

#### 443. *Anhydrous Uranyl Nitrate and its Complexes with Some Oxygen and Nitrogen Donors.*

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Reactions of uranium metal with mixtures of dinitrogen tetroxide and nitromethane, aliphatic esters, or methyl cyanide are described. The reactivity of mixtures containing esters varies widely with the ester used. From these reactions, the addition compounds  $\text{UO}_2(\text{NO}_3)_2 \cdot \text{N}_2\text{O}_4$ ,  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{MeCO}_2\text{Et}$ , and  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{MeCN}$  have been isolated. The thermal decomposition of the first two of these products has been studied by means of thermogravimetric and differential thermal analysis, and conditions are outlined for the isolation of pure anhydrous uranyl nitrate from the dinitrogen tetroxide addition compound. The ultraviolet and infrared spectra of these compounds are compared with those of uranyl nitrate.

ALTHOUGH the existence of anhydrous uranyl nitrate is now established,<sup>1-13</sup> knowledge of its chemistry is still very limited. In the course of investigations into the rates and mechanisms of reactions of uranium metal with mixtures of liquid dinitrogen tetroxide

<sup>1</sup> Comyns, *Chem. Rev.*, 1960, **60**, 115.

<sup>2</sup> Addison and Hodge, *J.*, 1961, 2987.

<sup>3</sup> Hoard and Stroupe, Atomic Energy Project Report A 1229, 1943; Zachariasen, *Acta Cryst.*, 1954, **7**, 795.

<sup>4</sup> Kennedy, *Chem. and Ind.*, 1958, 950; Fleming and Lynton, *ibid.*, 1959, 1409; 1960, 1415, 1416.

<sup>5</sup> Gatehouse and Comyns, *J.*, 1958, 3965.

<sup>6</sup> Allpress and Hambly, *Austral. J. Chem.*, 1959, **12**, 569.

<sup>7</sup> Ditte, *Compt. rend.*, 1879, **89**, 643.

<sup>8</sup> Marketos, *Compt. rend.*, 1912, **155**, 210.

<sup>9</sup> Späth, *Monatsh.*, 1912, **33**, 853.

<sup>10</sup> Gibson and Katz, *J. Amer. Chem. Soc.*, 1951, **73**, 5436.

<sup>11</sup> Jezowska-Trzebiatowska and Kedzia, *Bull. Acad. polon. Sci. Ser. Sci. chim.*, 1962, **10**, 213, 275, 283.

<sup>12</sup> Addison and Hodge, *J.*, 1961, 2490.

<sup>13</sup> Gibson, Beintema, and Katz, *J. Inorg. Nuclear Chem.*, 1960, **15**, 110.

and various other solvents,<sup>2,12,14</sup> we have prepared the compound  $\text{UO}_2(\text{NO}_3)_2 \cdot \text{N}_2\text{O}_4$  directly from the metal, and have also obtained a number of other addition compounds of anhydrous uranyl nitrate with organic donor molecules. The purpose of this Paper is to describe these reactions, and the attempts which have been made to obtain anhydrous uranyl nitrate from the addition compounds. Some properties of anhydrous uranyl nitrate prepared by thermal decomposition of  $\text{UO}_2(\text{NO}_3)_2 \cdot \text{N}_2\text{O}_4$  are also recorded.

#### EXPERIMENTAL

*Uranyl Nitrate-Dinitrogen Tetroxide.*—A piece of freshly-filed uranium metal was dissolved in excess of a 70 : 30 mole % mixture of dinitrogen tetroxide and nitromethane. Reaction rates for this system have been discussed elsewhere.<sup>2,14</sup> On addition of a large excess of dinitrogen tetroxide, a light yellow microcrystalline powder was precipitated which had the composition  $\text{UO}_2(\text{NO}_3)_2 \cdot \text{N}_2\text{O}_4$ . The same compound can be obtained in the form of large (1 cm.) yellow crystals by allowing dinitrogen tetroxide vapour to dissolve slowly in a concentrated solution of the yellow powder in nitromethane.

