strong axial interaction with the central metal atom will shift the spectrum of either platinum(II) or palladium(II) complexes. Thus in the paper by Chatt, Gamlen and Orgel[24] on the spectra of platinum(II) complexes, the bands of $PtCl_4^{2-}$ with maxima at 3895 and 3290 Å. in water are assigned to the transition $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$, respectively. In the case of the corresponding bands of $Pt(\text{di-amylamine})_2Cl_2$ it was found that the first band was unaffected and the second was shifted to longer wave lengths in going from the solvent hexane to ethanol. Certainly the interaction with hexane is weaker than with ethanol, yet the shift in the spectrum is *opposite* in direction to the shifts found by Harris, Livingstone and Reece.[22] According to theory then, one could invert the order of solvent interactions given by them and say that $C_6H_5NO_2$ interacts most strongly and H_2O least strongly. Unfortunately the theory is not well enough established for such a statement, since it does not explain why both bands are shifted by approximately the same amount in the case of both the Pt(II) and Pd(II) halide complexes. Accordingly the interpretation of these spectra in terms of solvent interactions must be viewed with caution at present.

Acknowledgment.—H.B,G. was the recipient of a summer research fellowship given by E. I. du Pont de Nemours and Co., Inc.

EVANSTON, ILLINOIS

[24] J. Chatt, G. A. Gamlen and L. E. Orgel, *J. Chem. Soc.*, 486 (1958).

[CONTRIBUTION FROM THE RALPH G. WRIGHT LABORATORY, SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

Isotopic Exchange Reactions. VI. Halogen Exchange in the System BCl_3–$POCl_3$[1,2]

BY ROLFE H. HERBER

RECEIVED SEPTEMBER 26, 1959

The isotopic halogen exchange between $POCl_3$ and BCl_3 has been investigated with the use of Cl^{36} labelled reactants. While a rapid (complete within one minute) exchange is noted at 0° when $POCl_3$ is present in excess, as well as in an equimolar mixture of the two components, no halogen exchange is observed in an excess of BCl_3. These data are interpreted on the basis of a structure previously proposed for the addition compound in which the bonding is through the phosphoryl oxygen. A mechanism for the rapid halogen exchange in $POCl_3$ rich systems is suggested, which does not necessitate the formation of a free tetrachloroborate anion as proposed in earlier studies of halogen exchanges in BCl_3.

In a previous paper[3] in this series it has been pointed out that isotopic halogen exchange between BCl_3 and other chlorine containing chemical species should be observed under conditions when the tetrachloroborate anion can be formed as a reaction intermediate in kinetically significant concentrations. It was also suggested that the formation of this anion occurred in the system BCl_3–$(CH_3)_4NCl$ and gave rise to the rapid halogen exchange which was observed. In the present study, the halogen exchange between BCl_3 and $POCl_3$ has been investigated with a view toward elucidating the nature of the bonding in the addition compound formed from these two components.

The formation of a crystalline 1:1 addition compound with a melting point of ~71–73° obtained from BCl_3 and $POCl_3$ has been amply reported in the literature,[4] with however little agreement on the nature of the chemical bonding which is involved in its formation. Thus the early work of Gutmann[5] suggests that electron deficient compounds such as $AlCl_3$ form anions in $POCl_3$ and then undergo ionic metathesis, so that under these conditions the addition compound may be expected to have the structure $POCl_2^+ \; BCl_4^-$. Similarly, Greenwood and Wade[6] consider the formation of the addition compound between $POCl_3$ and $GaCl_3$ to occur by coördinate bond formation involving one of the phosphoryl chloride chlorine atoms as the donor. Further, these authors cite evidence that at equilibrium, some 99.5% of the reactants are present as the covalent addition complex and about 0.5% as a $POCl_2^+GaCl_4^-$ ion pair formed by chloride ion transfer from the former to the latter.

