THE CHEMISTRY OF URANIUM. PART XXIX. THE KINETICS OF THE THERMAL DECOMPOSITION OF $(NMe_4)_2U(NO_3)_6$

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ABSTRACT

The thermal decomposition of $(NMe_4)_2U(NO_3)_6$ was studied in a dynamic nitrogen atmosphere. Isothermal kinetic studies indicated that the overall reaction consists of two consecutive reactions. The enthalpy of decomposition of the overall reaction was found to be 55 kJ mole^{-1}.

INTRODUCTION

The thermal decomposition of $Cs_2U(NO_3)_6$ under reduced pressure has been described previously [1]. It was noted that the gaseous products of the decomposition reaction consist of "oxides of nitrogen, mainly NO and NO_2" [2,3], but no specific identification of the gaseous products was done. During the kinetic studies of the thermal decomposition of $Cs_2U(NO_3)_6$, it was noted that the activation energy, as determined using Flynn and Wall's method [10], changed during the course of the reaction. This was interpreted as a possible change in the mechanism of the decomposition reaction. It was therefore of interest to investigate the kinetics of the thermal decomposition reaction of the nitrato complexes of uranium (IV) in more detail. In order to identify the gaseous products, the reaction was studied in a dynamic nitrogen atmosphere instead of vacuum. $(NMe_4)_2U(NO_3)_6$ was chosen for the study since it can be recrystallized from acetonitrile to give a pure crystalline compound.

EXPERIMENTAL

$(NMe_4)_2U(NO_3)_6$ was prepared as described in the literature [2,3], and was recrystallized from acetonitrile and petroleum ether.

Thermogravimetric studies

A Perkin-Elmer TGS-2 thermobalance was used to collect the thermogravimetric data. The temperature axis was calibrated using magnetic stan-

dards. A flow of approximately 60 cm³ min⁻¹ of nitrogen gas was maintained down the furnace tube, 27 mm i.d. An aluminium pan, similar to that used on the DSC-2, was used as sample holder.

Isothermal measurements were performed on ±10 mg samples in the temperature range 420—445 K. The data collected were fitted to a variety of kinetic expressions [4] using a Hewlett-Packard 9830A computer. The linearity of plots of calculated values of $f(\alpha_i)$ vs. time for each kinetic expression was taken as a criterion for identification of the rate equation. Reduced time plots (α vs. $t/t_{0.5}$) [5] and rate ($d\alpha/dt$) vs. reduced time [6] plots were also used to identify the rate equation.

Non-isothermal measurements were made at constant heating rates of 2.5 and 5 K min⁻¹.

Differential scanning calorimetry studies

A Perkin-Elmer DSC-2 instrument was used to obtain both the rate ($d\alpha/dt$) and the enthalpy of the decomposition reaction. Standard aluminium pans and lids were used as sample holders. Measurements were performed on ±10 mg samples. Nitrogen was used as purge gas.

DSC traces for enthalpy determinations were recorded using constant heating rates of 2.5 and 5 K min⁻¹. Baselines were recorded using an empty aluminium pan in the sample container of the DSC cell. The baseline was superimposed on the actual DSC trace. The areas of the peaks were then measured with a compensating planimeter from which the enthalpy was calculated. The instrument was calibrated using the heat of fusion of indium as standard.

Isothermal rate data were obtained by heating the sample rapidly (80 K min⁻¹) to a predetermined temperature in the DSC cell. The enthalpy changes that occurred at this temperature, which are proportional to the rate $d\alpha/dt$, were then recorded as a function of time.

The area under each isothermal thermogram was integrated with a planimeter for time increments. Dividing the area of each time increment by the total area under the curve gave the fraction of reactant decomposed (α) at the time. Reaction rate constants were determined in two different ways from the isothermal DSC trace:

(i) from maximum deflections from the baseline; and

(ii) from the reciprocal of the measured time interval between attainment of the reaction temperature (t_0) and the peak maximum (t_1) [9].

Using these rate constants, Arrhenius plots were constructed to obtain activation energies.

