

309. *The Chemistry of Nitrosyl Complexes. Part III.* Evidence for Compound Formation in Liquid Nitrosyl Chloride from Tracer Studies.*

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The rapid exchange of ^{36}Cl between the nitrosyl chloride addition compounds of ferric chloride and antimony pentachloride with liquid nitrosyl chloride is in agreement with the formulation of these compounds as nitrosonium salts. With the more covalent chlorides, arsenic trichloride, phosphorus oxychloride, and carbon tetrachloride, exchange is rapid with arsenic trichloride but very slow with phosphorus oxychloride and carbon tetrachloride. Phase studies indicate the formation of a compound, $\text{AsCl}_3 \cdot 2\text{NOCl}$, between arsenic trichloride and nitrosyl chloride but no compound formation between phosphorus oxychloride and nitrosyl chloride. The rapid exchange of ^{36}Cl between arsenic trichloride and nitrosyl chloride is attributed to the formation of this compound which behaves as a very weak electrolyte in the nitrosyl chloride solvent system.

The slow exchange of nitrosyl chloride with the non-electrolyte phosphorus oxychloride being assumed to occur through the presence of free chloride ions, the free chloride-ion concentration in nitrosyl chloride is calculated to be 10^{-8} g.-ion l^{-1} , and the ionic product $[\text{NO}^+][\text{Cl}^-] = 10^{-16}$ g.-ion 2 l^{-2} .

PREVIOUS studies in nitrosyl chloride have been mainly concerned with the behaviour of strong electrolytes¹ formed by the reaction of metal chlorides with the solvent. Thus complex formation occurs between nitrosyl chloride and ferric chloride to give the strong electrolyte nitrosonium tetrachloroferrite; and with antimony pentachloride to give nitrosonium hexachloroantimonate. The formation of these ionic compounds should lead to rapid exchange of ^{36}Cl between ferric chloride and antimony pentachloride and the solvent.

From the general behaviour in other systems, we would expect that arsenic trichloride and phosphorus oxychloride would behave as either weak or non-electrolytes in nitrosyl chloride. We have, therefore, studied the general properties of such solutions, with particular reference to the influence of the nature of the solute on the exchange of labelled chlorine. It was of interest to see if weaker compound formation also led to rapid exchange of chlorine with the solvent.

EXPERIMENTAL

Preparation of Compounds containing ^{36}Cl .—Radioactive nitrosyl chloride was prepared as described in Part II.

* Part II, *J.*, 1956, 150.

¹ Burg and Campbell, *J. Amer. Chem. Soc.*, 1948, **70**, 1954; Burg and McKenzie, *ibid.*, 1952, **74**, 3143.

Nitrosonium hexachloroantimonate. Radioactive nitrosyl chloride was condensed on a block of antimony metal cooled to -40° . The temperature was allowed to rise slowly, and reaction started. At room temperature, the excess of antimony was removed, leaving the yellow complex $\text{NOCl}_2\text{SbCl}_6$ (Found : Cl, 58.6. Calc. for NOSbCl_6 : Cl, 58.4%).

Arsenic trichloride. Radioactive tetramethylammonium chloride² (0.2 g.) was dissolved in anhydrous arsenic trichloride (10 ml.). Rapid exchange occurred³ and arsenic trichloride, containing ³⁶Cl, was distilled as required.

Phosphorus oxychloride. Radioactive tetraethylammonium chloride was dissolved in phosphorus oxychloride, and active phosphorus oxychloride was distilled as required.

Other Compounds.—(i) Carbon tetrachloride was dried (CaCl_2) and fractionally distilled immediately before use. (ii) Anhydrous ferric chloride was prepared by passing dry chlorine over heated iron wire. The product was sublimed into small ampoules in a stream of chlorine, and absorbed chlorine was removed under reduced pressure. The ampoules were sealed in a stream of nitrogen.

