28. *Chemistry of Nitrosyl Complexes. Part II.* Exchange of* ^{36}Cl *between Nitrosyl Chloride and Some Insoluble Metal Chlorides.*

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The exchange of radioactive chlorine (^{36}Cl) between zinc, mercury, and cadmium chlorides on the one hand, and liquid nitrosyl chloride on the other, has been studied. Rapid exchange occurs between the absorbed nitrosyl chloride and the metal chloride, followed by a slow heterogeneous exchange with the excess of solvent. The results are considered to favour the formation of unstable nitrosonium salts of the metal chlorides. The path for the heterogeneous exchange is the decomposition of the nitrosonium salt, and in agreement with this no exchange was found when a stable nitrosonium salt, nitrosonium chlorostannate, or chlorides that do not form complexes with nitrosyl chloride, *e.g.*, sodium or potassium chloride, were studied. Silver chloride does not form a complex with the nitrosyl chloride, no exchange being observed in the dark, but a slow heterogeneous exchange occurs in the light.

Nitrosyl chloride forms the following addition compounds with metals of the last two sub-groups of the transition metals: CuCl,NOCl; $ZnCl_2$,NOCl; $AuCl_3$,NOCl; $HgCl_2$,NOCl. Cadmium and silver chlorides have not been reported to form compounds, and the nature of the bonding of the nitrosyl chloride in the copper, zinc, and mercury chloride complexes is not known. Asmussen [1] and previous workers consider that the zinc and mercury compounds are best represented as loose addition complexes, as the nitrosyl chloride may be removed completely by gentle heat or by applying a vacuum. Addison and Lewis [2] have suggested that they may be nitrosonium chloro-complexes involving a polymeric complex ion. In order to obtain information on the bonding in these complexes, and to determine if compound formation occurs with silver and cadmium chlorides, we have investigated the exchange of radioactive chlorine (^{36}Cl) between nitrosyl chloride and the metal chlorides. The easy removal of nitrosyl chloride from these complexes affords a ready method for the study of the equivalence of the chlorine atoms in the compounds.

Experimental

Preparation of Compounds containing ^{36}Cl.—Nitrosyl chloride (15 ml.), prepared as described in Part I,* was condensed directly on to approx. 0·2 g. of active tetramethylammonium chloride. Exchange was complete within the time of separation at −5° and the active nitrosyl chloride was distilled off.

Zinc chloride. Active nitrosyl chloride was condensed on to a block of zinc, suspended on a glass hook. The temperature was allowed to rise slowly from −40° to room temperature. The zinc block was removed and the yellow complex formed, $ZnCl_2$,NOCl, was heated on an oil-bath at 120° for 30 min., giving a white powder (Found: Zn, as quinaldinate, 47·9; Cl, 51·9. Calc. for $ZnCl_2$: Zn, 48·0; Cl, 52·0%).

Cadmium chloride. Cadmium carbonate (approx. 8 g.) was added to 10 ml. of 11N-hydrochloric acid containing 0·1 ml. of $H^{36}Cl$ till a neutral solution was obtained. The solution was evaporated on a water-bath, and on cooling crystals of $CdCl_2,H_2O$ separated, and were then [3] heated in a stream of nitrogen at 120—140° for 3 hr. (Found: Cl, 38·8. Calc. for $CdCl_2$: 38·7%).

Mercuric chloride. Excess of active nitrosyl chloride was condensed on to 0·5 g. of mercury at −40°, and the temperature allowed to rise slowly. The compound was treated with another portion of active nitrosyl chloride to ensure that there was no unchanged mercury present. The yellow $HgCl_2$,NOCl formed was heated on a water-bath for 30 min. to give mercuric chloride (Found: Cl, 26·10. Calc. for $HgCl_2$: Cl, 26·15%).

Silver chloride. Hydrochloric acid (10 ml., containing $H^{36}Cl$) was treated with excess of

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* Part I, *J.*, 1955, 56.

[1] Asmussen, *Z. anorg. Chem.*, 1939, **243**, 127.

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

[3] Cf. Lister and Sutton, *Trans. Faraday Soc.*, 1941, **37**, 406.

silver nitrate solution, and the precipitated silver chloride was centrifuged, washed with water, alcohol, and ether, and dried at 120° in a vacuum.

Sodium chloride and potassium chloride. Hydrochloric acid (2 ml., containing $H^{36}Cl$) was neutralised with 2·98N-sodium hydroxide and gently evaporated to dryness; the active sodium chloride was dried in a vacuum (P_2O_5) for 6 hr. at 120°. Active potassium chloride was similarly prepared.

Nitrosonium chlorostannate. Excess of active nitrosyl chloride was condensed on to redistilled stannic chloride (1·5 ml.) at $-30°$. The temperature was allowed to rise slowly to $-5°$. If any stannic chloride remained unchanged the product fumed in the air; further treatment with active nitrosyl chloride gave a yellow product, not fuming in the air [Found : Cl, 54·2. Calc. for $(NO)_2SnCl_6$: Cl, 54·3].

