573. *The Reaction of Uranium with Solutions of Alkylammonium Nitrates in Dinitrogen Tetroxide; Some Properties of Alkylammonium Uranyl Nitrates.*

By C. C. ADDISON and N. HODGE.

The reaction of metallic uranium, or uranium oxides, with solutions of alkylammonium nitrates in liquid dinitrogen tetroxide is a satisfactory and rapid method for the preparation of alkylammonium uranyl nitrates $UO_2(NO_3)_2,MNO_3$ or $UO_2(NO_3)_2,2MNO_3$ (where M is $EtNH_3$, Et_2NH_2, Et_3NH, or Et_4N). With ethylammonium nitrate, both compounds can be prepared. With di- and tri-ethylammonium nitrate only the 1 : 1 compound is isolated; a mixture of the two compounds is obtained with tetraethylammonium nitrate. In the reactions with metallic uranium, uranium(IV) compounds are formed as intermediates and have a greater stability in these solutions than in dinitrogen tetroxide alone. Solutions of the 1 : 1 compounds in nitromethane have been studied by the methods of electrolysis, conductometric titration, light absorption, molecular weight, and ultraviolet spectra, and shown to contain the $[UO_2(NO_3)_3]^-$ ion. Solutions of the 1 : 2 compounds also contain this anion, and no evidence has been found for the existence of the ion $[UO_2(NO_3)_4]^{2-}$ in non-aqueous solvents. Some rates of reaction of uranium with alkylammonium nitrate solutions are recorded.

URANYL NITRATE combines with various other nitrates to give double salts which may contain the trinitrato- and the tetranitrato-uranyl complex anions $[UO_2(NO_3)_3]^-$ and $[UO_2(NO_3)_4]^{2-}$. These anions have been of interest in recent years because they represent one type of species involved in the solvent-extraction of uranium compounds, and because similar complexes are formed by some transuranium elements. The identity of the trinitratouranyl ion has been established with much greater certainty than that of the tetranitratouranyl ion. Compounds of general formula $M[UO_2(NO_3)_3]$ (where M = NH_4, K, Rb, or Cs) are known,[1,2] and an *X*-ray study of the rubidium salt leaves no doubt that the anion exists as a separate entity.[3] The anion has also been recognised in solution, by spectrophotometric study of solutions of uranyl nitrate in acetone containing tetrabutylammonium nitrate.[4] The salt $NMe_4[UO_2(NO_3)_3]$ has been crystallised from solutions of the appropriate nitrates in pure nitric acid.[5] In contrast, the existence of the tetranitratouranyl ion appears to have been deduced only from the stoicheiometry of double

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[1] Rimbach, *Ber.*, 1904, **37**, 461.

[2] Dieke and Duncan, "Spectroscopic Properties of Uranium Compounds," McGraw-Hill, New York, 1949, p. 138.

[3] Ref. 2, pp. 13 *et seq.*

[4] Kaplan, Hildebrandt, and Ader, *J. Inorg. Nuclear Chem.*, 1956, **2**, 153.

[5] Jander and Wendt, *Z. anorg. Chem.*, 1949, **258**, 1.

salts. Compounds of formula $M_2[UO_2(NO_3)_4]$ (where M = K,[6] NH_4,[6] NEt_4,[7] or NMe_4 [7]) have been described, but there is little evidence for the identity of such an anion.

Preparation of these compounds has often involved reactions in concentrated nitric acid. In these, and in the study of the complexes by extraction methods, water is inevitably present, and the chemical behaviour of both simple and complex nitrates is therefore restricted. Liquid dinitrogen tetroxide, however, is an excellent medium for the preparation of these compounds in pure, anhydrous form. The alkylammonium nitrates are formally basic in the dinitrogen tetroxide solvent system; uranium reacts rapidly with solutions of the alkylammonium nitrates, and alkylammonium uranyl nitrates can be crystallised readily from the solutions.

These compounds were studied for two main reasons. First, by using ethylammonium nitrate solutions it is possible to crystallise either the trinitrato- or the tetranitrato-uranyl compound. No complications then arise from the use of different cations or methods of preparation, and the properties of the two compounds, and their solutions in non-aqueous solvents, can be compared directly. Secondly, the study of these double salts in non-aqueous solvents involves the use of anhydrous uranyl nitrate, the existence of which has been subject to some doubt. We have now been able to prepare this compound in pure form by careful thermal decomposition of the addition compound $UO_2(NO_3)_2,N_2O_4$. It has a high solubility in a number of polar solvents such as nitromethane, and its association with the nitrate ion could therefore be studied by conductimetric and spectroscopic techniques.