Exchange Runs.—The apparatus and techniques employed were those described previously.³ Solid samples packed in small glass tubes open at both ends were added to the exchange vessel; with liquids, additions were made from a microburette. The burette was fitted with standard ground-glass joints for attachment to the exchange vessel. Activities were determined by precipitating the chloride as silver chloride and counting on G.E.C. 1.5 cm. planchets, with samples of infinite thickness.

In the experiments, inactive ferric chloride and carbon tetrachloride were employed with active nitrosyl chloride. For exchanges with antimony pentachloride, arsenic trichloride, and phosphorus oxychloride, active chlorides were used with inactive nitrosyl chloride.

A detailed study of the slow exchange between phosphorus oxychloride and nitrosyl chloride was carried out. The components were mixed and fractions were sealed in phials, which were allowed to attain 18° . After various intervals, a phial was broken, and the nitrosyl chloride allowed to evaporate. After complete removal of the nitrosyl chloride the activity of the chlorine in the remaining phosphorus oxychloride was determined. For 0.240M-phosphorus oxychloride solution, the percentage exchange after 0, 14, and 33 days was 0, 20.6, and 40.6, respectively.

Phase Studies.—The freezing points of mixtures of phosphorus oxychloride–nitrosyl chloride and arsenic trichloride–nitrosyl chloride were determined by the warming-curve technique.⁴ Thermometers were calibrated against the m. p. of ice, carbon tetrachloride, mercury, and chlorobenzene, and the sublimation point of solid carbon dioxide.

Conductivity Measurements in Liquid Nitrosyl Chloride.—The conductivities of arsenic trichloride, phosphorus oxychloride, and chloroform were determined in liquid nitrosyl chloride at -20° . The cell used was that described previously,³ and measurements were made with a Mullard conductivity bridge, type E 7566. A solution of the required liquid, in liquid nitrosyl chloride, was prepared in the cell by use of a weight pipette, and liquid nitrosyl chloride was added from a burette, designed to enable nitrosyl chloride to be maintained at -20° for long periods. This was attained by surrounding the burette with a glass envelope through which was circulated cold alcohol. The following Table contains the equivalent conductivities of the liquids in nitrosyl chloride.

Compound								
POCl ₃	Spec. conductivity (ohm ⁻¹ cm. ²)	0.173	0.194	0.208	0.220	0.230	0.240	0.242
	10 ³ × concn. (mole l. ⁻¹)	3.32	3.02	2.77	2.56	2.38	2.22	2.08
AsCl ₃	Spec. conductivity (ohm ⁻¹ cm. ²)	0.204	0.220	0.228	0.282	0.314	0.347	0.402
	10 ³ × concn. (mole l. ⁻¹)	2.86	2.65	2.47	2.06	1.85	1.68	1.48
CHCl ₃	Spec. conductivity (ohm ⁻¹ cm. ²)	0.104	0.111	0.119	0.126	0.133	0.140	0.148
	10 ³ × concn. (mole l. ⁻¹)	3.79	3.53	3.31	3.13	2.95	2.79	2.65

These values indicate that arsenic trichloride is a slightly better conductor than phosphorus oxychloride: the values for chloroform solutions were variable and the observed conductivity in the chloroform may well be associated with traces of impurity.

Conductometric Titration.—Arsenic trichloride was titrated with tetraethylammonium chloride in liquid nitrosyl chloride at -20° , an apparatus similar to that described for the

² Lewis and Wilkins, *J.*, 1955, 56.

³ Lewis and Sowerby, *J.*, 1957, 336.

⁴ Addison, Conduit, and Thompson, *J.*, 1951, 1303.

conductivity study being used. Fig. 1 shows the portion of the curve of the variation in conductivity of solutions of arsenic trichloride on addition of tetraethylammonium chloride, over the concentration range of the 1 : 1 compound. No breaks were observed at higher molecular ratios of the components, the conductivity rising smoothly with addition of tetraethylammonium chloride.

