ACTIVATION ENERGY STUDIES ON COMPLEXES OF URANYL FLUORIDE WITH AMIDIC LIGANDS

P.A.B. CARSTENS and T.P. KNOETZE

Department of Chemistry, Atomic Energy Corporation of South Africa Ltd., P.O. Box 582, Pretoria 0001 (South Africa)
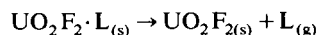
C.P.J. VAN VUUREN

Department of Chemistry, University of Pretoria, Pretoria, 0002 (South Africa)

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ABSTRACT

Complexes of UO_2F_2 with ten amidic ligands were prepared and characterized. It was shown that the complexes decompose according to the reaction

$$UO_2F_2 \cdot L_{(s)} \rightarrow UO_2F_{2(s)} + L_{(g)}$$

where L represents N,N-dimethylformamide (dmf), acetamide (aa), N-methylacetamide (nma), N,N-dimethylacetamide (dma), N,N'-dimethylurea (dmu) and N,N,N',N'-tetramethylurea (tmu). The mechanism for this decomposition reaction can be described by the equation

$$1 - (1 - \alpha)^{1/2} = kt$$

The activation energies of the decomposition reactions were determined. No relationship could be found between activation energy and any of the physical parameters studied in this work. Any relationship reported in the literature seems to be purely coincidental and system dependent. No universal relationship exists between activation energy and the physical parameters studied in this work.

INTRODUCTION

There are several arguments against the use of the Arrhenius equation to describe heterogeneous reactions [1–3]. In spite of all these objections, the temperature dependence of the reaction rate can be described by this equation in numerous solid state decomposition reactions [1,4,5]. In some cases a physical significance for activation energy (E_a) is postulated. A relationship linking the quantities r_c/r_i (the ratio of the Pauling covalent radius and the cation radius of the metal atom in hexacoordination) and ΣI_i (the sum of the ionization potentials of the metal atom in kJ mol^{-1}) with the activation energy of oxalate decomposition has been reported for some

metal oxalates [6]. A linear relationship between the anti-symmetric vibration ν_3 of the O–U–O group and the "activation energy" has also been reported [7,8].

The purpose of this study was to determine whether E_a has any physical significance in a system of complexes prepared from a homologous series of ligands. E_a was correlated with the infrared (IR) stretching frequencies, dissociation enthalpy (ΔH_r) and the DTG maximum temperature of the dissociation reaction. This temperature was used in preference to T_i, the initial temperature of decomposition. T_i is not a reliable measure of the thermal stability of a compound since it depends on the sensitivity of the measuring apparatus and on the experimental conditions [9].

The system of complexes must be chosen with great care. A solid state decomposition reaction of the type

$$ML_{(s)} \rightarrow M_{(s)} + L_{(g)} \tag{1}$$

was studied. UO_2F_2 was chosen as M because it is stable to thermal decomposition at elevated temperatures [10]. The uranyl ion in UO_2F_2 compounds also has an invariant structure with a O–U–O angle of $180°C$ and a coordination number of five in the equatorial plane [11]. In complexes of the type ML where $M = UO_2F_2$ it can be thus be expected that the nearest neighbours around the U atom will have a pentagonal bipyramidal spatial arrangement. The spatial arrangement around the U atom should thus have little influence on the physical parameters of the series of complexes. Another reason for the choice of UO_2F_2 is the fact that for the majority of $UO_2F_2 \cdot xL$ complexes, where L represents a neutral donor ligand, the value of x equals 1. The complexes of UO_2F_2 are thus relatively simple to investigate.

A series of amidic ligands was chosen with the aim of satisfying eqn. (1). Complexes of UO_2F_2 were prepared with formamide (form), N-methylformamide (nmf), N,N-dimethylformamide (dmf), acetamide (aa), N-methylacetamide (nma), N,N-dimethylacetamide (dma), urea (ur), N-methylurea (nmu), N,N'-dimethylurea (dmu) and N,N,N',N'-tetramethylurea (tmu). Some of these complexes have already been reported [12–16]. The fact that these ligands are thermally stable relative to other organic compounds (with the exception of ur and nmu which decompose) can be seen in their relatively high boiling points [17]. It was expected, with the exception of ur and nmu, that the ligands would not decompose during the thermal decomposition of the complexes, but that the reaction would take place according to eqn. (1). Another reason for the choice of amidic ligands is the fact that activation energy studies have never been carried out on a system with a homologous series of ligands. These amidic ligands provide a readily available homologous series. Therefore this is the first systematic study of this nature.

