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STUDY OF KINETICS OF THERMAL DECOMPOSITION OF URANYL NITRATE COMPLEXES WITH N-ALKYLCAPROLACTAMS BY MEANS OF NON-ISOTHERMAL GRAVIMETRY

Z. Lu[*], *L. Yang and J. Sun*

Central Laboratory, Suzhou University, Suzhou, Jiangsu 215006, P. R. China

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Abstract

The kinetics of thermal decomposition of a series of uranyl nitrate complexes with N-alkylcaprolactams (alkyl = C_2H_5, C_4H_9, C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$ or $C_{12}H_{25}$) was studied by means of non-isothermal gravimetry under a nitrogen atmosphere. From the TG-DTG curves, the kinetic parameters relating to the loss of two molecules of coordinated ligand were obtained by employing two groups of methods: (I) a group of conventional methods involving the Coats-Redfern, Freeman-Carroll, Horowitz-Metzger, Dharwadkar-Karkhanavala and Doyle (modified by Zsakó) equations; (II) a new method were suggested by J. Málek *et al.* The results obtained using two types of methods were compared, and it emerged that the results of method II were much more meaningful and reasonable in this work. Additionally, the effects of the molecular structure of the ligands on the kinetic data and models were studied and are discussed.

Keywords: complexes, kinetics, uranyl nitrate

Introduction

In a previous paper [1], we reported the preparation of a new series of uranyl nitrate complexes with N-alkylcaprolactams, $UO_2(NO_3)_2L_2$ ($L = CH_2(CH_2)_4CONR$, where $R = H$, C_2H_5, C_4H_9, C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$ or $C_{12}H_{25}$), their IR and UV-Vis spectra, their structures, the conductivities of their solution in nitrobenzene and/or water and their general thermal behaviour, measured with a combined TG-DTG-DSC technique.

As an extension of our studies of the title compounds, the present paper is devoted to an evaluation of the non-isothermal kinetic parameters and to the derivation of the mechanism for the stage of thermal decomposition of the com-

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[*] Corresponding author

plexes corresponding to the loss of two ligand molecules. Two groups of computational methods were applied for this purpose: (I) a group of conventional methods involving five different equations [2–6]; (II) a new method suggested by Málek, esták, Koga *et al.* [7–10]. The results obtained with the two types of methods were compared. Additionally, the effects of variation of the ligand structure on both kinetic parameters and models were investigated.

Experimental

The preparation and characterization of the compounds were reported previously [1].

A Perkin-Elmer TGA-7 Delta series thermogravimetric analyser was used to obtain the non-isothermal TG curves of the samples. The experiments were carried out in a dynamic pure nitrogen atmosphere at a flow rate of 20 ml·min^{-1}. The sample mass and heating rate used for method (I) were 5–10 mg and 5 deg·min^{-1}, respectively; while for method (II) the heating rate was 2.5, 5.0, 10.0 or 15.0 deg·min^{-1}, and approximately the same sample mass (3–4 mg) was used to minimize heat transfer and mass transfer limitation [11].

Survey of methods for kinetic analysis

Assuming the kinetic model function $f(\alpha)$ and the Arrhenius type of temperature dependence of the rate constant, the following equation is applied for kinetic analysis of the TA curves of the solid-state reaction:

$$\frac{d\alpha}{dt} = A\exp(-E/RT)f(\alpha) \tag{1}$$

where the symbols are those in common use. The kinetic model $f(\alpha)$ is derived on the basis of physico-geometric assumptions on the movement of the reaction interface [9]. Several computational methods based on the above equation have been presented in the literature. Flynn and Wall [12] grouped these methods into five classes: integral methods, differential methods, difference differential methods, methods applicable to initial rates, and non-linear or cyclic heating rate methods.

A group of conventional methods from among the above were used to process the experimental data in this paper: the methods of Coats-Redfern [2]; Freeman-Carroll [3]; Horowitz-Metzger [4]; Dharwadkar-Karkhanavala [5]; and Doyle, as modified by Zsakó [6] (below, all these methods will jointly be referred to as method I). As these methods have been described in the given literature references, the reader is referred to the original papers for further details. A previously reported computer program [13], with some modifications introduced earlier, was applied to aid the calculation, which allows use of the above five methods for up to 14 commonly cited kinetic models [14–17], listed in Table 1.