Electrolysis of Arsenic Trichloride in Liquid Nitrosyl Chloride.—The electrolysis was carried out in an apparatus similar to that used by Burg and McKenzie.¹ The electrodes were platinum cylinders, 4.5 cm. long and 0.7 cm. in diameter, and the electrolysis was carried out at -20° for 20 hr. The contents of the centre compartment were then frozen by liquid oxygen, and the anode and cathode fractions were removed. The concentration of arsenic in the former was always greater than that in the latter :

e.g., concn. of As in anode compartment = 0.0070 g./ml.
 " " cathode compartment = 0.0045 g./ml.

Owing to the low conductivity of these solutions, it was not possible to determine transport numbers, as the distance between the electrodes was not sufficient to ensure that there was no concentration change in the solution separating the anode and the cathode compartment.

DISCUSSION

Ferric chloride dissolves readily in nitrosyl chloride to give a highly conducting solution and behaves as a strong electrolyte in the system. The solutions are considered to contain nitrosonium chloroferrite, and on evaporation of the solvent, a solid of composition $\text{FeCl}_3 \cdot \text{NOCl}$ can be isolated. Tensimetric studies indicate that, in addition to the monosolvate, ferric chloride exists in solution as a disolvated molecule. Magnetic studies on these solutions show that the probable structure of such a complex involves solvation of the nitrosonium ion, and not further addition of chloride ion to the ferric ion.¹ The tetrachloroferrite ion may be expected to be labile with respect to chloride-ion exchange, and this exchange is analogous to the exchange of labelled water molecules with metal aquo-complexes in water. These exchanges are normally rapid. Antimony pentachloride behaves in a similar manner, reacting with nitrosyl chloride to yield nitrosonium chloro-antimonate. In many cases, the formulation of the compounds as salts containing an ion characteristic of the solvent is based on the isolation of a compound containing solvent molecules and the enhanced conductivity of the solvent on addition of the metal chloride. Huston⁵ has recently thrown doubt on this type of formulation. Aluminium chloride dissolves in carbonyl chloride to give a conducting solution and forms a monosolvate that was formulated as $(\text{COCl})^+(\text{AlCl}_4)^-$. Huston observed, however, that the exchange of labelled chlorine between aluminium chloride and carbonyl chloride was slow. A structure, as suggested above, for the complex would have led to a rapid exchange of chlorine between the aluminium chloride and the solvent.

The Table contains typical values for the exchange of labelled chlorine (^{36}Cl) between nitrosyl chloride and some soluble chlorides, and in agreement with the formulation above, ferric chloride and antimony pentachloride are exchanged completely within the time of separation. An interesting difference arises in the behaviour of the more covalent chlorides, for arsenic trichloride is exchanged rapidly with nitrosyl chloride but phosphorus oxychloride and carbon tetrachloride only very slowly. We have investigated the physical properties of solutions of arsenic trichloride and phosphorus oxychloride in liquid nitrosyl chloride to determine if the difference in the rates of exchange can be attributed to any major difference in the behaviour of such solutions.

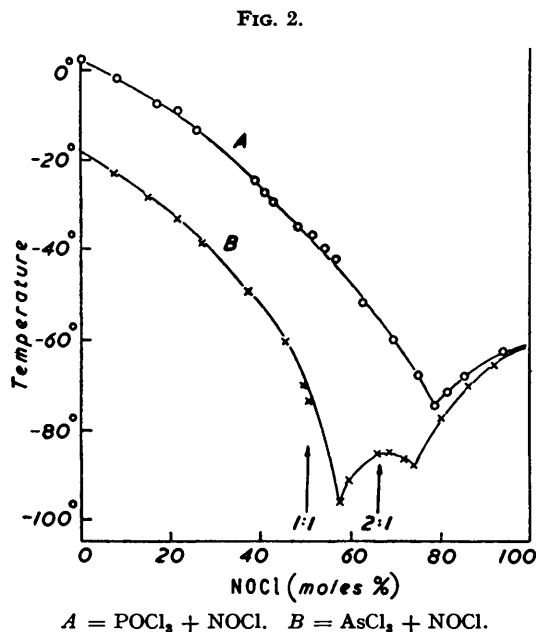
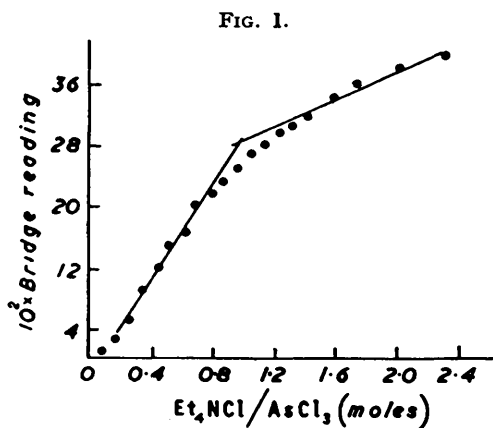
Thermal Measurements.—With ionic chlorides, arsenic trichloride forms stable, solid compounds involving the tetrachloroarsenite ion,⁶ $(\text{AsCl}_4)^-$, whereas phosphorus oxychloride normally solvates the chloride ion in solution but no solid derivatives of the corresponding ion, $(\text{POCl}_4)^-$, are known.⁷ We would, therefore, expect that, if compound

