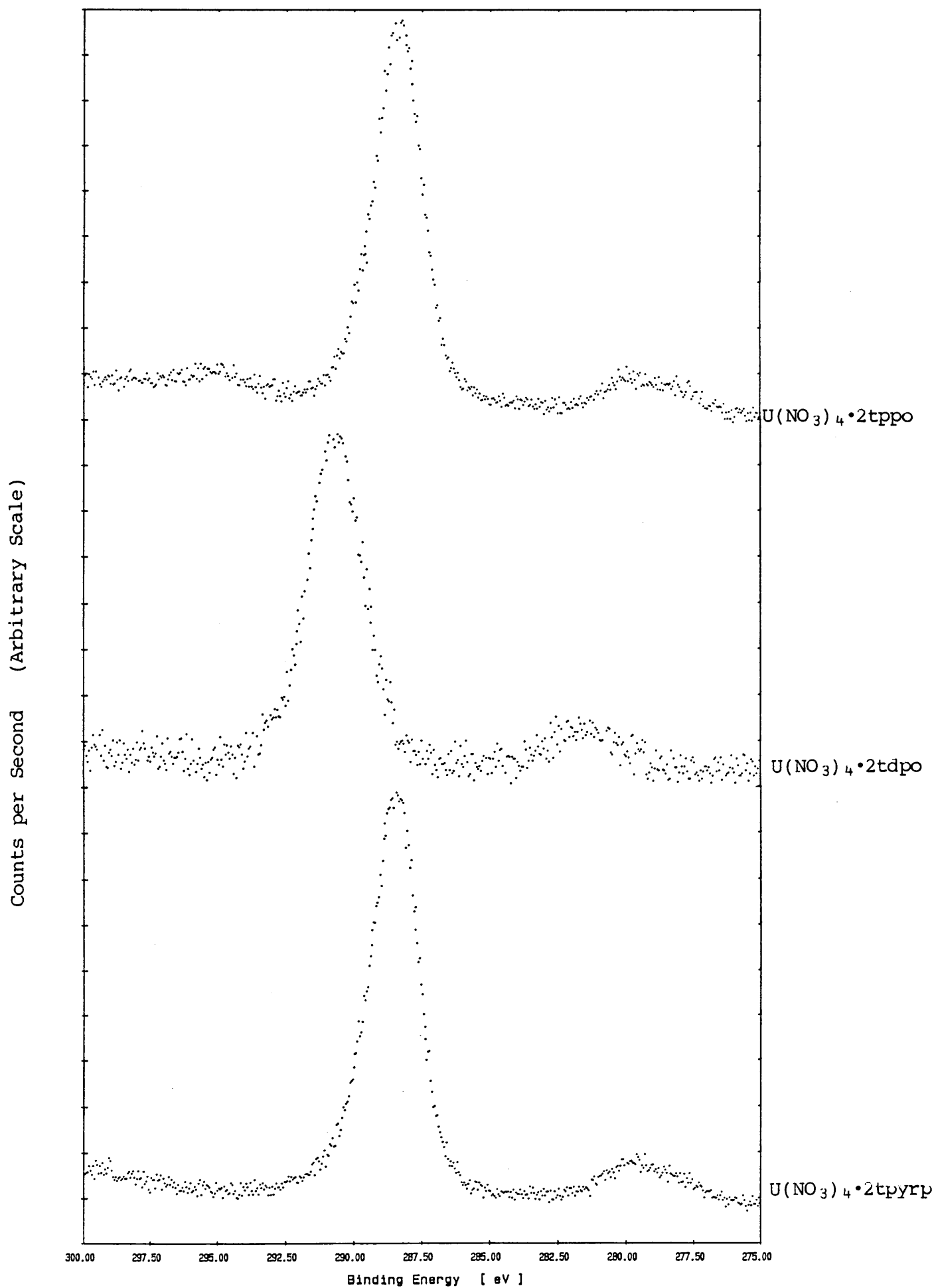


Figure 5.26 C1s XPS peaks for uranium(IV) complexes

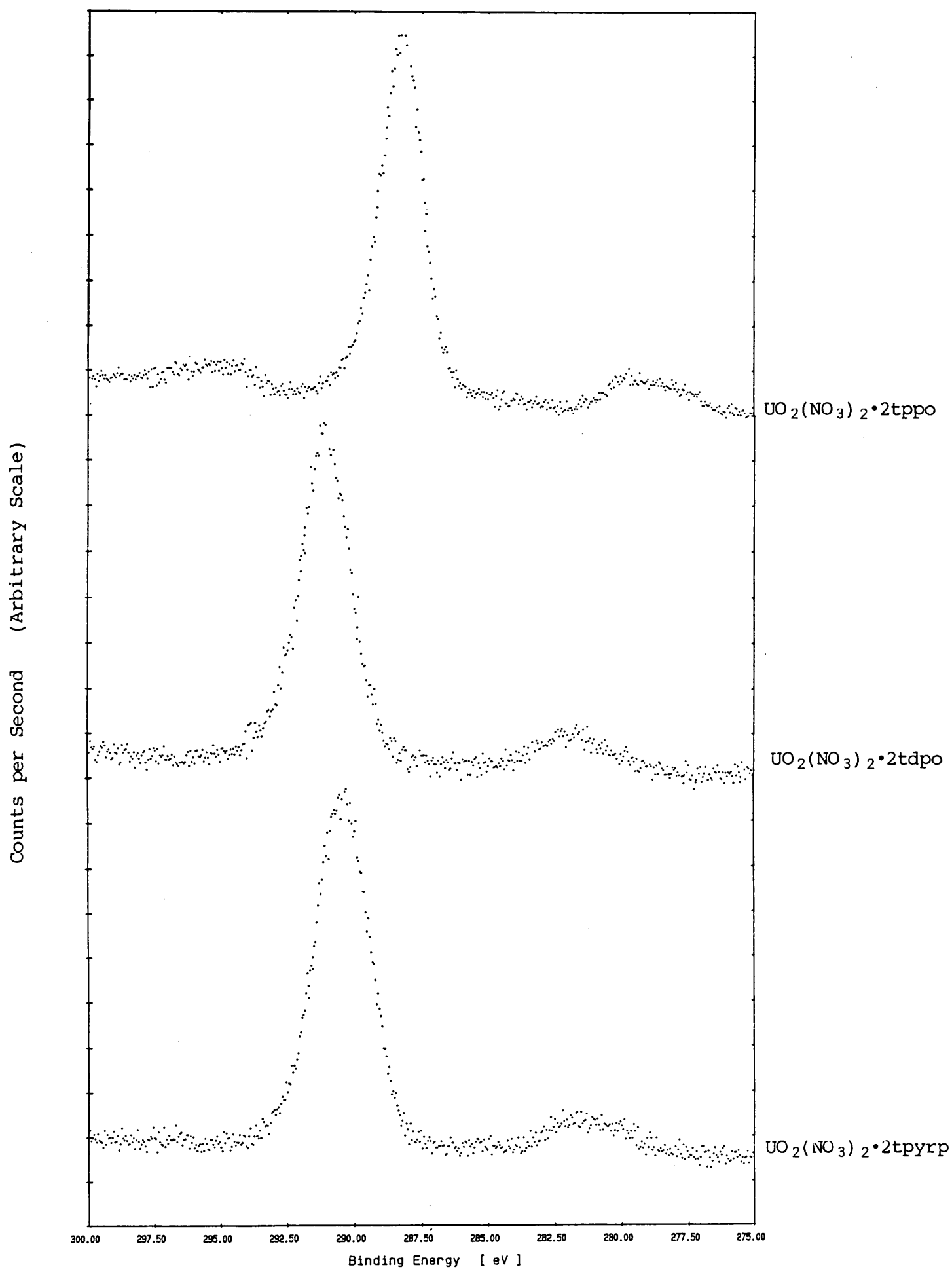


Figure 5.27 O 1s XPS peaks for uranyl(VI) complexes

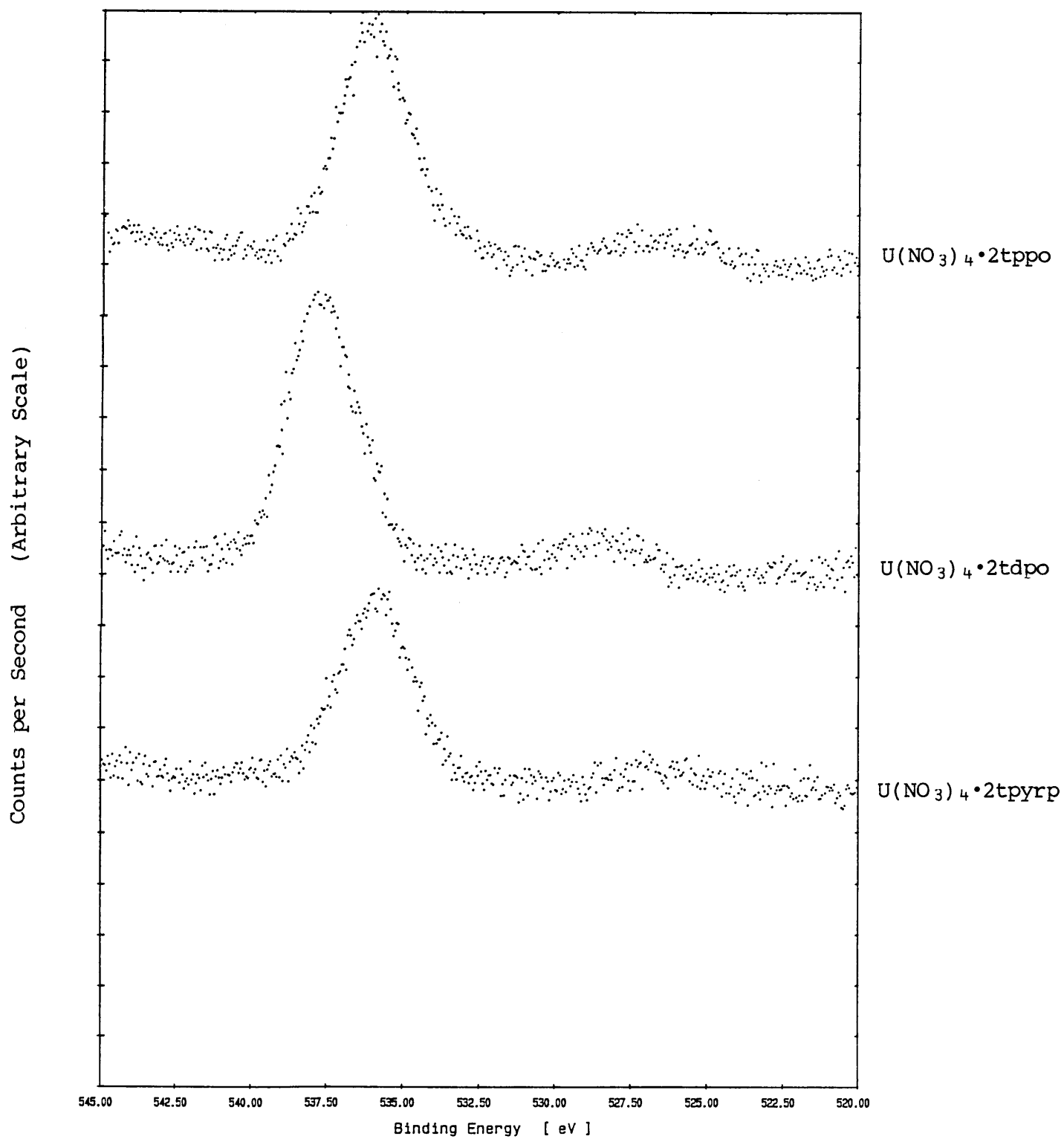


Figure 5.28 O1s XPS peaks for uranium(IV) complexes

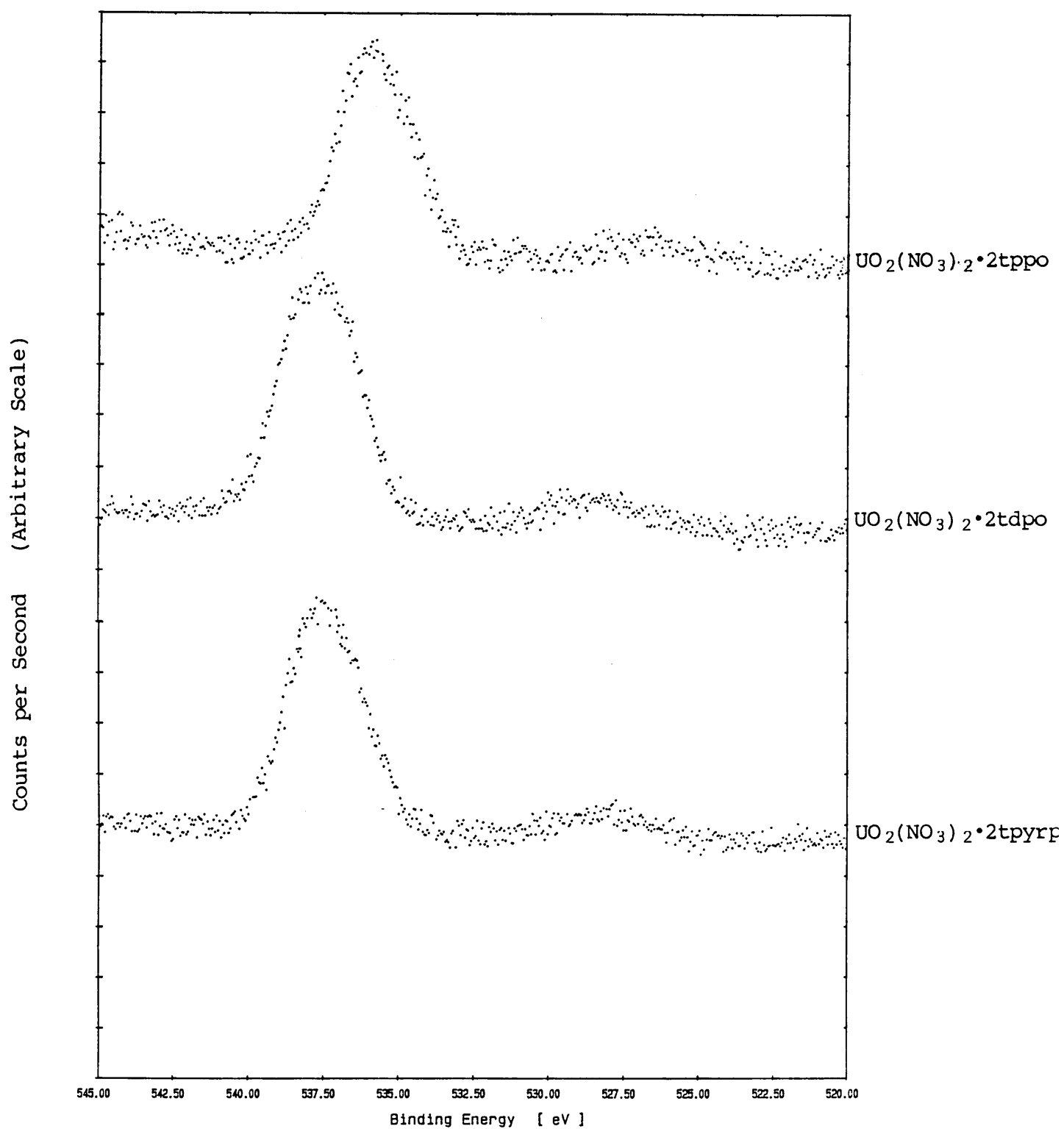


Figure 5.29 O1s XPS peaks for uranium(VI) complexes

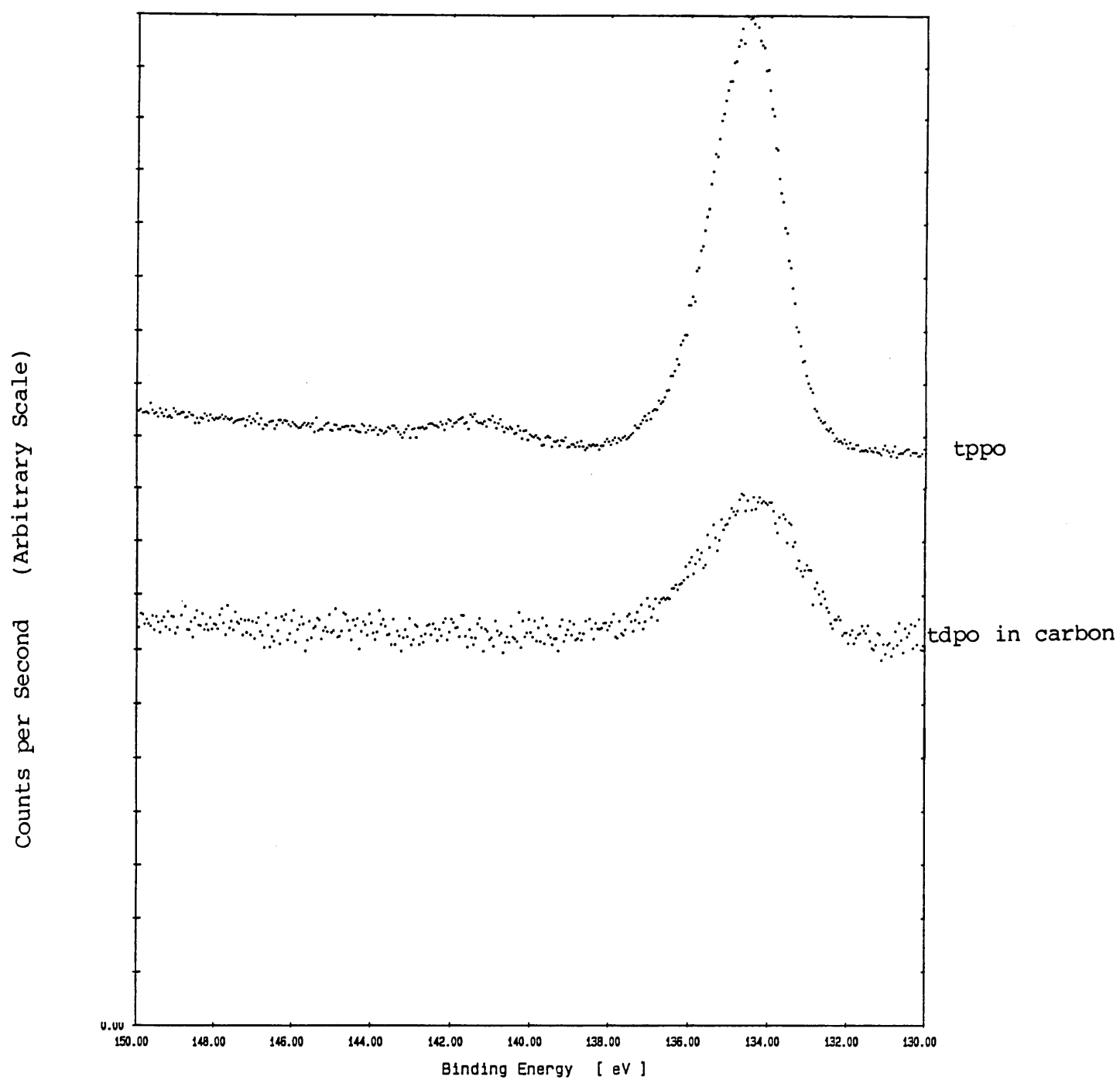


Figure 5.30 P2p XPS peaks in tppo and tdp

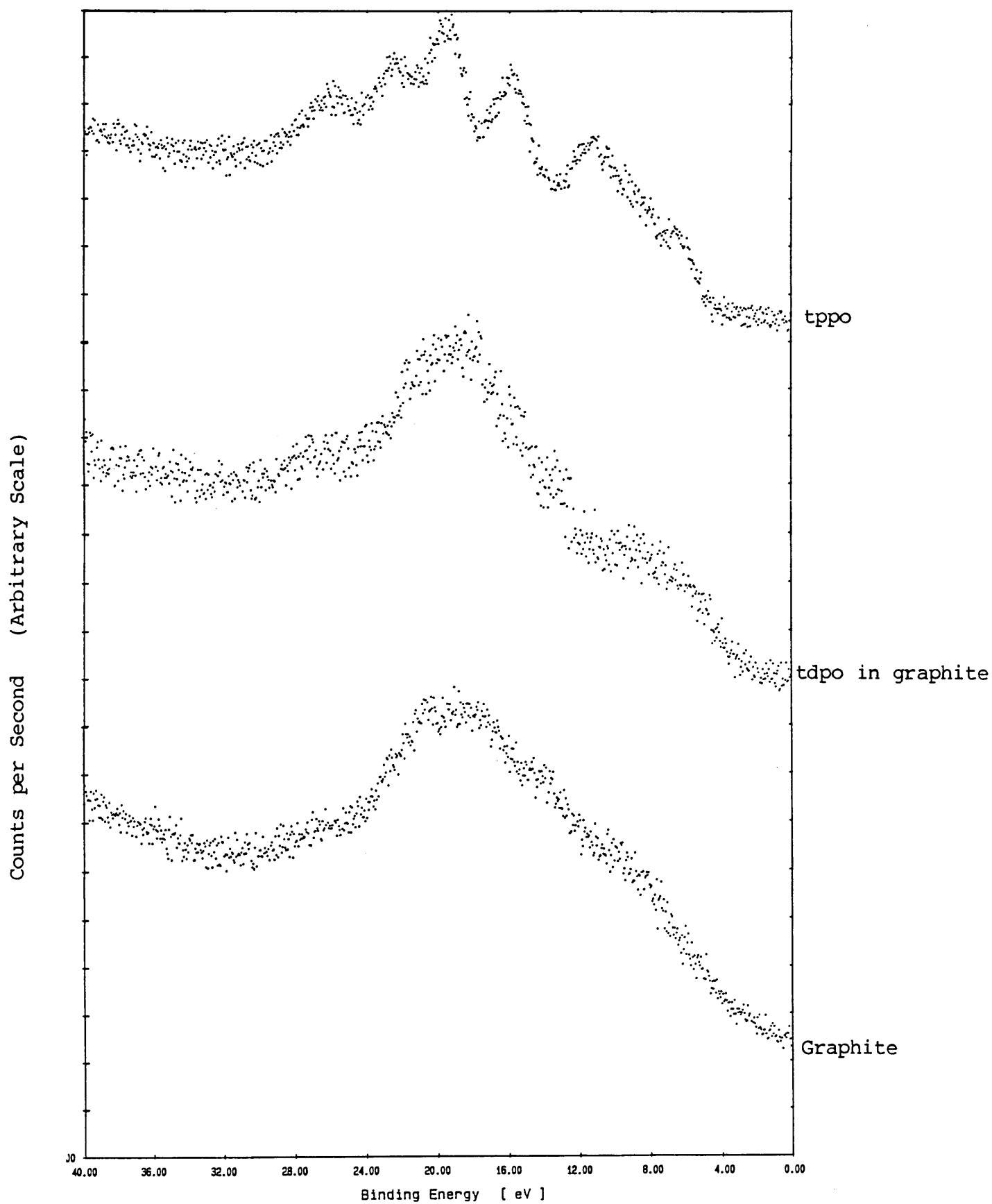


Figure 5.31 XPS data of the valence orbitals in tppo and tdp0

CHAPTER 6

DISCUSSION OF THE RESULTS OF THE STUDIES ON THE URANIUM(IV) NITRATE COMPLEXES

6.1 Kinetics studies

The uranium(IV) nitrate complexes decompose to uranyl(VI) nitrate complexes, thus in addition to the rupture of bonds (as previously described), oxidation of uranium(IV) to uranium(VI) occurs. The influence of the ligands on the decomposition reactions is an additional factor. No decomposition of the ligands; tdpo, tppo and tpyrp, was observed in the temperature range of this study. Both the reactants and solids are in the solid state in the experimental temperature ranges. The decomposition of all the uranium(IV) nitrate complexes is exothermic, while that of the lanthanide nitrates is endothermic.

A comparison between the mechanisms, activation energies, pre-exponential factors and temperature ranges for the uranium(IV) complexes' decomposition is given in table 6.1.