The product was analysed by means of the reaction of a known amount of it with 2N-sodium hydroxide solution in a stoppered bottle. After filtration of the uranate, portions of the filtrate were analysed for total nitrogen (by the Kjeldahl method) and for nitrite (by ceric sulphate titration). The uranate was dissolved in acid, reprecipitated as ammonium diuranate by carbonate-free ammonia, and ignited at 900° to  $\text{U}_3\text{O}_8$ . In spite of the strong bonding of the bulk of the tetroxide, small quantities (2—5%) are readily lost from the compound at room temperature unless an atmosphere of dinitrogen tetroxide is maintained, whereas it is difficult to remove traces of occluded tetroxide at low temperatures. This is shown in the analytical results for *samples* isolated at 0° and at 22° (At 0°, found: U, 47.9;  $\text{N}_2\text{O}_4$ , 19.4. At 22°, found: U, 49.3;  $\text{NO}_3^-$ , 25.6;  $\text{N}_2\text{O}_4$ , 18.1.  $\text{UO}_2(\text{NO}_3)_2 \cdot \text{N}_2\text{O}_4$  requires U, 49.0;  $\text{NO}_3^-$ , 25.5;  $\text{N}_2\text{O}_4$ , 18.9%).

*Thermal Decomposition of Uranyl Nitrate-Dinitrogen Tetroxide.*—The temperature at which the addition compound must be heated to obtain the anhydrous nitrate is highly critical, and does not appear to be greatly influenced by an applied vacuum. Jezowska-Trzebiatowska and Kedzia<sup>11</sup> obtained the pure anhydrous nitrate by thermal decomposition at 165°/10<sup>-5</sup> mm. for 110 min., but gave no reason for choosing this temperature. The Table lists the analyses for products obtained by heating at other temperatures. These results show that the pure nitrate is available under the conditions given in expt. 7. The temperature used, 163°, agrees closely with that used previously,<sup>11</sup> in spite of the fact that the present experiments were conducted at atmospheric pressure. It is also clear from the Table that a departure of more than a few degrees from 163° gives a product which is not fully dissociated (*e.g.*, expt. 3) or which contains uranium trioxide (expt. 9).

TABLE.

Thermal decomposition of  $\text{UO}_2(\text{NO}_3)_2 \cdot \text{N}_2\text{O}_4$  at atmospheric pressure.

Expt.	Temp.	Duration (hr.)	Composition of residue (%)		
			U	$\text{NO}_3$	$\text{N}_2\text{O}_4$
1	100°	0.75	—	—	15.6
2	157	6	59.8	—	—
3	157	14	60.0	—	—
4	160	18	60.2	32.3	0.2
5	161	18	60.2	—	—
6	163	4	60.5	—	0.1
7	163	20	60.5	31.6	0.0
8	165	3	62.1	31.3	0.0
9	176	0.5	61.8	—	0.0
	Calc. for $\text{UO}_2(\text{NO}_3)_2$ :		60.4	31.5	0.0

*Uranyl Nitrate-Bis(ethyl acetate).*—Uranium metal is readily attacked by a mixture of dinitrogen tetroxide and ethyl acetate. Using these liquids in 1 : 1 mole ratio, a green colour developed in the solution within minutes; after several hours at room temperature a bright yellow *solid* slowly crystallised (Found: U, 41.6; N, 4.9; C, 16.1; H, 2.7.  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{MeCO}_2\text{Et}$

<sup>14</sup> Addison, Sheldon, and Hodge, *J.*, 1956, 3900.

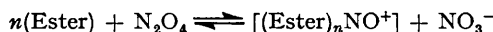
requires U, 41.7; N, 4.9; C, 16.8; H, 2.8%). The compound melts at 94° without decomposition. The same compound is obtained if the mother-liquor is evaporated or if excess of dinitrogen tetroxide is added to the medium. This is unusual as far as the transition metals are concerned; mixtures of the tetroxide with ethyl acetate have commonly been used in the preparation of anhydrous nitrates, but it is the addition compound with dinitrogen tetroxide which is usually precipitated. In view of the very high stability of  $\text{UO}_2(\text{NO}_3)_2 \cdot \text{N}_2\text{O}_4$ , it might have been expected to be the product of this reaction. That this is not the case is a reflection of the exceptional acceptor properties of the uranyl group towards esters, and the ethyl acetate complex may be compared with those formed by tributyl and triethyl phosphate.<sup>4</sup> The structure of the latter complexes involve a ring of six oxygen atoms equatorial to the uranyl group, and the structure of all complexes  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{S}$  (S = ester) may be essentially the same.

