480. Reactions of Uranium and Some Uranium Compounds with Nitrosyl Chloride, and with Liquid Nitrosyl Chloride–Dinitrogen Tetroxide Mixtures.

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The paper deals with reactions in the system uranium–nitrosyl chloride–dinitrogen tetroxide. Uranium does not react with liquid dinitrogen tetroxide, but does react when nitrosyl chloride is added. Uranyl compounds are always formed in the presence of dinitrogen tetroxide. At all concentrations up to 85% of NOCl, the product is the addition compound $UO_2(NO_3)_2,N_2O_4$. At higher concentrations of nitrosyl chloride, a compound $UO_2Cl_2,NOCl$ is produced (which is the corresponding compound on the nitrosyl chloride solvent system), but nitrate is present in the product at all concentrations below 98% of NOCl. In pure nitrosyl chloride the uranium(IV) oxidation state is stable, and uranium reacts with the liquid to give $UCl_4,xNOCl$; x is usually $\sim$2, but its variability suggests that 1 : 1 and 1 : 3 solvates may also exist. The nitrosyl chloride addition compounds have high thermal stability and are probably ionic complexes. These reactions of uranium metal are correlated by reference to the reactions of nitrosyl chloride with uranyl chloride, uranium tetra- and penta-chloride, the oxides UO_3 and U_3O_8, and uranyl nitrate–dinitrogen tetroxide, and to the solvolysis of uranium tetra- and penta-chloride by dinitrogen tetroxide.

REACTIONS involving non-aqueous inorganic solvents have usually been carried out in a single, pure solvent; by the use of mixed solvents, however, products can be varied by change in composition of the reaction medium.[1] Uranium does not react with dinitrogen tetroxide alone, but does react with liquid nitrosyl chloride and with mixtures of the two

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[1] Addison, *Roy. Inst. Chem. Monograph* No. 2, 1960.

solvents. Each of the pure liquids undergoes self-ionisation ($NOCl \rightleftharpoons NO^+ + Cl^-$; $N_2O_4 \leftarrow NO^+ + NO_3^-$) and thus represents a solvent system in its own right. In the mixture, the relative extent to which the two systems influence the reaction is revealed in the extent to which chlorides or nitrates appear in the products. A further feature of interest in the use of uranium arises from possible variations in its oxidation state; in dinitrogen tetroxide, uranium compounds tend to the U(VI) state, whereas the oxidising powers of nitrosyl chloride are much less pronounced.

The present paper gives a general review of reactions involving uranium metal, uranium halides, nitrosyl chloride, and dinitrogen tetroxide, and their interrelations. A more detailed study of the properties of individual compounds will be described in later papers.

RESULTS AND DISCUSSION

Reactions in Nitrosyl Chloride.—(a) *Uranyl chloride.* On addition of liquid nitrosyl chloride, uranyl chloride was converted rapidly into the 1 : 1 addition compound $UO_2Cl_2,NOCl$, which remained as a pale yellow powder on evaporation of the excess of solvent at room temperature. It is stable at room temperature in the absence of moisture, and there was no evidence of compounds involving other molecular ratios. In contrast, uranyl chloride normally combines with metal chlorides and alkylammonium chlorides to yield tetrachlorodioxouranate salts $M_2[UO_2Cl_4]$ (where M is a univalent cation), and the formula $UO_2Cl_2,2X$ predominates for the many molecular addition complexes which uranyl chloride forms with organic compounds.[2] Uranyl chloride–nitrosyl chloride is readily soluble in nitromethane; on electrolysis of a 0·06M-solution the uranium concentration increased in the anode compartment, and nitric oxide was evolved at the cathode, so that the compound may be represented in the ionic form $(NO^+)[UO_2Cl_3]^-$. The insolubility of uranyl chloride–nitrosyl chloride in nitrosyl chloride may suggest a dinuclear structure; many established mononitrosyl compounds, *e.g.*, $FeCl_3,NOCl$, $AlCl_3,NOCl$, and $SbCl_5,NOCl$ are soluble, whereas dinitrosyl compounds are generally insoluble.[3]

Uranyl chloride–nitrosyl chloride has high thermal stability, and heating at 220—240° for 2 hr. at 0·2 mm. was necessary to remove all nitrosyl chloride; pure uranyl chloride remained.

