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PART 30. THE EFFECT OF THE CATION ON THE THERMAL DECOMPOSITION OF HEXANITRATO URANATE (IV)

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The thermal decomposition reactions of various hexanitrate uranium(IV) species, $M_2U(NO_3)_6$ where $M = Cs^+$, NEt_4^+ , $AsPh_4^+$ and PPh_4^+ have been studied.

The overall decomposition reaction can be described in terms of an oxidation-reduction reaction in which the nitrate oxidizes the uranium. The enthalpies of decomposition were found to be very similar, approximately 55 kJ mole^{-1} except for the PPh_4^+ -salt which was only 27 kJ mole^{-1} .

The decomposition kinetics of all the compounds were studied and found to be complex — especially during the initial stages of the reaction.

The thermal decomposition of $(NMe_4)_2U(NO_3)_6$ was described in a previous publication [1]. Published data seems to indicate that the cation influence the stability of the hexanitrate uranium(IV) species. Ryan [2] reported that $(NEt_4)_2U(NO_3)_6$ decomposed “slightly” over a period of eighteen months at room temperature, while Bagnall [3] noted that $Cs_2U(NO_3)_6$ decomposed “more readily” at room temperature. In both cases the decomposition products were found to be uranyl nitrates, i.e. $(NEt_4)_2UO_2(NO_3)_4$ and $Cs_2UO_2(NO_3)_4$. Analysis of the gaseous products were not done. It was therefore of interest to investigate the thermal decomposition of $M_2U(NO_3)_6$, where $M = NEt_4^+$, $AsPh_4^+$, PPh_4^+ and Cs^+ , and to compare it with the data obtained for $(NMe_4)_2U(NO_3)_6$.

Experimental

Materials

The corresponding M_2UCl_6 , where $M = NEt_4^+$, PPh_4^+ and $AsPh_4^+$, was suspended in a mixture of acetone and acetonitrile. The suspension was cooled in ice and stirred, while the stoichiometric amount of $AgNO_3$, dissolved in acetonitrile, was added dropwise. The $AgCl$ was filtered off and small amounts of ethyl acetate were added to the cold filtrate to initiate precipitation. The resulting compound was then recrystallized from acetonitrile and petroleum ether mixtures. The caesium salt was prepared and recrystallized from an aqueous acidic nitric acid medium [3].

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Thermogravimetric studies

A Perkin-Elmer TGS-2 thermobalance was used to collect the thermogravimetric data. The temperature axis was calibrated using magnetic standards. A flow of approximately $60 \text{ cm}^3 \text{ min}^{-1}$ of nitrogen gas was maintained down the furnace tube, 27 mm i.d. An aluminium pan, similar to the one used on the DSC-2, was used as a sample holder.

Isothermal measurements were performed on $\pm 10 \text{ mg}$ samples in the temperature range 410–480 K. The samples were ground to a fine powder before any measurements were made. The data collected were fitted to a variety of kinetic expressions [7] using a Hewlett-Packard 9830A computer. The linearity of plots of calculated values of $F(\alpha_i)$ against time for each kinetic expression was taken as a criterion for identification of the rate equation. Reduced time plots (α vs. $t/t_{0.5}$) [8] and rate ($d\alpha/dt$) vs. reduced time [9] 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 the rate ($d\alpha/dt$) as well as the enthalpy of the decomposition reaction. Standard aluminium pans and lids were used as sample holders. Measurements were performed on $\pm 10 \text{ mg}$ samples in powder form. Nitrogen was used as a purge gas.

DSC traces for enthalpy determination 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, from which the enthalpies were calculated, were then measured with a compensating planimeter. The instrument was calibrated using the heat of fusion of Indium as standard.

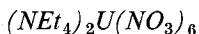
Isothermal rate data were obtained by heating the sample rapidly (80 deg min^{-1}) to a predetermined temperature in the DSC cell. The enthalpy changes that occurred at this temperature, which are proportional to the rate $d\alpha/dt$, was then recorded as a function of time.

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 enabled simultaneous DSC and EGD measurements to be made. Identification of the evolved gas was accomplished by introduction of an ethyl acetate/liq. nitrogen cold trap in between the DSC and TCD.