*Ethyl Propionate and Isopropyl Acetate.*—Mixtures of these esters with dinitrogen tetroxide gave little evidence of reaction with uranium. After seven days' immersion, a faint green colour was detected round the metal, but no product could be isolated from the solutions.

*Methyl Acetate.*—This ester gave slightly more reactive mixtures. After reaction for two days with uranium at room temperature, a very small amount of a yellow solid was obtained which melted at 114° with decomposition. It was probably the 1 : 2 addition compound with uranyl nitrate (Found: U, 42.8; Calc. for  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{MeCO}_2\text{Me}$ : U, 43.9%).

*Methyl Formate.*—Reaction rates with uranium were intermediate between those for methyl acetate and ethyl acetate. After reaction for 24 hr. *ca.* 1 g. of a yellow-brown microcrystalline solid was obtained by evaporation of the liquid. The ester is less strongly bonded, and the uranyl nitrate : ester ratio varies somewhat with the temperature. When the reaction and isolation were carried out near 20° throughout, the product had a uranium content of 49.6%, corresponding to  $\text{UO}_2(\text{NO}_3)_2 \cdot 1.42\text{HCO}_2\text{Me}$ . It melted at 78° to a yellow liquid which decomposed at 82°.

The readiness with which uranium reacts with these mixtures is mainly determined by two factors; first, the position of the equilibrium



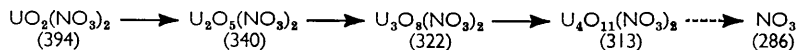
and secondly, the co-ordinating power of the particular ester towards uranyl nitrate. Except in the case of methyl formate, it is probably the first of these factors which is most sensitive to changes in the ester concerned.

*Methyl Cyanide.*—The 1 : 1  $\text{N}_2\text{O}_4$ –MeCN mixture reacted readily with uranium at room temperature to give a yellow, crystalline product, m. p. 180° (Found: U, 50.0. Calc. for  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{MeCN}$ : U, 50.0%).

## RESULTS AND DISCUSSION

*Thermal Decomposition.*—The decompositions of the compounds  $\text{UO}_2(\text{NO}_3)_2 \cdot \text{N}_2\text{O}_4$  and  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{CH}_3 \cdot \text{CO}_2\text{C}_2\text{H}_5$  have been compared using thermogravimetric analysis (Fig. 1) and differential thermal analysis (Fig. 2). In Fig. 1, the measured weights have been converted into values corresponding to 1 mole of initial compound, so that the vertical axis expresses molecular-weight units directly. On first heating, the tetroxide addition compound loses about 10% of its dinitrogen tetroxide content, and the differential thermal analysis curve (Fig. 2) shows that this occurs in the range 80–120°. Both techniques indicate that decomposition to the nitrate becomes appreciable at 163–165° (in agreement with the results in the Table); it is endothermic (Fig. 2), and uranyl nitrate is produced in a single stage (Figs. 1 and 2), the decomposition rate being at a maximum at 170–190°. The shape of the plateau at higher temperatures (Fig. 1) indicates that decomposition of pure uranyl nitrate is very slow at 200–220°, but becomes rapid between 260 and 300°. It is particularly interesting that the nitrate does not decompose directly to uranium trioxide. There is a definite break in the curve at 300°, corresponding to an apparent "molecular weight" of 313 (Fig. 1, inset). A sample of solid uranyl nitrate which had been allowed to equilibrate at 320° was shown by analysis to contain nitrogen, and the infrared spectrum indicated this to be present solely as nitrate. We may therefore consider the

thermal decomposition of solid uranyl nitrate as proceeding through a series of intermediate stages represented by:



the numbers in parentheses being the apparent molecular weights per atom of uranium. The break in the curve at 300° suggests that a solid of composition  $\text{U}_4\text{O}_{11}(\text{NO}_3)_2$  has a higher stability than the earlier decomposition stages. At 410°, there is a final break in the curve (Fig. 1, inset), and above 410°, decomposition to pure uranium trioxide occurs.

