631. *The Liquid Dinitrogen Tetroxide Solvent System. Part X.* The Reaction of Zinc with Liquid Nitrosyl Chloride–Dinitrogen Tetroxide Mixtures.*

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Rates of reaction of metallic zinc with solutions of nitrosyl chloride in dinitrogen tetroxide have been determined at 0° over the 0—40% nitrosyl chloride concentration range. The rate of reaction in a nitrosyl chloride solution is less than in a solution of dinitrogen trioxide of equivalent concentration, although this position is probably reversed at high concentrations. Over the major portion of the concentration range the rate of reaction is proportional to the square of the nitrosyl chloride concentration, and measurement of the electrical conductivities of the solutions supports the deduction that reaction with zinc takes place on impact of nitrosyl chloride molecules (rather than NO^+ ions) at the metal surface. In the 0—10% concentration range the increase in rate of reaction is more rapid; this may be due to an increase in the rate of the zinc–dinitrogen tetroxide reaction in a medium of higher dielectric constant.

The product of reaction, at concentrations up to about 85%, is a mixture of the compounds $Zn(NO_3)_2,2N_2O_4$ and $ZnCl_2,NOCl$. Above 85% of nitrosyl chloride, only the latter compound is obtained. This arises from the operation of the equilibrium

$$Zn(NO_3)_2 + NOCl \rightleftharpoons ZnCl_2 + N_2O_4$$

Evidence for the formulation of the compound $ZnCl_2,NOCl$, in the dimeric form in which the zinc ion is 4-co-ordinated, is considered. This is correlated with the existence of a compound $ZnCl_2,NOCl,N_2O_4$, stable over a narrow range of temperature.

Some preliminary experiments on the reaction between zinc and solutions of nitrosyl chloride in liquid dinitrogen tetroxide were reported in Part I (*J.*, 1949, S 211). The addition of nitrosyl chloride to the liquid tetroxide was observed to increase the rate of reaction, and two alternative mechanisms were postulated : (*a*) The addition of nitrosyl chloride may increase the concentration of NO^+ ions (the " solvent cations ") and reaction may involve electron transfer from the zinc atom to the NO^+ ion. (*b*) Reaction may occur as a result of collision of NOCl molecules with the metal surface.

The experiments described below were carried out in an attempt to determine which of these two mechanisms is the more probable. The increase in reaction rates and electrical conductivity produced on addition of nitrosyl chloride are of the same order as those produced by equivalent concentrations of dinitrogen trioxide. However, the product of reaction involving dinitrogen trioxide is the same compound $Zn(NO_3)_2,2N_2O_4$ as is formed with the pure

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* Part IX, preceding paper.

tetroxide, whereas the product of reaction with nitrosyl chloride solutions contains the compound $ZnCl_2,NOCl$, and the mechanisms of the two reactions appear to be quite different.

RESULTS AND DISCUSSION.

Rate of Reaction.—The variation in rate of reaction of zinc with concentration of nitrosyl chloride is shown in Fig. 1 (curve *A*) for the 0—40% concentration range at 0°. The slope of curve *A* shows a continual increase with increasing nitrosyl chloride concentration, compared with the decreasing slope obtained in dinitrogen trioxide solutions (Part IX, preceding paper) and the curves for the two solutes are therefore different in character. In a solution of nitrosyl chloride of concentration 8 g.-mols./l., the rate of reaction is 5 times that with the pure tetroxide, compared with an 8-fold increase for a corresponding concentration of dinitrogen trioxide. The maximum concentration (about 40%) employed in the present measurements was determined by the stability of the liquid mixtures at 0°, but the form of the curves indicates that (under experimental conditions so adjusted that the full concentration range could be used) the rate of reaction with nitrosyl chloride solutions would exceed the rate with dinitrogen trioxide solutions at higher concentrations.

FIG. 1.