RESULTS AND DISCUSSION

Ethylammonium Nitrate Solutions.—Solutions containing up to 58 wt. % of the nitrate in dinitrogen tetroxide separate immediately at room temperature into two layers. The upper layer contains the nitrate, the lower layer being almost pure tetroxide. For the preparation of the trinitratouranyl compound, dilute (10—20%) solutions were used. Uranium reacts readily on immersion in the upper layer; the product is concentrated in this layer, which increases in volume. Eventually the density of this layer exceeds that of dinitrogen tetroxide, and inversion occurs. The compound $(EtNH_3)[UO_2(NO_3)_3]$ separates from the lower layer as clear, yellow-green crystals.

Solutions containing more than 58% of ethylammonium nitrate are homogeneous. Reaction of these concentrated solutions with uranium is again rapid, and the analysis of the crystals which separate from this medium corresponds with the formula $(EtNH_3)_2[UO_2(NO_3)_4]$. The overall reactions are represented by the schemes:

$$U + EtNH_3NO_3 + 3N_2O_4 \longrightarrow (EtNH_3)[UO_2(NO_3)_3] + 4NO$$
$$(EtNH_3)[UO_2(NO_3)_3] + EtNH_3NO_3 \longrightarrow (EtNH_3)_2[UO_2(NO_3)_4]$$

Di- and Tri-ethylammonium Nitrate Solutions.—Solutions of these two nitrates behave similarly. Each nitrate gives a homogeneous solution in dinitrogen tetroxide at all concentrations, but separation into two phases occurs on solution of a third component, *e.g.*, a metal salt. As uranium reacted with a 10—20% solution, an immiscible liquid was formed at the metal surface, which rose as globules to form an upper liquid phase. As reaction proceeded, this layer increased in volume and density until inversion of the two layers occurred. From the lower layer the compounds $(Et_2NH_2)[UO_2(NO_3)_3]$ or $(Et_3NH)[UO_2(NO_3)_3]$ crystallised in pure form. Attempts to prepare the tetranitrato-uranyl compounds by the use of high alkylammonium nitrate concentrations gave only viscous yellow solutions which could not be induced to crystallise.

Tetraethylammonium Nitrate Solutions.—Tetramethyl- and tetraethyl-ammonium nitrate are only slightly soluble in dinitrogen tetroxide. Reaction of uranium with the relatively dilute solutions available is slow; and the product is also insoluble, which further inhibits reaction. When tetraethylammonium nitrate was used, analysis indicated

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[6] " Fluorescence of the Uranyl Salts," Carnegie Inst. Wash. Pub., Washington D.C. 1919, p. 208.
[7] Ref. 2, pp. 139, 140.

that the product was a mixture of $(Et_4N)[UO_2(NO_3)_3]$ and $(Et_4N)_2[UO_2(NO_3)_4]$, but in no case was either compound isolated in the pure state. Absolute nitric acid is probably a better medium for the preparation of the tetra-alkylammonium salts.[5]

Reaction of Uranium Oxides.—Whereas the oxides UO_3 and U_3O_8 do not react with liquid dinitrogen tetroxide at ordinary temperatures and pressures, they are readily dissolved by solutions of mono-, di-, and tri-ethylammonium nitrate, to yield the same products as described above.