EXPERIMENTAL

Preparation of complexes

All complexes were prepared by adding the ligand to a methanolic solution of uranyl fluoride (5 : 1 molar ratio). The resulting precipitates were washed with methanol, ether and petroleum ether before they were dried under vacuum. All chemicals used were synthesis grade.

Analyses and physical measurements

Uranium was analyzed by published methods [18] and by pyrohydrolysis in a thermobalance to U_3O_8 using wet O_2. Volatile decomposition products were determined by mass spectrometry. Positive ions were monitored.

IR spectra were recorded as nujol mulls between AgBr windows. Raman spectra were recorded with an argon laser with an incident wavelength of 514.5 nm. In both cases the resolution of the instruments was four wave-numbers. X-ray diffraction data were obtained using a Cu K_{α_1} source.

Thermal analysis

The thermal properties of the complexes were examined using a micro-processor-controlled thermobalance with a sensitivity of 1 μg. Nitrogen and argon were dried using a P_2O_5 column. These gases were utilized at a flow rate of 60 cm^3 min^{-1}. A furnace heating rate of 10°C min^{-1} was employed. Platinum sample pans were used and sample masses varied between 4 mg and 7 mg.

Isothermal decomposition of complexes was studied by rapidly heating the complexes to the desired temperature at a rate of 100°C min^{-1}. The decomposition reaction was terminated when no further mass loss could be detected. The course of the decomposition reactions was studied between α values of 0.2 and 0.8 (α having the normal meaning). During the very first part of the decomposition reaction the system is not necessarily at the required temperature [19]. When the values of α approaches unity, changes in mechanism are possible [20].

DSC studies were performed on an apparatus using the Calvet principle of heat flow. This apparatus is similar to that described previously [21]. Argon was used as carrier gas and a flow rate of 40 cm^3 min^{-1} was maintained over the sample.

RESULTS AND DISCUSSION

Determination of stoichiometry

All the complexes were of the type $UO_2F_2 \cdot xL$. From wet chemical analysis and thermogravimetry it became clear that $x = 1$ where L represents

nmf, dmf, aa, nma, dma, nmu, dmu and tmu. Where L represents ur the value of x is 2 and where L represents form $x < 1$.

Spectroscopic studies

The frequencies of the IR and Raman bands are given in Table 1. With a single exception there is a decrease in the CO stretching frequency with respect to that of the free amide [22,23]. This indicates that the ligands are attached to uranium through the oxygen atom of the ligand [12,22,24,25]. The fact that no decrease in the CO stretching frequency is observed for $UO_2F_2 \cdot$ dmu is difficult to explain since a decrease is expected. A decrease in the uranyl ν_1 and ν_3 frequencies is, however, observed for this complex.

In some of the complexes it was difficult to assign the ν_3 uranyl band due to the existence of multiple bands. It is, however, a well-established fact that a relationship exists between the ν_3 and ν_1 frequencies [26–28]. This relationship was determined for those complexes where ν_3 could be assigned without difficulty and the equation

$$\nu_3 = 2.278\nu_1 - 1006.850 \text{ cm}^{-1} \tag{2}$$

TABLE 1

Spectroscopic data of complexes (ν, cm^{-1}) [a]

Complex	CO stretch	ΔCO stretch	$\nu_1(UO_2^{2+})$	$\Delta\nu_1$	$\nu_3(UO_2^{2+})$	$\Delta\nu_3$
$UO_2F_2 \cdot x$ form	1674	12	865	51	966	52
$UO_2F_2 \cdot$ nmf	1653	14	869	48	968	50
$UO_2F_2 \cdot$ dmf	1649; 1666	23; 6	850	66	928	90
	1640; 1660 [12]		857 [12]		930 [12]	
	1640; 1675 [13]				940 [13]	
	1650, 1665 [14]				935 [14]	
$UO_2F_2 \cdot$ aa	1644; 1667	41; 18 [22]	865	51	965	53
	1675 [12]		854 [12]		955 [12]	
	1650 [13]				970 [13]	
$UO_2F_2 \cdot$ nma	1617	38	847	69	939	79
$UO_2F_2 \cdot$ dma	1624	19 [23]	853	63	938	80
	1630 [12]		852 [12]		941 [12]	
$UO_2F_2 \cdot$ 2ur	1653	33	831	85	914	104
	1659 [12]		834 [12]		915 [12]	
	1670 [14]				925 [14]	
$UO_2F_2 \cdot$ nmu	1645	43	850	66	928	90
$UO_2F_2 \cdot$ dmu	1620	0 [23]	850	66	934	84
			851 [12]		940 [12]	
$UO_2F_2 \cdot$ tmu	1620	27	853	63	936	82
					930 [12]	
					930 [13]	