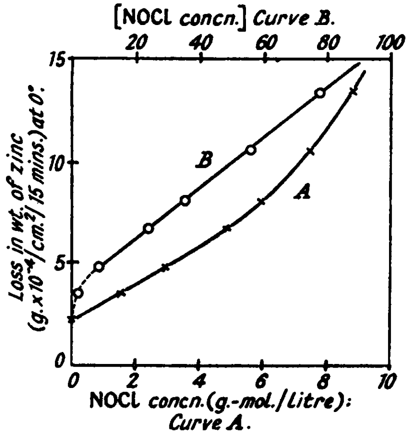
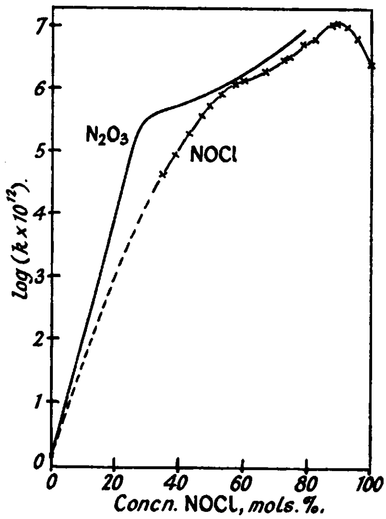


FIG. 2.



Curve *B* (Fig. 1) shows that linear relation exists between the rate of reaction and the square of the nitrosyl chloride concentration, for concentrations greater than about 2·4 g.-mols./l. (10%). The rate of reaction *R* may be represented by the expression

$$R = k[\mathrm{Zn}][\mathrm{NOCl}]^2 + k_1$$

The factor [Zn] is a constant since *R* is referred to unit area, and k_1 represents the contribution to the total rate of reaction made by the zinc–dinitrogen tetroxide reaction. In view of the linearity between *R* and $[NOCl]^2$, it appears that over the major portion of the concentration range it is unnecessary to consider as significant any mechanism other than that represented by the equations

$$\mathrm{Zn} + 2\mathrm{NOCl} \longrightarrow \mathrm{ZnCl_2} + 2\mathrm{NO} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

followed by

$$\mathrm{ZnCl_2} + \mathrm{NOCl} \longrightarrow \mathrm{ZnCl_2,NOCl}$$

Reaction is therefore considered to occur on impact of two nitrosyl chloride molecules at a zinc atom, rather than in a step-wise manner. In view of the experimental data, the reaction cannot be considered as occurring between the zinc atom and two NO^+ ions unless the degree of dissociation of the NOCl molecule into NO^+ and Cl^- ions is independent of nitrosyl chloride concentration. Such a condition is most unlikely in this system in view of the variation in dielectric constant of the medium with concentration.

At low concentrations (in the 0—2·4 g.-mol./l. range) represented by the broken portion of curve *B* (Fig. 1) the rate of reaction increases more rapidly than is required by equation (1).

There is no reason to doubt that the above mechanism is operative at low concentrations also, but in addition a further factor (which is either absent or negligible at high concentrations) increases the reaction rate by an amount which is clearly apparent at small reaction rates. Line *B*, when extrapolated, meets the rate axis at 3·80 × 10^{-4} g./cm.^{2}/15 minutes, compared with 2·25 × 10^{-4} for the zinc–pure tetroxide reaction. It is probable that the difference between these two rates finds explanation in the influence which the presence of nitrosyl chloride has on the zinc–tetroxide reaction. In Part VIII (*J.*, 1951, 2833) it has been postulated that this reaction takes place (at 0°) between zinc atoms and $[NO^+][NO_3^-]$ ion pairs. The equilibrium

$$N_2O_4 \rightleftharpoons 2NO_2 \rightleftharpoons [NO^+][NO_3^-] \rightleftharpoons NO^+ + NO_3^-$$

will be displaced towards the right-hand side by addition of a liquid which increases the dielectric constant of the medium. The dielectric constant of liquid nitrosyl chloride is 18·2 at 12° (Ketelaar, *Rec. Trav. chim.*, 1943, **62**, 289), and its addition to dinitrogen tetroxide ($\varepsilon = 2{\cdot}42$) will therefore result in an increase in the concentration of ion-pairs and/or free ions. Against this, any dissociation of nitrosyl chloride to give NO^+ and Cl^- ions would displace the above equilibrium to the left. In the case of nitrosyl chloride the net effect is a small displacement of the equilibrium to the right-hand side. When the two influences referred to above are complementary (as in the case of dinitrogen trioxide solutions) rather than opposed, a considerable increase in the rate of the zinc–dinitrogen tetroxide reaction results.