Table 1 Kinetic models used in method I

Kinetic model	Symbol	$f(\alpha)$	
Reaction order	*Fn*	$(1-\alpha)^n$	$n = 0, 1, 1/3, 1/2, 2/3, 2$
Phase boundary	*Rn*	$n(1-\alpha)^{1-1/n}$	$n = 2, 3$
Random nucleation	*Am*	$m(1-\alpha)[-\ln(1-\alpha)]^{1-1/m}$	$m = 2, 3, 4$
Diffusion	*D2*	$-\ln(1-\alpha)^{-1}$	
	D3	$\frac{1.5(1-\alpha)^{2/3}}{1-(1-\alpha)^{2/3}}$	
	D4	$\frac{1.5}{(1-\alpha)^{-1/3}-1}$	

However, as the above kinetic models are often based on a formal description of geometrically well-defined bodies, these mathematical formulae can hardly describe real heterogeneous systems, for which it has been shown that the processes involved are generally complex [10, 18–20]. An empirical kinetic model, SB(*m*, *n*), was proposed by esták and Berggren [21], and simplified by Gorbatchev [22]:

$$f(\alpha) = \alpha^m(1-\alpha)^n \tag{2}$$

which is believed to be able to accommodate the discrepancy of the real process from the idealized process with sufficient flexibility to describe real processes as closely as possible [9, 23].

What is more, it has been understood that the kinetic exponent in the kinetic model function, the activation energy and the pre-exponential factor are mutually correlated [24, 25], which is likely to lead, in kinetic analysis, to an apparent kinetic model, instead of an appropriate one, for a certain value of the apparent activation energy [8, 26]. Therefore, it can hardly be fruitful to ascertain all kinetic parameters from only one experimental TA curve unless the kinetic models or at least one kinetic parameter are *a priori* known [10]. Accordingly, a completely new method of kinetic analysis has been proposed by Málek *et al.* [7–10] which allows determination of the most suitable kinetic model and the calculation of a complete set of kinetic parameters.

For the same reason as above, here we merely outline the main procedures involved in the method, which was used and referred to as method II in the present study.

(1) Calculation of the activation energy by using multiple scan methods such as the Kissinger [27], Ozawa [28] or Friedman [29] equations. The true activation energy obtained in this step would be decisive for a reliable determination of the kinetic model in step 2.

(2) Determination of the kinetic model which best describes the measured set of TA data on the basis of a combination of the information from two specially defined functions $Y(\alpha)$ and $Z(\alpha)$, which can easily be obtained by simple transformation of the experimental data. The information includes the shape of function $Y(\alpha)$, and the α_M and α_P^∞ for which functions $Y(\alpha)$ and $Z(\alpha)$ have a maximum, respectively.

(3) Evaluation of the kinetic exponents by employing the appropriate equations once the kinetic model has been determined.

(4) Calculation of the pre-exponential factor.

The Kissinger method was used in the present paper to evaluate the activation energy E. All the foregoing calculations for method II were carried out with the aid of the computer program newly written by us, which will be reported separately.

Results and discussion

In our previous paper [1], the general behaviour of the complexes undergoing thermal decomposition has already been described and discussed in detail with the help of TG-DTG-DSC data. Briefly, most of the complexes seem to decompose in two steps:

$$[UO_2L_2](NO_3)_2(s) - UO_2(NO_3)_2(s) + 2\ L(g)$$

$$3UO_2(NO_3)_2(s) - U_3O_8(s) + 6NO_2(g) + 2O_2(g) \tag{3}$$

For the complexes with $R=C_2H_5$, C_4H_9 or C_6H_{18} in their ligand molecules, the second stage corresponding to the loss of two nitrate groups may even be faintly recognized as consisting of two sub-steps [1]: the release of oxygen, and then immediately nitrogen dioxide, which may be attributed to the time lag involved in the breaking of the nitrate group. The kinetic parameters in this paper were evaluated only for the first stage of decomposition, i.e. the stage involving the loss of ligand molecules, since this is the only clear-cut and non-overlapping stage. Because of the unusual decomposition pattern of the complex with $R=H$, which appears to complete almost the whole decomposition process within a very narrow temperature range, resulting in a TG curve too steep for enough data to be collected, no attempt at a kinetic study has been made.