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

Results and discussion



The TG, DSC and EGD curves for the decomposition of the compound, heating rate 5 deg. min⁻¹, are given in Fig. 1. TG data indicated that decomposition of the compound took place over the temperature range 410 to 455 K. The observed percentage mass loss was found to be 10.8% which agrees very well with the theoretical mass loss of 10.6% calculated for the reaction

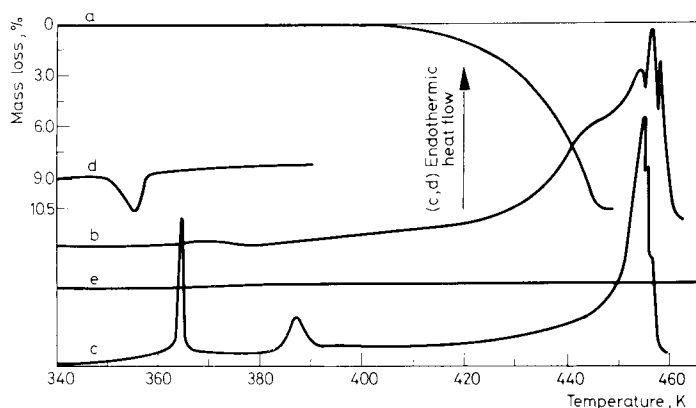
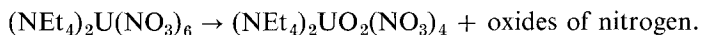
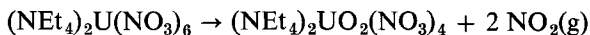


Fig. 1. TG, DSC and EGD curves for the thermal decomposition of $(\text{NEt}_4)_2\text{U}(\text{NO}_3)_6$. Heating rate 5 deg. min⁻¹. (a) TG trace; (b) EGD trace; (c) DSC trace; (d) DSC cooling curve; (e) EGD trace obtained with an ethyl acetate/liquid nitrogen trap

The infrared spectrum of the decomposition product showed absorption bands at 930 and 940 cm⁻¹ which can be assigned as due to the symmetric stretch of the UO₂ group [4]. These absorption bands were absent in the hexanitrate uranium(IV) species. The spectrum of the product agreed very well with the spectrum obtained for the compound $(\text{NEt}_4)_2\text{UO}_2(\text{NO}_3)_4$ prepared from $(\text{NEt}_4)_2\text{UO}_2\text{Cl}_4$ and 4 AgNO₃.

The DSC trace indicated three different endothermic peaks. The peak maxima were at 364, 388 and 477 K. The one at 477 K is associated with the decomposition of the compound as indicated by the TG and EGD traces. Decomposition of the compound is accompanied by melting of the product. The total enthalpy change measured for these two combined processes was 86 kJ mole⁻¹. When the EGD trace was recorded with an ethylacetate/liquid nitrogen cold trap (~ -80 °C) between the DSC and the TCD, no response was registered during decomposition of the compound. It can therefore be concluded that only NO₂(bp - 11°) is evolved during the decomposition and not NO(bp - 152°). The overall reaction can therefore be written as



The endothermic peaks at 364 and 388 K were not associated with any decomposition and could be due to phase changes, similar to the phase changes observed for KNO_3 [8]. The enthalpy changes associated with these changes were approximately 10 kJ mole^{-1} for the peak at 364 K and 6 kJ mole^{-1} for the one at 388 K.

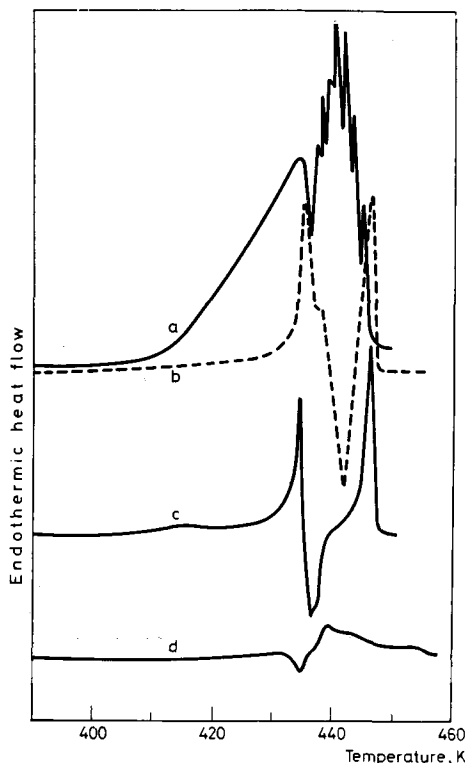


Fig. 2. DSC and EGD curves for the thermal decomposition of $(\text{AsPh}_4)_2\text{U}(\text{NO}_3)_6$. Heating rate $5 \text{ deg} \cdot \text{min}^{-1}$. (a) EGD trace, (b) DSC trace, (c) DSC trace — heating rate $2.5 \text{ deg} \cdot \text{min}^{-1}$ (d) EGD trace obtained with an ethyl acetate/liquid nitrogen trap

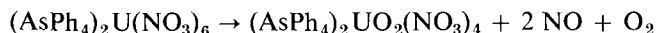
These changes were fully reversible. When the compound was heated at $2.5 \text{ deg} \cdot \text{min}^{-1}$ to 400 K and then cooled at a rate of $2.5 \text{ deg} \cdot \text{min}^{-1}$, only one peak was observed. This is indicated in Fig. 1, curve (d). It was an exothermic process and the enthalpy associated with it was approximately -15 kJ mole^{-1} which corresponds to the total heat measured for the endothermic processes at 364 K and 388 K.