Presence of U(IV) *in Alkylammonium Nitrate Solutions.*—In solutions which contain no strongly co-ordinating groups (*e.g.*, $NOCl-N_2O_4$ mixtures [8]) any oxidation state of uranium lower than U(VI) has only transitory existence. However, during the reaction of uranium metal with alkylammonium nitrate solutions, much quadrivalent uranium was present in the solutions, although efforts to isolate solid uranium(IV) compounds were unsuccessful. The presence of uranium(IV) gave to the solutions a brown colour which was quite different from that produced by dinitrogen trioxide or the uranyl compounds and persisted for some time after the removal of the metal from the solution. The presence of uranium(IV) was also shown by dropping a portion of the solution into dilute aqueous ammonia; grey-green UO_2,xH_2O was formed which could be separated, acidified, and titrated with potassium permanganate. Although the solutions were not examined quantitatively at this intermediate stage, the following general observations were made: (*a*) The greater the concentration of alkylammonium nitrate, the more uranium(IV) was present in solution for equivalent reaction times. This suggests the stabilisation of the U(IV) state by nitrate co-ordination, probably as the $[U(NO_3)_6]^{2-}$ ion. Neither this ion nor the simple uranium tetranitrate has been described, but corresponding compounds of plutonium (for which the quadrivalent state is more stable), *i.e.*, $K_2[Pu(NO_3)_6]$ [9] and $Pu(NO_3)_4,5H_2O$,[10] are well known. (*b*) The quantity of uranium(IV) in the solution varied with the cation present, in the increasing order $EtNH_3^+$, $Et_2NH_2^+$, Et_3NH^+, Et_4N^+. This is the reverse of the order in which these ions show hydrogen-bonding to the nitrate ion, and the quantity of uranium(IV) in solution therefore increases with increasing availability of the nitrate ions for co-ordination to the U(IV) ion.

It appears, then, that the optimum conditions for the preparation of salts of the $[U(NO_3)_6]^{2-}$ ion involve the use of high concentrations of tetraethylammonium nitrate, for which concentrated nitric acid is a better reaction medium than dinitrogen tetroxide.

Ionisation of Diethylammonium Uranyl Trinitrate.—Possible modes of ionisation of this typical compound are as follows:

$$(Et_2NH_2)[UO_2(NO_3)_3] \rightleftharpoons Et_2NH_2^+ + [UO_2(NO_3)_3]^- \quad (1)$$

$$\rightleftharpoons Et_2NH_2^+ + UO_2(NO_3)_2 + NO_3^- \quad (2)$$

$$\rightleftharpoons Et_2NH_2^+ + UO_2NO_3^+ + 2NO_3^- \quad (3)$$

$$\rightleftharpoons Et_2NH_2^+ + UO_2^{2+} + 3NO_3^- \quad (4)$$

In aqueous solution, ionic dissociation occurs; on electrolysis, uranium migrates to the cathode and is present in cationic form (equations 3 or 4). The compound is highly soluble in nitrobenzene ($\varepsilon = 35$). On electrolysis of a 0·067M-solution at 230 v and 20°, uranium became concentrated in the anode compartment, indicating the presence of the $[UO_2(NO_3)_3]^-$ ion in nitrobenzene (equation 1). Further information on the species present in very dilute solutions was obtained from cryoscopic molecular-weight measurements (Table 1). It is clear that at all higher concentrations the molecule dissociates into two ions only (equation 1), and that the trinitratouranyl ion undergoes further dissociation only at very high dilution.

Conductivity Measurements.—By using solutions of anhydrous uranyl nitrate in

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[8] Addison and Hodge, *J.*, 1961, 2490.

[9] Cunningham, " The Actinide Elements," Nat. Nuclear Energy Ser. Div. (IV), 1954, chapter 10, p. 371.

[10] Drummond and Welch, *J.*, 1956, 2565.

TABLE 1. *Dissociation of diethylammonium uranyl trinitrate in nitrobenzene.*

Molar concn.	0·0022	0·0068	0·0115	0·155
ΔT_f	0·044°	0·107°	0·158°	0·192°
Mean mol. wt.	155	193	220	245
Particles produced per mole of solute	3·42	2·75	2·41	2·16

nitromethane, it has been possible to study the formation of nitratouranyl ions in non-aqueous media. A solution of 0·141 g. of anhydrous uranyl nitrate in 10 ml. of nitromethane was titrated conductometrically with a 0·168M-solution of ethylammonium nitrate in nitromethane (Fig. 1). The initial very low conductivity of uranyl nitrate increases rapidly on addition of ethylammonium nitrate until the 1 : 1 ratio is achieved in solution. Thereafter conductivity falls slightly and there is no further break, so that the ionic dissociation

$$(EtNH_3)[UO_2(NO_3)_3] \longrightarrow EtNH_3^+ + [UO_2(NO_3)_3]^-$$

makes a much greater contribution to the total conductivity in nitromethane than does the ionic dissociation of uranyl nitrate or ethylammonium nitrate. The arrows (Fig. 1) indicate 1 : 1 and 2 : 1 molar ratios; the results provide convincing evidence (*a*) that the ion $[UO_2(NO_3)_3]^-$ has a high stability in nitromethane, and (*b*) that the ion $[UO_2(NO_3)_4]^{2-}$ does not exist in solution, even though a compound of empirical formula $UO_2(NO_3)_2,2EtNH_3NO_3$ can be obtained crystalline.