From table 6.1 it is clear that each uranium(IV) nitrate complex decomposes according to a different kinetic mechanism. Each kinetic model describes a different process, and it is thus debatable whether comparisons of the activation energies and the pre-exponential factors for the different reactions, are trivial. Nevertheless, a trend was observed

Table 6.1 Kinetic results of the decomposition of the uranium(IV) nitrate complexes

Complex	Kinetic equation	Temperature range	Activation energy (kJ·mol ⁻¹)	Pre-exponential factor ln(A/min ⁻¹)
U(NO ₃) ₄ ·2tdpo	kt=-ln(1-α)	98°C-156°C	127,0	40,0
U(NO ₃) ₄ ·2tppo	kt=1-(1-α) ^{1/2}	130°C-162°C	109,4	30,0
U(NO ₃) ₄ ·2tpyrp [19]	kt=($\frac{1}{1-\alpha}$)-1	87°C-112°C	185	48

for the activation energy values and the pre-exponential factors. With an increase in the decomposition onset temperature, a decrease in the activation energy values and pre-exponential factors was observed.

6.1.1 U(NO₃)₄·2tdpo

The average correlation coefficient for the fit of the Avrami-Erofe'ev equation, with $n = 1$, to the experimental data was calculated to be 0,998. The next best fit was for the Avrami-Erofe'ev equation, with $n = \frac{3}{2}$, with an average correlation coefficient of 0,994. The contracting volume equation, $kt = 1-(1-\alpha)^{0,33}$ also showed a high correlation coefficient value (0,993).

Figure 6.1 gives the reduced time plots for two sets of experimental data, and for the three models that best describe the data. From these reduced time plots it is

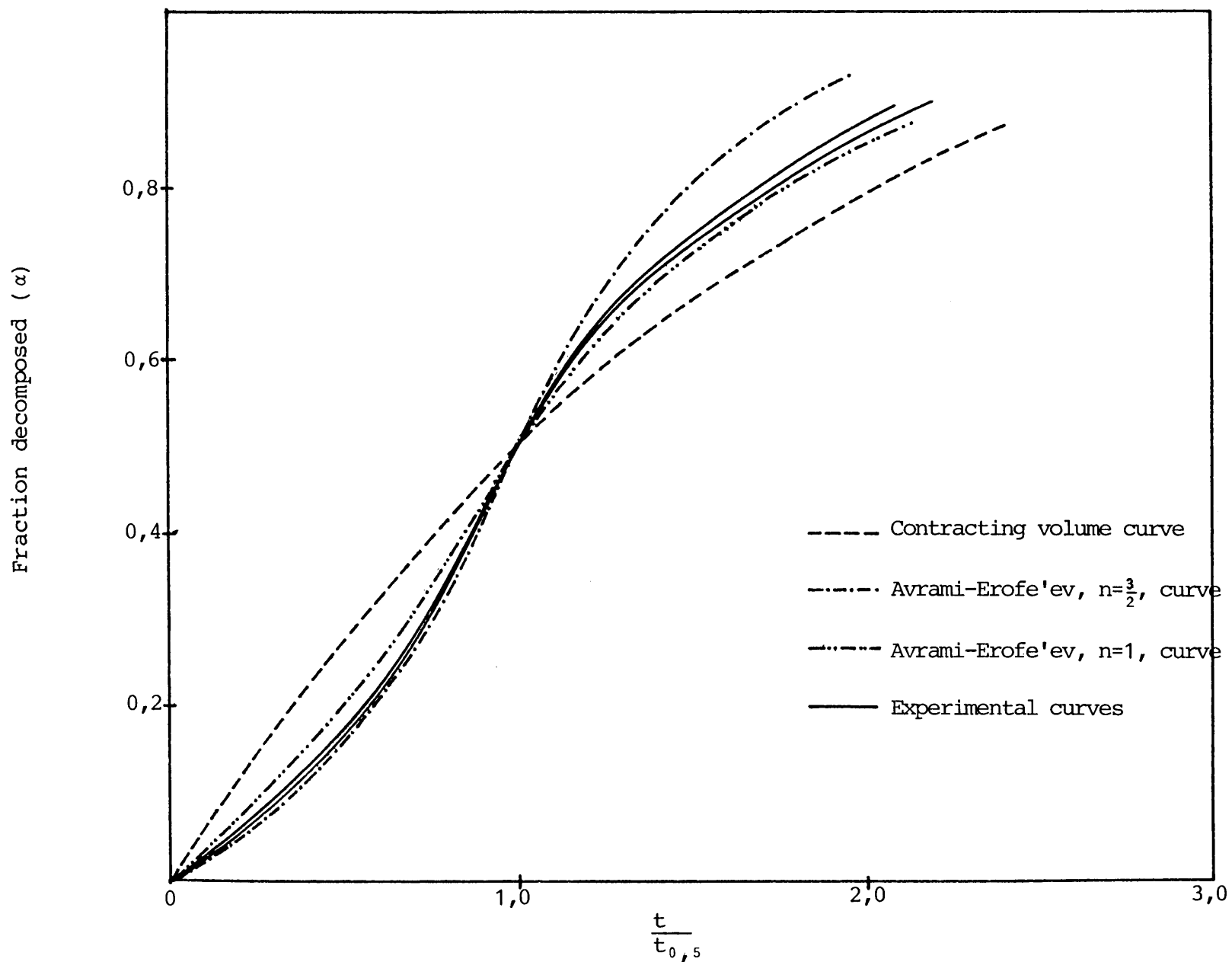