Reaction with Iron.—It is of interest to compare the behaviour of iron in nitrosyl chloride–dinitrogen tetroxide mixtures with that of zinc. Iron reacts very slowly with dilute solutions of nitrosyl chloride, but reaction is rapid in 50% solution. Although an accurate reaction rate–concentration curve corresponding to curve *A* (Fig. 1) has not been obtained for iron, observation of the reaction over a range of nitrosyl chloride concentration suggests that the curve would be of the same form as curve *A*, but would follow a cube rather than a square law with respect to concentration, as required by the reaction $Fe + 3NOCl = FeCl_3 + 3NO$.

Electrical Conductivities.—The specific conductivities of liquid mixtures of nitrosyl chloride and dinitrogen tetroxide (determined at −10°) are shown in Fig. 2. The specific conductivity of pure nitrosyl chloride was found to be 2·73 × 10^{-6} ohm^{-1} cm.$^{-1}$ at −10°, in good agreement with Burg and Campbell's value of 2·88 × 10^{-6} ohm^{-1} cm.$^{-1}$ at −20° (*J. Amer. Chem. Soc.*, 1948, **70**, 1964). The general form and position of the conductivity curve indicate that no appreciable ionisation takes place in the system. The small increase in conductivity which occurs on addition of dinitrogen tetroxide to nitrosyl chloride is probably due to ionisation of the tetroxide, but the maximum specific conductivity does not exceed 10^{-5} ohm^{-1} cm.$^{-1}$. Conductivity values for this system therefore support the deduction that the reaction of zinc takes place on impact with nitrosyl chloride molecules rather than with NO^+ ions produced by ionisation of the NOCl molecules. The conductivity curve for dinitrogen trioxide–tetroxide mixtures is superimposed in Fig. 2 for comparison. The curve is similar in form, and range, to the nitrosyl chloride curve, but the increase in conductivity on addition of the solute to the tetroxide is more rapid in the case of dinitrogen trioxide. This may reflect the relative dieletric constants of the trioxide and nitrosyl chloride.

Products of Reaction.—When zinc is added to a mixture of nitrosyl chloride and dinitrogen tetroxide, the simultaneous reactions occurring may be summarised as follows :

$$(a)\quad Zn + 2NOCl = ZnCl_2 + 2NO \qquad (b)\quad Zn + 2N_2O_4 = Zn(NO_3)_2 + 2NO$$
$$ZnCl_2 + NOCl = ZnCl_2,NOCl \qquad Zn(NO_3)_2 + 2N_2O_4 = Zn(NO_3)_2,2N_2O_4$$

Since the extrapolation of line *B* (Fig. 1) passes through the rate axis at a point above that representing the tetroxide reaction alone, it was to be expected that the product of reaction for mixtures of nitrosyl chloride and dinitrogen tetroxide of any composition would be a mixture of $ZnCl_2,NOCl$ and $Zn(NO_3)_2,2N_2O_4$. The product was obtained by adding a block of pure zinc (about 5 g.) to 20 ml. of the liquid at 0°. About 0·2—0·6 g. of product was formed in ten hours according to the concentration. The excess of liquid was decanted, the zinc block removed, and the nitrosyl chloride and dinitrogen tetroxide adhering to the solid were allowed to evaporate at room temperature; the product then remained as a very pale yellow crystalline mass. For nitrosyl chloride concentrations up to about 85%, the product was found to contain chloride and nitrate. When heated gently, the crystals evolved dinitrogen tetroxide, and softened to a yellow pasty mass. On being heated further, nitrosyl chloride was evolved, and when gas evolution ceased, the remaining solid was shown to be a mixture of zinc chloride and zinc nitrate. The properties of the product were therefore consistent with its formulation as a mixture of the compounds $ZnCl_2,NOCl$ and $Zn(NO_3)_2,2N_2O_4$. As the nitrosyl chloride content of the reaction mixture increased within the 0—85% range, the proportion of $ZnCl_2,NOCl$ in the product also increased; this is illustrated in the following table:

Initial NOCl concn. (%) in reaction mixture ...	0	13	36	45·4	78	90	100
Chloride content of product, %	0	19·8	28·2	27·0	44·3	52·7	52·7

Prolonged keeping of the reaction mixture during preparation of the product led to some decrease in the nitrosyl chloride content. This no doubt accounts for the slight discrepancies in the above table, but there is clearly a trend towards a high chlorine content in the product.