[a] Numbers in brackets indicate references; ν_1 for anhydrous $UO_2F_2 = 916$ cm^{-1}; ν_3 for anhydrous $UO_2F_2 = 1018$ cm^{-1}.

was obtained. The square of the correlation coefficient (R^2) for this fit is 0.975 and eqn. (2) was used to assign the remaining ν_3 bands. In all complexes a decrease in both the ν_1 and ν_3 frequencies is observed compared with the values of ν_1 and ν_3 of anhydrous UO_2F_2 (Table 1). This can be seen as an indication that electron density is transferred from the ligand (O-donor) to the uranium.

In general there is good agreement between the frequencies obtained during this study (Table 1) and those reported previously [12–14]. However, experimental conditions are not always defined clearly [12,13] and this leads to difficulty when comparing results. For $UO_2F_2 \cdot aa$, values of 1675 cm^{-1} [12] and 1650 cm^{-1} [13] are reported for the CO stretching frequency. No explanation is given for the difference.

X-ray powder diffraction

The X-ray powder diffraction patterns of all the complexes were obtained. Each pattern is unique, indicating a unique structure for every complex. The

TABLE 2

X-ray powder diffraction data

$UO_2F_2 \cdot nmf$			$UO_2F_2 \cdot nma$			$UO_2F_2 \cdot nmu$		
2θ	d (Å)	Rel. I (%)	2θ	d (Å)	Rel. I (%)	2θ	d (Å)	Rel. I (%)
10.775	8.2038	65.3	11.894	7.4342	29.5	12.152	7.2773	22.7
13.223	6.6901	100.0	14.422	6.1364	100.0	12.899	6.8575	10.6
14.694	6.0232	35.1	16.986	5.2154	9.5	13.135	6.7345	8.2
16.290	5.4368	3.1	18.841	4.7059	12.7	13.638	6.4874	100.0
17.988	4.9271	3.7	22.327	3.9785	16.3	16.318	5.4273	2.4
19.964	4.4436	47.8	24.286	3.6617	11.8	18.188	4.8734	4.0
20.700	4.2873	39.0	25.055	3.5511	6.5	20.338	4.3628	2.9
23.310	3.8129	76.5	25.449	3.4971	10.2	21.989	4.0388	7.0
24.840	3.5813	8.2	26.488	3.3621	22.8	22.283	3.9862	7.4
25.204	3.5305	28.9	27.049	3.2936	12.8	22.796	3.8976	3.1
26.691	3.3370	8.2	28.381	3.1420	7.8	23.846	3.7284	2.5
29.488	3.0265	10.8	29.166	3.0592	5.1	24.683	3.6037	17.7
31.539	2.8342	15.1	30.302	2.9471	6.3	25.108	3.5437	6.1
33.051	2.7079	11.0	33.208	2.6955	2.2	25.432	3.4993	2.4
33.595	2.6654	19.8				26.620	3.3457	6.9
						27.491	3.2417	3.9
						27.776	3.2091	6.5
						29.321	3.0434	2.7
						30.823	2.8984	9.6
						31.901	2.8029	2.0
						33.221	2.6945	2.4

X-ray powder diffraction data for the complexes of UO_2F_2 with nmf, nma and nmu, which are reported for the first time, are given in Table 2.

Thermal decomposition

The thermal decomposition of the complexes was studied under a nitrogen atmosphere and the evolved gases were monitored by mass spectrometry. An initial mass loss was observed from a temperature of $30\,^\circ C$ for the complexes of UO_2F_2 with form and nmf (Fig. 1). Decomposition of the ligand was observed where L represents form, ur and nmu (Figs. 1 and 2), but the decomposition products could not be identified positively. The complexes with L = form, nmf, ur and nmu were not studied further because they do not satisfy the prerequisite set in eqn. (1).