⁵ Huston, *J. Inorg. Nuclear Chem.*, 1956, **2**, 128.

⁶ Gutmann, *Z. anorg. Chem.*, 1951, **266**, 331.

⁷ *Idem, ibid.*, 1952, **270**, 179.

formation involved such ions, it would be more pronounced in the case of arsenic trichloride. Fig. 2 shows the liquidus curves for mixtures of arsenic trichloride and phosphorus oxychloride with nitrosyl chloride. The solutions are miscible over the whole concentration range. With phosphorus oxychloride, a simple eutectic was observed at -74° , with a composition of 78 moles % of nitrosyl chloride, showing the absence of any compound formation between the components. However, with arsenic trichloride, a maximum is found at a concentration of 68 moles % of nitrosyl chloride, indicating that a compound, with a molecular composition $2\text{NOCl}, \text{AsCl}_3$, is formed. There was no apparent break in the curve at the 1:1 mole ratio. The shape and height of the maximum suggest that the compound has not a very great stability, and is probably highly dissociated. This compound may be considered either as a weak addition compound or as an ionic compound analogous to the chloroferrite addition compound discussed above. In the formulation



as an ionic compound, the structure may be either $[(\text{NO})(\text{NOCl})]^+[\text{AsCl}_4]^-$ (I) or $(\text{NO})_2^+[\text{AsCl}_5]^{2-}$ (II). Structure (I) involves the solvation of the nitrosonium ion, in a similar manner to that postulated for nitrosonium chloroferrite. In agreement with this structure is the fact that even the most strongly donating chloro-compounds only give a tetrachloroarsenite ion in arsenic trichloride solutions. Consistently with structure (II), a phase study of the aluminium chloride-nitrosyl chloride system shows that aluminium chloride gives two complexes⁸ with molecular compositions $\text{AlCl}_3, \text{NOCl}$ and $\text{AlCl}_3, 2\text{NOCl}$. The disolvate, which is formulated as a solvated nitrosonium derivative, is much more unstable than the monosolvate and is found to have an incongruent m. p. at 17.5° . Thus, if structure (I) is correct, we would have expected some indication of the formation of a monosolvate in the phase diagram, although the larger size of the ion $[\text{AsCl}_5]^{2-}$ than of the ion $[\text{AlCl}_4]^-$ may account for the increased stability of a compound of structure (I).

Electrochemical Studies.—The conductivities of solutions of phosphorus oxychloride and arsenic trichloride in liquid nitrosyl chloride indicate that these liquids behave as either very weak electrolytes or non-electrolytes. The values of the equivalent con-

⁸ Houtgraaf and de Roos, *Rec. Trav. chim.*, 1953, **72**, 963.

ductivities of these solutions do not differ significantly from those of solutions of chloroform, which may be considered to be a non-electrolyte in this system. The high degree of dissociation of the arsenic trichloride complex, deduced from the phase diagram, therefore probably involves dissociation into nitrosyl chloride and arsenic trichloride rather than

Exchange of radio-chlorine between nitrosyl chloride and some soluble chlorides.