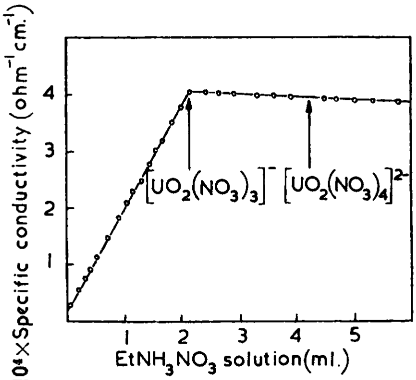

FIG. 1. *Conductometric titration of anhydrous uranyl nitrate with ethylammonium nitrate in nitromethane.*

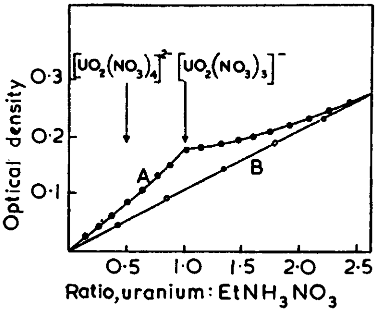

FIG. 2. *Variation in light absorption by a solution of anhydrous uranyl nitrate* (A) *in nitromethane on dilution with a solution of ethylammonium nitrate in nitromethane and* (B) *in nitromethane alone.*

Light Absorption Measurements.—The above observations were confirmed during a study of the applicability of Beer's law to these solutions. The light transmitted in a Hilger " Spekker " absorptiometer when a 0·084M-solution of anhydrous uranyl nitrate in nitromethane was diluted with nitromethane obeys Beer's law (line B, Fig. 2). When a solution of ethylammonium nitrate in nitromethane was used as diluent (curve A, Fig. 2) optical density is not proportional to concentration; a single sharp break occurs at the 1 : 1 ratio, but there is again no evidence for the $[UO_2(NO_3)_4]^{2-}$ ion.

Conductivity and light-absorption measurements similar to those described above have been carried out with di-, tri- and tetra-ethylammonium nitrates also, and the results are similar.

Ultraviolet Absorption Spectra.—Solutions of mono-, di-, or tri-ethylammonium uranyl trinitrate in nitromethane give almost identical ultraviolet spectra, which are shown as the full line in Fig. 3. The spectrum consists of a series of bands spaced regularly 14 mμ apart, which are characteristic of the excited electronic states of the uranyl group. The three bands at 440, 454, and 468 mμ are the most pronounced and the most important when complex-formation by the uranyl group is being considered. When the uranyl ion becomes part of a nitrato-complex ion, the interaction of nitrate ions with the uranyl ion leads to enhanced absorption at these wavelengths, and these spectra therefore provide a useful means of showing the presence of complex ions. This is illustrated in Fig. 3 by the spectrum of the compound $UO_2(NO_3)_2,N_2O_4$, shown as a broken line. The chemistry of solutions of this compound (which will be discussed in detail together with that of the anhydrous nitrate in a later paper) indicates that $[UO_2(NO_3)_3]^-$ ions are not present to any appreciable extent. When alkylammonium nitrate is added to the solution, there is immediate enhancement of the absorption at the three higher wavelengths. Characteristics of the spectrum for each of the compounds studied are collected in Table 2. The spectra of the first three compounds are quite consistent with the simple dissociation to alkylammonium and trinitrato-uranyl ions. The striking observation is that the spectrum of ethylammonium uranyl tetranitrate is virtually identical with the spectra of the compounds in which the presence of the trinitratouranyl ion can be accepted. Since the co-ordination of one NO_3^- ion to the $UO_2(NO_3)_2$ molecule brings about such a pronounced enhancement of the " uranyl " peaks, it would be expected that the co-ordination of a second NO_3^- ion would also be reflected in the spectrum. We therefore believe that this compound ionises in nitromethane as follows:

