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THE CHEMISTRY OF URANIUM
PART XXI. A THERMOGRAVIMETRIC STUDY OF THE DECOMPOSITION OF $(Net_4)_2UCl_6$ AND $(Net_4)_2UBr_6$

J. G. H. DU PREEZ AND C. P. J. VAN VUUREN
Uranium Chemistry Research Unit, University of Port Elizabeth, P.O. Box 1600, Port Elizabeth, 6000 (South Africa)

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ABSTRACT

The thermal decomposition reactions of $(Net_4)_2UX_6$, X = Cl, Br, were studied in nitrogen and oxygen atmospheres. Isothermal and dynamic techniques were used to estimate activation energies for the reactions in nitrogen. The bromo complex seems to be more resistant towards decomposition than the chloro complex.

INTRODUCTION

The solution chemistry of uranium (IV), in the presence of various anionic and neutral donor ligands, has been investigated extensively over the last few years[1]. Very little fundamental information is available on the thermal behaviour of uranium (IV) halides. Van Wazer and John[2] reported a kinetic study of the oxidation of uranium tetrachloride in an oxygen atmosphere. The oxidation process consisted of two independent steps which were described as:

(i) $UCl_4 + O_2 \rightarrow UO_2Cl_2 + Cl_2 : E_a = 50$ kJ mol^{-1}
(ii) $3UO_2Cl_2 + O_2 \rightarrow U_3O_8 + 3Cl_2 : E_a = 189$ kJ mol^{-1}

In addition, UO_2Cl_2 was found to decompose to U_3O_8 when ignited in air, while UO_2 was the product when nitrogen instead of air was used[3]. The oxidation of UBr_4 by oxygen was described by similar reactions[3], i.e.,

(i) $UBr_4 + O_2 \rightarrow UO_2Br_2 + Br_2$
(ii) $3UO_2Br_2 + O_2 \rightarrow U_3O_8 + 3Br_2$

The reactions were studied in the temperature range 150–200°C, but no energy parameters such as activation energies, are reported.

The present investigation was undertaken in an attempt to elucidate the solid-state decomposition kinetics and, if possible, the mechanism of the decomposition of the hexahalo uranium (IV) species. Isothermal and dynamic thermogravimetric studies were therefore performed on $(Net_4)_2UCl_6$ and $(Net_4)_2UBr_6$ in oxygen and nitrogen atmospheres.

EXPERIMENTAL

Materials

$(Net_4)_2UCl_6$ and $(Net_4)_2UBr_6$ were prepared by mixing stoichiometric amounts of the corresponding uranium (IV) halide, dissolved in acetone, and tetraethylammonium halide, dissolved in acetonitrile. The pale green solids were recrystallized from boiling acetonitrile, vacuum dried and analysed. The analytical results are given in Table I.

TABLE I

ANALYTICAL RESULTS

Compound	*Uranium (%)*		*Halide (%)*	
	Calc.	*Found*	*Calc.*	*Found*
$(Net_4)_2UCl_6$	33,47	33,5	29,96	29,8
$(Net_4)_2UBr_6$	24,35	24,4	49,05	49,1

Thermogravimetric measurements

A Perkin-Elmer TGS-2 thermobalance was used to collect all data. The temperature axis was calibrated using magnetic standards. A flow of approximately 60 ml min^{-1} of the required gas, oxygen or nitrogen, was maintained down the furnace tube, 27 mm i.d. A platinum cup was used as sample holder.

Isothermal measurements were performed on ± 7 mg samples in the temperature range 600–700 K.

The data collected were fitted to a variety of kinetic rate laws[4] using a Hewlett-Packard 9830A computer. The minimum standard deviation in alpha obtained from the least-squares fitting of the best straight line was used as the criteria for the most applicable rate law.

Dynamic measurements were made at constant heating rates of 2.5, 5, 10 and 20 K min^{-1}, using sample weights of ± 7 mg. In order to check the effect of sample size on the activation energy, sample weights varying between 3 and 15 mg were used at a constant heating rate of 5 K min^{-1}. The data obtained were processed to give values for the energy of activation (E_a) using the integral technique proposed by Coats and Redfern[5]. Reaction orders $n = 0$; 0.5; 0.67; and 1.0 were used for the calculations. The value of n, giving the minimum standard deviation from the least-squares fitting of the best straight line, was used as the order describing the reaction.