The dissociation reaction

$$UO_2F_2 \cdot L_{(s)} \rightarrow UO_2F_{2(s)} + L_{(g)} \tag{3}$$

takes place when L represents dmf, aa, nma, dma, dmu and tmu. In these complexes no decomposition of the ligands was observed. This observation does not agree with that previously reported [13]. The DTG maximum temperatures for the dissociation reactions are given in Table 3. The thermal decomposition curve for $UO_2F_2 \cdot dmf$ is given in Fig. 3. This curve is representative of reaction (3) for the six ligands mentioned above.

Differential scanning calorimetry

The dissociation enthalpy (ΔH_r) of the reaction, $UO_2F_2 \cdot L_{(s)} \rightarrow UO_2F_{2(s)} + L_{(g)}$, was obtained for the complexes with dmf, aa, nma, dma, dmu and tmu (Table 3). With the exception of $UO_2F_2 \cdot dmu$, the values of ΔH_r are similar in the complexes studied. In all cases a single endothermic peak was observed.

Kinetics from isothermal TG

It is an established fact that it is possible to discern between mechanisms for solid state decomposition reactions by using isothermal methods [20]. The rate equation is given by

$$g(\alpha) = kt \tag{4}$$

where $g(\alpha)$ is a function of α that describes the reaction mechanism. For the correct choice of reaction mechanism a plot of $g(\alpha)$ vs. time t is linear [29] and the rate constant k can be obtained from the slope.
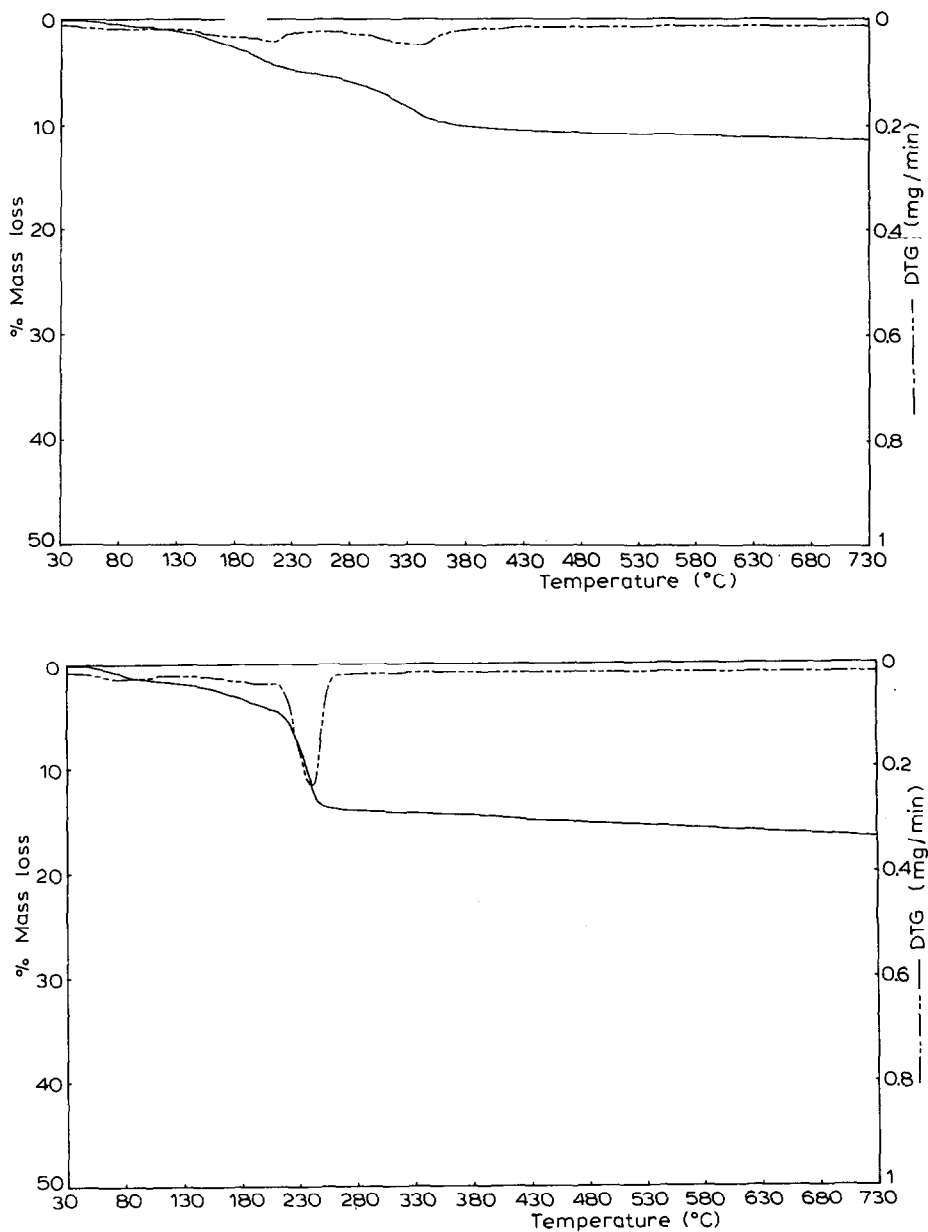
Fig. 1. Thermal decomposition curves of $UO_2F_2 \cdot x$form (top) and $UO_2F_2 \cdot nmf$ (bottom) under nitrogen atmosphere.