Figure 6.1 Reduced time plots for $U(NO_3)_4 \cdot 2tdpo$

clear that of the 19 different kinetic models, the Avrami-Erofe'ev equation, with $n = 1$, best describes the experimental data.

Using the rate constants, calculated from the Avrami-Erofe'ev equation ($n = \frac{3}{2}$), an activation energy of $128,8 \text{ kJ}\cdot\text{mol}^{-1}$ and a pre-exponential factor of $\ln(A/\text{min}^{-1}) = 39,8$ were determined. The activation energy calculated from the rate constants derived from the contracting volume equation is $142,9 \text{ kJ}\cdot\text{mol}^{-1}$ and the pre-exponential factor ($\ln(A/\text{min}^{-1})$) is $43,3$. The activation energy and pre-exponential factor seem to be independent of the kinetic model, as the values determined from the different models are approximately the same. The best approximation of the activation energy and pre-exponential factor seems to be that calculated from a mathematical expression, that exactly describes the decomposition data.

6.1.2 $\text{U}(\text{NO}_3)_4 \cdot 2\text{tppo}$

The contracting area equation, $kt = 1-(1-\alpha)^{0,5}$, showed the best fit to the experimental decomposition data of $\text{U}(\text{NO}_3)_4 \cdot 2\text{tppo}$, with an average correlation coefficient of $0,998$. The contracting volume equation, $kt = 1-(1-\alpha)^{0,33}$, gave an average correlation coefficient value of $0,996$ and the values for the Avrami-Erofe'ev equations, with $n = 1, \frac{3}{2}, 2$ and 3 , also showed high values ($> 0,980$).