(b) *Uranyl nitrate–dinitrogen tetroxide.* The compounds $UO_2Cl_2,NOCl$ and $UO_2(NO_3)_2,N_2O_4$ are corresponding compounds in the nitrosyl chloride and dinitrogen tetroxide solvent systems. The reaction

$$UO_2(NO_3)_2,N_2O_4 + 3NOCl \rightleftharpoons UO_2Cl_2,NOCl + 3N_2O_4 \quad \ldots\ldots \quad (1)$$

was examined, first, by addition of liquid nitrosyl chloride to uranyl nitrate–dinitrogen tetroxide. The mixture was kept at —7° for 6 hr., and the mixed solvents were then evaporated. After four successive treatments with nitrosyl chloride, approximately half of the uranyl nitrate was converted into chloride, and four further treatments were necessary for complete conversion. The equilibrium lies well to the left-hand side, since both uranyl chloride and uranyl chloride–nitrosyl chloride are converted completely into uranyl nitrate–dinitrogen tetroxide by a single treatment with liquid dinitrogen tetroxide.

(c) *Uranium tetrachloride and pentachloride.* These reactions were carried out primarily to determine the influence of nitrosyl chloride on the lower-valency states of uranium, and the products have been given preliminary examination only. The green tetrachloride underwent an immediate change, and after evaporation of the excess of liquid a bright orange powder remained, in which the uranium was still in the quadrivalent state (compare the behaviour of dinitrogen tetroxide discussed below). When this product was heated, nitrosyl chloride was evolved, but the orange compound has a high thermal stability,

[2] Katz and Robinowitch, " The Chemistry of Uranium," McGraw-Hill, New York, 1951, pp. 583, 584.

[3] Burg and McKenzie, *J. Amer. Chem. Soc.*, 1952, **74**, 3143.

and heating at 240° for several hours under a vacuum was necessary to remove all the nitrosyl chloride. Most of the residue also sublimed at this temperature, condensing as green crystals of uranium tetrachloride, so that the orange product is an addition compound $UCl_4,xNOCl$. However, in contrast to the uranyl chloride addition compound, the value of x is not definite: in different preparations, it varied between 1·8 and 2·3. It is probable that the main product is $UCl_4,2NOCl$, but that less stable compounds having molecular ratios 1 : 1 and 1 : 3 are also formed. Vapour-pressure–composition data are being determined to define this system more precisely.

Uranium pentachloride reacted immediately on immersion, becoming orange-yellow. The increase in weight on evaporation of solvent at room temperature was 31·0% ($UCl_5 \longrightarrow UCl_5,2NOCl$ requires 31·5%). With ferric chloride and aluminium chloride, 2 : 1 as well as 1 : 1 addition compounds with nitrosyl chloride are known,[3] the additional molecule of nitrosyl chloride being combined with the NO^+ ion, *i.e.*, as $[NO^+,NOCl][FeCl_4^-]$. This formulation may also be applied to the compound $UCl_5,2NOCl$ to retain the maximum co-ordination number of 6 in the uranium chloro-complex. Like the uranyl chloride addition compound, the addition compounds with uranium tetra- and penta-chloride are probably ionic compounds $(NO^+)_2[UCl_6]^{2-}$ and $[NO^+,NOCl][UCl_6]^-$. However, on microscopic examination of the latter it appeared that both orange and yellow particles were present. Disproportionation to U(IV) and U(VI) may therefore have occurred, but in the direct reaction with uranium tetra- or penta-chloride there was no evidence that nitrosyl chloride acts as an oxidising agent.

(d) *Uranium oxides.* Uranium trioxide reacted slowly with liquid nitrosyl chloride. Complete reaction according to the equation $UO_3 + 3NOCl \longrightarrow UO_2Cl_2,NOCl + N_2O_3$ required 7 days' immersion in the liquid at −7°. The oxide U_3O_8 reacted even more slowly, and its reactivity depended to some extent on its method of preparation. The most active sample was prepared by heating ammonium diuranate to 650°; after immersion for 7 days at −7° in liquid nitrosyl chloride, 40 wt. % of the oxide had been converted into $UO_2Cl_2,NOCl$. Samples of the oxide obtained by heating ammonium diuranate to the more usual 900—1000° reacted much more slowly.

