

*The Chemistry of Nitrosyl Complexes. Part I. Evidence for the Self-ionisation of Liquid Nitrosyl Chloride from Tracer Studies.*

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Complete exchange has been observed between tetramethyl- or tetraethylammonium chloride (enriched with  $^{36}\text{Cl}$ ) and nitrosyl chloride within 10 minutes at  $-5^\circ$  or 3 minutes at  $-36^\circ$ , respectively. The results are considered to favour a self-ionisation of the nitrosyl chloride rather than an ion-transfer process. The latter may occur in the other solvent systems examined by tracer methods. The exchange is not photochemical.

In connection with the investigation of certain addition compounds in nitrosyl chloride, we have studied the exchange of chloride ion, labelled with  $^{36}\text{Cl}$ , with nitrosyl chloride. In many solvents a small amount of self-ionisation has been postulated to account for the reactions which occur in them. Isotopic exchange reactions have been used in an attempt to detect such ionisation since in a solvent system  $\text{X} \rightleftharpoons \text{Y}^+ + \text{Z}^-$  the addition of either labelled  $\text{Y}^+$  or labelled  $\text{Z}^-$  to the solvent should rapidly lead to labelling in X. In the case of nitrosyl chloride a self-ionisation  $\text{NOCl} \rightleftharpoons \text{NO}^+ + \text{Cl}^-$  has been suggested by (Burg and Campbell, *J. Amer. Chem. Soc.*, 1948, **70**, 1964; Burg and McKenzie, *ibid.*, 1952, **74**, 3143) and hence rapid exchange between chloride ion and solvent would be expected. In our preliminary experiments (Lewis and Wilkins, *Chem. and Ind.*, 1954, 634) tetramethylammonium chloride was the soluble chloride but its limited solubility made exchange studies at temperatures lower than  $-5^\circ$  difficult. Tetraethylammonium chloride, which is much more soluble in nitrosyl chloride, could be used at  $-36^\circ$ .

#### EXPERIMENTAL

*Preparation of Tetramethylammonium Chloride containing  $^{36}\text{Cl}$ .*—Tetramethylammonium hydroxide (5 c.c.; 25% w/w solution) was treated with 3.12N-hydrochloric acid containing  $^{36}\text{Cl}$  (0.48  $\mu\text{c}/\text{c.c.}$  of solution; supplied by the Radiochemical Centre, Amersham) until a neutral solution was obtained (about 5 c.c.), and then evaporated. The solid chloride was dried in a vacuum for 12 hr. at  $118^\circ$  over phosphoric oxide (Found: Cl, 32.2. Calc. for  $\text{C}_4\text{H}_{12}\text{NCl}$ : Cl, 32.4%).

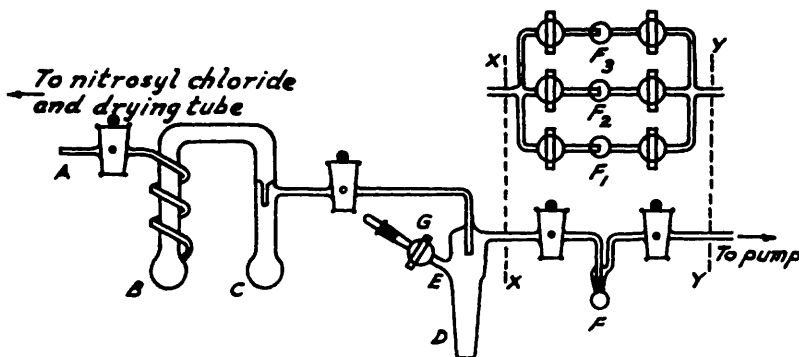
*Preparation of Tetraethylammonium Chloride containing  $^{36}\text{Cl}$ .*—Hydrochloric acid containing  $^{36}\text{Cl}$  (5 c.c. as above) was treated with tetraethylammonium hydroxide (about 8.7 c.c.; 25% w/w solution) until a neutral solution resulted and this was gently evaporated to dryness. The residue was recrystallised from acetone and the resulting needles were dried as above (Found: Cl, 21.3. Calc. for  $\text{C}_8\text{H}_{20}\text{NCl}$ : Cl, 21.4%). On one occasion a small amount of the crude active residue from the evaporation was recrystallised from ethylene dichloride (Vernon, Goldberg, and La Rochelle, *J. Amer. Chem. Soc.*, 1951, **73**, 2844) but the product was almost inactive and exchange must have taken place in the hot solvent.