Evolved gas detection

A thermal conductivity detector of a Servomex gas chromatograph was used for gas detection. The outlet of the DSC-2 purge gas was coupled to the detector which enables simultaneous DSC and EGD measurements to be made. Identification of the evolved gas was accomplished by introduction of a cold trap inbetween the DSC and TCD.

Infrared spectra were recorded using a Perkin-Elmer Model 457 IR spectrometer.

RESULTS AND DISCUSSION

TG, DSC and EGD studies

The TG curve for the decomposition of the compound, $(NMe_4)_2U(NO_3)_6$, at a heating rate of 5 K min^{-1} is given in Fig. 1. The observed percentage mass loss, 12.3%, suggested that the decomposition reaction may be represented as the oxidation reaction

$$(NMe_4)_2U(NO_3)_6 \rightarrow (NMe_4)_2UO_2(NO_3)_4 + \text{oxides of nitrogen}$$

The infrared spectrum of the decomposition product was found to be similar to that of $(NMe_4)_2U(NO_3)_6$ except for a sharp absorption band at 930 cm^{-1} which is characteristic of the UO_2^{2+} group. The six absorption bands observed at 1525, 1285, 1030, 810, 745 and 705 cm^{-1} in both $(NMe_4)_2U(NO_3)_6$ and $(NMe_4)_2UO_2(NO_3)_4$ indicated that the nitrate ions are co-ordinated to the uranium [7].

The DSC trace, represented in Fig. 2, shows only endothermic changes. A broad endotherm appears between 413 and 463 K. It is, however, quite clear that this peak cannot be regarded as a single endothermic peak, but is in fact the resultant of different endotherms. The general profile of the EGD curve (Fig. 2) agrees fairly well with that of the DSC curve. This endothermic peak, which corresponds to the decomposition reaction, indicates that the reaction is more complicated than is suggested by the TG curve. It seems as if the overall reaction is occurring in different steps. The total enthalpy change for the overall reaction was found to be 55 kJ mole^{-1}.

When a cold trap (liquid N_2/ethyl acetate $\sim$—80°C) was introduced between the DSC and TCD, no traces of gas evolution could have been
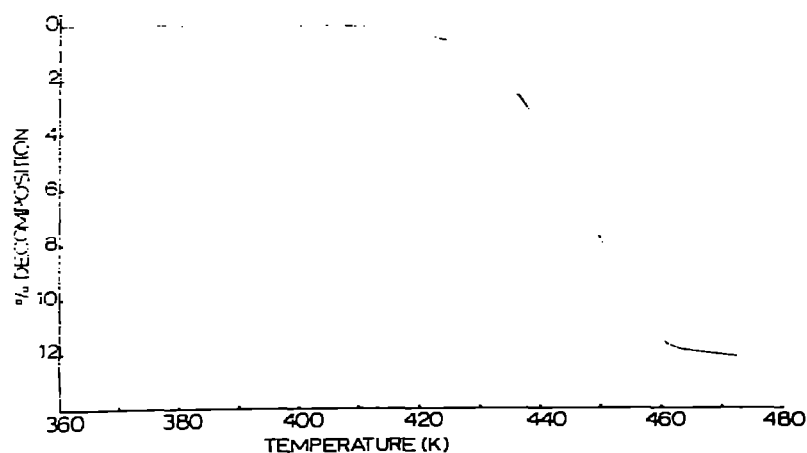