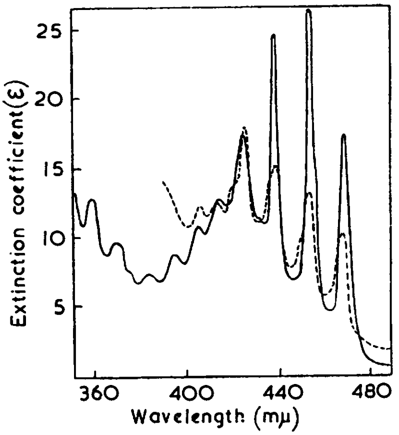

FIG. 3. *Ultraviolet absorption spectra of nitromethane solutions.*

Full line: $(EtNH_3)[UO_2(NO_3)_3]$, $(Et_2NH_2)[UO_2(NO_3)_3]$, and $(Et_3NH)[UO_2(NO_3)_3]$.
Broken line: $UO_2(NO_3)_2,N_2O_4$.

TABLE 2. *Ultraviolet absorption spectra of solutions of alkylammonium uranyl nitrates in nitromethane.*

Compound	$\lambda_{max.}$ (mμ)	ε	$\lambda_{max.}$ (mμ)	ε	$\lambda_{max.}$ (mμ)	ε	$\lambda_{max.}$ (mμ)	ε
$EtNH_3[UO_2(NO_3)_3]$	425	17·6	440	25·0	455	26·8	468	18·3
$Et_2NH_2[UO_2(NO_3)_3]$	426	17·3	440	24·5	455	27·0	469	17·3
$Et_3NH[UO_2(NO_3)_3]$	426	17·4	440	25·0	454	27·1	468	17·9
$(EtNH_3)_2[UO_2(NO_3)_4]$	425	17·7	439	25·3	455	27·0	469	17·9
$UO_2(NO_3)_2,N_2O_4$	427	16·3	438	15·2	454	13·8	468	10·8

$$(EtNH_3)_2[UO_2(NO_3)_4] \longrightarrow 2EtNH_3^+ + [UO_2(NO_3)_3]^- + NO_3^-$$

and that even if the complex ion $[UO_2(NO_3)_4]^{2-}$ exists in the solid state (which must now be regarded as doubtful) there is no evidence for its existence in solution.

The apparent upper limit of three nitrate ions in a uranyl complex is not set by the nitrate ions, since the existence of the tetranitratozincate ion, for example, has been established [11] for nitromethane solutions. It is presumably a consequence of the peculiar stability of the $[UO_2(NO_3)_3]^-$ ion. From an *X*-ray study of the rubidium salt,[3] each nitrate ion is believed to be bidentate, and the uranium atom is then surrounded by a ring of six oxygen atoms in a plane at right angles to the uranyl group. This structure is believed to occur in the uranyl nitrate hydrates also.[12]

Nitromethane was selected as solvent in these experiments because the solutions are

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[11] Addison and Hodge, *J.*, 1954, 1138.
[12] Gatehouse and Comyns, *J.*, 1958, 3965.

stable. Solutions in other non-aqueous solvents give closely similar spectra. For example, fresh solutions in cyclohexanone are bright yellow and their spectra resemble those in Fig. 3, but the solutions darken rapidly owing to oxidation of the solvent.

Other Properties of Diethylammonium Uranyl Trinitrate.—The crystals are bright yellow and very deliquescent. They show only weak fluorescence to ultraviolet radiation. [Anhydrous uranyl nitrate is also weakly fluorescent, whereas the compound $UO_2(NO_3)_2,N_2O_4$ and the uranyl nitrate hydrates are strongly fluorescent.] The compound did not dissolve in, or react with, ether, benzene, carbon tetrachloride, or dioxan.

The compound melted sharply at 115° to a clear yellow liquid. On further heating, no change occurred until 166°, when diethylnitrosamine and nitric acid were identified in the evolved gases. Loss in weight at this temperature was only 1·2% per hour, and 2·1% per hour at 173°. At 176°, violent decomposition occurred, leaving a residue of uranium trioxide. This decomposition at a critical temperature was typical of all the alkylammonium uranyl nitrates.