*Preparation of Nitrosyl Chloride.*—Nitrogen dioxide (obtained by heating commercial lead nitrate in a metal bomb) was passed through a 2-ft. column of moist potassium chloride (Whittaker, Lundstrom, and Merz, *Ind. Eng. Chem.*, 1931, **23**, 1410), and the evolved nitrosyl chloride dried by passing through three 2-ft. columns of anhydrous calcium chloride. The gas was condensed to a deep-red liquid in a spiral worm (similar to *B* in the Figure) cooled in solid carbon dioxide-acetone.

*Exchange Runs.*—The apparatus (Figure) was thoroughly dried before an exchange run, being flamed under vacuum. Manipulations involving the tetraethylammonium chloride were carried out in a Tower's Manipulator Box. The spiral worm containing the liquid nitrosyl chloride was warmed and the middle fraction of evolved gas further dried by passing through a short length of calcium chloride, attached at *A*, and condensed in the bulb *B*. The nitrosyl chloride was again fractionally distilled and the middle fraction condensed in bulb *C*; this was fractionated into the exchange vessel *D*, up to a calibrated mark (about 5 c.c.). The procedure after this differed slightly depending upon which active chloride was used. (a) A known amount of tetramethylammonium chloride (about 18 mg.) was added to the nitrosyl chloride (about

$-7^{\circ}$ , just below the b. p.) by inverting a side-arm (not shown in the figure) attached at *E*. The liquid was vigorously stirred by manual magnetic stirring for about 5 min. during which the chloride dissolved; about one-third of the nitrosyl chloride was boiled off and condensed in one of the receivers *F*. The nitrosyl chloride solution was just prevented from boiling and after about 20 min. and then 60 min. the remaining nitrosyl chloride was removed and collected in the other receivers *F*<sub>2</sub> and *F*<sub>3</sub>. (b) A known amount of tetraethylammonium chloride (about 50 mg.) packed in a small glass tube open at both ends was added through the vacuum-tap *G* to the nitrosyl chloride cooled in freezing ethylene dichloride (about  $-36^{\circ}$ ). The chloride was soon dissolved from the open tube and was stirred for 1–2 min. as described in (a). The nitrosyl chloride was removed at this temperature by applying a vacuum (vapour pressure of nitrosyl chloride at  $-36^{\circ} = 170$  mm., Burg and McKenzie, *loc. cit.*), it being possible to remove a fraction of nitrosyl chloride about 3 min. after the chloride had been added. Further fractions of nitrosyl chloride after about 10 and 30 min. were removed in the same way. In both (a) and (b), runs were carried out in the light and in the dark and the residue was analysed for chloride (Volhard; see below).

**Counting Procedure.**—Because of the relatively small amounts of activity involved after the necessarily large dilution of active chloride by inactive nitrosyl chloride, counting was done on solid samples where a higher efficiency of counting was obtained than with the more convenient counting in solution. The nitrosyl chloride was converted into a solid suitable for counting as follows: the nitrosyl chloride from *F* was almost completely solidified and added



to excess of sodium hydroxide solution, forming sodium chloride and sodium nitrite. The chloride was precipitated from the acidified (nitric acid) solution with silver or lead nitrate solution. The solid was washed with water, alcohol, and ether and dried at about  $100^{\circ}$  for 30 min. Most of the counting was done on silver chloride and although the results obtained were sufficiently accurate for our purposes, the silver chloride darkened on exposure to light and the activity changed by a small amount. In addition, the solid was usually crystalline, difficult to powder finely, and therefore not "matting" well by our methods. Lead chloride had none of these disadvantages and was used towards the end of the work. Matted samples were made on G.E.C. large flat planchets by a method very similar to that described by Popjak (*Biochem. J.*, 1950, **46**, 560) and by Adamson and Wilkins (*J. Amer. Chem. Soc.*, 1954, **76**, 3381). The amounts used were always the same and more than half of that required for "infinitely thick." The latter is about 190 mg./sq. cm. estimated from Feather's equation (see Taylor, "The Measurements of Radio Isotopes," Methuen, London, 1951, p. 71) and roughly confirmed experimentally. The variation of count with the amount of material was therefore very slight at the thicknesses used. Reproducibility was within 5%. Standard electronic equipment was employed for counting in conjunction with a G.E.C. mica end-window counter and a Panax Universal lead castle. Because of the low counts recorded, no resolving time correction was necessary (Taylor, *op. cit.*, p. 86). The usual allowance was made for background. The results are tabulated.