Solute	Con- ditions	Time of contact (min.)	Activity of NOCl (counts/ min.)	Value for 100% exchange (counts/ min.)	Solute	Con- ditions	Time of contact (min.)	Activity of NOCl (counts/ min.)	Value for 100% exchange (counts/ min.)	
NOFeCl ₄	-20°, in dark	2½	144	146	POCl ₃ ...	-20°, in light	5	3	140	
		3½	140				50	2		
		70	143				75	2		
NOSbCl ₆	-20°, in light	6	135	132	-20°, in dark	-20°, in dark	60	0	134	
		11	134				100	1		
		25	136				285	0		
		56	138				285	0		
AsCl ₃ ...	-20°, in light	5	269	265	CCl ₄ ...	-30°, in light	8	292*	161	
		28	274				42	302		
		51	274				75	293		
	91	265	98	289						
	-20°, in dark	5	132	134						
		20	137							

* Original NOCl = 302 counts/min.

into ionic components. A conductometric titration between arsenic trichloride in liquid nitrosyl chloride and a strong base in the nitrosyl chloride solvent system, tetraethylammonium chloride, gave a break in the conductivity curve at a molecular ratio of Et₄NCl : AsCl₃ = 1 : 1. No break occurred at any other concentration. Phosphorus oxychloride under similar conditions gave no break in the conductivity curve. This may be taken to indicate that, in nitrosyl chloride, arsenic trichloride forms a monobasic acid, which may be considered as [(NO)(NOCl)]⁺[AsCl₄]⁻, whilst phosphorus oxychloride is probably a non-electrolyte. An electrolysis of a solution of arsenic trichloride in nitrosyl chloride between nickel or platinum electrodes also agreed with the arsenic's being present in the anion, as arsenic concentrated in the anode compartment.

The exchange of labelled chlorine between nitrosyl chloride and arsenic trichloride may then occur by the formation of this weak addition compound, whilst phosphorus oxychloride, which does not form a similar compound, may be expected to be exchanged slowly.

The bimolecular rate constant for the exchange of phosphorus oxychloride with chloride ion in acetonitrile has been determined over a temperature range,³ and at 18° the calculated rate constant is 66 sec.⁻¹ mole⁻¹ l. If we assume that the exchange between phosphorus oxychloride and nitrosyl chloride occurs by a similar bimolecular process involving chloride ion (present owing to the self-dissociation of liquid nitrosyl chloride), we can calculate the chloride-ion concentration in liquid nitrosyl chloride. The rate of the phosphorus oxychloride-nitrosyl chloride exchange reaction is given by

$$R = \frac{0.693}{t_{\frac{1}{2}}} \cdot \frac{3[\text{POCl}_3][\text{NOCl}]}{[3[\text{POCl}_3] + [\text{NOCl}]]}$$

and if we assume the above bimolecular mechanism, $R = k_2[\text{POCl}_3][\text{Cl}^-]$ where k_2 is the rate constant and $[\text{Cl}^-]$ is the concentration of chloride ion due to the self-ionisation of nitrosyl chloride. This requires that the rate constant, k_2 , is the same as that in acetonitrile. Normally, for a bimolecular mechanism, involving an ion and a neutral molecule, the rate constant is slightly increased on decrease of the polarity of the solvent, and therefore the concentration of free chloride ion in nitrosyl chloride will probably be lower than this calculated value. As phosphorus oxychloride is a non-electrolyte in this system, we

may then consider that the concentration of nitrosonium ion is equal to the concentration of chloride ion. Hence, the ionic product for nitrosyl chloride $K = [\text{NO}^+][\text{Cl}^-]$ will reduce to $K = [\text{Cl}^-]^2$. From the above data, the chloride-ion concentration in nitrosyl chloride at 18° is 10^{-8} g.-ion l.⁻¹ and the ionic product is 10^{-16} g.-ion² l.⁻².

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