In the preparation of zinc chloride, mercuric chloride, and nitrosonium hexachlorostannate, moisture was rigidly excluded. The preparations were carried out in B14 flasks fitted with guard tubes of phosphoric oxide. All the preparations were subsequently handled in a Towers Manipulator Box.

Exchange Runs.—Exchange runs were carried out essentially as described in Part I. A known weight of the metal chloride was added through a side-arm to liquid nitrosyl chloride, which was fractionally distilled into the exchange vessel to a calibrated mark. The liquid was stirred by manual magnetic stirring to ensure complete mixing. Known fractions of nitrosyl chloride were distilled from the exchange vessel after various time intervals. It was important in all experiments to use finely divided solids, as incomplete reaction was observed with coarsely powdered samples.

The activity of the samples was determined by precipitating the chloride as silver chloride and matting this to infinite thickness on G.E.C. 1·5-cm. planchets. Allowance was made for the background count.

The initial activity of the metal chloride was found by hydrolysing the compound in dilute aqueous sodium hydroxide and precipitation of the chloride as silver chloride; the final activity was obtained from the metal chloride remaining in the exchange vessel after all excess of nitrosyl chloride had been removed.

In the heterogeneous studies, it was found more accurate to use active metal chloride, and determine the rate of attainment of activity of the nitrosyl chloride. Use of active nitrosyl chloride and determination of the rate of fall in activity usually involved small changes, as a large excess of nitrosyl chloride was employed in the experiments.

RESULTS AND DISCUSSION

All the metal chlorides except auric chloride are insoluble in liquid nitrosyl chloride. Therefore the exchange reactions with nitrosyl chloride may be considered in two parts : (*a*) the exchange of the combined nitrosyl chloride with the metal chloride, (*b*) the heterogeneous exchange of the chloride, or addition complex if formed, with the liquid nitrosyl chloride. Exchange of the chloride in the copper complex was not carried out, as the compound decomposed very rapidly to a mixture of cuprous and cupric chloride, even in the absence of light.

Table 1 contains typical values for the exchange of nitrosyl chloride with the metal

TABLE 1. *Exchange of nitrosyl chloride with zinc, mercury, cadmium, and silver chlorides.* (Temp. —15°).

Metal chloride	Expt. no.	Required for 1 : 1 compound (counts/min.)	Found (counts/min.)	Time of contact (min.)
$ZnCl_2$	(i)	570	565	263
	(ii)	821	808	44
	(iii)	240	234 *	5
	(iv)	570	541	5 (in dark)
$HgCl_2$	(i)	399	320	30
	(ii)	524	500 *	5
	(iii)	634	616	5 (in dark)
$CdCl_2$	(i)	186	250	5
	(ii)	300	340	5 (in dark)
AgCl	(i)	270	400	90 (in dark)

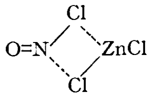
* Using active NOCl and inactive complex.

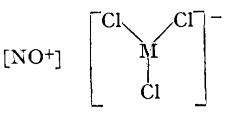
chlorides. The change in activity of chloride in zinc and mercury chlorides agrees with the formation of a 1 : 1 complex, in which the chlorine rapidly exchanges with the combined nitrosyl chloride. After allowance has been made for the heterogeneous exchange, by determining the activity of the supernatant nitrosyl chloride, values of the exchange showed that no higher complex than a 1 : 1 complex is formed during 6 hr.

The experiments with zinc and mercuric chloride in the dark showed that the exchange was not photochemical. Experiments were carried out using both active metal chloride and active nitrosyl chloride. The change in activity corresponded to partial compound formation in the case of cadmium chloride, but no compound formation with silver chloride for reactions carried out in the dark. If a 1 : 1 complex is assumed with cadmium chloride and nitrosyl chloride, a 60% conversion into the complex occurs; this incomplete formation may be associated with the protective nature of the film formed when metallic cadmium react with nitrosyl chloride. Zinc and mercury react rapidly to form the metal chloride–nitrosyl chloride complex, but the reaction with cadmium is very quickly inhibited by the formation of a protective film of chloride over the metal surface. We were not able to isolate any compound with cadmium chloride, for the nitrosyl chloride is completely removed from the product on standing at room temperature.

The rapid exchange indicates that the nitrosyl chloride is combined with the metal chloride and does not correspond to a physical absorption of the gas into chloride lattice. The complex may be formulated as (I) or (II). Structure (I) would give a fall of 25% in the activity of the metal chloride, and to account for the observed fall of *ca.* 33% would require the breaking and formation of a number of zinc–chlorine bonds. The complex involves the bonding of two chlorine atoms to a nitrogen atom which, as discussed in Part I, is considered unlikely. The change in activity is readily explained by structure (II), in which a nitrosonium compound is formed. The complexes would then correspond to nitrosyl chloride complexes of many other metal chlorides, which have been established as nitrosonium chloro-complexes.[4]

(I)





(II)

The ions $(ZnCl_3)^-$, $(CdCl_3)^-$, and $(HgCl_3)^-$ have been established in melts of alkali-metal chlorides with the corresponding metal chloride.[5] The stability of the compounds is found to depend upon the radius of the alkali-metal ion. No complexes are formed with lithium chloride, but sodium chloride gives a compound with an incongruent melting point, and potassium, rubidium, and ammonium chlorides give compounds with a congruent melting point. The radius [6] of the nitrosonium ion is 1·40 Å, compared [7] with potassium 1·33 Å and rubidium 1·48 Å; hence, from these considerations compound formation to give the $(MCl_3)^-$ ion is possible.