(e) *Uranium metal.* Nitrosyl chloride was condensed on to uranium metal at −70° and allowed to warm slowly. Reaction was slow below −40°, but the rate increased rapidly above this temperature; reaction was very vigorous at −20°, with evolution of nitric oxide. The controlled low-temperature reaction gave a bright orange, homogeneous powder; all the uranium was in the U(IV) oxidation state, and the product was identical with that formed by direct addition of uranium tetrachloride to nitrosyl chloride. The empirical formula of several such products was near $UCl_4,2{\cdot}3NOCl$, so that again the product probably consists of the disolvate $UCl_4,2NOCl$ together with the trisolvate $UCl_4,3NOCl$, having comparable stability and indistinguishable under the microscope. The reaction is considered to involve initial electron-transfer from uranium to the NO^+ ion (present as a result of self-ionisation of the liquid): $U + NO^+ \longrightarrow U^+ + NO$. This process will then continue stepwise until the uranium ion reaches the minimum oxidation state which is stable in nitrosyl chloride: $U + 4NO^+ \longrightarrow U^{4+} + 4NO$. During this reaction there was no evidence of the formation of products involving lower oxidation states of uranium.

When the reaction was allowed to proceed vigorously at about −20°, the product was a mixture of $UCl_4,xNOCl$ with the pale yellow uranyl compound $UO_2Cl_2,NOCl$. The production of the latter must be due to side reactions, probably involving the oxides of nitrogen which are produced copiously under these conditions. [Results given below indicate that any nitrogen dioxide present would immediately oxidise U(IV) to the uranyl compound.]

Dry gaseous nitrosyl chloride has little effect on a freshly filed uranium-metal surface at 100°, a faint stain appearing after prolonged treatment. However, if the nitrosyl chloride is not scrupulously dried, reaction is vigorous.

Solvolysis by Dinitrogen Tetroxide.—Reactions of uranium halides in liquid dinitrogen tetroxide were studied to determine the extent to which any such halides initially produced in the mixed solvent nitrosyl chloride–dinitrogen tetroxide would be influenced by the presence of the tetroxide.

On immersion in the liquid tetroxide at 20°, uranium tetrachloride changed, first, to an orange compound [which may be the unstable $U(NO_3)_4$], then to the lemon-yellow $UO_2(NO_3)_2,N_2O_4$. Nitrosyl chloride was continuously evolved, and complete solvolysis

$$UCl_4 + 4N_2O_4 \longrightarrow UO(NO_3)_2,N_2O_4 + 4NOCl$$

required 36 hr. at 20°. The corresponding reaction

$$UCl_5 + 4N_2O_4 \longrightarrow UO_2(NO_3)_2,N_2O_4 + 4NOCl + \tfrac{1}{2}Cl_2$$

was complete in 20 hr. at 20°. Neither chloride is soluble in dinitrogen tetroxide, and the slowness of these solvolyses is largely due to this. When dinitrogen tetroxide is added to a solution of either chloride in nitromethane, the reaction is complete within 30 min. at 20°. The rapid conversion of uranyl chloride–nitrosyl chloride into uranyl nitrate–dinitrogen tetroxide has been referred to above (equation 1); uranyl chloride behaves similarly.

In the presence of dinitrogen tetroxide, uranium(IV) and uranium(V) are therefore oxidised to the uranium(VI) state, and solvolysis of the higher uranium chlorides is a fairly ready process. The influence which a particular metal, its valency state, and the covalent character of its chloride have on the extent to which solvolysis occurs is not yet understood. Zinc chloride,[4] the titanium and zirconium halides,[5] and the alkylammonium halides[6] are readily solvolysed, whereas the anhydrous chlorides AgCl, NaCl, KCl, $FeCl_3$, and $CrCl_3$ do not react with pure dinitrogen tetroxide.