EXPERIMENTAL

Alkylammonium nitrates were prepared by solvolysis of the chlorides in dinitrogen tetroxide, as already described for $EtNH_3NO_3$,[11] $Et_2NH_2NO_3$,[13] and Et_3NHNO_3.[14] The alkylammonium uranyl nitrates were separated from mother-liquor by washing them with nitromethane and dinitrogen tetroxide. Ethylammonium uranyl tetranitrate could not be treated in this way, being highly soluble in both solvents. This compound was given prolonged filtration on a sintered-glass plate in an argon atmosphere. The products were analysed by distilling the amine constituent into standard acid. Nitrate was determined in the residue by the Kjeldahl method. Uranium was precipitated as ammonium diuranate and ignited to U_3O_8 (Table 3).

Molecular-weight determinations were carried out in conventional apparatus with purified nitrobenzene (m. p. 5·75°). Results in Table 1 were calculated by assuming a molar depression constant of 6·89.[15]

Conductivity measurements were carried out in an apparatus similar to that already described.[16]

Ultraviolet absorption spectra were measured by using a Unicam S.P. 500 spectrophotometer, with fused silica cells, at a temperature close to 20°.

TABLE 3. *Analysis of alkylammonium uranyl nitrates.*

	Required (%)			Found (%)		
	$[R_4N]$	U	NO_3	$[R_4N]$	U	NO_3
$(EtNH_3)[UO_2(NO_3)_3]$	9·2	47·4	37·0	9·3	47·6	36·2
$(EtNH_3)_2[UO_2(NO_3)_4]$	15·1	39·0	40·6	15·9	39·0	39·8
$(Et_2NH_2)[UO_2(NO_3)_3]$	14·0	44·9	35·1	14·2	44·7	35·2
$(Et_3NH)[UO_2(NO_3)_3]$	18·3	42·5	33·3	18·6	42·4	34·0

Rates of Reaction of Uranium.—Rates of reaction with three solutions of diethylammonium nitrate in dinitrogen tetroxide are compared in Fig. 4 with corresponding rates of reaction in nitromethane–dinitrogen tetroxide mixtures. Uranium discs were rotated in the solutions at 20°, at a speed of 350 r.p.m., as described elsewhere.[17] The rate of solution of uranium is constant during the first 6 hours' immersion and varies only slightly on longer immersion.

Where metal–dinitrogen tetroxide reactions are brought about by the introduction of a third component, rates of reaction vary widely with composition of the solution.[17] This is illustrated by curves (d) and (e) of Fig. 4. With the diethylammonium nitrate solutions, however, reaction rates are almost independent of concentration. Furthermore, solutions of the mono-, tri-, and tetra-ethylammonium nitrate of various concentrations also gave results lying very close to curves (a), (b), and (c), Fig. 4. In all alkylammonium nitrate solutions the reactive species is considered [17] to be the complex ion $[R_3N \longrightarrow NO^+]$ where R = H or Et, and reaction rate should be highly concentration-dependent. To explain the apparent anomaly, the influence of dinitrogen trioxide and of stirring rate was therefore examined.

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[13] Addison, Conduit, and Thompson, *J.*, 1951, 1298.
[14] Addison and Hodge, *Chem. and Ind.*, 1953, 1315.
[15] Roberts and Bury, *J.*, 1923, 2037.
[16] Addison, Hodge, and Lewis, *J.*, 1953, 2631.
[17] Addison, Sheldon, and Hodge, *J.*, 1956, 3900.

TABLE 4. *Influence of* N_2O_3 *on the* U–N_2O_4 *reaction.*

Wt. % of N_2O_3 in N_2O_4	U * dissolved	Wt. % of mixture (col. 1) in $MeNO_2$	U * dissolved	U * dissolved in corresponding $MeNO_2$–N_2O_4 mixture
2·10	0·0	28·7	1·79	1·80
4·00	0·01	30·8	1·89	1·90
5·15	0·03	31·6	1·93	1·93
10·0	0·10	—	—	—
16·0	0·22	—	—	—

* Units are mg./cm.^{2}/2 hr.