From the reduced time plots (figure 6.2) it is clear that

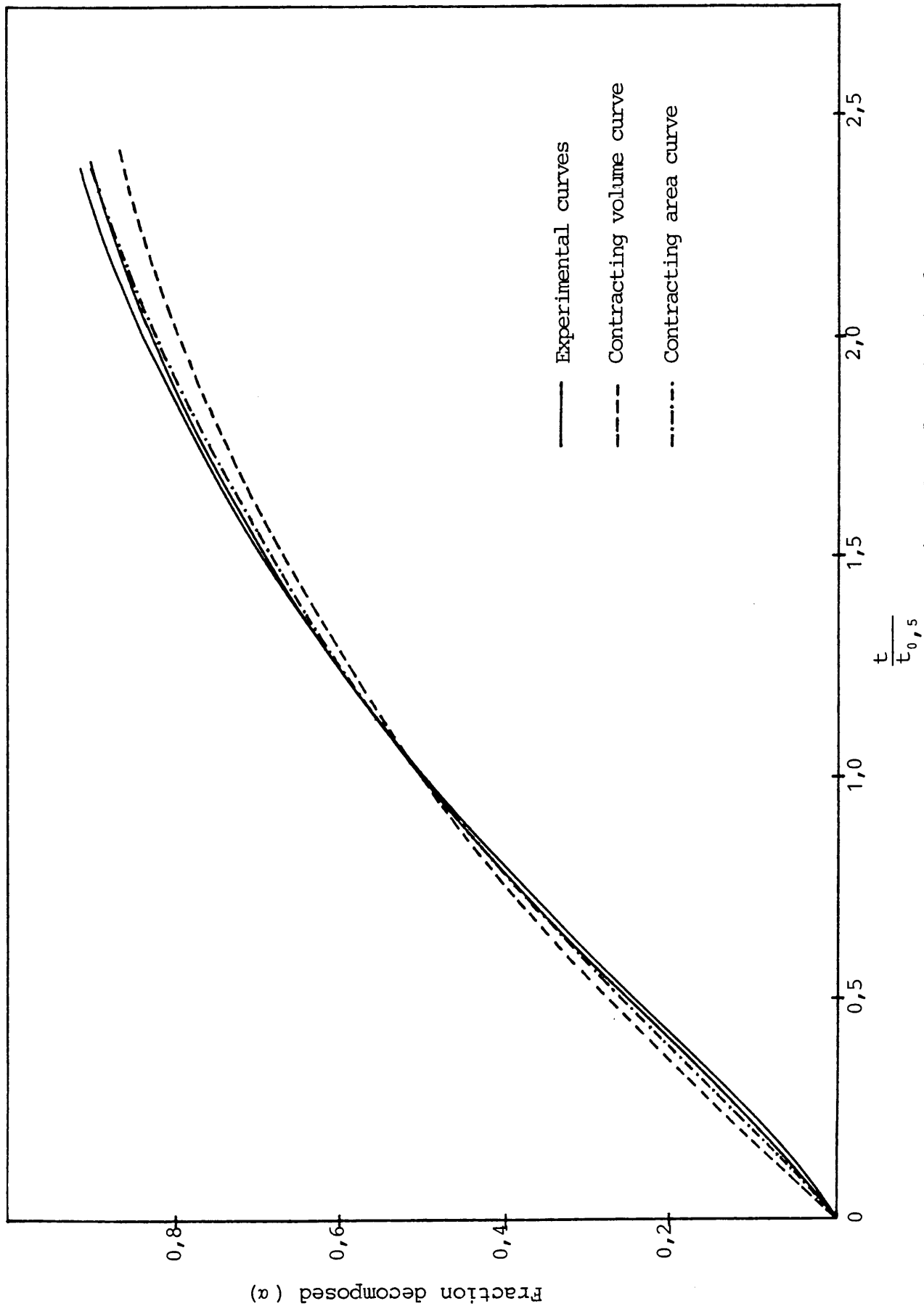


Figure 6.2 Reduced time plot for $\text{U}(\text{NO}_3)_4 \cdot 2\text{tppo}$

of the nineteen kinetic models, the contracting area equation is the best fit to the experimental data. The activation energy value, calculated from the contracting volume equation, is $104,4 \text{ kJ}\cdot\text{mol}^{-1}$ and the pre-exponential factor ($\ln(A/\text{min}^{-1})$) is $27,4$. These values are approximately the same as those for the contracting area equation (table 6.1).

As was the case for the lanthanide nitrates, it seems that the kinetic models are only mathematical descriptions of the decomposition data. The reason for this behaviour seems to be the same as for the decomposition kinetics of the lanthanide nitrates (paragraph 4.2.4).

6.2 Structural studies

In the uranium(IV) nitrate complexes, uranium is ten co-ordinated, two oxygen atoms from each nitrate group being bonded to the uranium atom together with two oxygen atoms from the neutral donor ligands. The uranium(VI) ion in the uranyl complexes is eight co-ordinated, where two nitrate groups are exchanged for two oxygen atoms. All these complexes belong to different space groups and different structures (figures 5.8 - 5.18).

Studies concerning $\text{UCl}_4\cdot 2\text{L}$ and $\text{UBr}_4\cdot 2\text{L}$ complexes (L = phosphine and arsine oxides) showed that uranium in these complexes is six co-ordinated with the neutral ligands in trans-positions [47]. Only the compound $\text{UCl}_4\cdot 2\text{tppo}$ showed

the ligands in cis-positions, due to a more stable crystal packing [71]. The uranium(IV) and uranyl nitrate complexes studied, showed trans-positions for all neutral ligand groups.

6.2.1 Bond angles

The U-O-P angles in $\text{UCl}_4 \cdot 2\text{tppo}$ and $\text{UCl}_4 \cdot 2\text{hmpa}$ (hmpa = hexamethyl phosphoramidate) are approximately the same ($165,1(5)$ and $163(2)^\circ$) [71]. A somewhat smaller value of $159,8(4)^\circ$ was reported in the complex $\text{UCl}_4 \cdot 2\text{tppa}$ (tppa = tetramethylphosphoramidate) [70]. Table 6.2 summarizes the U-O-P angles in the complexes studied. In all the uranium(IV) nitrate complexes, significantly higher values ($168,4(9)$ - $171,5(8)^\circ$) of the U-O-P angles were observed than in the uranium(IV) halide complexes ($159,8(4)$ - $165,1(5)^\circ$).

Table 6.2. Bond angles ($^\circ$) in the uranium(IV) and uranyl complexes

Complex	U-O-P	Smallest UO-N-OU	Biggest UO-N-OU
$\text{U}(\text{NO}_3)_4 \cdot 2\text{tpyrp}$	$171,5(8)$	$113(2)$	$120(2)$
$\text{U}(\text{NO}_3)_4 \cdot 2\text{tdpo}$	$168,4(9)$	$113(2)$	$117(2)$
$\text{U}(\text{NO}_3)_4 \cdot 2\text{tppo}$	$170,8(7)$	$110(2)$	$112,9(14)$
$\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{tpyrp}$	$161,1(2)$	$114,5(5)$	$114,5(5)$
$\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{tdpo}$	$179,3(6)$	$121(2)$	$125(2)$
$\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{tppo}$	$159,2(3)$	$113,8(7)$	$113,8(7)$

The U-O-P angles in the uranyl nitrate complexes differ from $159,2(3)^\circ$ for the tppo complex to $179,3(6)^\circ$ for the tdp complex. The angles in the uranyl nitrate tppo complex ($159,2(3)^\circ$) and the uranyl nitrate tpyrp complex ($161,1(2)^\circ$) are approximately the same as observed in the six-coordinated uranium(IV) halide complexes [70,71]. The U-O-P angle of $179,3(6)^\circ$ in $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{tdpo}$ showed the two neutral ligands in an approximately linear position to the uranium ion.

The UO-N-OU angles in the uranium(IV) nitrate complexes vary from $110(2)$ to $120(2)^\circ$. The smallest UO-N-OU angles in the nitrate groups in each complex ($110(2) - 113(2)^\circ$) show the occurrence of a distortion from the equilateral triangle (120°) around the N atom. If it is assumed that the nitrate groups with the biggest distortion from the equilateral triangle structure are the groups that decompose, then the oxygen-uranium bonds as summarized in table 6.3 are involved in the decomposition reactions (figures 5.8 - 5.18).

Table 6.3. Oxygen-Uranium pairs in the uranium(IV) complexes involved in the decomposition reactions

Complex	Oxygen-Uranium pairs
$\text{U}(\text{NO}_3)_4 \cdot 2\text{tpyrrp}$	O(24)-U, O(25)-U
$\text{U}(\text{NO}_3)_4 \cdot 2\text{tdpo}$	O(8) -U, O(7) -U
$\text{U}(\text{NO}_3)_4 \cdot 2\text{tppo}$	O(54)-U, O(55)-U and (O(50)-U, O(51)-U)*

*() denotes less certain data

When comparing the oxygen-uranium pairs proposed in table 6.3 to the structures of the decomposition products, it seems that in $\text{U}(\text{NO}_3)_4 \cdot 2\text{tdpo}$ (figure 5.8) either the O(8)-U or the O(7)-U bond is ruptured, resulting in an U=O(1) bond with the remaining oxygen in the $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{tdpo}$ molecule (figure 5.14). This change only involves slight changes in the positions of all atoms between the uranium(IV) nitrate and its decomposition product, uranyl nitrate. No rearrangement of co-ordinated groups is necessary. It proved difficult to predict whether the U-O(7) or the U-O(8) bond is ruptured, as these two bond lengths are approximately the same. It seems that either of these bonds can be ruptured and that the rupturing occurs on a random base in the nitrate groups showing the biggest distortion from an equilateral triangle.

In the $\text{U}(\text{NO}_3)_4 \cdot 2\text{tppo}$ complex it seems that the O(54)-U or O(55)-U bond and the O(50)-U or O(51)-U bond are ruptured during thermal treatment (figure 5.10). This also results in a product requiring little deviation from the reactant's structure (figure 5.16). The structure of the $\text{U}(\text{NO}_3)_4 \cdot 2\text{tpyrp}$ complex indicates that the O(24)-U or O(25)-U bond is ruptured to form the U=O(19) bond in the uranyl nitrate complex (figures 5.12 and 5.18).