The addition compound  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{MeCO}_2\text{Et}$  behaves quite differently on thermal decomposition. A break in the thermogravimetric curve at 120° (Fig. 1) corresponds to

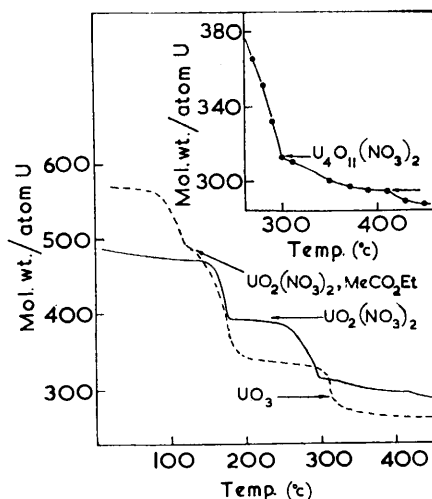


FIG. 1. Thermogravimetric analysis (heating rate 1.5°/min.). The inset graph gives the results for  $\text{UO}_2(\text{NO}_3)_2 \cdot \text{N}_2\text{O}_4$  at the higher temperatures on an extended scale. Full line  $\text{UO}_2(\text{NO}_3)_2 \cdot \text{N}_2\text{O}_4$ . Dashed line  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{MeCO}_2\text{Et}$ .

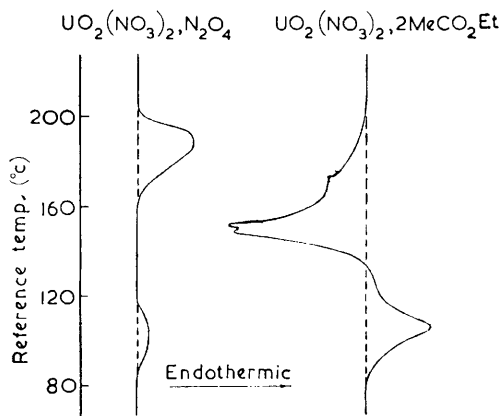


FIG. 2. Differential thermal analysis (heating rate 2°/min.).

the loss of one molecule of ethyl acetate; only ethyl acetate is evolved during this stage, and this is an endothermic process (Fig. 2). The second stage, in the temperature range 120—200°, involves an intramolecular reaction between the oxidising nitrate groups and the remaining molecule of ethyl acetate; this is an exothermic reaction (Fig. 2), and differential thermal analysis indicates at least two steps in this reaction. Samples of the addition compound were heated in this temperature range, and formaldehyde and acetaldehyde were detected in the vapours evolved. The reaction product (represented by the plateau at 200—300°, Fig. 1) has an apparent molecular weight much less than that of uranyl nitrate, and contains carbon. It is not a simple chemical entity, and its apparent molecular weight changes somewhat with rate of heating. Further decomposition occurs at 300° to give finally a mixture of uranium oxide and uranium carbide.

A similar intramolecular reaction between the nitrate groups and the organic ligand has been observed on heating the compound  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{MeCN}$  at 140°.

*Ultraviolet Absorption Spectra.*—Fig. 3 shows the spectra of solutions of anhydrous uranyl nitrate and of the complexes referred to above, in appropriate solvents. In all four cases the vibrational band structure characteristic of excited electronic states of the uranyl group is retained, although absorption is weak in methyl cyanide and ethyl acetate. Previous work<sup>2</sup> has shown that association of nitrate ions with uranyl nitrate, to give the

complex-ion  $[\text{UO}_2(\text{NO}_3)_3]^-$ , results in enhancement of the absorption at the "uranyl" peaks at about 440, 454, and 468  $\mu$  to a much greater extent than occurs in spectrum A (Fig. 3). It is therefore clear that this complex-ion is absent in all four solutions. According to Jezowska-Trzebiatowska and Kedzia<sup>11</sup> the spectra of solutions of anhydrous uranyl nitrate in diethyl ether, acetone, heptan-2-one, dioxan, and formamide also show vibrational band structure, but the spectrum of a solution in acetylacetone does not.