The isothermal decomposition curve of $UO_2F_2 \cdot dmf$ at 223.9 °C (Fig. 4) is representative of the complexes satisfying eqn. (3) at their respective decomposition temperatures. The decomposition reaction of these complexes can
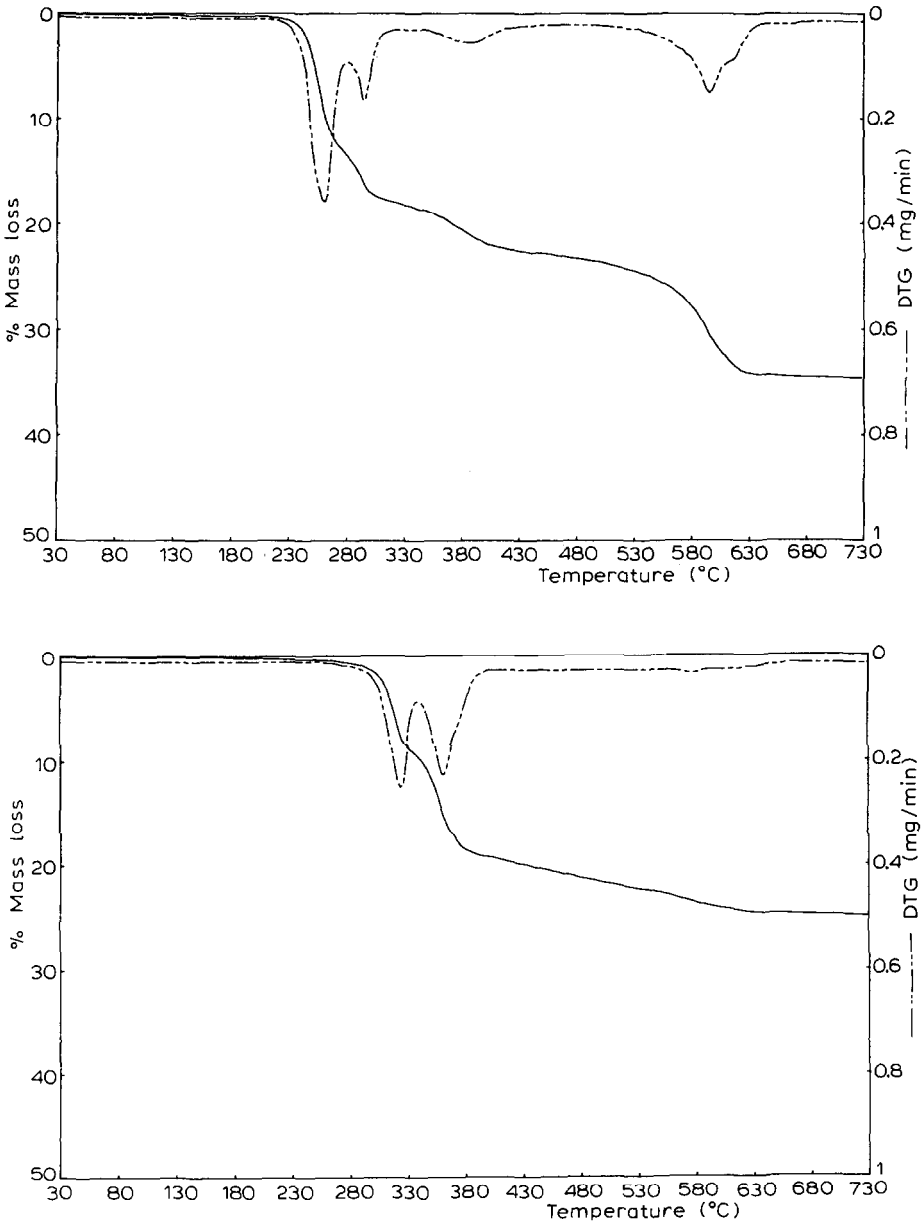
Fig. 2. Thermal decomposition curves of $UO_2F_2 \cdot ur$ (top) and $UO_2F_2 \cdot nmu$ (bottom) under nitrogen atmosphere.