6.2.2 Bond lengths

U-O(ligand) bond lengths of 2,24(1) Å were reported for the complexes $\text{UCl}_4 \cdot 2\text{L}$ (L = hmpa and tppo) [71]. The U-O-(ligand) bond lengths in the uranium(IV) nitrate complexes

studied are approximately the same and no significant bond lengthening or shortening was observed in the different complexes (table 6.4). A strong U-O(L) interaction is implied by the bond lengths, which are appreciably shorter than those in e.g. eight co-ordinated U(IV) compounds [71]. The U-O(ligand) bond lengths in the uranyl nitrate complexes all are significantly longer than in the uranium(IV) complexes, implying a weaker uranium-ligand interaction in the uranyl nitrates. The uranium-ligand bonds in these complexes are regarded as highly ionic [47].

Table 6.4. Average bond lengths (Å) in the uranium(IV) and uranyl complexes

Complex	Average bond lengths (Å)		
	U-O(L)	U-O(NO ₂)	O-P(L)
U(NO ₃) ₄ •2tpyrp	2,241(10)	2,513(29)	1,479(11)
U(NO ₃) ₄ •2tdpo	2,226(10)	2,481(34)	1,514(12)
U(NO ₃) ₄ •2tppo	2,230(11)	2,443(94)	1,540(12)
UO ₂ (NO ₃) ₂ •2tpyrp	2,341(3)	2,562(6)	1,502(3)
UO ₂ (NO ₃) ₂ •2tdpo	2,294(7)	2,538(14)	1,507(7)
UO ₂ (NO ₃) ₂ •2tppo	2,371(5)	2,507(8)	1,495(5)

An increasing O-P(ligand) bond length from the tpyrp (1,479(11) Å) to the tdpo (1,514(12) Å) to the tppo complex (1,540(12) Å) is observed in the uranium(IV) complexes. It seems that the P-O bond of 1,46(1) Å in free tppo (and probably the other ligands too) is only slightly affected by the co-ordination to U(NO₃)₄ and obviously maintains a strong double-bond character [71]. Nevertheless the in-

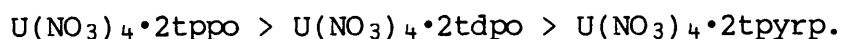
creasing P-O bond length implies a slightly decreasing P-O bond order that could result from an increasing ligand-uranium interaction. This is possibly the result of a delocalization of the oxygen electrons towards the uranium ion and implies a neutral ligand donor strength order for the ligand studied. The order is established as



This ligand donor strength order is the same as that derived from XPS and thermal data (paragraphs 6.3 and 6.4).

No significant O-P(ligand) bond lengthening or shortening was observed in the uranyl nitrate complexes.

The U-O(NO₂) bond lengths in the three uranium(IV) nitrate complexes differ greatly. Although the error ranges overlap, it seems that the average U-O(NO₂) bond length in the tppo complex is the smallest, and the longest U-O(NO₂) average bond length occurs in the tpyrp complex (table 6.4). If it is assumed that the longer the U-O(NO₂) bond, the easier it ruptures, then an order of stability can be established;

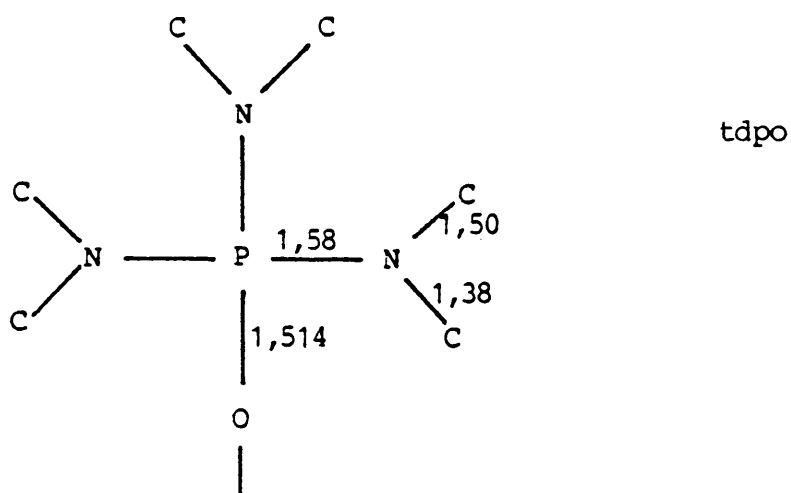
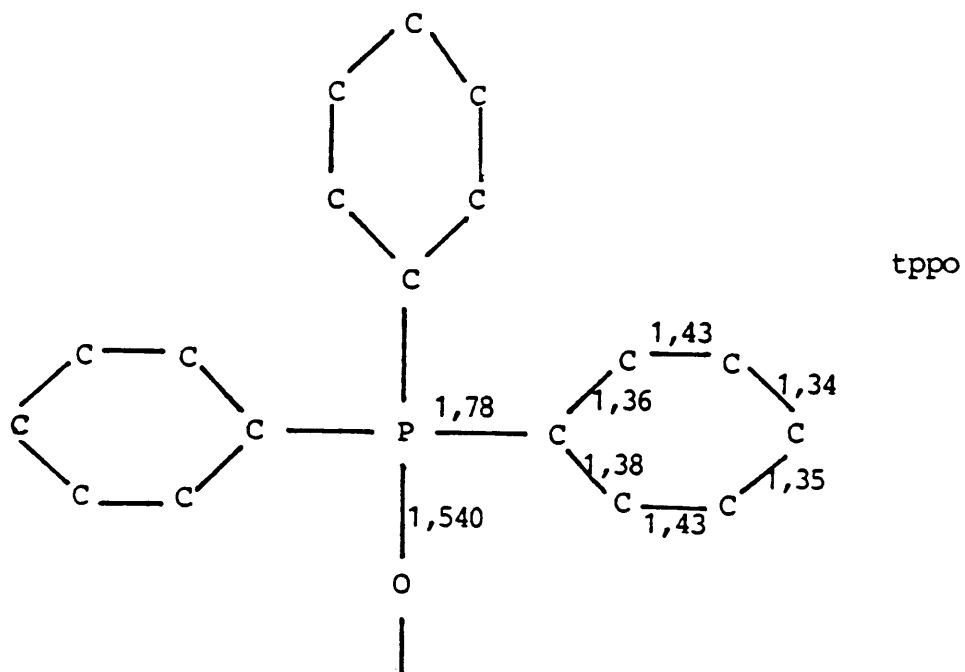


This stability order is the same as the proposed ligand donor strength order.

The U-O(NO₂) bonds in the uranyl complexes are all significantly longer than the bonds in their uranium(IV) nitrate complexes. This is probably due to the influence of the U=O bonds in the oxynitrates.

6.2.3 Lattice energies and ligand sizes

In potentiometric studies it was found that the order of donor strength of P=O ligands is inversely proportional to the size of the ligands [26]. Figure 6.3 gives the lengths of some bonds in the ligands, tppo, tdpo and tpyrp.



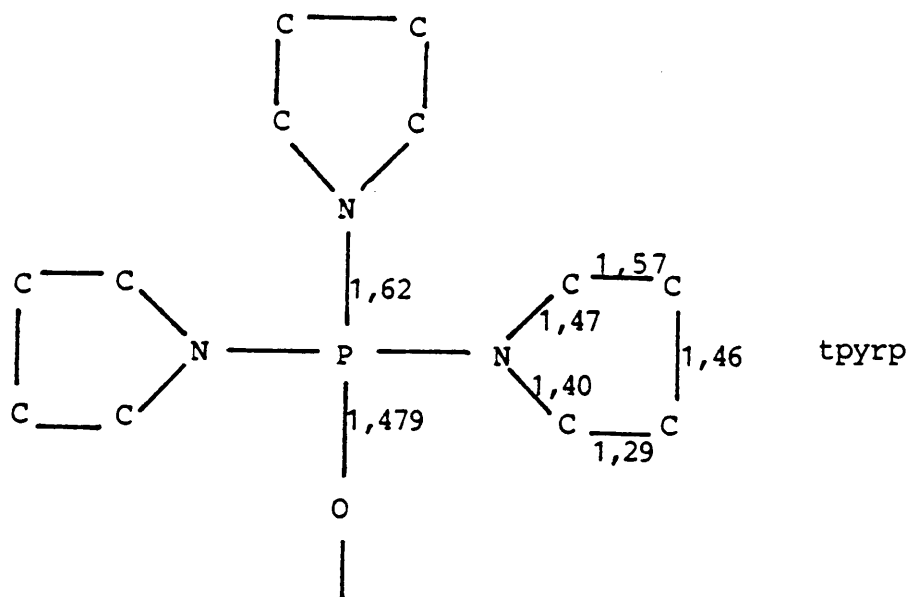
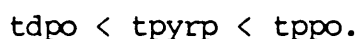


Figure 6.3 Bond lengths in tppo, tdpo and tpyrp.

From figure 6.3 an order of increasing size of the ligands can be established:



According to the mentioned theory, it follows that tdpo is the strongest electron donor, followed by tpyrp and then tppo. However, as it was also found that for P=O ligands, with sizes of the same order, a larger dipole moment on the ligand indicates that it is a stronger electron donor [26].

The lattice energy can be taken as proportional to

$$\frac{v \times z^+ \times z^-}{r^+ + r^-},$$

where v is the total number of the ions, z^+ and z^- are cationic and anionic charges and r^+ and r^- are cationic and anionic radii [27]. Since the uranium(IV) complexes are

not spherical, their radii cannot be accurately determined, but an approximation can be made. The radius of the $U(NO_3)_4 \cdot 2L$ species can be approximated as

$$\text{radius } U^{4+} + \frac{4}{6} \text{ radius } NO_3^- + \frac{2}{6} \text{ radius } L.$$

In the lattice energy equation, the only differing factor for the three uranium(IV) nitrate complexes is the radius of the ligand, as the other radii and charges are approximately the same. The lattice energies of the uranium(IV) complexes can thus be taken as approximately proportional to

$$\frac{X}{Y + \frac{1}{3} \text{ radius } L},$$

with X and Y constants for all the complexes. It is clear that the larger the ligand, the smaller the lattice energy is. A large lattice energy can be regarded as a large driving force for a reaction [26]. According to this approximation, $U(NO_3)_4 \cdot 2tppo$ has to be more stable than $U(NO_3)_4 \cdot 2tpyrp$, with $U(NO_3)_4 \cdot 2tdpo$ the least stable of the three. It must be borne in mind that this is an approximation and that factors such as electron donor strength or dipole moment are not taken into consideration.