The product obtained from reaction mixtures containing more than about 85% of nitrosyl chloride could not be distinguished from the compound $ZnCl_2,NOCl$ (chloride content 52·7%). There are two reasons for this. First, the proportion of this compound formed is a function of the square of the nitrosyl chloride concentration, so the proportion of nitrate formed will become very small. Secondly, the following reaction between products and reacting liquid can take place in either direction according to conditions:

$$Zn(NO_3)_2 + 2NOCl \rightleftharpoons ZnCl_2 + 2N_2O_4 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

At high nitrosyl chloride concentrations, the equilibrium will be displaced to the right, and the zinc nitrate initially formed by reaction of zinc with the tetroxide will therefore be converted into chloride. In the dinitrogen tetroxide solvent system the forward reaction (equation 2) becomes an acid–base reaction, and the reverse reaction is an example of solvolysis. The validity of the equilibrium represented by equation (2) has been established as follows.

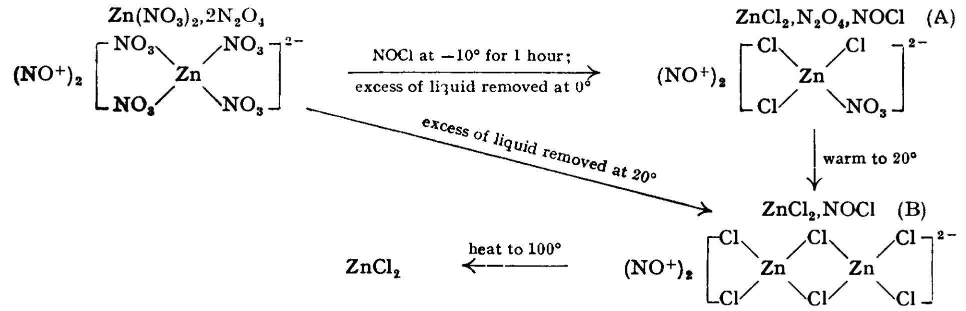
Zinc Nitrate–Nitrosyl Chloride Reaction.—About 1 g. of the crystalline compound $Zn(NO_3)_2,2N_2O_4$ was treated with 15 ml. of pure nitrosyl chloride for 1 hour at −10°. The temperature was then allowed to rise to about 20°; nitrosyl chloride and dinitrogen tetroxide evaporated, leaving a free-flowing white powder, which was shown to be the compound $ZnCl_2,NOCl$.

Zinc Chloride–Dinitrogen Tetroxide Reaction.—Pure zinc chloride was obtained from the compound $ZnCl_2,NOCl$ by heating it to remove nitrosyl chloride. About 0·5 g. of zinc chloride was treated with 10 ml. of liquid dinitrogen tetroxide at 20°. The liquid rapidly developed a red coloration due to nitrosyl chloride. After several hours the liquid was allowed to evaporate, and the resulting solid product analysed. The chlorine content was 11·93%; the product at this stage being assumed to be a mixture of the compound $ZnCl_2,NOCl$ and $Zn(NO_3)_2,2N_2O_4$ this chlorine content is equivalent to a zinc content of 20·96%. Analysis gave Zn, 21·16%. By this single treatment approximately half of the chlorine originally present as zinc chloride was removed as nitrosyl chloride. Successive treatments with dinitrogen tetroxide reduced the chlorine content of the product, and after six such treatments the product was converted completely into the compound $Zn(NO_3)_2,2N_2O_4$. A similar reaction took place when the compound $ZnCl_2,NOCl$ was employed instead of zinc chloride.

The above experiments indicate that, although equation (2) is completely reversible under appropriate conditions, the forward (or acid–base reaction) occurs more completely than the reverse (or solvolytic) reaction. The equilibrium (equation 2) favours the formation of zinc chloride, and in consequence the product obtained from mixtures containing a high concentration of nitrosyl chloride contains no detectable quantity of nitrate.