Table 2 Kinetic parameters obtained by method I(five methods) for thermal decomposition of uranyl nitrate complexes with N-alkylcaprolactams

Parameter	Method[a]	Complex $UO_2(NO_3)_2[CH_2(CH_2)_4CONR]_2$					
		$R = C_2H_5$	C_4H_9	C_6H_{13}	C_8H_{17}	$C_{10}H_{21}$	$C_{12}H_{25}$
E / kJ·mol^{-1}	FC	76.84	77.93	71.20	102.90	98.35	71.13
	HM	83.07	84.08	75.41	112.90	107.98	78.66
	DK	78.35	79.95	71.17	108.32	105.02	69.34
	CR	77.01	79.60	71.02	99.06	96.41	71.54
	DZ	85.86	87.83	79.99	115.34	106.59	74.81
ln A	FC	12.7	12.6	12.2	19.0	18.3	11.6
	HM	14.1	14.0	12.1	20.4	19.9	13.5
	DK	12.8	13.0	11.0	20.1	19.2	11.4
	CR	12.6	12.4	10.8	18.3	18.0	12.0
	DZ	15.0	15.0	14.9	20.5	19.6	13.0
$K.M$[b]	FC	n = 0.57	n = 0.52	n = 0.49	n = 0.50	n = 0.46	n = 0.59
	HM	$R2$	$F1/2$	$F0$	$F1/2$	$F1/2$	$R2$
	DK	$F1/2$	$R2$	$F1/2$	$F1/2$	$R2$	$F1/2$
	CR	$F1/2$	$R2$	$R2$	$F1/2$	$F1$	$F1/2$
	DZ	$F1/2$	$F1/2$	$R2$	$F1/2$	$R2$	$R2$
r	FC	0.9828	0.9946	0.9840	0.9806	0.9973	0.9884
	HM	0.9965	0.9955	0.9948	0.9953	0.9958	0.9929
	DK	0.9992	0.9985	0.9986	0.9993	0.9978	0.9979
	CR	0.9986	0.9987	0.9905	0.9985	0.9993	0.9960
Dm[c]	DZ	0.0052	0.0034	0.0034	0.0016	0.0024	0.0018

[a] FC, Freeman-Carrol method; DK, Dharwadlkar-Karkhanavala method; DZ, Doyle method modified by Zsakó; HM, Horowitz-Metzger method; CR, Coats-Redfern method; [b] K.M, Kinetic modle (ref. able 1); [c] Dm, Minimum standard deviation

In addition, we review here some other conclusions drawn from the results obtained in the previous work [1], as these are considered helpful for a discussion of the kinetic study in this paper. They are briefly summarized as follows:

(1) Generally, the initial temperature T_i defined by the TG curves, and the peak temperature T_p defined by the DTG curves for the first stage of decomposition of the complexes $UO_2(NO_3)_2L_2$, increase slightly with increasing length of the substituting alkyl groups.

(2) The DSC curves indicate two peaks for all the complexes: a weakly endothermic one, followed by a medium exothermic peak. The endothermic peak, not accompanied by any mass loss and probably due to a solid-state phase transition or melting, for complexes with $R=C_6H_{13}$, C_8H_{17}, $C_{10}H_{21}$ or $C_{12}H_{25}$, is lo-

cated far below the initial decomposition temperature, whereas for complexes with R=H, C_2H_5 or C_4H_9, the first peak falls in the temperature range in which thermolysis just takes place.

The results obtained from kinetic analysis using the two groups of methods in the present study are presented separately below.

Method I

The results from the five conventional methods for six complexes are tabulated in Table 2, which shows no large or regular variation in the values of E and A among these complexes. From Table 2, it can also be seen that, with a few exceptions, the most probable kinetic model for the studied system is either $n=1/2$ or R2.

