59. *Exchange of Chlorine-36 between Chloride Ion and Phosphorus Oxychloride, Arsenic Trichloride, or Selenium Oxychloride.*

By J. LEWIS and D. B. SOWERBY.

Complete exchange has been observed within the time of separation between ionic chlorides (containing ^{36}Cl) and the solvents, phosphorus oxychloride, arsenic trichloride, and selenium oxychloride. A kinetic study of the exchange between labelled tetraethylammonium chloride and phosphorus oxychloride in chloroform, nitrobenzene, and acetonitrile indicates that exchange occurs by a bimolecular mechanism, being of the first order with respect to the phosphorus oxychloride and tetraethylammonium chloride. It is considered that in pure phosphorus oxychloride and arsenic trichloride the exchange between the ionic chloride and the solvent proceeds by the formation and dissociation of the ions $[POCl_4]^-$ and $[AsCl_4]^-$ rather than by a self-ionisation of the solvent.

IT has been postulated, to explain the properties of some solutions, that certain solvents undergo a limited degree of self-ionisation. For phosphorus oxychloride,[1] arsenic trichloride,[2] and selenium oxychloride [3] the following equilibria have been suggested:

$$POCl_3 \rightleftharpoons POCl_2^+ + Cl^-$$

$$AsCl_3 \rightleftharpoons AsCl_2^+ + Cl^-, \text{ followed by } Cl^- + AsCl_3 \rightleftharpoons AsCl_4^-$$

$$2SeOCl_2 \rightleftharpoons [SeOCl_2,SeOCl]^+ + Cl^-$$

As each ionisation involves the formation of a chloride ion, the addition of labelled chloride (^{36}Cl) to such systems should result in rapid exchange between the solute and the solvent, as occurs with nitrosyl chloride and tetraethylammonium chloride.[4]

Clusius and Haimerl [5] found a slow exchange of labelled chlorine with phosphorus oxychloride and hydrogen chloride, but that arsenic trichloride underwent complete exchange within the time of separation (1 hr.). The exchange between arsenic trichloride and chlorine has also been shown to be slow in carbon tetrachloride.[6] As these exchanges probably do not involve chloride ions, we have investigated the exchange of ^{36}Cl between chloride ion and these solvents.

EXPERIMENTAL

Phosphorus Oxychloride.—Phosphorus oxychloride was distilled to remove the bulk of hydrogen chloride and phosphoric acid, and refluxed over sodium wire for 4 hr. In the fractional distillation, after the sodium had been removed, the fraction boiling at 105·5° was collected.

Arsenic Trichloride.—Arsenic trichloride was refluxed with arsenic for 4 hr., then fractionally distilled. The middle fraction was kept over sodium wire for 2 days, then again distilled and the fraction of b. p. 130·0° was collected.

Selenium Oxychloride.—Selenium oxychloride was distilled; the middle fraction, b. p. 176·5°, was collected.

Compounds containing ^{36}Cl.—These were prepared and purified as described previously.[4]

Exchange Runs.—The apparatus used was similar to that described by Lewis and Wilkins [4] but modified to allow the liquid studied to be fractionally distilled directly into the exchange vessel. Exchange with phosphorus oxychloride was carried out with tetraethylammonium chloride, but tetramethylammonium chloride was used with arsenic trichloride as its solubility is the greater therein. Sodium and potassium chloride were used with selenium oxychloride.

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[1] Gutmann, *Monatsh.*, 1952, **83**, 164.

[2] *Idem, Z. anorg. Chem.*, 1951, **266**, 331.

[3] Smith, *Chem. Rev.*, 1938, **23**, 165.

[4] Lewis and Wilkins, *J.*, 1955, 56.

[5] Clusius and Haimerl, *Z. physikal. Chem.*, 1942, **51**, *B*, 347.

[6] Owen and Johnson, *J. Inorg. Nucl. Chem.*, 1956, **2**, 260.