On the other hand the recent work of Sheldon and Tyree,[7] on the donor properties of $POCl_3$ and related compounds, suggests rather strongly that addition compound formation with solvates such as $AsCl_3$, $SnCl_3$ and $TiCl_4$ occurs *via* bonding through the oxygen atom. This view is supported by the observation that the P–O stretching frequency is shifted some 50–100 cm.$^{-1}$ relative to its value in the pure solvent, when compound formation is observed. Clearly, while the interpretation of this shift is not unambiguous, it suggests strongly that electron pair donation by the oxygen atom is probably taking place. This proposed bonding through the oxygen atom also has been suggested by Groene-

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[1] The experimental portions of this research were carried out under contract AT(11-1)-67, Project 19, between the U. S. Atomic Energy Commission and the University of Illinois in the W. A. Noyes Laboratory of Chemistry, University of Illinois.

[2] Presented in part as paper No. 610 at the XVIIth Congress of the International Union of Pure and Applied Chemistry, Munich, Germany, 1959.

[3] R. H. Herber, THIS JOURNAL, **80**, 5080 (1958).

[4] (a) Gustavson, *Z. Chem.*, **7**, 417 (1871); *Ber.*, **4**, 975 (1871); (b) A. B. Burg and M. K. Ross, THIS JOURNAL, **65**, 1637 (1943); (c) The formation of a crystalline addition compound between PCl_3 and BCl_3 has been reported by M. A. Stieber, *Compt. rend.*, **116**, 1524 (1893). However, this system has been investigated carefully from −78° to room temperature by R. R. Holmes (private communication) who finds no evidence for compound formation over this temperature range, so that Stieber's compound is probably the $POCl_3 \cdot BCl_3$ compound cited earlier by Gustavson.

[5] V. Gutmann, *Monatsh. Chem.*, **83**, 279 (1952); *Z. anorg. u. allgem. Chem.*, **270**, 179 (1952).

[6] N. N. Greenwood and K. Wade, *J. Chem. Soc.*, 1516 (1957).

[7] J. C. Sheldon and S. Y. Tyree, Jr., THIS JOURNAL, **81**, 2290 (1959).

veld[8] and by Lindqvist and his co-workers[9] and others. Indeed Gutmann and his co-workers[10] have recently accumulated further data which are consistent with bonding through the oxygen atom in the formation of solvates and addition compounds of $POCl_3$.

By studying the halogen exchange between BCl_3 and $POCl_3$ in an excess of either reagent as well as in the equimolar system, we have attempted to elucidate the bonding involved in the formation of the addition compound formed from these two halides.

Experimental

Boron Trichloride-Cl^{36}.—Radiochlorine labelled BCl_3 was prepared by exchange with chlorine-36 labelled tetramethylammonium chloride using the method described earlier.[3] Samples having a specific activity in excess of 500 c.p.m./cm. in the gas phase counting assembly used for all radioassays in this work[11] were routinely prepared.

Phosphorus Oxychloride.—Hooker Electrochemicals Co. $POCl_3$ was transferred to the vacuum line and after discarding generous head and tail fractions, a middle cut was distilled into ampoules containing purified mercury. These ampoules then were sealed off and stored in the dark for four to six weeks. During this time the two liquids were shaken periodically to ensure complete reaction of any chlorine with the mercury. The $POCl_3$ then was fractionally distilled into all-glass breakoff tip ampoules and stored in the dark until used.

Phosphorus Oxychloride-Cl^{36}.—Radiochlorine labelled $POCl_3$ was prepared by a modification of the method of Lewis and Sowerby,[12] taking advantage of the rapid heterogeneous exchange between $POCl_3$ and radiochlorine labelled tetramethylammonium chloride. The separation of labelled $POCl_3$ after exchange with BCl_3, although feasible as a method of obtaining the tagged compound, was less convenient than the above method and was not commonly used.

Exchange Run Procedure.—The experimental method used to follow the isotopic exchange kinetics was essentially that described earlier.[13] The two components were effectively separated for radioassay purposes by distilling off either the excess BCl_3 at 0° or the excess $POCl_3$ at room temperature. A number of determinations of possible incomplete separation of excess BCl_3 from labelled $POCl_3$ were made and showed that the apparent "zero time exchange" was not larger than 0.68% and was thus neglected. Since all of the exchange experiments were carried out at 0°, an ice-water bath in a high efficiency glass dewar was used to thermostat the reaction mixture. Liquid nitrogen was employed as a coolant to stop the reaction at the desired time.