*Infrared Spectra.*—Certain features of the spectrum of uranyl nitrate hexahydrate are significant with respect to the spectrum of the anhydrous nitrate itself. Differences between the hexahydrate spectra obtained by Gatehouse and Comyns<sup>5</sup> and by Allpress and Hambly<sup>6</sup> have been attributed<sup>6</sup> to differences in experimental technique, and in particular to the extent to which cell windows were protected. We have redetermined this spectrum, using (a) mull cells in which sodium chloride windows were protected by polythene sheets, and (b) silver chloride windows on which the hydrate was spread by evaporation from a thin film of aqueous solution. The results agree most closely with those of Allpress and Hambly.<sup>6</sup> Since the unidentate and bidentate nitrate groups possess the same elements of symmetry, they give rise to the same six infrared-active vibrations. The spectrum is entirely consistent with covalent bonding of the nitrate groups (in agreement with the crystal structure<sup>4</sup>), and in contrast to Gatehouse and Comyn's observations,

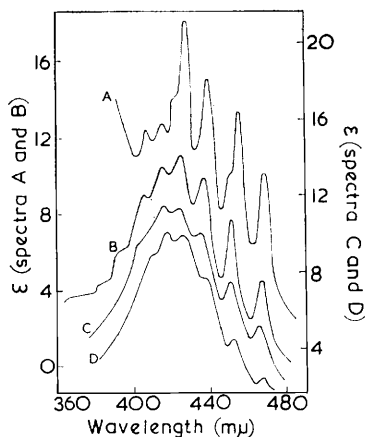


FIG. 3. Ultraviolet spectra of solutions of uranyl nitrate. A,  $\text{UO}_2(\text{NO}_3)_2 \cdot \text{N}_2\text{O}_4$  in nitromethane. B,  $\text{UO}_2(\text{NO}_3)_2$  in nitromethane. C,  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{MeCN}$  in methyl cyanide. D,  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{MeCO}_2\text{Et}$  in ethyl acetate.

we find no evidence for the band around  $1380 \text{ cm}^{-1}$  characteristic of the nitrate ion. In the present context the main feature of interest is the  $1621 \text{ cm}^{-1}$  band, which Allpress and Hambly<sup>6</sup> assigned to the bending frequency for water. From experiments in which changes in this band were observed as the hexahydrate was converted to lower hydrates (to be described in a later Paper), we find that it readily splits into two bands in the  $1600$ — $1640 \text{ cm}^{-1}$  region; the independent variation in intensity of these two bands with water content and temperature indicates strongly that one of them is due to the nitrate group. This implies that the nitrate groups exist in at least two different environments in the hexahydrate crystal, which is feasible in view of the crystallographic evidence<sup>4</sup> that the molecule is irregular, and that the U—O distances for the bidentate nitrate are  $2.40$  and  $2.57 \text{ \AA}$ . It is relevant that the  $1621 \text{ cm}^{-1}$  band is absent in the spectrum<sup>6</sup> for anhydrous  $\text{K}[\text{UO}_2(\text{NO}_3)_3]$ , but occurs strongly in anhydrous uranyl nitrate (see below).

The spectrum of uranyl nitrate-dinitrogen tetroxide consists of the following bands (the nomenclature used for the assignments is that normally used for the unidentate group<sup>15</sup>):  $2970\text{w}$ ;  $2540\text{w}$ ;  $2510\text{w}$ ;  $2300\text{w,sp}$ ;  $2263\text{w,sp}$ ;  $2039\text{w}$ ;  $1819\text{w}$ ;  $1766\text{w}(\text{N}_2\text{O}_4)$ ;  $1731\text{w}$ ;  $1633\text{w}$  and  $1607\text{m}(\text{NO}_3)$ ;  $1530\text{s}$  and  $1458\text{m}[\nu_4(\text{NO}_3)]$ ;  $1302\text{s}[\nu_1(\text{NO}_3)]$ ;

<sup>15</sup> Herzberg, "Molecular Spectra and Molecular Structure, Vol. 2, Infra-red and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, 1945, pp. 65, 179.