Approx. 50 mg. of the appropriate active chloride were packed into a small glass tube, open at both ends, and added to the solvent in the exchange vessel through a vacuum tap. The liquid was stirred magnetically until dissolution was complete. After various times fractions of the solvent were removed by applying a vacuum; the solvent vapour was condensed by liquid oxygen. The activities of the samples were determined, after hydrolysis in sodium hydroxide solution, by precipitating the chloride as silver chloride and matting to infinite thickness on G.E.C. 1·5 cm. planchets.

Stability of Tetra-alkylammonium Chlorides.—To investigate the stability and state of the tetra-alkylammonium chlorides in the solvents, solutions of tetraethylammonium chloride in phosphorus oxychloride, and of tetramethylammonium chloride in arsenic trichloride, were prepared. Excess of solvent was removed under a vacuum at 18°, *i.e.*, in the same conditions applying in the exchange runs. In both cases white, crystalline, apparently homogeneous solids were obtained. Gutmann [2] found that, when excess arsenic trichloride was removed in a vacuum from tetramethylammonium chloride at 40°, the white compound $Me_4N,AsCl_4$ remained; but when excess was removed at 0°, a solvate $Me_4N,AsCl_4,2AsCl_3$, was obtained.[7] The substance obtained in the present experiment was a mixture of the solvate with approx. 14% of the non-solvated tetrachloroarsenite (Found: C, 8·6; H, 2·1; As, 33·2; Cl, 53·3. Calc. for $C_4H_{12}NAs_3Cl_{10}$ containing 13·7% of $C_4H_{12}NAsCl_4$: C, 8·6; H, 2·15; As, 33·2; Cl, 53·7%). When the temperature was raised to 40°, the remaining substance was $Me_4N,AsCl_4$ (Found: Cl, 49·0. Calc. for $C_4H_{12}N,AsCl_4$: Cl, 48·8%). With phosphorus oxychloride, the residue always contained a small amount of oxychloride. It was difficult to remove this even in a vacuum during many days (Found: P, 0·64; Cl, 22·9. Calc. for Et_4NCl containing 3·2% of $POCl_3$: P, 0·65; Cl, 22·9%).

Conductivity of Tetraethylammonium Chloride in Phosphorus Oxychloride.—It is essential, in an exchange study, that the nature of the added solute in the solvent be known (see Lewis and Wilkins [4]). Tetraethylammonium chloride was shown from conductivity measurements to exist in phosphorus oxychloride as a strong electrolyte. The conductivity was measured in a cell of 25 ml. capacity, fitted with a B24 socket for the electrode assembly. The cell constant of the electrodes was 0·283. Phosphorus oxychloride was added from a burette, which was fitted with a ground-glass joint, so that moisture could be excluded. The general procedure was that employed by Addison, Hodge, and Lewis.[8] The specific conductivity of pure phosphorus oxychloride was found to be $3{\cdot}7 \times 10^{-6}$ ohm^{-1}. Conductivities were measured at 20° with either a Mullard Conductivity Bridge, or an A.C. bridge circuit of the type described by Haszeldine and Woolf.[9] The equivalent conductivities of tetraethylammonium chloride in phosphorus oxychloride are shown in the Table. Extrapolation of the plot of equivalent conductivity against (concentration)$^{0{\cdot}5}$ for the most dilute solutions, gave a value of 45 ohm^{-1} cm.^{2} for Λ_∞. The average value of the Onsager coefficient, obtained from the slope of this graph, was 232·5, whilst the calculated value (obtained by using [1] $\eta = 0{\cdot}01145$ poise and $\varepsilon = 13{\cdot}9$) was 254·0 at 20°. Thus tetraethylammonium chloride is completely dissociated in phosphorus oxychloride at the dilutions considered. Gutmann has shown tetramethylammonium chloride to be completely dissociated in arsenic trichloride.[2]

Et_4NCl (10^{-4}M)	9·45	9·81	10·1	10·9	11·3	12·3	14·2	19·7	21·3	24·4
Λ (ohm^{-1} cm.^{2})	37·8	37·6	37·5	37·1	36·9	36·8	36·4	36·4	35·8	34·8
Et_4NCl (10^{-4}M)	25·6	28·5	31·9	33·2	36·2	37·9	41·9	46·9	49·8	53·1
Λ (ohm^{-1} cm.^{2})	34·5	33·7	33·1	33·3	32·8	32·3	32·0	30·8	29·9	28·9