Fig. 1. TG curve for the thermal decomposition of $(NMe_4)_2U(NO_3)_6$. Heating rate 5 K min^{-1}.
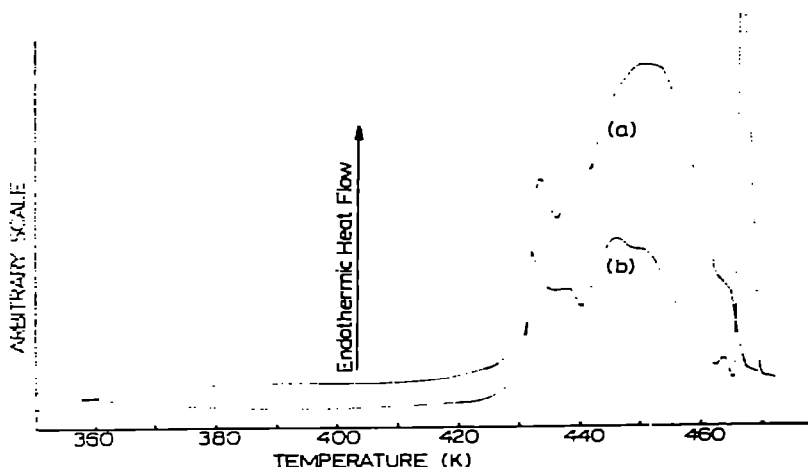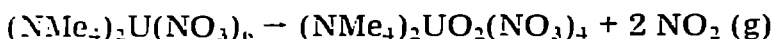
Fig. 2. EGD (a) and DSC (b) curves for the thermal decomposition of $(NMe_4)_2U(NO_3)_6$. Heating rate 5 K min^{-1}.

detected during the decomposition reaction. It must therefore be concluded that only NO_2 (b.p. $-11°C$) is evolved during the reaction and not NO (b.p. $-152°C$). The overall decomposition (redox) reaction can therefore be written as

$$(NMe_4)_2U(NO_3)_6 \rightarrow (NMe_4)_2UO_2(NO_3)_4 + 2\ NO_2\ (g)$$

The sharp endothermic peak at 468 K is due to the melting of the decomposition product. The enthalpy change was found to be 27 kJ mole^{-1}.

Kinetic studies

The isothermal decomposition curves were recorded in the temperature range 420—445 K. The data seem to fit two kinetic equations equally well:

(i) a first-order rate equation, $-\ln(1 - \alpha) = kt$ (Fig. 3); and

(ii) the Jander equation, $[1 - (1 - \alpha)^{1/3}]^2 = kt$ (Fig. 4)

A reduced time plot (α vs. $t/t_{0.5}$; Fig. 5) eliminated the possibility of describing the kinetics by the Jander equation. It further indicated that the first-order rate data deviated slightly from the calculated reduced time plots for the first-order rate equation. Reduced time plots of experimental data obtained 423 and 435 K gave exactly the same degree of fit with the calculated data for a first-order rate equation. It seems, therefore, as if the mechanism of the overall decomposition reaction can approximately be described by the kinetic equation $[-\ln(1 - \alpha] = kt$. However, a 100% fit of the experimental with the calculated data is required to draw any conclusions regarding the kinetic expressions [8].