**Stability of Organic Cationic Chlorides in Liquid Nitrosyl Chloride.**—As found by Burg and McKenzie (*loc. cit.*), tetramethylammonium chloride was stable in boiling nitrosyl chloride. This was shown by analysing (for chloride; Volhard) the white residue remaining at the end of an exchange run after removal of the nitrosyl chloride under a vacuum (Found, for three experiments: Cl, 32.5, 32.35, 32.4. Calc. for  $C_4H_{12}NCl$ : Cl, 32.4%). Tetraethylammonium chloride

was also stable in contact with liquid nitrosyl chloride at  $-30^\circ$ , but it was extremely difficult to remove all the nitrosyl chloride in a vacuum, even during several hours, and the residue was always very pale yellow. Nevertheless, the chloride content of the residue closely corresponded to that for the original compound (Found, for three experiments : Cl, 21.6, 21.65, 21.55. Calc.

Run no.	Inactive chloride		Active chloride		Dilution of chloride in $\text{NR}_4\text{Cl}$	Conditions	Time of contact (min.)	Activity of mixture (counts/min.)	Activity of $\text{NOCl}$ (counts/min.)
	NaCl (g.)	NOCl (g.)	$\text{Me}_4\text{NCl}$ (mg.)	$\text{Et}_4\text{NCl}$ (mg.)					
1	—	7.65	17.8	—	719	In light, $-5^\circ$	10	—	92
							22	—	87
							57	—	86
2	—	7.84	17.7	—	741	In dark, $-5^\circ$	10	—	80
							25	—	83
							60	—	81
	6.0	—	15.2	—	739	Mixed at room temp.	—	87	—
6.0	—	32.8	—	342	—		174	—	
3	—	7.68	—	50.6	445	In dark, $-36^\circ$	3	—	106
				43.7			8	—	94
					50	—	101		
	0.70	—	—	4.21	471	Mixed at room temp.	—	109	—
0.70	—	—	6.31	314	—		150	—	
4	—	7.68	—	6.50	299	In light, $-36^\circ$	14	—	145
							31	—	138
	0.40	—	—	3.79	298	Mixed at room temp.	—	142	—

In runs 1—3, the activity of nitrosyl chloride was determined in terms of silver chloride, in run 4 in terms of lead chloride.

for  $\text{C}_8\text{H}_{20}\text{NCl}$ : Cl, 21.4%), and decomposition, if it occurred, must have been very slight. The removal of nitrosyl chloride at  $100^\circ$  in a vacuum led to decomposition of both salts, as shown by very low chloride contents of the residues.

## DISCUSSION

The similar values (see Table) for the activity of the evolved nitrosyl chloride after various contact times, and their close agreement with those obtained by similar dilution of the active chloride with inactive sodium chloride, substantiate complete exchange within the time of separation. The method used almost certainly precludes exchange induced by the separation procedure. A photochemical path for exchange has been ruled out by work in the dark. Great care was taken to exclude moisture from the system to eliminate exchange paths involving water. These would probably be slow anyway as Burg and Campbell (*loc. cit.*) found that the reaction between water and nitrosyl chloride is slow at room temperature, and that the water can be recovered from the mixture.