Conductivity of Tetraethylammonium Chloride in Nitrobenzene and Acetonitrile.—In order to determine the degree of dissociation of tetraethylammonium chloride in nitrobenzene and acetonitrile, the conductivity of the salt at various dilutions was determined at 25° by the above procedure. Analysing the results of measurements in nitrobenzene by Fuoss and Shedlovsky's [10] method and using the Debye–Hückel limiting law for the determination of the activity coefficients gave the value Λ_∞ 38·53 ohm^{-1} cm.^{2}, in good agreement with the value 38·55 ohm^{-1} cm.^{2} obtained by Witschonke and Kraus.[11] The dissociation constant was $1{\cdot}3 \times 10^{-2}$ compared with Witschonke and Kraus's value of $1{\cdot}25 \times 10^{-2}$. In these calculations

[7] Lindqvist and Andersonn, *Acta Chem. Scand.*, 1954, **8**, 128.

[8] Addison, Hodge, and Lewis, *J.*, 1953, 2631.

[9] Haszeldine and Woolf, *Chem. and Ind.*, 1950, 544.

[10] Fuoss and Shedlovsky, *J. Amer. Chem. Soc.*, 1949, **71**, 1496.

[11] Witschonke and Kraus, *ibid.*, 1947, **69**, 2472.

the viscosity [12] was taken as 0·01811 poise and the dielectric constant as 34·8. The conductivity values are shown in the Table.

Et$_4$NCl (10^{-3}M)	3·07	3·29	3·54	3·83	4·60	5·10	5·74	6·56	7·65	9·18
Λ (ohm^{-1} cm.^{2})	30·9	30·6	30·4	29·9	29·3	28·9	28·1	27·6	26·3	25·0

The data for the conductivity of tetraethylammonium chloride in acetonitrile at 25° are given below. The value of Λ_∞ was found by extrapolation to be 187 ohm^{-1} cm.^{2}. The calculated value of the Onsager coefficient (obtained by using [12] $\eta = 0{\cdot}0034$ poise and $\varepsilon = 37{\cdot}5$) was 358, whilst the experimental value was 362, showing that the salt is completely dissociated over the range studied. Thus applying Fuoss and Shedlovsky's procedure to a 0·0114M-solution gives the degree of dissociation as 0·98.

Et$_4$NCl (10^{-3}M)	2·31	2·44	2·57	3·31	3·70	4·49	5·23	6·98	8·37	8·97	10·46
Λ (ohm^{-1} cm.^{2})	170	170	169	167	166	162	161	158	157	156	154

Kinetic Experiments.—Purification of solvents. Nitrobenzene was dried over phosphoric oxide, distilled under reduced pressure from phosphoric oxide, and finally fractionally distilled. Chloroform was shaken, four times, with half its own volume of distilled water, dried ($CaCl_2$, then P_2O_5), and distilled immediately before use. Acetonitrile was purified by repeated distillation from phosphoric oxide.[13]

The water content of the solvent was determined before a kinetic run by titration with Karl Fischer reagent. In all cases the solvents contained <0·005% of water.

Exchange between Phosphorus Oxychloride and Chloride Ion in Acetonitrile, Nitrobenzene, and Chloroform.—Solutions of phosphorus oxychloride were prepared by using a weight pipette. The separation procedure used for mixtures of tetraethylammonium chloride and phosphorus oxychloride was as follows: In the cases of chloroform and acetonitrile the tetraethylammonium chloride was precipitated by pouring the mixed solutions into dry ether at −70°. Precipitation was >75% complete and there was little tendency for coprecipitation. Owing to difficulty in separation, it was impossible to follow the increase in activity of the phosphorus oxychloride with time. With nitrobenzene, however, great difficulty was experienced with the above separation, as the nitrobenzene froze on being added to the ether solution and the separated tetraethylammonium chloride was often contaminated with phosphorus oxychloride. The precipitated tetraethylammonium chloride was removed on a sintered-glass plate, washed at least twice with dry ether, and dissolved in 10 ml. of water. The activity of the solution was determined by using a skirted counter (20th Century Electronics Ltd., Type M6) in conjunction with standard counting equipment. The chloride ion concentration was estimated by titration with N/100-mercuric nitrate with sodium nitroprusside as indicator. Over the concentration range used, the activity was found to be proportional to the chloride ion concentration.