A method utilizing the reaction rate to obtain information about the reaction mechanism has been described in the literature [6]. This method involves plots of $d\alpha/dt$ vs. reduced time. It seems to be superior to the method described by Sharp et al. [5] on the grounds of greater differences in the shapes of the master curves. Isothermal DSC measurements yielded
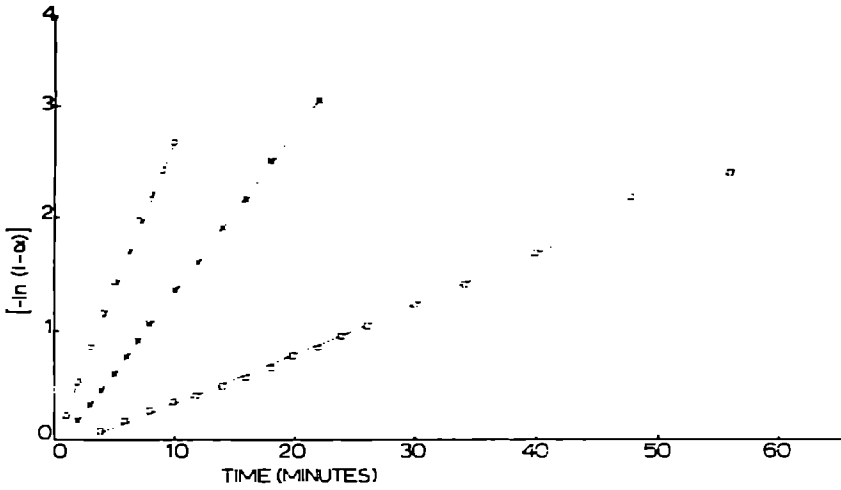
Fig. 3. Plots of $-\ln(1-\alpha)$ vs. t for the isothermal decomposition reaction. $\square$, $T = 420$ K; $\times$, $T = 423$ K; , $T = 435$ K.
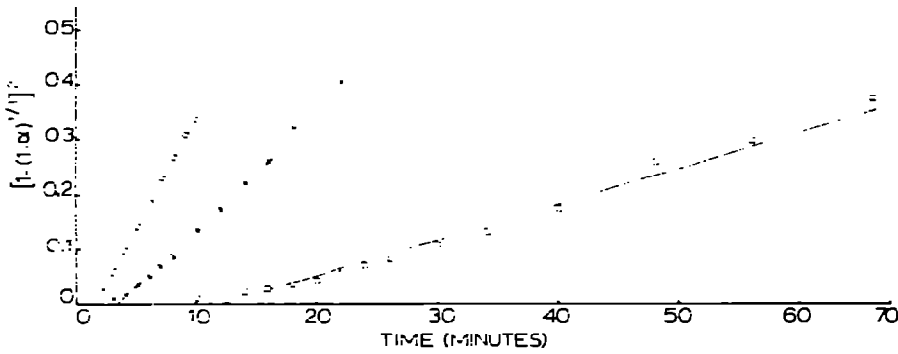

Fig. 4. Plots of $[1-(1-\alpha)^{1/3}]^2$ vs. t for the isothermal decomposition reaction. $\square$, $T = 420$ K; $\times$, $T = 423$ K; , $T = 435$ K.

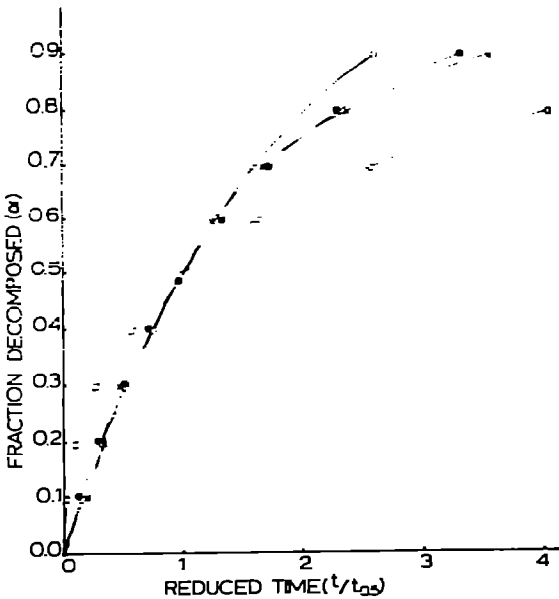Fig. 5. Reduced time plots. $\square$, $[1-(1-\alpha)^{1/3}]^2 = kt$; $\circ$, $1-(1-\alpha)^{1/3} = kt$; $\bullet$, $\ln(1-\alpha) = kt$; $\times$, experimental curve; $T = 430$ K.
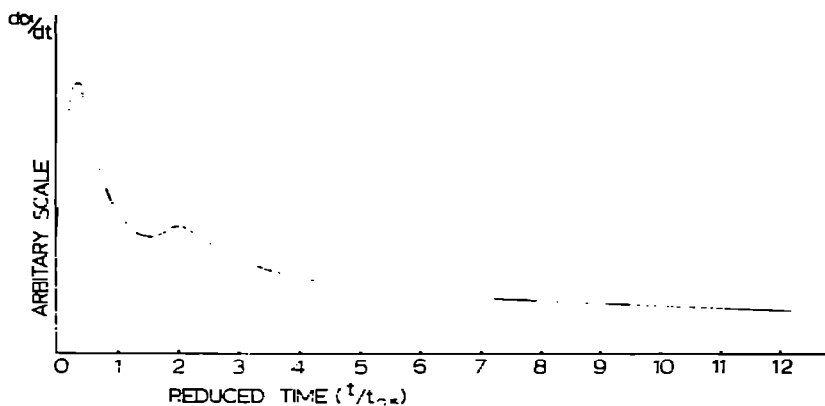
Fig. 6. Rate vs. reduced time plot.

the rate data directly. A plot of $d\alpha/dt$ vs. $t/t_{0.5}$ for the decomposition of $(NMe_4)_2U(NO_3)_6$ is given in Fig. 6.