At first sight, the above results appear reliable because of the high value of the correlation coefficient (r), or the low value of the standard deviation (D_m), which indicate nearly perfect linearity. As a matter of fact, it is interesting that, for a given complex and a given method, the r values for several different kinetic models are all very high. It is considered reasonable therefore, to suspect the authenticity of the kinetic models determined and the kinetic parameters calculated with only the r value as the criterion, because a small difference in r would make a large difference in E and the kinetic model.

Method II

Table 3 gives the complete kinetic parameters and models obtained from method II, together with some important features of the functions $Y(\alpha)$ and $Z(\alpha)$ provided by the calculation. Figures 1 and 1 selectively show some typical $Y(\alpha)$ and $Z(\alpha)$ dependences.

Table 3 Kinetic parameters and feature of $y(\alpha)$ and $z(\alpha)$ functions obtained using method II by J. Málek *et al.*

Complex[a]	E / kJ·mol^{-1}	α_M	α_P^∞	KM[b]	m	n	ln A
$R = C_2H_5$	87.31	0.483	0.576	SB	0.874	0.936	20.2
$R = C_4H_9$	91.68	0.469	0.585	SB	0.836	0.947	21.1
$R = C_6H_{13}$	97.53	0.251	0.649	SB	0.264	0.789	22.4
$R = C_8H_{17}$	112.9	0.281	0.724	SB	0.228	0.584	25.3
$R = C_{10}H_{21}$	115.7	0.259	0.718	SB	0.202	0.579	24.8
$R = C_{12}H_{25}$	112.9	0.166	0.612	SB	0.197	0.992	22.7

[a] Complex $UO_2(NO_3)_2[CH_2(CH_2)_4CONR]_2$ [b] Kinetic model

From Table 3, it can be seen that the activation energy E, like the temperature T_p for the corresponding complexes, increases with increase of the length of the substituting alkyl group in the ligand molecule. This may be attributed to the fact that the presence of the alkyl group, which is generally considered to be electron-repelling [30, 31] brings about an increase in the electron density on the O atom through the inductive effect along the R–N–C=O bonding, and

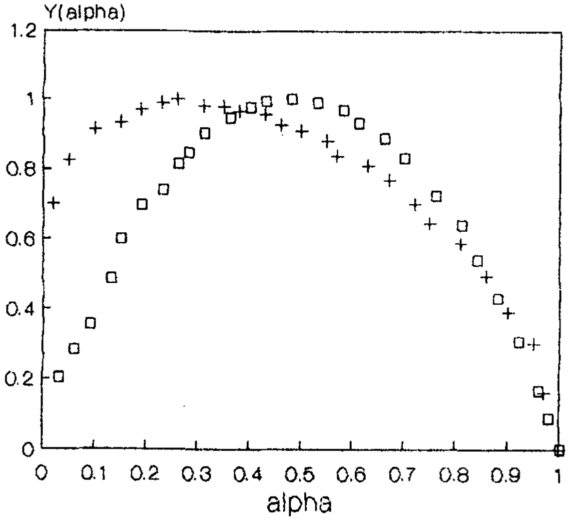

Fig. 1 Normalized $Y(\alpha)$ function corresponding to the N-alkylcaprolactam decomposition kinetic data measured at a heating rate of 5 deg·min^{-1} for complexes $UO_2(NO_3)_2[CH_2(CH_2)_4CONR]_2$ with $R=C_2H_5$ (o), $R=C_{10}H_{21}$ (+)