Vapor Pressure Studies.—The determination of vapor pressures above the $POCl_3$–BCl_3 systems was carried out in the usual manner, special care being taken to prevent accidental transfer of the powdery addition compound to the manometer system during warmup. Again, in these experiments carried out at 0°, an ice-water bath was used as a thermostat and at least six pressure readings were taken at each composition point—half of these representing cooling to 0° and half representing warming to 0°. In general, good agreement between these two sets of pressure readings was obtained and only the average values are here reported.

Experimental Results

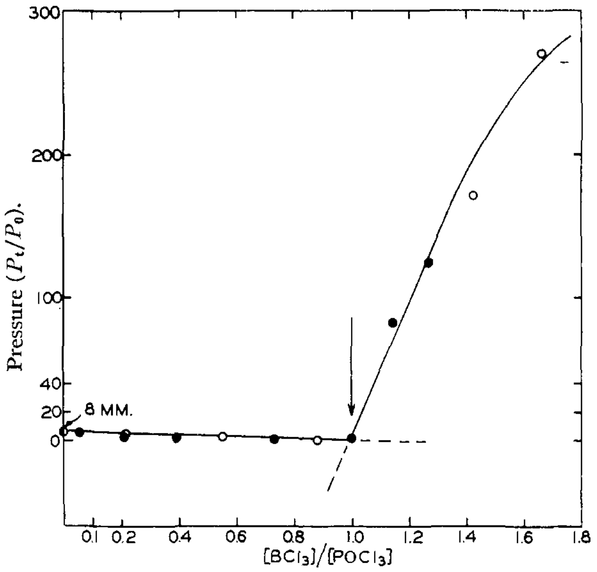

Fig. 1.—Vapor pressure–composition curve for the system BCl_3-$POCl_3$.

The Composition of the Addition Compound.—The results of the vapor pressure-composition studies are summarized in Fig. 1 in which the closed and open circles represent replicate runs and give an idea of the reproducibility of the data. Clearly there is a very well defined compound having a composition ratio of unity. The addition compound is a white solid which is not very soluble in an excess of either reagent, since a homogeneous solution could not be obtained either in a more than ten-fold excess of $POCl_3$ or a five-fold excess of BCl_3. When a cold finger containing an equimolar mixture of the two components—that is, the powdery dry solid—is warmed to room temperature, it is found that a small increase in pressure is noted and that buildup of the addition compound can be observed at an ice cooled position elsewhere in the vacuum system. Whether the addition compound itself sublimes or whether the transfer is effected through a prior dissociation into the two components was not directly determined, although secondary evidence indicated that dissociation into the components is taking place.

Exchange Run in an Excess of BCl_3.—In a typical exchange experiment, 2.41 mmoles of BCl_3 and 0.56 mmole of labelled $POCl_3$ were dosed into a reaction vessel and warmed to 0°. Periodically, BCl_3 samples were removed for gas phase radioassay and then returned to the reaction vessel which had meanwhile been maintained at liquid nitrogen temperature. No transfer of chlorine activity to the BCl_3 was noted in 43 hr. At the end of this interval, the two components were separated at −78° and the $POCl_3$ activity redetermined. The initial and final specific activities were identical within ±1.5%, in agreement with the observed absence of halogen exchange.

Exchange Run in an Excess of $POCl_3$.—In a typical exchange experiment, 0.56 mmole of BCl_3 and 1.11 mmoles of $POCl_3$ were handled as above. Complete halogen exchange within one minute was observed by noting the decrease in activity of the initially labelled $POCl_3$ to a value which agreed well with that calculated from an activity balance.

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(8) W. L. Groeneveld, *Rec. trav. chim.*, **75**, 594 (1956); *ibid.*, **76**, 1005 (1957).

(9) I. Lindqvist, *Acta Chem. Scand.*, **12**, 135 (1958); I. Lindqvist and C. I. Branden, *ibid.*, **12**, 134 (1958), I. Lindqvist, paper No. 608, XVIIth Congress IUPAC, Munich, 1959.