RESULTS AND DISCUSSION

(1) Decomposition reactions in oxygen

The TG and DTG curves for the decomposition of $(Net_4)_2UCl_6$ in oxygen,

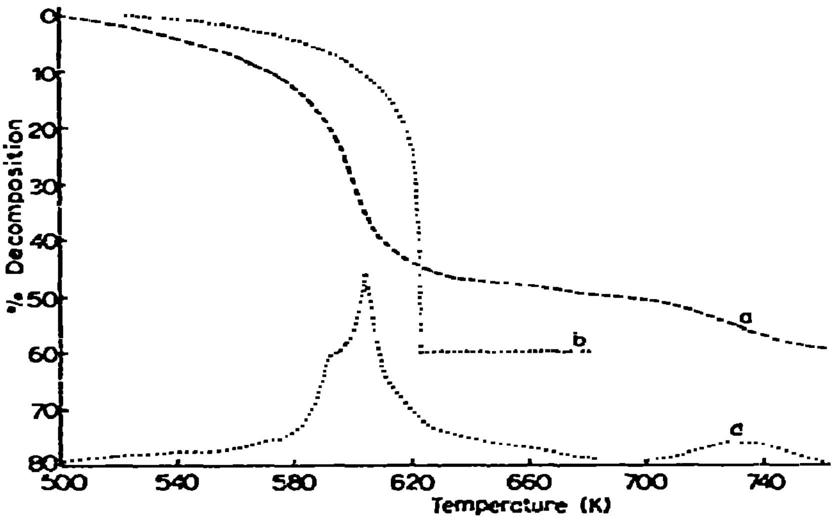


Fig. 1. TG and DTG curves for the decomposition of $(Net_4)_2UCl_6$ in oxygen. Heating rate: (a) 2.5 K min^{-1}; (b) 5 K min^{-1}.

using a heating rate of 2.5 K min^{-1} are given in Fig. 1. It seems to suggest a two-step decomposition process:

(i) $(Net_4)_2UCl_6 \rightarrow$ product A
(ii) Product A $\rightarrow U_3O_8$

Product A had no definite composition and it seems to be a mixture of UO_2, U_3O_8 and UO_2Cl_2, similar to the decomposition described for UBr_4. A surprising fact was that $(Net_4)_2UO_2Cl_4$ seems to be ruled out as a stable intermediate in the decomposition reaction. The decomposition reaction was found to be very sensitive to the heating rate (β). When $\beta \geq$ K min^{-1}, a highly exothermic reaction occurred over the α range 0.4 to 1.0. The DTG curve given in Fig. 1 (shoulder at 602 K to the main peak) suggested that the initial stages of the decomposition might be described by the reaction:

$$(Net_4)_2UCl_6 \rightarrow (Net_4)UCl_5 + Net_4Cl$$

although no stable intermediate of such a nature could have been detected. This type of dissociation reaction is not uncommon and was observed[6] in the thermal decomposition of $(C_nH_{2n+1}NH_3)_2MnCl_4$. The thermal decomposition of the bromo complex, $(Net_4)_2UBr_6$, in an oxygen atmosphere was found to be different from the chloro analogue discussed above. The TG and DTG curves (Fig. 2) suggested that the overall decomposition process could be represented by the following three individual processes:

(i) $(Net_4)_2UBr_6 + O_2 \rightarrow (Net_4)_2UO_2Br_4 + Br_2$
(ii) $(Net_4)_2UO_2Br_4 \rightarrow UO_2Br_2 + 2(Net_4)_2Br$
(iii) $3UO_2Br_2 + O_2 \rightarrow U_3O_8 + 3Br_2$

It was noticed that simultaneously with the formation of the yellow $(Net_4)_2UO_2Br_4$,

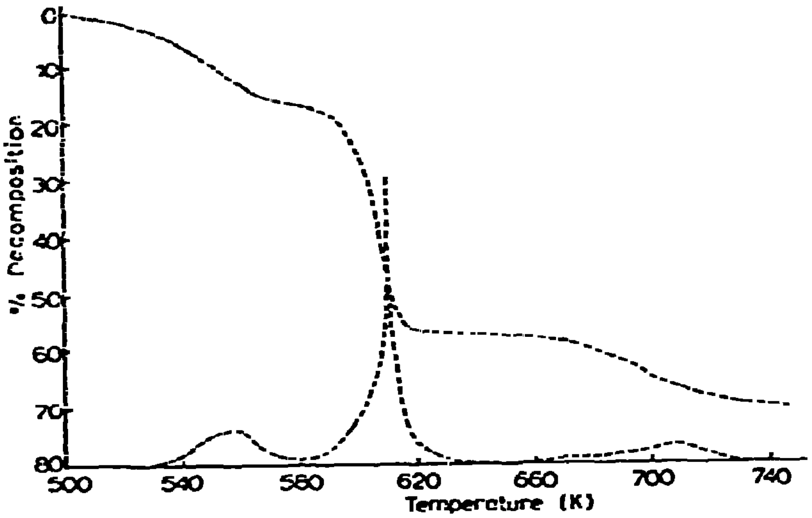


Fig. 2. TG and DTG curves for the decomposition of $(Net_4)_2UBr_6$ in oxygen. Heating rate 5 K min^{-1}.