Complete exchange, as evidence for self-ionisation in any solvent system, is complicated by the fact that usually an alternative path can account for the transfer of labelled atoms between solvent and solute. In the case of liquid ammonia, for example, the exchange of ammonium chloride containing  $^{15}\text{N}$  with the solvent can be explained as well by a direct proton transfer,  $^{15}\text{NH}_4^+ + \text{NH}_3 \rightleftharpoons ^{15}\text{NH}_3 + \text{NH}_4^+$ , as by ionisation of the ammonia. In addition, in liquid ammonia traces of water could interfere with the interpretation of the results, since water in a concentration of only  $1 : 10^7$  in liquid ammonia gives a detectable quantity of ammonium ions *via* the fast reaction  $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$  (Ogg, *J. Chem. Phys.*, 1954, **22**, 560). Similar ambiguity will exist for other protonic solvents. In addition, the exact mode of ionisation of the solute must be known; the absence of exchange of thionyl compounds in liquid sulphur dioxide could arise from incomplete ionisation, *e.g.*,  $\text{SOCl}_2 \rightleftharpoons \text{SOCl}^+ + \text{Cl}^-$ , provided the ion  $\text{SOCl}^+$  did not exchange with the solvent.

In the case of non-protonic solvents the alternative to a self-ionisation path for exchange involves transfer of a heavier particle, *e.g.*, an oxide ion in the cases of sulphur dioxide (cf. Johnson, Norris, and Huston, *J. Amer. Chem. Soc.*, 1951, **73**, 3052) and dinitrogen tetroxide, although this seems less probable than a proton transfer. Favouring this idea with the sulphur

dioxide system is the fact that there is an affinity of sulphite ion for sulphur dioxide, normal sulphites being converted by liquid sulphur dioxide into the metabisulphite. The activated complex for the oxide ion transfer reaction will have to contain the sulphur atoms in equivalent positions, *viz.*,  $\left[ \begin{array}{c} \text{O} \\ \diagup \text{S} \cdots \text{O} \cdots \text{S} \diagdown \text{O} \\ \text{O} \end{array} \right]^{2-}$  which is not the usual arrangement of this assortment of atoms in the metabisulphite ion, namely,  $\left[ \begin{array}{c} \text{O} \\ \diagup \text{S} \text{---} \text{S} \diagdown \text{O} \\ \text{O} \end{array} \right]^{2-}$  (Wells, "Structural

Inorganic Chemistry," Oxford, 1950, p. 332). That this is not an insuperable difficulty, however, is shown by the fact that although there is a rapid exchange between nitric oxide and nitrogen dioxide enriched with  $^{15}\text{N}$  (Liefer, *J. Chem. Phys.*, 1940, **8**, 301) and the activated complex must be  $(\text{O}-\text{N} \cdots \text{O} \cdots \text{N}-\text{O})$ , dinitrogen trioxide nevertheless has the unsymmetrical structure  $\left[ \begin{array}{c} \text{O} \\ \diagup \text{N}-\text{N}-\text{O} \\ \text{O} \end{array} \right]$  (d'Or and Tarte, *Bull. Soc. roy. sci. Liège*, 1953, **22**, 276).

Interaction between  $\text{NO}^+$  and  $\text{NOCl}$  is very likely in view of the acceptor and donor properties of these molecules. Solvation of the nitrosonium ion has been in fact established for the aluminium and ferric chloride addition compound (Burg and McKenzie, *loc. cit.*; Houtgraaf and De Roos, *Rec. Trav. chim.*, 1953, **72**, 963). The structure of the complex is  $[\text{:}\ddot{\text{O}}=\ddot{\text{N}}-\ddot{\text{Cl}}-\ddot{\text{N}}=\ddot{\text{O}}\text{:}]^+$  in which the nitrogen atoms are equivalent, and therefore complete exchange between labelled nitrosonium complexes and nitrosyl chloride would occur independently of self-ionisation.

Tetramethylammonium chloride has been shown by conductivity studies to dissolve in nitrosyl chloride to give chloride ions (Burg and McKenzie, *loc. cit.*). Exchange of the chloride ion *via* a nitrosonium ion transfer mechanism,  $^{36}\text{Cl}^- + \text{NOCl} \rightleftharpoons \text{NO}^{36}\text{Cl} + \text{Cl}^-$ , seems much less likely especially since *both* chloride ion and nitrosyl chloride are electron donors (see also Burg and Campbell, *loc. cit.*). The complete exchange observed is, however, in accordance with the self-ionisation  $\text{NOCl} \rightleftharpoons \text{NO}^+ + \text{Cl}^-$  put forward by Burg and his co-workers (*loc. cit.*).