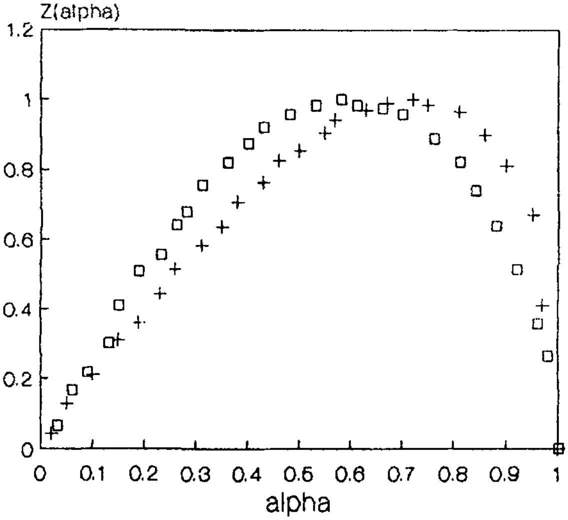

Fig. 2 Normalized $Z(\alpha)$ function corresponding to the N-alkylcaprolactam decomposition kinetic data measured at a heating rate of 5 deg·min^{-1} for complexes $UO_2(NO_3)_2[CH_2(CH_2)_4CONR]_2$ with $R=C_2H_5$ (o), $R=C_{10}H_{21}$ (+)

consequently an increase in the number of $-CH_2-$ units in R could result in a stronger U–O coordinate bond [32, 33]. This assumption also seems to be favoured by the general trend in the shift for $\bar{\nu}_{CO}$, caused by coordination, in the IR spectra for all the studied complexes [1].

It is really of interest to note that, through the decomposition kinetic models determined for all the complexes are SB(*m*, *n*), the values of their kinetic exponents *m* and *n* are different and seem to vary regularly. These values, and especially those of *m*, can be classified into two groups according to their magnitude: $m > 0.8$ for complexes with $R = C_2H_5$ or C_4H_9; and $m < 0.3$ for the others. This appears to be comparable with the two different temperature ranges in which the first peak of the DSC curves falls, as described above in conclusion 2. As this phenomenon is difficult for us to explain in set terms at present, we simply put forward an assumption on a trial basis. With $m \rightarrow 0$, the mathematical expression of the SB(*m*, *n*) model tends to be that of RO(*n*) [10, 34]:

$$\lim m \rightarrow o \quad \alpha^m(1 - \alpha)^n = (1 - \alpha)^n \tag{3}$$

Therefore, the decomposition processes for complexes with C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$ or $C_{12}H_{25}$ with a much lower value of *m* seem to be less complicated than those for the others, with higher values of *m* because of the relatively high regularity and homogeneous degree of the sample for complexes with $R = C_6H_{13}$ to $C_{12}H_{25}$, due to the fact that their solid-state phase transition or melting occurs before the initial decomposition [1].

Conclusion

For the title complexes, the information provided by decomposition kinetic analysis employing the two groups of methods used in this paper differs. The results obtained from method II, i.e. the method of Málek, esták, Koga *et al.*, are much more reliable and reasonable, revealing the complexity and diversity of the decomposition processes, as predicted by their thermal behaviour observed in our previous study, though these phenomena are as yet hard to interpret satisfactorily, and further investigation is therefore needed.

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Zusammenfassung — Mittels nichtisothermer Gravimetrie wurde in Stickstoff die Kinetik der thermischen Zersetzung einer Reihe von Uranylnitratkomplexen mit N-Alkylkaprolaktamen (Alkyl=C_2H_5, C_4H_9, C_6H_{13}, C_8H_{17}, $C_{10}H_{21}$ oder $C_{12}H_{25}$) untersucht. Unter Anwendung zweier Arten von Methoden wurden anhand der TG-DTG-Kurven die kinetischen Parameter bezüglich der Abgabe zweier koordinierter Ligandenmoleküle ermittelt: (I) eine Gruppe herkömmlicher Methoden, wie z.B. die Gleichungen von Coats-Redfern, Freeman-Carroll, Horowitz-Metzger, Dharwadkar-Karkhanavala und Doyle (modifiziert durch Zsakó); (II) eine neue, von Málek et al vorgeschlagene Methode. Die mittels der zwei verschiedenen Methoden erhaltenen Ergebnisse wurden miteinander verglichen und es zeigte sich, daß die Ergebnisse der Methode II in vorliegender Arbeit sinnvoller und akzeptabler sind. Zusätzlich wurde der Einfluß der Molekülstruktur der Liganden auf die kinetischen Daten und das kinetische Modell untersucht und diskutiert.