be described by the equation

$$1 - (1 - \alpha)^{1/2} = kt$$

In all cases studied this equation gave a fit with an R^2 value of 0.997 or
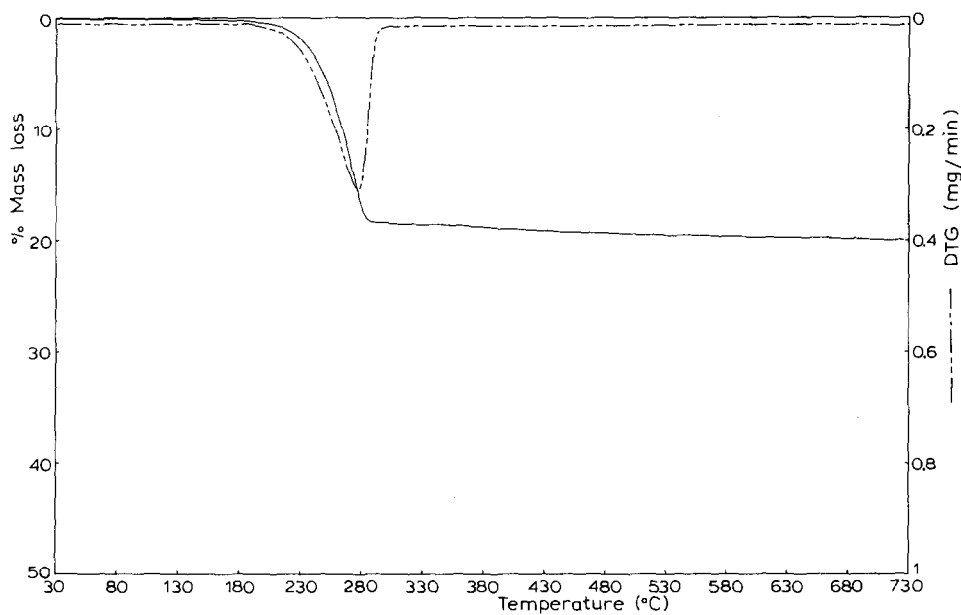
Fig. 3. Thermal decomposition curve of $UO_2F_2 \cdot dmf$ under nitrogen atmosphere.
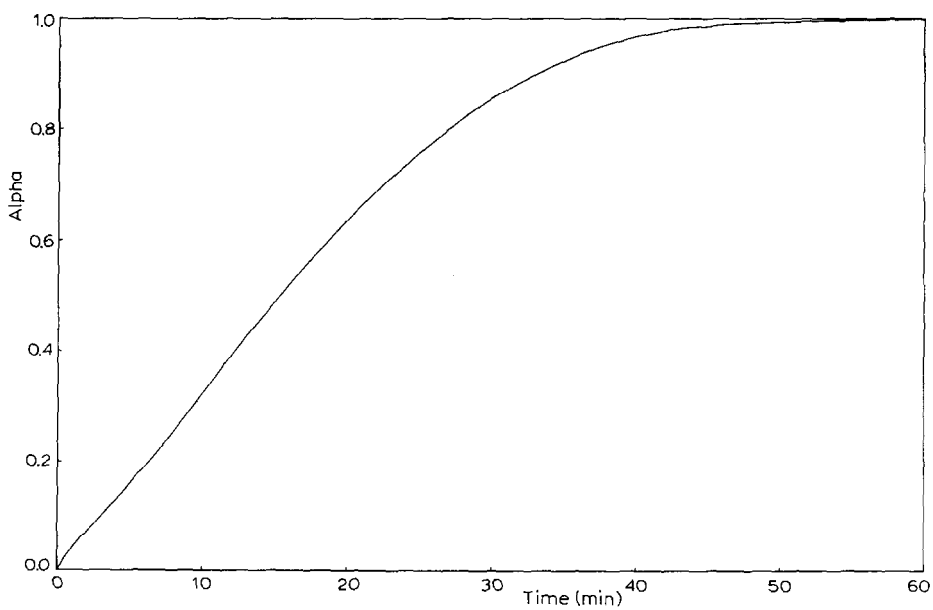
Fig. 4. Isothermal decomposition curve of $UO_2F_2 \cdot dmf$ under argon atmosphere at $223.9\,^\circ C$.