Structure of the Compound $ZnCl_2,NOCl$.—The empirical formula for this compound, first determined by Sudborough (*J.*, 1891, **59**, 655), has been confirmed by Asmussen (*Z. anorg. Chem.*, 1939, **243**, 127), by Partington and Whynes (*J.*, 1948, 1952), and in the present work. Asmussen regards the compound as a loose addition compound (analogous to $HgCl_2,NOCl$ and $AlCl_3,NOCl$), since nitrosyl chloride may be removed as such by gentle heat. However, the $ZnCl_2 : NOCl$ ratio of 1 : 1 is so clearly defined that it is permissible to consider a possible structure for the compound. The more stable addition compounds of metallic chlorides with nitrosyl chloride have for some time been accepted as nitrosyl compounds; Klinkenberg (*Rec. Trav. chim.*, 1937, **56**, 749; *Chem. Weekblad*, 1938, **35**, 197) has shown by crystallographic methods that the compounds $SnCl_4,2NOCl$ and $PtCl_4,2NOCl$ are isomorphous with $(NH_4)_2[SnCl_6]$ and $(NH_4)_2[PtCl_6]$ respectively, and should therefore be formulated as $(NO^+)_2[SnCl_6]^{2-}$ and $(NO^+)_2[PtCl_6]^{2-}$. The formulation of the compound $ZnCl_2,NOCl$ as a nitrosyl compound should not be dismissed on the grounds of lower stability alone, since it is well known that the stability of co-ordination complexes varies widely with the metal involved. The compound $AlCl_3,NOCl$ is of a lower order of stability than the corresponding platinum and tin compounds, and is dismissed by Asmussen (*loc. cit.*) as a loose addition compound, but Burg and Campbell (*loc. cit.*) have observed this compound to be a strong electrolyte in solution in pure nitrosyl chloride, and formulate it as $(NO^+)[AlCl_4]^-$. The stability of the compound $ZnCl_2,NOCl$ is of a similar order to that of the aluminium compound. However, the formulation of the complexes mentioned above as nitrosyl salts of chloro-complexes involves the use of co-ordination numbers for aluminium, tin, and platinum which are known to be characteristic of these metals; the corresponding structure for the zinc complex, *i.e.*, $(NO^+)[ZnCl_3]$, involves 3-co-ordination, whereas the formation of two linear *s–p* bonds, or four tetrahedral *s–p*^{3} bonds is predominant in the co-ordination chemistry of zinc. Many compounds of empirical formula $MZnCl_3$ are known, where M is a univalent metal ion. Since M may also be ½Mg or ½Ba (Partington, " General and Inorganic Chemistry," Macmillan, 1947, p. 388), these solids are to be considered as composed of essentially ionic crystals, or in the dimeric form $M_2[Zn_2Cl_6]$. The former appears to be the more probable alternative for these metal salts, but the chemistry of the compound $ZnCl_2,NOCl$ provides some evidence for considering that the zinc is in a 4-co-ordinate complex, and therefore that the molecule may be a dimer.

In the zinc nitrate–nitrosyl chloride reaction discussed above, the warming of the reaction mixture from –10° to 20° resulted in the formation of the compound $ZnCl_2,NOCl$. If this warming is carried out slowly, it is possible to detect an intermediate stage. The reactions are summarised below.



The removal of excess of liquid at 0° gave compound (A) as a very pale yellow, free-flowing powder, which was stable provided that the atmosphere of nitrosyl chloride and dinitrogen tetroxide was maintained. When the temperature was increased to about 20°, dinitrogen tetroxide (containing no more than a trace of nitrosyl chloride) was evolved, leaving compound (B). Compounds (A) and (B) were almost identical in appearance. The solid formed on heating (B) until evolution of nitrosyl chloride ceased was shown to be pure zinc chloride. In view of the ready evolution of dinitrogen tetroxide, (A) may be a simple lattice compound. On the other hand, when it is formulated as a nitrosyl compound as shown, the zinc ion is 4-co-ordinated, and the 4-co-ordination may be maintained on evolution of the tetroxide by representing compound (B) in the dimeric form as shown.

Burg and Campbell (*loc. cit.*) have shown that mononitrosyl salts (*e.g.*, $NO[AlCl_4]$, $NO[SbCl_6]$, and $NO[FeCl_4]$) are readily soluble in liquid nitrosyl chloride, whereas those dinitrosyl salts tested, $(NO)_2[SnCl_6]$ and $(NO)_2[TiCl_6]$, are quite insoluble. It is relevant that both compounds (A) and (B) are insoluble in liquid nitrosyl chloride, which is consistent with their formulation as dinitrosyl salts.

EXPERIMENTAL.

Preparation of Nitrosyl Chloride and Nitrosyl Chloride–Dinitrogen Tetroxide Mixtures.—These were prepared precisely as described in Part II (*J.*, 1949 S 218). The use of phosphoric oxide as a drying agent for nitrosyl chloride has been found to be undesirable unless the condensed product is given further purification by fractional distillation. When the calcium chloride drying tubes were replaced by a phosphoric oxide drying train, the nitrosyl chloride vapour appeared to react with the phosphoric oxide. Nitric oxide was produced, which dissolved in the condensed nitrosyl chloride, converting the colour of the liquid from blood-red to black.