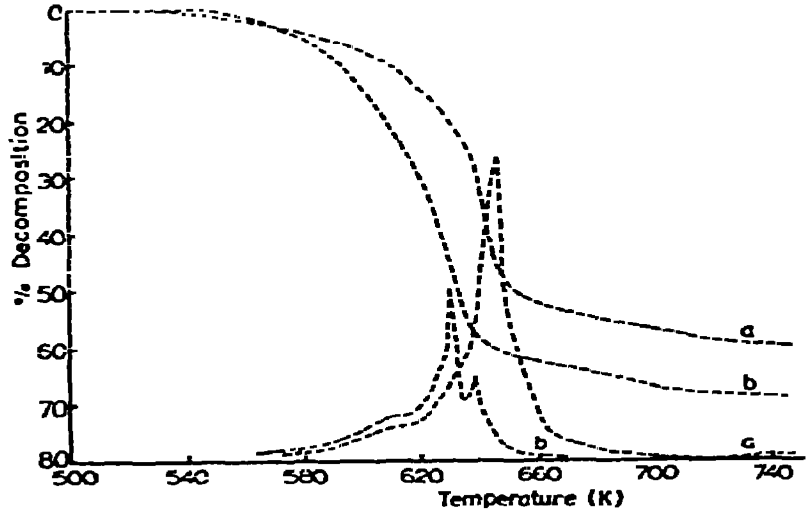


Fig. 3. TG and DTG curves for the decomposition of: (a) $(Net_4)_2UCl_6$, and (b) $(Net_4)_2UBr_6$ in nitrogen. Heating rate 5 K min^{-1}.

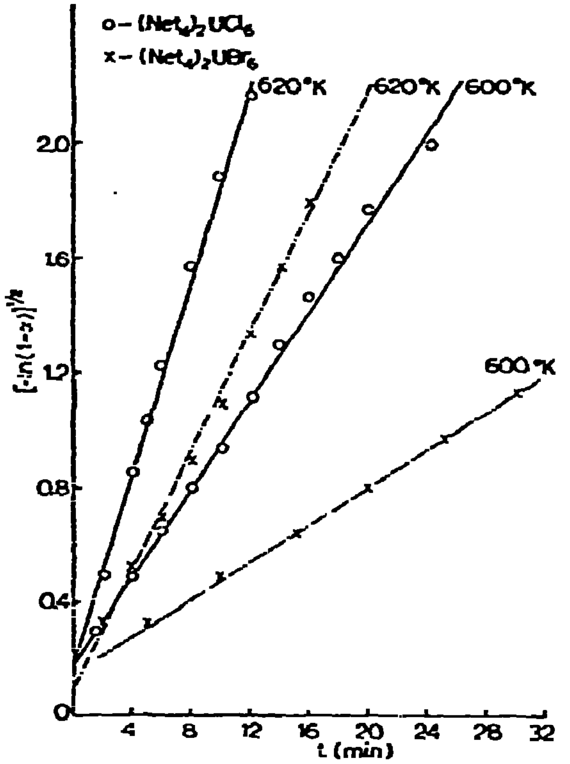
a black impurity, probably UO_2 and/or U_3O_8, was formed, similar to the decomposition[3] of UBr_4. The reaction was found to be less sensitive to the heating rate, since it became exothermic only when $\beta \geqslant 10$ K min^{-1}.

(2) Decomposition reactions in nitrogen

The decomposition reactions of the complexes in a dynamic N_2 (99.5%) atmosphere were found to differ from their analogues in oxygen. The TG and DTG curves obtained using a heating rate of 5 K min^{-1} (Fig. 3) suggested similar reactions for both compounds, i.e.,

$$3(Net_4)_2UX_6 \rightarrow U_3O_8 + 6Net_4X + 6X_2$$

The oxygen present in the N_2 seems to be sufficient for the oxidation reaction to occur.