(10) V. Gutmann and M. Baaz, private communication. The author is very grateful to Prof. Gutmann and Dr. Baaz for making available to him a considerable amount of unpublished data relating to conductimetric studies in (dilute) phosphoryl chloride solutions.

(11) R. H. Herber, *Rev. Sci. Inst.*, **28**, 1049 (1957).

(12) J. Lewis and D. B. Sowerby, *J. Chem. Soc.*, 123 (1957).

(13) R. H. Herber and A. W. Cordes, *J. Chem. Phys.*, **28**, 361 (1958).

Exchange Run in the Equimolar System.—0.70 mmoles each of $POCl_3$ and labelled BCl_3 were dosed into a reaction vessel and handled as above. The first BCl_3 sample was isolated for counting after 1 minute by cooling the reaction vessel to −78° and distilling off the BCl_3 into a separate cold finger. The observed specific activity (58.7 c.p.m./cm.) agreed well with that calculated for complete exchange (58.0 c.p.m./cm.). Nine samples of BCl_3 isolated in an identical manner over a 1120 minute interval gave a specific activity ratio to that calculated for complete exchange from an activity balance of 0.954 ± 0.043.

From the above results it is clear that while in an excess of BCl_3 there is no halogen exchange between the addition compound and the solvent in 43 hr. at 0°, there is rapid exchange of the addition compound with excess $POCl_3$ and between the two components in an equimolar system.

Exchange Runs with Stepwise Variation of Concentration.—To clarify the above data further an exchange experiment was carried out in which the boron trichloride to phosphoryl chloride concentration ratio was varied in a stepwise manner from a value smaller than unity to a value in excess of unity. In a typical run, the reaction vessel was initially charged with 1.188 mmoles of labelled BCl_3 having a specific activity of 131.1 ± 1.0 c.p.m./cm.

$POCl_3$ then was added in a stepwise manner as summarized in Table I. The specific activity of the BCl_3 was determined in the usual manner after the system had been maintained at 0° for 5 minutes. From these data it is clear that while there is essentially no halogen exchange in the boron trichloride rich system, rapid halogen exchange is noted when the $POCl_3$ to BCl_3 ratio is unity or larger, in agreement with the earlier exchange runs at a single concentration ratio.

TABLE I

HALOGEN EXCHANGE BETWEEN $POCl_3$ AND LABELLED BCl_3 UNDER CONDITIONS OF STEPWISE VARIATION IN CONCENTRATION

$POCl_3$, mmole	$[POCl_3]/[BCl_3]$	Specific activity of BCl_3 Exp., c.p.m./cm.	Calcd. compl. exch., c.p.m./cm.
0.0	0.0	131.1	. . .
.332	.279	147.7	102.5
.359	.581	130.8	82.9
.332	.861	148.9	70.5
.166	1.00	56.9	65.6
.442	1.37	57.6	55.3
.553	1.84	53.5	46.2
.415	2.18	43.9	41.2

A similar experiment with chlorine-36 labelled $POCl_3$ and inactive BCl_3 was carried out to ensure that complete reversibility of the exchange system was obtained. This run is summarized in Table II and again shows no exchange of halogens in the BCl_3 rich system and rapid exchange in the $POCl_3$ rich system, with complete randomization of the tracer within 5 minutes at 0°.

TABLE II

HALOGEN EXCHANGE BETWEEN LABELLED $POCl_3$ AND BCl_3 UNDER CONDITIONS OF STEPWISE VARIATION IN CONCENTRATION

$POCl_3$, mmole	$[POCl_3]/[BCl_3]$	Specific activity of BCl_3 Exp., c.p.m./cm.	Calcd. for compl. exch., c.p.m./cm.
0.0	0.0	0.0	0.0
.628	.384	.198	7.51
.574	.735	.122	11.46
.219	.870	.267	12.57
.219	1.00	.442	13.55
.628	1.38	13.4	15.72
.574	1.73	16.8	17.18
.655	2.13	17.1	18.43