1278s[ $\nu_1(\text{NO}_3) + \text{N}_2\text{O}_4$ ]; 1173s; 1028s[ $\nu_2(\text{NO}_3)$ ]; 943s [ $\nu_3(\text{UO}_2^{2+})$ ]; 804m[ $\nu_6(\text{NO}_3)$ ]; 754  $\text{cm}^{-1}$  [ $\nu_3$  or  $\nu_5(\text{NO}_3)$ ]. This spectrum has many features in common with that of the hexahydrate. In the present case the uranyl group is surrounded equatorially by six oxygen atoms, four of which are provided by two essentially bidentate nitrate groups, and two by a molecule of co-ordinated dinitrogen tetroxide. The symmetrical stretching frequency  $\nu_1$  for the uranyl group is not observed; this implies that the uranyl group is more nearly linear than in the hexahydrate. The bands at 2300 and 2263  $\text{cm}^{-1}$  have the characteristic sharpness, and the frequency, of the  $\text{NO}^+$  ion.<sup>16</sup> Again, absorption near 1730  $\text{cm}^{-1}$  is observed for many compounds in which the NO group is co-ordinated to a metal.<sup>17</sup> However, the bands are weak, and there is no other physical or chemical evidence to suggest that the NO group exists in either form in the compound. They are regarded as overtone bands, since they also occur in the spectra of  $\text{K}[\text{UO}_2(\text{NO}_3)_3]$  (at 2300, 2270, and 1733  $\text{cm}^{-1}$ )<sup>6</sup> and anhydrous copper nitrate (at 2299 and 1733  $\text{cm}^{-1}$ ).<sup>18</sup>

The spectrum of uranyl nitrate-bis(ethyl acetate) can be interpreted in the same manner. The bands are as follows: 3008m; 2990m (C-H stretch); 2556w; 2367w; 2292w; 2050w; 1968w; 1901w; 1800w; 1774w; 1732w; 1642vs (C=O stretch); 1604s,sh( $\text{NO}_3$ ); 1541vs and 1479s[ $\nu_4(\text{NO}_3)$ ]; 1390s (C-H bend); 1328vs[ $\nu_1(\text{NO}_3)$ ]; 1271vs (C-O stretch); 1161m; 1125m; 1045s(skeletal); 1032s[ $\nu_2(\text{NO}_3)$ ]; 943vs [ $\nu_3(\text{UO}_2^{2+})$ ]; 860m[ $\nu_1(\text{UO}_2^{2+})$ ]; 812m[ $\nu_6(\text{NO}_3)$ ]; 749m  $\text{cm}^{-1}$  [ $\nu_3$  or  $\nu_5(\text{NO}_3)$ ]. Some stretching frequencies (particularly that of C=O) for the ethyl acetate molecule are shifted on co-ordination in metal complexes,<sup>19</sup> and the assignment of bands due to ethyl acetate in the above spectrum has been made with this in mind. The nitrate groups are again covalent, since the strong 1032  $\text{cm}^{-1}$  band is quite distinct from the skeletal vibration of ethyl acetate, and is infrared-inactive in the nitrate ion. Again, there are strong bands which are clearly assignable to  $\nu_1$  and  $\nu_4$  for the covalent nitrate, and there is no reason to suppose that the 1390  $\text{cm}^{-1}$  band is other than the C-H bending frequency.