Reaction of Uranium Metal with Nitrosyl Chloride–Dinitrogen Tetroxide Mixtures.—Our interest in these mixtures arises from the fact that, although dinitrogen tetroxide is a relatively unreactive liquid, its reactivity can be stimulated by mixing with other liquids, *e.g.*, inert organic solvents such as nitromethane,[7] organic donor solvents,[7] and dinitrogen trioxide.[8] Such mixtures retain all the essential features of the dinitrogen tetroxide solvent system, apart from solubility properties and reactivity. Nitrosyl chloride is also a suitable additive, and mixtures are readily prepared by passage of the tetroxide vapour through (say) calcium chloride. Experiments were therefore conducted to determine the composition ranges over which the products of reaction with uranium remained characteristic of the N_2O_4 system, and the results are summarised in Table 1.

TABLE 1. *Products of reaction of uranium with* N_2O_4–NOCl *mixtures.*

NOCl (wt. %)	Reaction product after removal of solvents at room temp.
0	No reaction with uranium
All concns. up to 84%	$UO_2(NO_3)_2,N_2O_4$
84—98	Mixture of $UO_2(NO_3)_2,N_2O_4$ and UO_2Cl_2,NOCl, the proportion of the latter increasing with NOCl concn.
99	Mixture of UO_2Cl_2,NOCl and UCl_4,*x*NOCl
100	UCl_4,*x*NOCl

The striking feature is that the nitrosyl chloride concentration can be increased to 84% before any chloride appears in the product. In view of the reactions discussed earlier, and the absence of reaction between uranium and the pure tetroxide, the reaction mechanism

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[4] Addison and Lewis, *J.*, 1951, 2843.

[5] Gutmann and Tannenberger, *Monatsh.*, 1956, **87**, 421.

[6] Addison, Conduit, and Thompson, *J.*, 1951, 1298.

[7] Addison, Sheldon, and Hodge, *J.*, 1956, 3900.

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

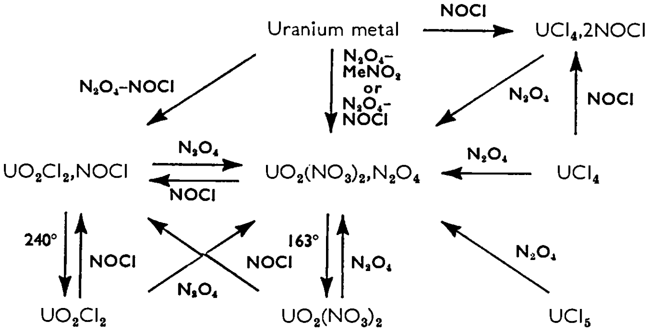
must involve initial attack by nitrosyl chloride, followed by oxidation and solvolysis of the chloride by dinitrogen tetroxide:

$$\mathrm{U + 6NOCl \longrightarrow UCl_4,2NOCl + 4NO} \qquad (2)$$

$$\mathrm{UCl_4,2NOCl + N_2O_4 \longrightarrow UO_2Cl_2,NOCl + 3NOCl} \qquad (3)$$

$$\mathrm{UO_2Cl_2,NOCl + 3N_2O_4 \longrightarrow UO_2(NO_3)_2,N_2O_4 + 3NOCl} \qquad (4)$$

If the product is isolated at an early stage in the reaction, it is seen to consist of the yellow uranyl nitrate–dinitrogen tetroxide contaminated by a bright orange compound. The latter contains uranium in an oxidation state lower than U(VI), and is probably the uranium tetrachloride–nitrosyl chloride addition compound.



From the experiments with dilute solutions of dinitrogen tetroxide in nitrosyl chloride, it is clear that the presence of any tetroxide in the liquid mixture results in ultimate oxidation of U(IV) to U(VI). With 1% of tetroxide, appreciable oxidation to uranyl chloride occurs, and with mixtures containing 2% of tetroxide no uranium tetrachloride remains in the product.

The reactions of dinitrogen tetroxide and nitrosyl chloride with uranium, and the interconversion of nitrates and chlorides, are summarised in the annexed scheme.