TABLE 3

DTG maximum temperatures obtained from thermogravimetric curves, dissociation enthalpies (ΔH_r) and activation energies for the reaction $UO_2F_2 \cdot L_{(s)} \rightarrow UO_2F_{2(s)} + L_{(g)}$

Complex	DTG maximum temperature (°C)	ΔH_r (KJ mol^{-1})	Activation energy (kJ mol^{-1})
$UO_2F_2 \cdot dmf$	275	90.35	133.7
$UO_2F_2 \cdot aa$	274	84.65	124.5
$UO_2F_2 \cdot nma$	314	90.76	149.7
$UO_2F_2 \cdot dma$	314	94.80	127.7
$UO_2F_2 \cdot dma$	345	163.13	173.1
$UO_2F_2 \cdot tmu$	311	95.72	166.2
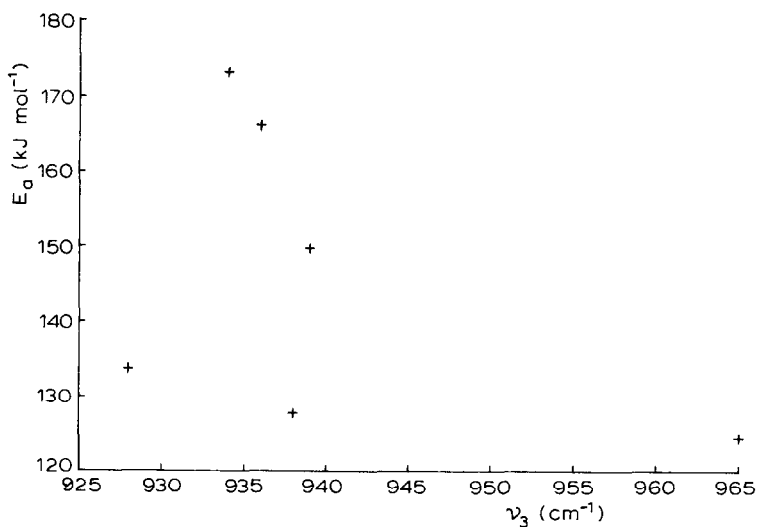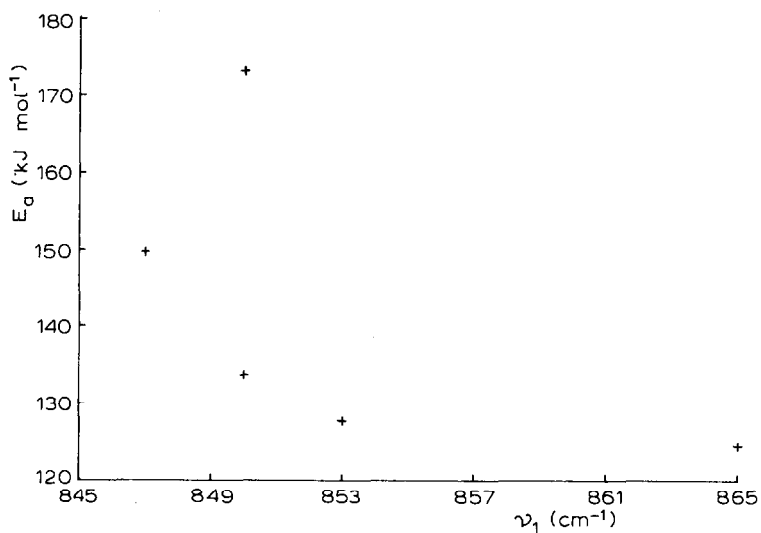
better. This mechanism describes a phase boundary that moves through a compound [19]. The activation energies for the decomposition reactions were determined from a plot of ln k vs. T^{-1} and are given in Table 3.