The spectrum of anhydrous uranyl nitrate is highly unusual, but characteristic and reproducible. (Spectra taken by using either Nujol or Halocarbon oil as a mulling agent were in agreement, so that no interaction with mulling agent occurred during the course of the measurements.) In the absence of other co-ordinating groups, the equatorial ring of oxygen atoms round the uranyl group cannot be achieved unless some of the nitrate groups employ all three oxygen atoms in co-ordination. There is an indication of such behaviour in the structure of cupric nitrate,<sup>20</sup> and strong bonding of this type may provide an explanation for features in the uranyl nitrate spectrum which have not been observed for any other anhydrous nitrate. To a first approximation, the spectrum may be regarded as that of a solid containing both covalent nitrate groups and nitrate ions; the tentative assignments given below are made on this basis, frequencies being represented by  $\nu(\text{NO}_3)$  and  $\nu(\text{NO}_3^-)$ , respectively. The following bands were observed: 2464w; 1860w; 1820w; 1781w; 1656w; 1641s and 1625s [ $\nu_4(\text{NO}_3)$ ]; 1419vs and 1357vs[ $\nu_3(\text{NO}_3^-)$ ]; 1240s[ $\nu_1(\text{NO}_3)$ ]; 1067m[ $\nu_2(\text{NO}_3)$ ]; 980vs[ $\nu_3(\text{UO}_2^{2+})$ ]; 804s, 784m, 762s, and 750s  $\text{cm}^{-1}$  [ $\nu_3$ ,  $\nu_5$ ,  $\nu_6(\text{NO}_3)$  and  $\nu_4(\text{NO}_3^-)$ ]. There is no band near 860  $\text{cm}^{-1}$  which can be assigned to  $\nu_1$  for the uranyl ion. For a covalent nitrate group, the  $\nu_4$ - $\nu_1$  separation is a measure of the degree of covalency,<sup>21</sup> the asymmetric  $\text{NO}_2$  stretch,  $\nu_4$ , being the most sensitive frequency. The symmetric  $\text{NO}_2$  stretch,  $\nu_1$ , at 1240  $\text{cm}^{-1}$  is unusually low for a covalent nitrate (it occurs at 1297, 1278, and 1328  $\text{cm}^{-1}$  for the three addition compounds discussed above.) Assuming this assignment for the 1240  $\text{cm}^{-1}$  band, it should follow that  $\nu_4$  occurs at high frequency; consistent with this, the  $\nu_4$  band which occurs at 1536, 1430, and 1541  $\text{cm}^{-1}$  in the three

<sup>16</sup> Millen and Watson, *J.*, 1957, 1369.

<sup>17</sup> Griffith, Lewis, and Wilkinson, *J. Inorg. Nuclear Chem.*, 1958, 7, 38.

<sup>18</sup> Addison and Gatehouse, *J.*, 1960, 613.

<sup>19</sup> Lappert, *J.*, 1961, 817.

<sup>20</sup> Wallwork, *Proc. Chem. Soc.*, 1959, 311; Duffin and Wallwork, *Acta Cryst.*, 1963, in the press.

<sup>21</sup> Ferraro, *J. Mol. Spectroscopy*, 1960, 4, 99.



addition compounds is missing in the spectrum of anhydrous uranyl nitrate, and this frequency is represented entirely by the double band at 1625, 1641  $\text{cm}^{-1}$ . Absorption in the region represented by the bands at 1419 and 1357  $\text{cm}^{-1}$  has only been observed previously for compounds containing the nitrate ion. In this case, however, it should be accompanied by the  $\nu_2(\text{NO}_3^-)$  absorption around 830  $\text{cm}^{-1}$ , and this is not observed.

*Chemical Properties of Uranyl Nitrate-Dinitrogen Tetroxide.*—The electrical conductivity and ultraviolet spectrum of this compound in nitromethane solution,<sup>2</sup> and its infrared spectrum, indicate that it does not exist in the form  $\text{NO}^+[\text{UO}_2(\text{NO}_3)_3]^-$ . On prolonged electrolysis of solutions in nitromethane, uranium trioxide is precipitated at the cathode and the yellow colour in the anode compartment decreases in intensity; the small degree of ionisation which does occur therefore gives a cation which contains the uranyl group. The compound reacts immediately on contact with benzene or toluene, giving an intense red colour, and nitro-derivatives can be separated from the solution. After twenty-four hours' immersion in excess of toluene, the residue contained 30% of uranium but no dinitrogen tetroxide. Anhydrous uranyl nitrate behaves similarly, but is rather less reactive.

The co-ordinated dinitrogen tetroxide is readily replaced by pyridine, with which the compound reacts immediately. The product,  $\text{UO}_2(\text{NO}_3)_2 \cdot 2\text{py}$ ,<sup>22</sup> can be recrystallised from pure pyridine, or from ethyl acetate containing pyridine.

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<sup>22</sup> Barr and Horton, *J. Amer. Chem. Soc.*, 1952, **74**, 4431.

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