EXPERIMENTAL

The preparation of dinitrogen tetroxide and nitrosyl chloride, the preparation of the mixtures, and their analysis were carried out as already described.[9]

Uranyl Chloride.—Passage of hydrogen chloride gas over the hydrate for 24 hr. at 300° gave anhydrous uranyl chloride as a yellow powder (Found: U, 69·7. Calc. for UO_2Cl_2: 69·8%).

Analysis of Uranyl Chloride–Nitrosyl Chloride.—Both acid and alkaline hydrolysis were employed. A weighed sample was sealed in a thin-walled phial, which was broken by being shaken in a bottle containing 0·1N-hydrochloric acid. The temperature was kept at 0° to reduce the vigour of the hydrolysis. Chlorine was determined as silver chloride. Uranium was precipitated as ammonium diuranate by addition of carbonate-free ammonia, and the precipitate was ignited at 900° to the oxide U_3O_8. In the alkaline hydrolysis, 2N-sodium hydroxide at 0° was used. Nitrogen was determined separately after alkaline hydrolysis in 5N-sodium hydroxide. Under these conditions, nitrogen contents obtained by the Kjeldahl method, and by determining nitrite by potassium permanganate titration, were in agreement. When hydrolysis was carried out in sodium hydroxide solutions more dilute than 5N, nitrite analyses were less satisfactory. Two alternative reactions are possible:[10]

$$\mathrm{NOCl + 2NaOH = NaNO_2 + NaCl + H_2O}$$

$$\mathrm{3NOCl + 4NaOH = 3NaCl + NaNO_3 + 2NO + 2H_2O}$$

but the second reaction is not significant at higher alkali concentrations. The product from the reaction of uranyl chloride with nitrosyl chloride reaction gave: N, 3·45%; on acid hydrolysis, U, 58·4; Cl, 26·8%; on alkaline hydrolysis, U, 58·4; Cl, 26·6% (Calc.

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[9] Addison and Thompson, *J.*, 1949, S218.

[10] Perret and Perrot, *Compt. rend.*, 1931, **193**, 937.

for $UO_2Cl_2,NOCl$: U, 58·5; Cl, 26·2; N, 3·45%). In removing the last traces of excess of nitrosyl chloride from the addition compound, we were anxious that the latter should not be decomposed, and the slightly high chlorine content probably represents nitrosyl chloride adsorbed on the powder.

During thermal decomposition of uranyl chloride–nitrosyl chloride, the evolved gas was absorbed in a sodium hydroxide–calcium oxide tube, and its chloride content determined; the weight of evolved gas was determined directly from loss in weight of the addition compound. The residue gave: U, 69·5; Cl, 20·6% (Calc. for UO_2Cl_2: U, 69·8; Cl, 20·8%). In the evolved gas, Cl = 54·8% (Calc. for NOCl: 54·2%).

Uranyl Nitrate–Dinitrogen Tetroxide.—Such material was obtained by reaction of uranium metal (or the oxide UO_3 or U_3O_8) with mixtures of nitromethane and dinitrogen tetroxide. It is normally obtained as a yellow powder [11] but from solutions rich in nitromethane it can be crystallised as large (1 cm.) yellow crystals. Removal of dinitrogen tetroxide to leave the pure anhydrous nitrate can only be carried out under special conditions, which are not appropriate for analysis, and reaction products believed to consist of this compound (see Table 3) were analysed by hydrolysis in 2N-sodium hydroxide. After filtration of the uranate, total nitrogen was determined in the filtrate by the Kjeldahl method, and nitrite by titration with potassium permanganate solution. The uranate was dissolved in acid, reprecipitated as ammonium diuranate, and ignited to U_3O_8.

Uranium Chlorides.—These were prepared by passing an excess of dry chlorine over a mixture of the oxide U_3O_8 and carbon in a silica tube at 600°. The pentachloride and tetrachloride condensed as separate bands in the cool parts of the tube, the pentachloride predominating. For analysis, the latter was dissolved in water at 0° and oxidised by nitrous acid, and uranium and chloride were determined as U_3O_8 and AgCl respectively (Found: U, 57·4; Cl, 42·1. Calc. for UCl_5: U, 57·3; Cl, 42·6%). The tetrachloride was prepared by heating the pentachloride at 200° in a current of dry carbon dioxide, followed by sublimation at 600—650°. The product was dissolved in dilute sulphuric acid, and uranium determined by titration with potassium permanganate (Found: U, 62·5; Cl, 38·0. Calc. for UCl_4: U, 62·7; Cl, 37·3%).