Composition of Mixtures.—The composition of the reaction mixtures used was determined from the m. p., the liquidus curve given in Fig. 3, Part II (*loc. cit.*), being used. In the measurements of rate of reaction with zinc, the m. p. of the liquid was determined before and after each experiment. Since the b. p. of nitrosyl chloride (–5·5°) is appreciably higher than that of dinitrogen trioxide (–27·3°), solutions of nitrosyl chloride were more stable than solutions of the trioxide (see Part IX, preceding paper).

Rate of Reaction.—The experimental technique employed has been described in Part VIII (*loc. cit.*). Since preliminary experiments showed that the quantity of zinc reacting, per unit area, was proportional to the time of immersion during the first 15 minutes, rates of reaction recorded in Fig. 1 were determined for 15-minute immersion periods.

The reaction between zinc and dinitrogen tetroxide involves active species which are in equilibrium with the tetroxide (Part VIII, *loc. cit.*); provided that the metal surface is "wetted" by the tetroxide, the active species has direct access to the surface, and a stirring rate of 40 r.p.m. was found to be sufficient to disperse the trioxide produced by reaction. Similar conditions apply to dinitrogen trioxide–tetroxide mixtures (preceding paper). However, if the reaction with nitrosyl chloride solution involves impact of nitrosyl chloride molecules at the metal surface, it appeared possible that the products of reaction might present a barrier to the diffusion of nitrosyl chloride to the surface. The influence of stirring rate on the rate of reaction of zinc is given in the following table; the measurements were carried out at 0°, a 40·1% solution of nitrosyl chloride in dinitrogen tetroxide being used:

Stirring rate (revs. per min.)	0	10	108	150	250
Rate of reaction of zinc (g. × 10^{-4}/cm.^{2}/15 mins.)	8·4	9·0	13·5	13·5	13·3

The rate of reaction increases at first with increase in rate of stirring, whereas a decrease occurs with pure tetroxide. At stirring rates above 100 r.p.m. the rate of reaction is independent of stirring rate, and diffusion is not significant. The measurements recorded in Fig. 1 were carried out at 250 r.p.m.

Briner and Pylkoff's data (*J. Chim. physique*, 1912, **10**, 640) were used in the calculation of the density of $NOCl–N_2O_4$ mixtures.

Electrical Conductivity.—Specific conductivities were determined by means of a Mullard Measuring Bridge Type G.M. 4140/1, in conjunction with a Mullard Cell Type G.M. 4221. The liquid was contained in a 10 × 2·5 cm. Pyrex tube fitted with a B.24 ground-glass joint and a side-arm carrying a thermometer which dipped into the liquid. The electrode assembly (cell constant = 2·46) was fitted into a B.24 ground-glass cone, so that a closed system was maintained during measurement.

Analysis of Reaction Products.—(a) $ZnCl_2,NOCl–Zn(NO_3)_2,2N_2O_4$ *mixtures.* A weighed quantity of the solid, contained in a sealed tube, was hydrolysed by breaking the tube under the surface of excess of 0·1N-sodium hydroxide solution in a stout, stoppered bottle. The resulting solution was acidified with nitric acid and boiled to remove nitrous acid. Chlorine was then determined as silver chloride, and zinc gravimetrically as the 8-hydroxyquinoline complex [Found, for *compound* (A): Zn, 22·68. $ZnCl_2,N_2O_4,NOCl$ requires Zn, 22·3%. Found, for solid formed on heating (B): Zn, 48·02; Cl, 52·25. Calc. for $ZnCl_2$: Zn, 47·97; Cl, 52·03%].

(b) ZnCl,NOCl. This compound was hydrolysed, and chlorine and zinc determined in the acidified solution, as above. The nitrosyl chloride content was determined from the loss in weight on heating a sample of the compound to zinc chloride. The zinc content in the product remaining after evolution of nitrosyl chloride was determined by conversion into the nitrate by means of concentrated nitric acid, followed by ignition to zinc oxide [Found for compound (B): Zn, 32·2. Calc. for $ZnCl_2,NOCl$: Zn, 32·4%].

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