6.2.4 X-ray powder diffraction

The X-ray powder diffraction data (table 5.1) of the compounds, $U(NO_3)_4 \cdot 2tpyrp$, $U(NO_3)_4 \cdot 2tppo$ and $U(NO_3)_4 \cdot 2tdpo$ were compared and found to be completely different, indi-

cating different crystal structures for the different complexes. This observation was confirmed by the crystal structure data (paragraph 5.2). $\text{U}(\text{NO}_3)_4 \cdot 2\text{tdpo}$ belongs to the $P\bar{1}$ space group with a triclinic structure, $\text{U}(\text{NO}_3)_4 \cdot 2\text{tppo}$ belongs to the $P2_1/n$ space group with a monoclinic structure and $\text{U}(\text{NO}_3)_4 \cdot 2\text{tpyrp}$ belongs to the $P4_12_12$ space group with a tetragonal structure.

The small observed difference in the X-ray powder diffraction data of $\text{U}(\text{NO}_3)_4 \cdot 2\text{tdpo}$ at 25°C and 83°C (figure 5.5) can be regarded as a symmetry change in the crystal rather than a major structural change. This is also in agreement with the small enthalpy value of 10,1 kJ·mol⁻¹ observed for this process. It seems that this symmetry change could be explained as a transition from the centro-symmetric $P\bar{1}$ space group to the non-centro-symmetric $P1$ space group, or vice versa, as refinement of these two space groups showed approximately the same R - and R_w -values.

6.3 XPS studies

Uranium is part of the actinide series in which the 5f electronic states become filled. The free-atom electronic configuration of uranium is $6s^2 6p^6 5f^3 6d^1 7s^2$ [44]. In uranium the 5f, 6s, 6p and 7s levels are considered as valence levels [45].

Structures on the spectra that will be discussed include X-ray ghost lines, multiplet splitting, shake-up satellites and asymmetric metal core levels.

X-ray ghost lines are due to excitations arising from impurity elements in the X-ray source. The most common ghost is $\text{AlK}\alpha_{1,2}$ from a $\text{Mg K}\alpha$ source. This arises from secondary electrons produced inside the source hitting the thin aluminium window (present to prevent these same electrons hitting the sample) [66].

Multiplet splitting of core-level peaks occurs when the system has unpaired electrons in the valence levels. The 4f levels of the rare earth metals show strong multiplet splitting [66]. Multiplet splitting occurs as a result of coupling between unpaired electrons remaining in a core orbital (following photo-electron emission) with unpaired electrons from an unfilled outer shell, such as f electrons in lanthanides and actinides. A decrease in f electron density, e.g. charge delocalization to a ligand, will decrease the splitting [67].

The loss of a core electron by photo-emission appears to increase the nuclear charge to the valence electrons associated with that atom. This major perturbation gives rise to substantial reorganization of the valence electrons (referred to as relaxation) which may involve excitation of one of them to a higher unfilled level ("shake-up"). This process leads to a discrete structure on the higher binding energy side of the photo-electron peak. These structures are called shake-up satellites. Very strong satellites are observed for certain transition metal and rare earth compounds which have unpaired valence electrons.

In a solid metal a distribution of unfilled one-electron levels exists above the Fermi energy which is available for shake-up-type events following core electron emission. In the case of asymmetric metal core peaks, instead of discrete satellites, the core level peak itself is accompanied by a high binding energy tail. The higher the density of the states at the Fermi level, the more likely is observation of this effect [66].

Shake-off satellites are other structures that can be produced on the XPS-spectra when "shake-up" valence electrons leave an ion, and vacancies in both the core level and a valence level result. Shake-off satellites are very rarely observed in the solid state [66].

In a study concerning uranium(IV) chlorides and -bromides, Thibaut and co-workers [48] found that for decreasing halogen electronegativity

- (i) the U5f valence peak comes closer to zero binding energy;
- (ii) the splitting between U5f and valence band peaks decreases;
- (iii) the U5f peak intensity decreases with respect to the U4f core peaks and to $U6p_{3/2}$;
- (iv) the U4f core level binding energy decreases
- (v) the shake-up satellites appear closer to the main peak; and
- (vi) the shake-up satellites have increasing intensity relative to the main peak.

Valence charge redistribution (and thus binding energy differences) arises from the influence of the chemical environment as well as from structural differences. A change in the effective radius of the valence shell may cause a change in the binding energy values [53]. The symmetry of the uranium ion is thus another factor that can influence the binding energy values.

The equivalent cores approximation is a method by which an atomic core which lacks one electron is considered chemically equivalent to the complete core of the next element in the periodic table [67]. Best has pointed out that it should be possible to correlate X-ray absorption data with thermodynamic data using the equivalent cores approximation as a base [68]. Application of this method to solid compounds is very complicated, and very little experimental or theoretical work on this method could be found in the literature.

6.3.1 The U4f energy region: 370 eV to 401 eV

Thibaut and co-workers [48] found that valence photo-electron spectra are much less affected by surface conditions (impurities) than U4f core level peaks. The U4f photo-electrons, with a kinetic energy of about 400 eV lower than the valence electrons, have a shorter mean free path in the solid, and therefore originate from a thinner surface layer. They found that for differently-prepared UCl_3 samples, the U4f spectra are notably different, but not the valence data. An increasingly covalent character in the

halogen group, from F to Br, which involves an increasingly strong U5f participation in the bonding orbitals, was found for the uranium(IV)halides [48]. This tendency results in an increase in the U4f shake-up satellite intensities. The electronic transitions observed due to the shake-up satellite structures in the U4f region correspond to the excitation of an electron of a molecular orbital with strong ligand character to an orbital mainly of 5f character based on the metal centre. The intensities of the satellite peaks are indicative of the 5f admixture in the lowest unoccupied molecular orbital [49].

For all the uranium(IV) nitrate complexes, satellite structures accompanying the $U4f_{7/2}$ peak were observed with peak maximum values just above 390 eV (figures 5.22 and 5.23). The intensity of the satellite peak of the tpyrp complex is the smallest, and that of tppo complex the biggest. This indicates a stronger U5f participation in the tppo complex. The decreasing satellite peak heights in the tppo, tdpo and tpyrp complexes are in the same order as the decreasing thermal stability of the complexes. It thus seems that the stronger the participation of the U5f orbitals in the bonds in the complex, the more stable the complex is. The $U4f_{5/2}$ satellite structures are concealed by nearby N1s peaks.

The multiplet splitting for the U4f peaks in $U(NO_3)_4 \cdot 2tpyrp$ and $U(NO_3)_4 \cdot 2tppo$ are determined as 10,90 eV and 10,85 eV respectively, thus approximately the same (figure 5.22) and

table 5.8). The value for $\text{U}(\text{NO}_3)_4 \cdot 2\text{tdpo}$ (11,55 eV) is noticeably higher, indicating an increase in 4f electron density on the uranium ion in the tdpo complex. The multiplet splitting for the U4f peaks in uranium metal is 10,85 eV and is the same as that recorded in the literature [66].

The $\text{U}4f_{7/2}$ binding energy peak maxima for $\text{U}(\text{NO}_3)_4 \cdot 2\text{tpyrp}$ and $\text{U}(\text{NO}_3)_4 \cdot 2\text{tppo}$ are approximately the same (384,75 eV and 384,80 eV, figure 5.22 and table 5.8). The $\text{U}4f_{7/2}$ binding energy peak maximum for $\text{U}(\text{NO}_3)_4 \cdot 2\text{tdpo}$ (385,85 eV) is approximately 1,05 eV higher than the maxima in the other two complexes, indicating a decreasing covalent character or an increasing ionic character in the bonds concerning the tdpo-complex's U4f orbitals. The U4f binding energies in the complexes studied are significantly higher than that in UF_4 ($\text{U}4f_{5/2}$ at 392,8 eV and $\text{U}4f_{7/2}$ at 382,0 eV [48]). The nitrate complexes of uranium(IV) seem thus to be more ionic than UF_4 .

The $\text{U}4f_{7/2}$ and $\text{U}4f_{5/2}$ peaks were observed at higher binding energies in the uranyl complexes than in the uranium(IV) compounds, suggesting a more ionic nature of the uranyl nitrate complexes (figure 5.23 and table 5.8). No satellite structures were observed in the U4f region for the uranyl complexes, indicating very little or no U5f activity. Distinct tails on the higher binding energy side of each core level peak suggest a high density of electronic states at the Fermi level. In the uranium(IV) nitrate com-

plexes, these tails are concealed by the satellite structures. It is clear from the valence band spectra (figures 5.20 and 5.15) that a high density of electronic states exists in the vicinity of the Fermi level (0 eV to 25 eV).

During the decomposition of the uranium(IV) nitrate complexes, a more ionic type of compound is formed and it seems that the UO_2^{2+} ion behaves as a single species as was found for uranylhalide compounds [48]. It must, however, be borne in mind that the U4f binding energies increase with an increase in metal oxidation states [48].

The shift in the $\text{U4f}_{7/2}$ peak maxima as a result of the decomposition reactions are summarized below.

		Binding Energy
		Difference
$\text{U}(\text{NO}_3)_4 \cdot 2\text{tpyrp}$	$\rightarrow \text{UO}_2(\text{NO}_3)_2 \cdot 2\text{tpyrp}$	3,10 eV
$\text{U}(\text{NO}_3)_4 \cdot 2\text{tdpo}$	$\rightarrow \text{UO}_2(\text{NO}_3)_2 \cdot 2\text{tdpo}$	1,90 eV
$\text{U}(\text{NO}_3)_4 \cdot 2\text{tpo}$	$\rightarrow \text{UO}_2(\text{NO}_3)_2 \cdot 2\text{tpo}$	1,10 eV

The greatest shift towards a more ionic U4f bond was observed for the tpyrp complex, and the smallest shift for the tppo complex. If it is possible to consider these binding energy differences as indications of the relative values of the chemical reaction energy or enthalpy values, then an increasing binding energy difference must accompany an increasing (negative) enthalpy value. The increasing binding energy difference from the tppo to the tpyrp complex follows the same order as the increasing enthalpy

values for the decomposition reactions (paragraphs 5.1 and 6.4). This method of comparing the binding energy differences can thus be a means of predicting thermodynamic characteristics, which includes the thermal stability and ligand donor strength of similar compounds.