When the addition compounds with nitrosyl chloride were dissolved in water or dilute acids, the uranium was oxidised to the U(VI) state by the nitrous acid produced, and these solutions could not be used for analysis. The nitrosyl chloride was therefore removed from the addition compound by heating under a vacuum, and the remaining chloride determined as stated above.

Metallic Uranium–Nitrosyl Chloride Reaction.—Relevant analyses are given in Table 2.

TABLE 2. *Products of reaction of uranium with nitrosyl chloride.**

Prepn. no.	Temp. of liquid NOCl	NOCl (%) in product	Analysis (%) of product after removal of NOCl at 240°		
			U(IV)	UO_2^{2+}	Cl
1	Below −40°	28·9	62·8	0	35·0
2	−30 to −20°	31·8	49·3	13·6	—
3	−30 to −20°	30·4	37·2	23·0	—

* $UCl_4,2NOCl$ and $UCl_4,3NOCl$ require 25·6 and 34·1% of NOCl, respectively.

In preparation 1, almost all of the product obtained after removal of nitrosyl chloride could be sublimed as the green tetrachloride. A trace of uranium(IV) oxide dichloride, $UOCl_2$, remained as unsublimable residue, and accounts for the somewhat low chlorine content. Under conditions of more vigorous reaction (preparations nos. 2 and 3) the quantity of uranyl compound produced was variable, though it appeared to increase with vigour of reaction. The evolved gases were passed through activated alumina, which absorbs nitrosyl chloride and any nitrogen dioxide; nitric oxide is not absorbed and was recognised by the formation of brown fumes in contact with atmosphere.

Reaction of Uranium with N_2O_4–NOCl *Mixtures.*—In all experiments, the liquid mixture was present in large excess. Over the 0—40% NOCl range, reaction was very slow. For example, freshly filed uranium metal was held in a sealed tube at 20° with a mixture containing 37% of nitrosyl chloride; a thin film of product developed after 24 hr. Reaction became more

[11] Gibson and Katz, *J. Amer. Chem. Soc.*, 1951, **73**, 5436.

vigorous at concentrations above 40% of nitrosyl chloride. Analyses of products obtained at some higher concentrations are given in Table 3.

TABLE 3. *Reaction of uranium with* N_2O_4-NOCl *mixtures.*

Expt. no.	NOCl (wt. %)	Temp. of reaction mixture	Analysis (%) of product		
			U(VI)	N_2O_4	Cl
1	70·0	−8°	50·0	18·7	0
2	84·1	−9	49·4	18·3	Trace
3	96·4	−22	53·2	—	22·0
4	97·8	−35	56·7	Trace	26·0
	$UO_2(NO_3)_2,N_2O_4$ requires		49·0	18·9	0
	UO_2Cl_2,NOCl requires		58·5	0	26·2

In none of these experiments was uranium(IV) detected in the final product. With 70·0% and 84·1% of nitrosyl chloride, analysis shows the product to be $UO_2(NO_3)_2,N_2O_4$. This is one of the most stable of the metal nitrate–dinitrogen tetroxide addition compounds, but unless isolated with great care it readily loses a small amount of dinitrogen tetroxide. This is reflected in the slightly high uranium, and slightly low N_2O_4, analyses in expt. nos. 1 and 2. Over the narrow concentration range 84—97·8% of nitrosyl chloride, the product changes to uranyl chloride–nitrosyl chloride (expt. no. 4). At higher concentrations (about 99%) no trace of nitrate is found in the product (*i.e.*, no brown fumes are given off on ignition) but uranium(IV) chloride occurs in the product. This is recognised by sublimation, and by titration of an aqueous solution of the product after removal of nitrosyl chloride under a vacuum.

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