Discussion of Results

The absence of chlorine exchange between BCl_3 and $POCl_3$ in the BCl_3 rich systems clearly indicates that the bonding in the addition compound cannot be of the type $POCl_2^+ BCl_4^-$ since the tetrachloroborate anion so formed would immediately lead to halogen exchange due to the kinetic equivalence of the sp^3 bonded[14] chlorines in this species. It seems reasonable then, in view of the demonstrated stoichiometry of the addition compound, that the bonding is that suggested by Sheldon and Tyree,[7] Groeneveld,[8] Lindqvist[9] and others. In this structure the phosphoryl oxygen donates an unshared pair to complete the boron octet and presumably none of the six halogen atoms is directly involved in the bonding.

The observed exchange in $POCl_3$ rich systems must then be due to processes, characteristic of phosphoryl chloride as a solvent, which are unlikely—on the basis of energetic considerations—in boron trichloride solvent systems. The relatively high dielectric constant of $POCl_3$ (13.9 at 25°)[15] compared to that of BCl_3 (1.0 at 0°) suggests that ionic processes may occur much more readily in the former than in the latter solvent. On this basis it is suggested that in $POCl_3$ rich systems the observed rapid halogen exchange between the two components occurs by the mechanism

$$POCl_3 \rightleftarrows POCl_2^+ + Cl^- \qquad (1)$$

$$Cl^- + Cl_3{}^*BOPCl_3 \rightleftarrows [Cl_4{}^*BPOCl_3]^- \rightleftarrows Cl^{*-} + Cl_3BOPCl_3 \qquad (2)$$

The bracketed reaction intermediate may be envisioned as an activated complex configuration in which two chlorine atoms are both partially bonded to the central boron atom at one of the regular tetrahedral positions. The formation of a tetrachloroborate anion is thus not necessary to account for the observed exchange data. Indeed it is difficult to see how this ion could be formed *as such* in the $POCl_3$ rich system and not be involved in the addition compound formation in the BCl_3 rich system. The more facile scission of the boron–chlorine bond in passing through the suggested activated complex configuration is then presumably a reflection of the electron donating property of the coördinate bond, as well as of the change of structure of the boron adduct from a planar triangle to a tetrahedron. Finally, the very

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[14] H. A. Levy and L. O. Brockway, THIS JOURNAL, **59**, 2085 (1937).

[15] V. Gutmann, *Monatsh. Chem.*, **83**, 164 (1952). This paper summarizes a number of physical constants for $POCl_3$ and discusses the role of this liquid as an ionizing solvent.

rapid randomization of the chlorine activity in the $POCl_3$ rich systems is consistent with an ion-molecule interaction and may be taken as indicative of the rate with which equilibrium is established in (1) and (2), above, in the ionizing solvent $POCl_3$.[16]

Per contra, the absence of exchange in BCl_3 rich systems may be taken as a reflection of the fact that (a) most of the $POCl_3$ in the system is tied up as the addition compound and thus not available for participation in equilibrium 1; and (b) any free phosphoryl chloride is likely present as the undissociated molecule, since the solvent nature of boron trichloride is such as to repress the self ionization equilibrium on the one hand and to hinder the migration of free chloride ions through the solution (as required by (2)) on the other.

The observed rapid halogen exchange in a reaction system composed of an equimolar mixture of BCl_3 and $POCl_3$ is in consonance with the suggested mechanism, since the decomposition of the addition complex, and resultant evaporation of BCl_3 into the gas phase of the reaction vessel, leaves behind a phase which is rich in $POCl_3$ and in which the exchange then can occur as suggested. This decomposition of the addition compound into its components suggests relatively weak bonding in the coördinate bond, in agreement with the results obtained by Sheldon and Tyree.[7] These workers were able to show that while CCl_4 and $SiCl_4$ formed no addition compounds with $POCl_3$, both $AsCl_3$ and $SnCl_4$ formed "weak" compounds and $TiCl_4$ formed two "strong" compounds. On the basis of electronegativity considerations (C and Si ~2.5, B and As ~2.0, Sn ~1.7 and Ti ~1.6) the formation of a "weak" compound between BCl_3 and $POCl_3$ is thus not unexpected. The experimental observation in the present study that a clean separation between $POCl_3$ and BCl_3 could be obtained by distillation into a liquid nitrogen cooled trap of the volatile material evolved from the addition compound held at −78° is further evidence of this weak compound formation and is in qualitative agreement with the observations of Burg and Ross[4b] who showed that the addition compound dissociation has a ΔF^0_{298} of -4.6 kcal. mole^{-1} and that the vapor is some 89.5 to 91.2% dissociated.