The ion $(MCl_3)^-$ is polymeric in structure, with each metal atom surrounded by six chloride ions, *i.e.*, a distorted perovskite structure.[8] The $(MCl_3)^-$ ion which occurs in aqueous solution is presumably tetrahedral in structure, the fourth position being occupied by a water molecule, as these complexes are usually monohydrated. In agreement with this polymeric structure of the $(MCl_3)^-$ ion is the insolubility of the complexes in liquid nitrosyl chloride. This formulation of the complex is also related to the behaviour of zinc and mercury chloride in other chloro-solvent systems. With strong chloro-donor compounds insoluble complexes are formed; *e.g.*, with phosphorus pentachloride. Groeneveld [9] has isolated 1 : 1 complexes which have been shown to be salts, $(PCl_4)^+(MCl_3)^-$.

Heterogeneous Exchange.—In addition to the exchange of the combined nitrosyl chloride

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[4] Addison and Lewis, *Quart. Rev.*, 1955, **9**, 115.

[5] Belyaev and Mironov, *Zhur. obschei Khim.*, 1952, **22**, 1734; Bloom and Heymann, *Proc. Roy. Soc.*, 1947, *A*, **188**, 392.

[6] Ketelaar and Palmer, *J. Amer. Chem. Soc.*, 1937, **59**, 2629.

[7] Wells, " Structural Inorganic Chemistry," Oxford, 2nd edn., 1950, p. 70.

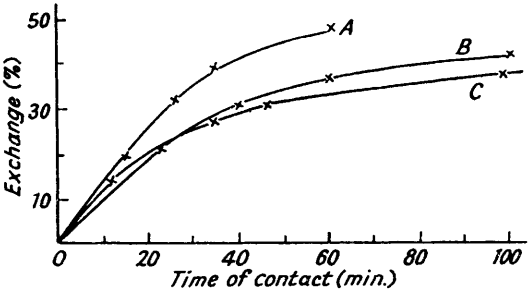
[8] *Idem, op. cit.*, p. 290.

[9] Groeneveld, *Rec. Trav. chim.*, 1952, **71**, 152.

with the metal chloride, a slow heterogeneous exchange occurs between the solvent and the complex. Values for this exchange are shown in the figure. The percentage exchange for the cadmium complex was calculated on the assumption of 100% compound formation, so the actual values are in excess of those shown. The rates of the reactions were found to depend on the degree of division of the solids, and were not photochemical. A possible path for the exchange is the formation of the addition complex with exchange of the chlorine atoms, as discussed above, followed by dissociation of the complex and slow transference of the activity to the solution.* When chlorides which did not form complexes with nitrosyl chloride, or which formed very stable nitrosonium chloro-complexes, were studied, no exchange was observed with liquid nitrosyl chloride. Table 2 gives the values of the exchange for sodium and potassium chloride and for nitrosonium chlorostannate, which is the most stable nitrosyl chloride addition compound known[10] and has been shown by Klinkenberg[11] to be a true salt. Thus the dissociation to nitrosyl chloride, responsible for the exchange with the zinc, cadmium, and mercury chlorides, will not occur. In the case of hydrogen chloride and stannic chloride, however, rapid exchange of chloride has been observed for solid, liquid, and gaseous stannic chloride with gaseous hydrogen chloride;[12] the complex, $SnCl_4,2HCl$, is very unstable and readily dissociates and forms an obvious path for the exchange.

TABLE 2. *Exchange of nitrosyl chloride with metal chlorides.*

Compound	Temp.	Time of contact (min.)	Activity of NOCl for 100% exchange (counts/min.)	Activity of NOCl (counts/min.)
NaCl	−10°	240	210	3
	−10	310	342	0
KCl	−20	360	197	2
$[NO]_2^+[SnCl_6]^{=}$	−20	90	410	3
	−15	303	205	0



Heterogeneous exchange between solvent and complex.

A, $CdCl_2,NOCl$.
B, $HgCl_2,NOCl$.
C, $ZnCl_2,NOCl$.

Silver chloride was found to exchange with liquid nitrosyl chloride in the presence of light, but no exchange was observed in the dark (see Table 1). The photochemical decomposition of silver chloride and nitrosyl chloride is the probable path of the exchange reaction.

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* These differences in the rate of reaction of heterogeneous systems may be accounted for alternatively by changes in the nature and area of the surfaces of the solids.

[10] Whynes, Thesis, London, 1948.

[11] Klinkenberg, *Rec. Trav. chim.*, 1937, **56**, 749.

[12] Howald and Willard, *J. Amer. Chem. Soc.*, 1955, **77**, 2046.