$\text{Cs}_2\text{U}(\text{NO}_3)_6$, $(\text{AsPh}_4)_2\text{U}(\text{NO}_3)_6$ and $(\text{PPh}_4)_2\text{U}(\text{NO}_3)_6$

TG, infrared and elemental analysis indicated that the solid decomposition product of all three compounds corresponded to the uranyl complex i.e. $\text{M}_2\text{UO}_2(\text{NO}_3)_4$

where $M = Cs^+$, $AsPh_4^+$ and PPh_4^+ . The DSC traces obtained for the decomposition reactions differ considerably from one another, as well as from those obtained for $(NEt_4)_2U(NO_3)_6$ (Fig. 1) and $(NMe_4)_2U(NO_3)_6$ (1). For $Cs_2U(NO_3)_6$ a broad endothermic peak is observed. The enthalpy of decomposition was measured to be 57 kJ mole^{-1} . Both the $AsPh_4^+$ and PPh_4^+ -salts showed an initial endothermic peak which is followed by an exothermic peak. A sharp endothermic peak, due to the melting of the decomposition product, followed the decomposition peaks. It was possible to separate the melting peak from the decomposition peaks by using a slower heating rate. e.g. $2.5 \text{ deg. min}^{-1}$ — see Fig. 2. The total enthalpy changes for the decomposition was 53 kJ mole^{-1} for the $(AsPh_4)_2U(NO_3)_6$ but only 27 kJ mole^{-1} for $(PPh_4)_2U(NO_3)_6$.

EGD measurements suggested that, except for $(AsPh_4)_2U(NO_3)_6$, the gas evolved during the decomposition was NO_2 . A very "noisy" curve was obtained when the trace was recorded without a cold trap between the DSC and TCD. With a cold trap a very small peak was obtained suggesting that NO was evolved. The simultaneous evolution of two different gases with different thermal conductivities could give rise to such a "noisy" curve. A possible reaction which will explain the evolution of NO can be written as



The decomposition kinetics

The isothermal decomposition kinetics of all the compounds studied were found to be complex. In all cases the data fitted more than one kinetic equation equally well.

Reduced time plots, α vs $t/t_{0.5}$, suggested that the decomposition kinetics, except in the case of $(NEt_4)_2U(NO_3)_6$, can be described by the first order law, $-\ln(1 - \alpha) = kt$. It was, however, not possible to obtain a 100% fit of the experimental data with the calculated reduced time plots for a first order rate law and therefore no conclusive results could have been drawn from these results [6]. Rate versus reduced time plots indicated that the decomposition kinetics are extremely complex for small values of α , i.e. $\alpha < 0.2$, and no simple kinetic equation can be used to describe the decomposition kinetics. (See Fig. 3.) The thermal reaction of $(NEt_4)_2U(NO_3)_6$ seems to be described by linear kinetics, $\alpha = kt$, over the alpha range 0 to ± 0.5 , as illustrated in Fig. 4. A different mechanism seems to describe the decomposition reaction over the alpha range ± 0.5 to 1.

Considering all the results it can be concluded that the cation plays an important role in the decomposition of the hexanitrate uranate(IV) salts; the exact nature is still not known. The results can be summarized as follows:

1. All the salts studied seems to be described by an oxidation reaction in which the nitrate ions oxidize the uranium(IV) to uranium(VI) with the evolution of NO_2 gas as the only volatile product, except in the case of the $AsPh_4^+$ salt. A mixture of gases, probably NO_2 , NO and O_2 , was detected for the decomposition of this salt.

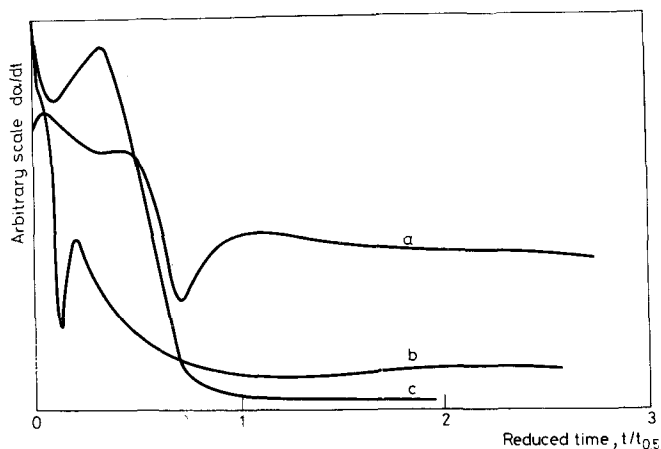


Fig. 3. Reduced time plots. (a) $(\text{AsPh}_4)_2\text{U}(\text{NO}_3)_6$, $T = 415 \text{ K}$; (b) $(\text{PPh}_4)_2\text{U}(\text{NO}_3)_6$, $T = 420 \text{ K}$; (c) $\text{Cs}_2\text{U}(\text{NO}_3)_6$, $T = 460 \text{ K}$