A test of the proposed mechanism lies in the measurement of conductivities of dilute solutions of BCl_3 in $POCl_3$ and of $POCl_3$ in BCl_3. If the present suggestions are correct, the former should show the moderate conductance to be expected from the self ionization of $POCl_3$, *without however any increase due to the presence of the BCl_3 solute.* Any increase in conductivity above this value (aside from possible activity effects) would be at variance with our suggested mechanism and could be taken as an indication of the formation of tetrachloroborate anions. The dilute solutions of $POCl_3$ in BCl_3 solvent, on the other hand, should show essentially zero conductance if the present suggestions are valid. Conductimetric measurements of this type currently are being undertaken[17] and should shed further light on the nature of $POCl_3$ as an ionizing solvent.

The author is indebted to the Hooker Electrochemical Company for their generosity in providing samples of $POCl_3$ and to Professors P. E. Yankwich and A. Kuppermann for illuminating discussions of this work, as well as to Professor R. R. Holmes for preliminary data on possible compound formation in the PCl_3–BCl_3 system.

NEW BRUNSWICK, NEW JERSEY

[16] NOTE ADDED IN PROOF.—Baaz and Gutmann (*Monatsh.*, **90**, 426 (1959)) have suggested the equilibrium $Cl_5SbOPCl_3 \rightleftarrows SbCl_6^- + POCl_2^+$ to account for observed conductivities in liquid $POCl_3$. While such a step is not ruled out completely in the present instance, it is likely that the Cl^- ion in (2) originates from a solvent molecule dissociation rather than from transfer of a chloride ion from the addition compound $POCl_3$.

[17] In the laboratory of Professor V. Gutmann, Technische Hochschule, Vienna.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Acid Ionization Constants of Alcohols. II. Acidities of Some Substituted Methanols and Related Compounds[1,2]

BY P. BALLINGER AND F. A. LONG

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The acid ionization constants of twelve simple alcohols have been determined by a conductivity procedure for dilute solutions in water at 25°. The values of K_{HA} range from 5.8×10^{-13} for trichloroethanol to 3×10^{-16} for methanol and allyl alcohol. For several of the alcohols comparisons can be made of their relative acidities in water with the relative acidities reported by Hine and Hine for the solvent 2-propanol. The qualitative agreement is good. A plot of pK *versus* σ^* for the aqueous ionization of a set of simple substituted methanols leads to a straight line with slope $\rho^* = 1.4$. The data lead to an extrapolated pK value for ethanol in water of 15.9. Using this, the relative acidities of methanol, water and ethanol are found to be in the ratio 3:2:1 for the solvent water. Data also are given for ionization of two of the alcohols in deuterium oxide. The resulting K^H/K^D values of 4.5 for 2,2,2-trifluoroethanol and 4.9 for 2-chloroethanol fit in well with data for carboxylic acids and phenols.

A previous communication gave details of a conductivity procedure for determining ionization constants for uncharged acids with pH values in the range 10 to 16.[3] The method has been illustrated for ionization of the alcohols 2,2,2-trifluoroethanol and 2-chloroethanol in the solvents H_2O and D_2O.[3,4] The present paper gives results for a number of other alcohols, most of them simple substituted methanols.

In view of the importance of alcohols, it is not

[1] Work supported by a grant from the Atomic Energy Commission.

[2] Presented in part at Symposium on Electrolytes of the XLVIIth meeting of the Societa Italiana per il Progresso delle Scienze, Trieste, Italy, June 1959.

[3] P. Ballinger and F. A. Long, THIS JOURNAL, **81**, 1050 (1959).

[4] P. Ballinger and F. A. Long, *ibid.*, **81**, 2347 (1959).