CONCLUSIONS

The activation energies of the decomposition reactions of the complexes (Table 3) were compared with the uranyl ν_1 and ν_3 frequencies (Fig. 5) and
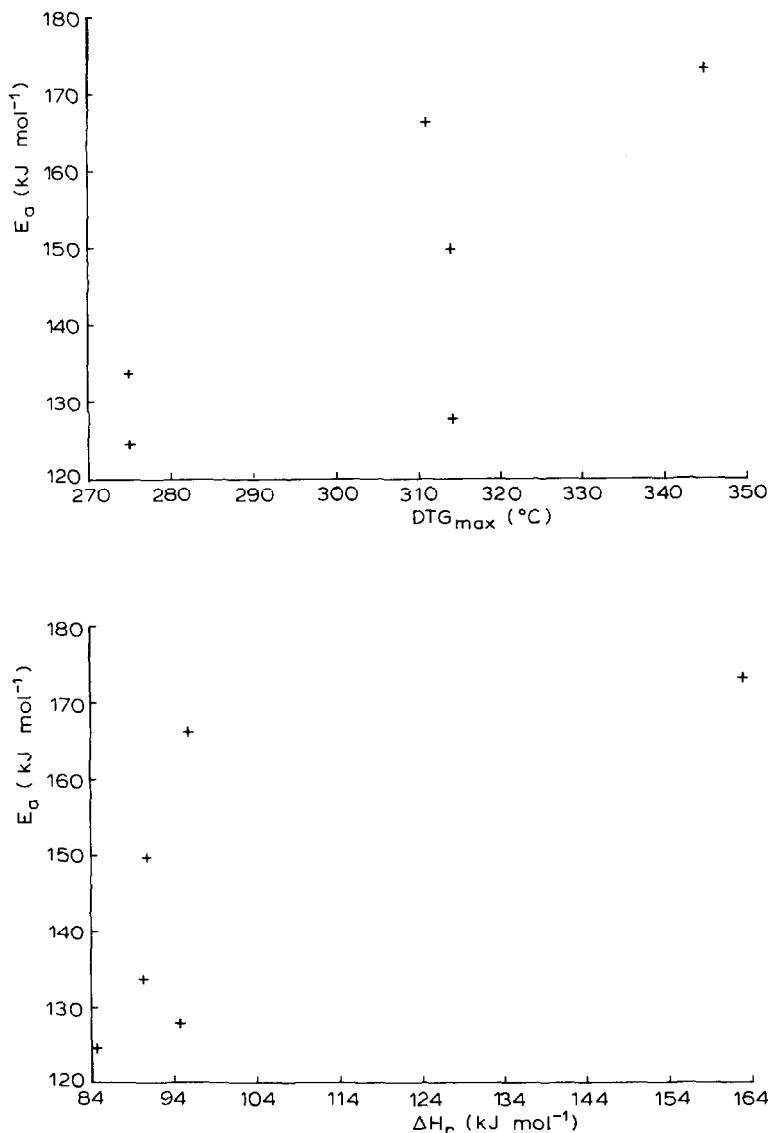

Fig. 6. DTG maximum temperature (top) and ΔH_r (bottom) vs. E_a.

with the DTG maximum temperature and ΔH_r (Fig. 6). From Figs. 5 and 6 it is clear that no relationship exists between the activation energy of the decomposition reaction and any of the physical parameters used in this study, even though a homologous series of ligands was used in the preparation of the complexes. Any relationship reported in the literature seems to be purely coincidental and system dependent. No universal relationship between activation energy and any of the above-mentioned physical parameters exists.

ACKNOWLEDGEMENTS

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