(a) *Influence of dinitrogen trioxide.* Some of the nitric oxide formed in the reaction of uranium with these solutions dissolves to give dinitrogen trioxide. Since this is known [18] to increase the reaction rate of zinc with dinitrogen tetroxide, it was necessary to determine the extent to which it might also enhance a uranium–dinitrogen tetroxide reaction. The results are given in Table 4. Uranium discs were rotated at 350 r.p.m. and 0° in N_2O_3–N_2O_4 mixtures (column 1). At high N_2O_3 concentrations, the solution rate becomes appreciable. However, in the alkylammonium nitrate solutions the trioxide concentration is less than 5%, and hence has a negligible effect on the solution rate of uranium. The solutions in column (1) were diluted with nitromethane, and the values given in column (3) represent the total wt. % of nitrogen oxides in nitromethane. The rate of reaction of uranium with these solutions (column 4) is the same as with corresponding solutions containing dinitrogen tetroxide only (column 5). The trioxide influences reaction rates by increasing the dielectric constant of the medium (and thus the N_2O_4 self-ionisation) and, when nitromethane or other polar substance is already present, the influence of dinitrogen trioxide is negligible.

FIG. 4. *Rates of reaction of uranium with liquid dinitrogen tetroxide containing*: (a) 0·084M-$Et_2NH_2NO_3$, (b) 0·052M-$Et_2NH_2NO_3$, (c) 0·027M-$Et_2NH_2NO_3$, (d) 0·86M-$MeNO_2$, (e) 0·072M-$MeNO_2$.

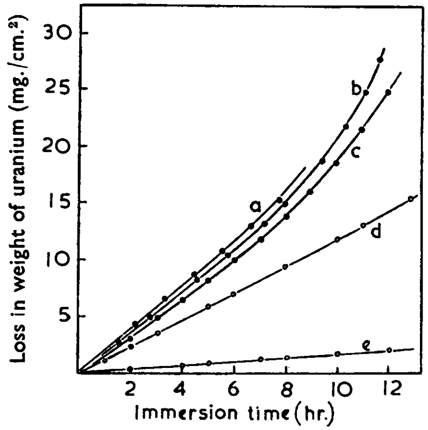
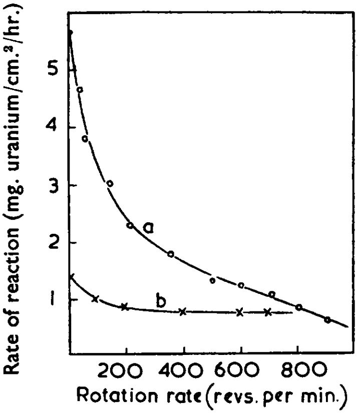


FIG. 5. *Influence of stirring rate on reaction of uranium with* (a) 0·052M-*solution* of $Et_2NH_2NO_3$ *in liquid dinitrogen tetroxide and* (b) $MeNO_2$–N_2O_4 *mixture containing* 35·3 wt. % *of* N_2O_4.



(b) *Influence of stirring rate.* Rates of reaction were determined in a diethylammonium nitrate solution at 20°, at various rotation speeds, and the results are shown in Fig. 5. The reaction rate falls continuously with increasing rotation speed, and approaches zero as rotation rates reach 1000 r.p.m. This variation is much more pronounced than in any other metal–dinitrogen tetroxide system studied.[17] The results are compared in Fig. 5 with those for a nitromethane–dinitrogen tetroxide solution. In the latter case, reaction rate is independent of stirring at speeds above 350 r.p.m.; the uranium surface is in contact with a homogeneous solution, and reaction rate is dependent only on desorption of metal ions from the surface. The results with diethylammonium nitrate solutions are interpreted satisfactorily on the basis of the two liquid phases present in the system. On initial immersion, the whole of the uranium surface is in contact with a homogeneous solution. When small amounts of uranium salts

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[18] Addison, Lewis, and Thompson, *J.*, 1951, 2838.

enter the liquid, two phases are formed (which will be present as an emulsion in these experiments). The phase which contains almost all the alkylammonium nitrate tends to adhere to the metal surface, and reaction rates are therefore high in unstirred systems. This phase is removed from the surface by stirring, and the surface is then brought into contact (to an extent which depends on rotation rate) with the second liquid phase which consists of almost pure dinitrogen tetroxide. Uranium does not react with this phase, and the results in Fig. 5 therefore reflect the difference in the reactivity of uranium with the two phases. The rate of reaction of uranium with these solutions is therefore determined more by stirring rate than by solute concentration, which accounts for the very small concentration effect noted in Fig. 4.

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