The broad low peaks at binding energy values between 374 eV and 380 eV seem to be X-ray ghost peaks.

6.3.2 The Valence band energy region: 0 eV to 40 eV

According to Fuggle and co-workers, the valence band in clean uranium metal has a width of approximately 4 eV, is asymmetric and the peak position would be at the Fermi level [69]. The value of 0,95 eV observed for the U5f peak of uranium metal agrees well with Fuggle's findings (figure 5.20). U6p_{3/2} and U6p_{1/2} peaks were observed at binding energies of respectively 17,1 and 26,9 eV.

Veal and Lam found that a valence band exists in UO₂, consisting of U6d, U7s and O2p electrons, at about 6 eV above the Fermi level [44]. They found a U6p_{3/2} peak at 18 eV, a U6p_{1/2} peak at 28,5 eV, a O2s_{1/2} peak at 23 eV and a O2p peak at approximately 6 eV. Taking into consideration the shift of 7 to 8 eV in the U4f_{7/2} peaks in the uranium(IV) nitrate complexes in comparison to the value in uranium metal, it seems possible that the shoulders at approximately 6,4 eV on all the spectra of the uranium(IV) nitrate complexes are due to U5f activity (figure 5.20). The satellite struct-

ures accompanying the U4f peaks also indicate U5f activity. Thibaut and co-workers found that the stronger the U5f participation in the bonding orbitals, the more diffuse the valence band and U5f peaks become [48]. Except for $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{tpyrp}$ with a shoulder at 7,2 eV on the broad valence peak, no shoulders were found on the valence band spectra of the uranyl nitrates (figure 5.21). This indicates no U5f activity in the bonding orbitals in the uranyl nitrates, and is in good agreement with the electronic structure of these complexes, which predicts that the U5f level should not be occupied. The shoulder at 7,2 eV on the spectrum of the tpyrp complex could be due to P, N, C and O peaks.

A broad valence band peak with a maximum binding energy of approximately 9,9 eV was observed for all the $\text{U}(\text{NO}_3)_4 \cdot 2\text{L}$ complexes (figure 5.20). This broad peak could be due to a combination of $\text{P}3\text{p}_{1/2}$, $\text{P}3\text{p}_{3/2}$, $\text{N}2\text{p}_{1/2}$, $\text{C}2\text{p}_{1/2}$ and $\text{O}2\text{p}_{1/2}$ peaks. This broad valence band peak is at a slightly higher binding energy (approximately 10 to 11 eV) for all the uranyl complexes (figure 5.21).

The broad peaks between 16 and 25 eV on the uranium(IV) nitrate and uranyl nitrate complexes' XPS-spectra consist mainly of $\text{U}6\text{p}_{3/2}$ and $\text{O}2\text{s}_{1/2}$ peaks. Due to the overlapping of these peaks, resulting from their energies being in close proximity, it proved difficult to determine the exact positions of the $\text{U}6\text{p}_{3/2}$ peaks (figure 5.20, figure 5.21 and table 5.9). The $\text{U}6\text{p}_{1/2}$ peaks are separated to a greater

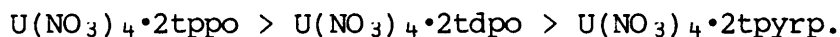
degree from the other valence band peaks. The $U6p_{1/2}$ peak for $U(NO_3)_4 \cdot 2tppo$ at 29,5 eV indicates a more ionic bond in the $U6p$ orbitals in the $tppo$ complex than in both the other two complexes, with binding energies of 28,5 eV in their $U6p$ orbitals. The $U6p_{1/2}$ binding energy values for $UO_2(NO_3)_2 \cdot 2tppo$ and $UO_2(NO_3)_2 \cdot 2tdpo$ are the same (30,0 eV) and that for $UO_2(NO_3)_2 \cdot 2tpyrp$ is only 0,1 eV higher. These values for the uranyl nitrate complexes are all higher than in the uranium(IV) nitrate complexes, indicating as was the case for the $U4f$ peaks, more ionic-type bonds in the uranyl complexes.

Comparing the $U6p_{1/2}$ peak values in the uranium(IV) nitrates, it seems that the co-ordination groups in the $tppo$ complex are slightly more electronegative than in $U(NO_3)_4 \cdot 2tdpo$, with the lowest electronegativity observed in the $tpyrp$ complex. This implies that of the three ligands, $tppo$ is the strongest electron donor and $tpyrp$ the weakest electron donor. The same conclusion was reached in a previous paragraph, when using the bond lengths in the molecules.

The shift of the $U6p_{1/2}$ peak maxima resulting from the decomposition reactions, are summarized below:

Binding Energy		
Difference		
$U(NO_3)_4 \cdot 2tpyrp$	$\rightarrow$ $UO_2(NO_3)_2 \cdot 2tpyrp$	1,6 eV
$U(NO_3)_4 \cdot 2tdpo$	$\rightarrow$ $UO_2(NO_3)_2 \cdot 2tdpo$	0,7 eV
$U(NO_3)_4 \cdot 2tppo$	$\rightarrow$ $UO_2(NO_3)_2 \cdot 2tppo$	0,5 eV

The same order of decreasing binding energy differences of the ligands is observed as that for the U4f peak differences, indicating again (see paragraph 6.3.1) a possible stability order for the uranium(IV) nitrate complexes of



This stability order or ligand donor strength order is the same as that derived from all other experimental techniques.

It seems that the valence band is of the utmost importance in the interpretation of the XPS-data when evaluating the electronic structures, and its influence on the kinetic and thermodynamic characteristics of the complexes.

6.3.3 The N1s energy region: 403 eV to 413 eV

Two N1s peaks were observed on the spectra of $\text{U}(\text{NO}_3)_4 \cdot 2\text{L}$ and $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{L}$, with $\text{L} = \text{tdpo}$ and tpyrp (figures 5.22 and 5.23, table 5.8). The N1s peak above 409 eV on all the spectra is due to the N in the NO_3^- groups. The N1s peak between 403 eV and 405 eV originates from the ligand nitrogen atom. No ligand nitrogen peak was observed for $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{tppo}$, and the peak at 403,15 eV for $\text{U}(\text{NO}_3)_4 \cdot 2\text{tppo}$ seems to be due to the satellite structure accompanying the $\text{U}_{4f_{5/2}}$ peak, as well as impurities in the compound.

The N1s orbitals in the ligand in the tdpo complex seem to be involved with slightly more ionic-type bonds than those

in the tpyrp complex, for both the uranium(IV) and uranyl complexes (table 5.8).

The average binding energy difference of 7,6 eV between the two types of N1s peaks is high and indicates noticeable differences in the character of the two nitrogen bonds. The ligands' nitrogen atoms seem to be involved in stronger covalent bonds than those of the nitrate groups, with a stronger ionic character.

6.3.4 The P2p, C1s and O1s XPS peaks

Peaks due to ionization from orbitals having a P2p character were observed at 134,40 eV for tppo and at 134,50 eV for tdpo. The P2p peaks in the complexes are all at significantly higher binding energies (approximately 2 to 5 eV). The higher binding energy values are a direct result of the co-ordination of the neutral ligand to the uranium ion and indicate a more ionic character of the ligands in the complexes. The insignificant change in the P2p binding energy values between the uranium(IV) and uranyl complexes indicates that the bonding ligand orbitals are not significantly influenced by the decomposition of the uranium(IV) nitrate complexes.

As the carbon atoms in the different complexes are all of different types, their binding energies cannot be compared. It is noted that all the values for the C1s peaks shifted to slightly higher binding energy values during

decomposition of the various uranium(IV) nitrate complexes (table 5.8, figures 5.26 and 5.27).

The O1s peak observed for uranium metal is due to atmospheric oxygen always present, even under severe vacuum conditions. The O1s peaks in the complexes have binding energy values of approximately 6 to 7 eV higher than atmospheric oxygen, indicating the influence of the co-ordination of the nitrate groups to the uranium ions. These higher values indicate a strong ionic character of the nitrate groups attached to the uranium ion.

6.4 Thermal stability

Comparing the temperatures at onset of decomposition with the enthalpy values, as listed in table 6.5, it seems possible to establish an order of stability for the complexes; i.e $U(NO_3)_4 \cdot 2tppo > U(NO_3)_4 \cdot 2tdpo > U(NO_3)_4 \cdot 2tpyrp$.

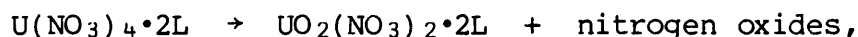
Table 6.5 Decomposition onset temperatures and reaction enthalpy values for the thermal decomposition of the uranium(IV) nitrate complexes

Complex	Decomposition onset temperature* ($^{\circ}C$)	Enthalpy ($kJ \cdot mol^{-1}$)
$U(NO_3)_4 \cdot 2tppo$	130	-24,1
$U(NO_3)_4 \cdot 2tdpo$	98	-133,4
$U(NO_3)_4 \cdot 2tpyrp$ [19]	87	-165

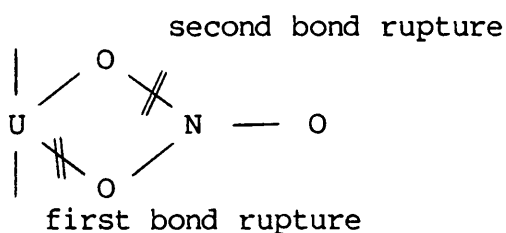
* The decomposition onset temperatures were determined from the TG curves, using a heating rate of $5^{\circ}C \cdot min^{-1}$.

6.5 Conclusions

For the thermal decomposition reactions,



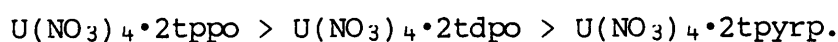
it is inevitable that a U-O(NO₂) bond will be ruptured, followed by a N-O bond rupture. Schematically one nitrate group can be represented as follows;



Together with these bond ruptures, an oxidation of uranium(IV) to uranium(VI) occurs.

Stabilization of the uranium(IV) nitrate complexes is accomplished by the electron donor properties of the neutral donor ligand. The electrostatic forces, which attract neutral oxygen-donor molecules to the positively-charged nuclei are due to the permanent electric dipoles in the molecules. The approximation was made that in the donor molecules, the dipole results from the charge of an electron located at the centre of the oxygen atom and an equal and opposite charge located along the P-O bond [26].