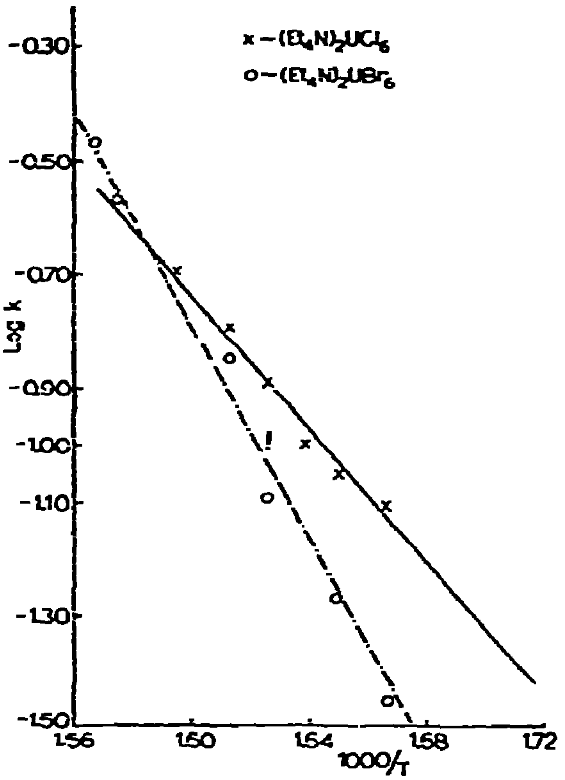


Fig. 4. Plots of $[-\ln(1-\alpha)]^{\frac{1}{2}}$ versus time for $(Net_4)_2UCl_6$ and $(Net_4)_2UBr_6$.

Fig. 5. Arrhenius plots for $(Net_4)_2UCl_6$ and $(Net_4)_2UBr_6$.

TABLE 2

ACTIVATION ENERGIES AS OBTAINED FROM ISOTHERMAL AND DYNAMIC MEASUREMENTS

Compound	*Isothermal (Arrhenius plots) (kJ mol^{-1})*	*Dynamic (Coats-Redfern eqn) (kJ mol^{-1})*
$(Net_4)_2UCl_6$	115	156
$(Net_4)_2UBr_6$	181	185

Isothermal studies indicated that the Erofeev equation, $[-\ln(1-\alpha)]^{\frac{1}{2}} = kt]$, was consistently the most applicable rate law for both decomposition reactions (see Fig. 4). Values for the activation energies were obtained from Arrhenius plots (Fig. 5) and are listed in Table 2.

Treatment of the dynamic data using the Coats-Redfern equation indicated zero-order decomposition kinetics, $n = 0$, for both reactions. The activation energies obtained from this equation (Table 2) are average values obtained using different sample sizes and heating rates as indicated in Table 3. These values seem to be fairly insensitive to sample size and heating rate.

TABLE 3

ACTIVATION ENERGIES FROM DYNAMIC DATA USING DIFFERENT HEATING RATES AND SAMPLE SIZES

Compound	*Heating rate ($K\ min^{-1}$)*	*Sample size (mg)*	*Activation energy ($kJ\ mol^{-1}$)*
$(Net_4)_2UCl_6$	5	4,35	155
		5,52	147
		6,90	151
		9,45	170
		13,16	158
	5	6,95	156
	10	7,10	156
	20	6,80	162
$(Net_4)_2UBr_6$	5	3,07	179
		7,48	179
		10,96	187
		15,74	188
	5	7,00	185
	10	7,10	191
	20	7,05	188

The isothermal and dynamic data suggested a similar mechanism, random nucleation, for both reactions. The consistent higher activation energy obtained for the bromo complex suggested that the complex is more resistant to decomposition than the chloro complex. It is, however, clear that in order to describe the mechanism of the decomposition reactions, various factors, such as cation effect, atmosphere, etc. will have to be investigated carefully.

CONCLUSION

Isothermal and dynamic decomposition studies indicated that $(Net_4)_2UX_6$ where X = Cl and Br decomposes to yield U_3O_8. The nature of the decomposition reaction is determined by the atmosphere used. A dynamic oxygen atmosphere produced an exothermic reaction under non-isothermal conditions; $\beta \geqslant 5\ K\ min^{-1}$ for $(Net_4)_2UCl_6$ and $\beta \geqslant 10\ K\ min^{-1}$ for $(Net_4)_2UBr_6$. Isothermal studies in dynamic nitrogen atmosphere suggested similar mechanisms for both decomposition reactions. The bromo complex was found to be more resistant towards decomposition than the chloro complex.

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