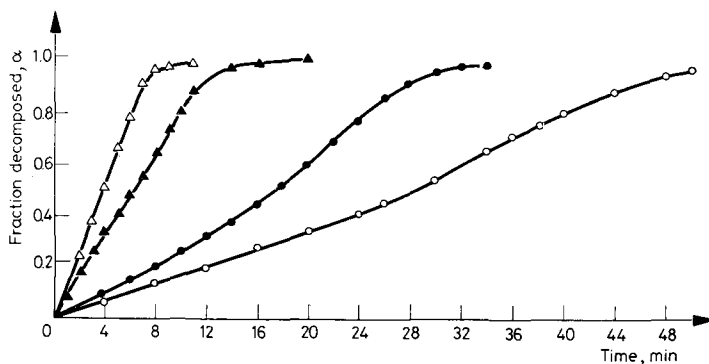


Fig. 4. Isothermal decomposition curves for $(\text{NEt}_4)_2\text{U}(\text{NO}_3)_6$. $\triangle T = 435 \text{ K}$, $\blacktriangle T = 425 \text{ K}$, $\bullet T = 420 \text{ K}$, $\circ T = 417 \text{ K}$

2. The enthalpies of decomposition for the various salts, $\text{NMe}_4^+ - (\text{I})$, $\text{AsPh}_4^+ -$ and $\text{Cs}^+ -$, were found to be very similar, $\pm 55 \text{ kJ mole}^{-1}$. For the PPh_4^+ salt, ΔH was found to be $\pm 30 \text{ kJ mole}^{-1}$ less than the other salts.

3. $(\text{NEt}_4)_2\text{U}(\text{NO}_3)_6$ is unique in so far that it is the only nitrate which showed a reversible phase change before decomposition occurred.

4. The kinetics of all the compounds studied were found to be complex and different from each other.

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RÉSUMÉ — On a étudié la décomposition thermique des diverses espèces d'hexanitrate d'uranium IV de formule:



La réaction générale de la décomposition peut être décrite par une réaction d'oxydo-réduction, dans laquelle le nitrate oxyde l'uranium. On a trouvé que les enthalpies de décomposition étaient très similaires, environ $55 \text{ kJ} \cdot \text{mole}^{-1}$, à l'exception du sel de PPh_4^+ dont la valeur n'était que $27 \text{ kJ} \cdot \text{mole}^{-1}$.

On a étudié la cinétique de décomposition de tous les composés. Elle est complexe, spécialement pendant les étapes initiales de la réaction.

ZUSAMMENFASSUNG — Die thermischen Zersetzungsreaktionen verschiedener Hexanitraturan (IV)-Arten der Formel $M_2U(NO_3)_6$ ($M = Cs^+$, NEt_4^+ , $AsPh_4^+$ und PPh_4^+) wurden untersucht.

Die allgemeine Zersetzungsreaktion kann durch eine Oxidations-Reduktionsreaktion beschrieben werden, in der Uran durch Nitrat oxidiert wird. Die Zersetzungsenthalpien erwiesen sich als sehr ähnlich, annähernd $55 \text{ kJ} \cdot \text{mol}^{-1}$ mit Ausnahme des PPh_4^+ -Salzes, dessen Wert nur $27 \text{ kJ} \cdot \text{mol}^{-1}$ betrug.

Die Zersetzungskinetik sämtlicher Verbindungen wurde studiert und für komplex gefunden, besonders in den Anfangsstadien der Reaktion.

Резюме — Изучены реакции термического разложения различных соединений гексанитратурана(IV) типа $M_2U(NO_3)_6$, где $M = Cs^+$, Et_4N^+ , Ph_4As^+ и Ph_4P^+ . Полное разложение их может быть описано на основе реакции окисления-восстановления, в которой нитрат окисляет уран. Найдено, что для всех соединений энтальпии разложения очень подобны и составляли приблизительно 55 кдж.моль^{-1} , за исключением Ph_4P^+ — соли, для которой это значение составляло только 27 кдж.моль^{-1} . Для всех соединений изучена кинетика реакций разложения и найдено, что это сложный процесс и особенно во время началь стадий реакций.