Taking into consideration the decomposition onset temperatures, the enthalpy values, the bond lengths and the XPS data, an order of stability was established;



From the crystal and molecular structure data, it seems that tppo is the strongest donor ligand, followed by tdpo and then tpyrp. It can be concluded that the stronger the electron donor properties of the ligand, the more stable the uranium(IV) nitrate complex. The stronger the uranium 5f orbital participation in the bonds in the complexes, the more stable the complexes are.

The average U-O(NO₂) bond distances also showed a similar trend, that is in U(NO₃)₄•2tppo the smallest average U-O(NO₂) distance was observed and in U(NO₃)₄•2tpyrp the longest average U-O(NO₂) distance occurs. The longer the average U-O(NO₂) distance, the easier it is for that bond to rupture. From the O-P(ligand) bond lengths it is possible to establish a donor strength order for the ligands;



A stronger electron donor ligand thus stabilizes the uranium(IV) ion by resulting in a stronger participation of the uranium(IV) ion's valence orbitals in the bonds in the complexes. This results in a stronger or more stable bond between the uranium(IV) ion and the nitrate group and thus a greater thermal stability.

When comparing the activation energy values (table 6.1) with the thermal stability, no useful conclusions could be made, as, with increasing thermal stability, it was found that the activation energy values also increase. The activation energies were calculated using different kinetic models, thus

the significance of its comparison is questioned. It must also be borne in mind that activation energy in the solid state does not have the same meaning as activation energy in both the liquid and gaseous states. Factors such as imperfections, particle sizes and pre-treatment can influence the value to a great extent [8]. It also seems that the activation energy and pre-exponential factor values for different kinetic models cannot be compared to each other. Activation energy in the solid state seems to be associated with a definite process, for example, three-dimensional diffusion, first order kinetics or the contracting volume model.

REFERENCES

1. C.H. Bamford and C.F.H. Tipper, Chemical Kinetics, Reactions in the solid state, 22 (1980).
2. R.C. Mackenzie, Talanta, 16, (1969) 1227.
3. P.D. Garn, Thermoanalytical methods of investigation, Academic Press, New York (1965).
4. Chemistry of the solid state, Ed. W.E. Garner, Butterworth, London (1955) Chapter 7.
5. J. Sestak, V. Satavo and W.W. Wendlandt, Thermochim. Acta, 7 (1973) 333.
6. J.W. Christian, Transformations in metals and alloys, 1 (1975).
7. P.W.M. Jacobs, Mater. Sci. Res., 4 (1969) 37.
8. P.D. Garn, J. Therm. Anal., 13 (1978) 581.
9. F.A. Cotton and G. Wilkinson, Advanced inorganic chemistry, 3rd edition (1972) 1056.
10. W.W. Wendlandt and J.L. Bear, J. Inorg. Nucl. Chem., 12 (1960) 276.

11. K.C. Patil, R.K. Gosavi and C.N.R. Rao, *Inorg. Chim. Acta*, 1 (1967) 155.
12. J. Del Pino, P.M. Chukurov and B.N. Ivanov-Emin, *Zh. Neorg. Khim.*, 30 12 (1985) 3052.
13. P.M. Chukurov, J. Del Pino and B.N. Ivanov-Emin, *Zh. Neorg. Khim.*, 3 1 (1986) 262.
14. K.W. Bagnall, P.S. Robinson and M.A.A. Stewart, *J. Chem. Soc. (A)*, (1961) 4060.
15. I.I. Chernyaev, *Complex compounds of uranium*, Israel Program for Scientific Translations, Jerusalem, (1979).
16. A. Litthauer, *Thermal stability of hexanitrate uranate(IV) complexes*, M.Sc thesis, UPE (1979).
17. J.G.H. du Preez and C.P.J. van Vuuren, *J. Inorg. Nucl. Chem.*, 36 (1974) 81.
18. J.E. Flemming and H. Lynton, *Chem. Ind. (London)*, (1960) 1415.
19. M.E. Brown, C.P.J. van Vuuren and A. Litthauer, *Thermochim. Acta*, 49 (1981) 247.
20. P.W. Atkins, *Physical Chemistry*, Oxford University Press, Belfast, 3rd edition (1986) 476.

21. J.M. Dyke, G.D. Josland, A. Morris, P.M. Tucker and J.W. Tyler, J. Chem. Soc., Faraday Trans. 2, 77 (1981) 1273.
22. J.B. Wagener and C.P.J. van Vuuren, personal inquiry.
23. J.H. Flynn, Thermochim. Acta, 37 (1980) 225.
24. A.C.T. North, D.C. Philips and F. Mathews, Acta Cryst., A34 (1968) 351.
25. G.M. Sheldrick, 'SHELX' program system 1976, University of Cambridge, England.
26. J.G.H. du Preez, P.L. Gellatly and H.E. Rohwer, J. Inorg. Nucl. Chem., 39 (1977) 1173.
27. A.F. Kapustinskii, Quart. Rev., 10 (1956) 283.
28. K.M. Mackay and R.A. Mackay, Introduction to modern inorganic chemistry, 2nd edition, Intertext books, London (1973).
29. F. Vratny and J.M. Honig, Trans. Faraday Soc., 56 (1960) 1051.
30. Gatehouse, J. Inorg. Nucl. Chem., 8 (1958) 79.
31. D. Dollimore, Thermochim. Acta, 117 (1987) 331.
32. D.A. Young, Decomposition of solids, Volume 1, International Encyclopedia of physical chemistry and chemical physics, Pergamon Press, London (1966).

33. C.J. Keattch and D. Dollimore, An Introduction to thermogravimetry, Heyden, London (1975).
34. J.P. Redfern, in R.C. Mackenzie, Differential Thermal Analysis, Volume 1, Chapter 5, Academic Press, London (1970).
35. J. Noll, Angewandte Chemie, 62 (1950) 567.
36. W.E. Garner, Chemistry of the solid state, Butterworths, London (1955).
37. J.H. Sharp, G.W. Brindley and B.N. Narahaki Achar, J. Amer. Ceram. Soc., 49 (1966) 379.
38. R.M. Dell and V.J. Wheeler, 5th Int. Symp. Reactivity of Solids, Munich, (1964) 395.
39. Alekseenko, Lemenkova and Serebrennikov, Zhur. Neorg. Khim., 4 (1959) 1382.
40. K. Negase, Bull. Chem. Soc., Jpn., 45 (1972) 2166.
41. A. Glasner and M. Steinberg, J. Inorg. Nucl. Chem., 16 (1961) 279.
42. W. Komatso, in G.M. Schwab, Reactivity of Solids, Proc. 5th Int. Symp., Elsevier, Amsterdam (1965) 182.
43. G.M. Sheldrick, 'SHELX' program system, University of Cambridge, England (1976).

44. B.W. Veal and D.J. Lam, Phys. Rev. B, 10 12 (1974) 4902.
45. J.M. Dyke, N.K. Fayad, A. Morris, I.R. Trickle and G.C. Allen, J. Chem. Phys., 72 6 (1980) 3822.
46. J.C. Fuggle, A.F. Burr, L.M. Watson, D.J. Fabian and W. Lang, J. Phys. F: Metal Phys., 4 (1974) 335.
47. J.G.H. du Preez, B.J. Gellatly, G. Jackson, L.R. Nassimbeni and A.L. Rodgers, Inorg. Chim. Acta, 27 (1978) 181.
48. E. Thibaut, J. Boutique, J.J. Verbist, J. Levet and H. Noël, J. Am. Chem. Soc., 104 (1982) 5266.
49. C.M. Demanet and J.G.H. du Preez, Inorg. Chim. Acta, 77 (1983) L167.
50. F.J. Grunthaner, P.J. Grunthaner, R.P. Vasquez, B.F. Lewis, J. Maserjian and A. Madhukar, J. Vac. Sci. Technol., 16 (1979) 1443.
51. S. Brennan, J. Stohr, R. Jaeger and J.E. Rowe, Phys. Rev. Lett., 45 (1980) 1414.
52. R.P. Vasquez, M.H. Hecht, F.J. Grunthaner and M.L. Naiman, Appl. Phys. Lett., 46 (1985) 361.

53. R.P. Vasquez, X-Ray Photoelectron Spectroscopy and Spectroscopic ellipsometry studies of some structurally and/or chemically inhomogeneous materials, Ph.D. study, University of California, 1986.
54. C.S. Fadley, Electron Spectroscopy: Theory, Techniques and Applications, edited by C.R. Brundle and A.D. Baker, Academic Press, New York (1978).
55. K.L. Mampel, Z. Phys. Chem. A, 187 43 (1940) 235.
56. W.E. Garner and H.R. Hailes, Proc. Roy. Soc. A, 139 (1933) 576.
57. E.G. Prout and F.C. Tompkins, Trans. Faraday Soc., 42 (1946) 482.
58. B.V. Erofeev, C.R. Acad. Sci., U.R.S.S., 52 (1946) 511.
59. M. Avrami, J. Chem. Phys., 9 (1941) 177.
60. S.J. Gregg and R.I. Razouk, J. Chem. Soc., (1949) 536.
61. W.D. Spencer and B. Topley, J. Chem. Soc., (1929) 2633.
62. J.B. Holt, J.B. Cutler and M.E. Wadsworth, J. Amer. Ceram. Soc., 45 (1962) 133.
63. W. Jander, Z. Anorg. Allg. Chem., 163 (1927) 1.

64. A.M. Ginstling and B.I. Brounshtein, Zh. Prikl. Khim., 23 (1950) 1249.
65. K.W. Bagnall, D. Brown, P.J. Jones and T.G.H. du Preez, J. Chem. Soc. A, (1965) 3594.
66. D. Briggs and M.P. Seah, Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy, John Wiley and Sons, New York (1983).
67. C.R. Brundle and A.D. Baker, Electron Spectroscopy: Theory, Techniques and Applications, Volume 1, Academic Press, London (1977).
68. P.E. Best, J. Chem. Phys., 49 (1968) 2797.
69. J.C. Fuggle, A.F. Burr, L.M. Watson, D.J. Fabian and W. Lang, J. Phys. F: Metal Phys., 4 (1974) 335.
70. M.R. Caira and L.R. Nassimbeni, J. Inorg. Nucl. Chem., 39 (1977) 455.
71. G. Bombieri, D. Brown and R. Graziani, J. Chem. Soc. Dalton, (1975) 1873.