A considerable difference between the experimentally obtained curve and the calculated curves [6] for a first-order rate process and the Jander equation is observed. Integration of the isothermal DSC response yielded an α—time curve which agrees very well with that obtained from the isothermal mass loss curves (Fig. 7). The isothermal DSC data suggested that the redox reaction can be described by two consecutive reactions. A considerable amount of overlap of these reactions exist.
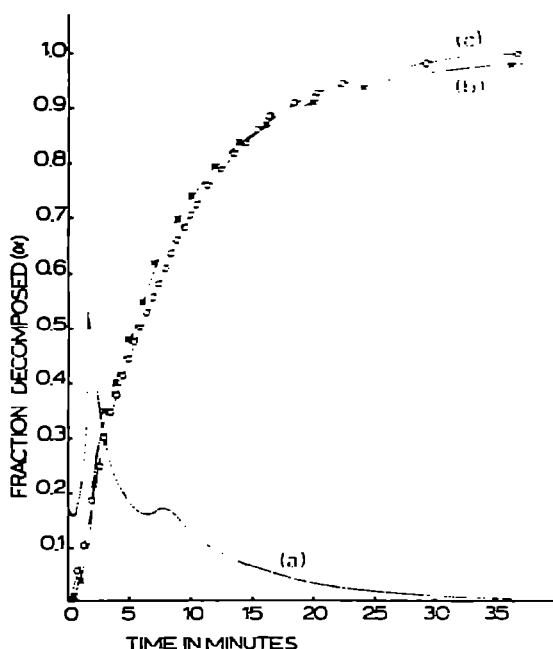

Fig. 7. Isothermal decomposition (arbitrary units and α) of $(NMe_4)_2U(NO_3)_6$ at 430 K. (a) DSC response; (b) α values obtained from numerical integration of DSC response; (c) thermogravimetric data.

The first reaction reached its maximum rate after 1.5 min (at 430 K), and can possibly be represented as the oxidation of the uranium(IV) by a nitrate ion to uranium(V), i.e.

$$(NMe_4)_2U(NO_3)_6 \rightarrow (NMe_4)_2UO(NO_3)_5 + NO_2 \qquad (1)$$
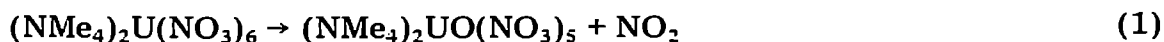
It was not possible to isolate the uranium(V) intermediate because of the considerable amount of overlap of the two reactions. The second reaction, which reached its maximum rate after 7.5 min (at 430 K), can be linked to the oxidation of the uranium(V) to uranium(VI) by a second nitrate ion, i.e.

$$(NMe_4)_2UO(NO_3)_5 \rightarrow (NMe_4)_2UO_2(NO_3)_4 + NO_2 \qquad (2)$$
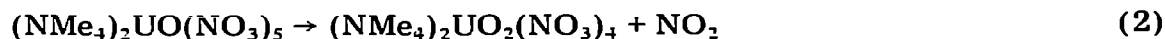
The general shape of the curve, however, suggested a nucleation and growth type of mechanism for each reaction, but a detailed analysis of the curve is required to make any meaningful conclusions regarding the mechanism.

Estimates of activation energies for the two different reactions from measured magnitudes of reciprocal time and maximum deflection values are 182 and 145 kJ mole^{-1}, respectively, for reaction (1), and 153 and 157 kJ mole^{-1}, respectively, for reaction (2).

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