For the fast exchanges (in nitrobenzene and acetonitrile), a two-compartment flask, similar to that described by Rich and Taube,[14] was used. In one compartment a solution of tetraethylammonium chloride was placed, and in the other a solution of phosphorus oxychloride. The solutions were allowed to gain the required temperature, and then mixed by shaking. The reaction was considered to be quenched on addition to the cold ether. In all these experiments it was essential to exclude water, and all reactions were carried out in apparatus fitted with standard ground-glass joints. All manipulations were performed in a closed system.

For exchange in acetonitrile, preliminary experiments showed that the rate of exchange at 0° was fast, and kinetic measurements were carried out at −10° and −20°. The temperature of exchange was maintained within ±0·3° by adding powdered solid carbon dioxide to acetone, contained in a large Dewar flask. The range of values in nitrobenzene was limited as, owing to the relatively high m. p. of the solvent, runs could only be carried out at correspondingly higher temperatures. As the reaction was fast at the lowest convenient concentration of tetraethylammonium chloride, we only obtained values over a very limited range of halide concentration. Thus it was not possible to verify the order of the exchange reaction in nitrobenzene.

Each run involved the determination of three separations, which were taken in the range 1—2 half-lives. There was good agreement between observed and calculated activities at infinite time, based on the exchange of all the chlorine atoms in the phosphorus oxychloride. The

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[12] Weissberger and Proskauer, "Organic Solvents," Interscience Publ., Inc., New York, 1955.

[13] Walden and Birr, *Z. physikal. Chem.*, 1929, **144**, *A*, 269.

[14] Rich and Taube, *J. Phys. Chem.*, 1954, **58**, 1.

reaction was shown not to be photochemical from experiments carried out in the dark. Table 1 contains typical values for the exchange reactions. The rate of exchange was calculated from the above data by the equation :[15]

$$R = \frac{0{\cdot}693 \times 3[\mathrm{POCl_3}][\mathrm{Et_4NCl}]}{t_{\frac{1}{2}} \times (3[\mathrm{POCl_3}] + [\mathrm{Et_4NCl}])}$$

Exchanges with Arsenic Trichloride.—The exchange of tetraethylammonium chloride with arsenic trichloride in nitrobenzene, acetonitrile, and chloroform was attempted by the above techniques. In all cases, arsenic trichloride was coprecipitated. When excess of trichloride was employed, the precipitate was a mixture of the solvated complexes (Et_4NAsCl_4 and $Et_4NAsCl_4,2AsCl_3$) whilst with excess of tetraethylammonium chloride the precipitate contained some of the monosolvate.

DISCUSSION

Table 2 contains typical values for the exchange of labelled chloride ions with chlorine-containing solvents. The constancy of the activity of the separated solvent and the agreement with a standard, prepared from active chloride diluted with the calculated amount of inactive sodium chloride corresponding to the chloride content of the solvent, shows that there is complete exchange of the chloride within the time of separation. This is in agreement with the presence of some self-ionisation of the solvents. Runs carried out in the dark preclude a photochemical path for the reaction. The time of separation in the case of

TABLE 1. *Exchange of tetraethylammonium chloride and phosphorus oxychloride in organic solvents.*

Run no.	Temp.	Et_4NCl (10^{-3}M)	$POCl_3$ (10^{-3}M)	$t_{\frac{1}{2}}$ (sec.)	Run no.	Temp.	Et_4NCl (10^{-3}M)	$POCl_3$ (10^{-3}M)	$t_{\frac{1}{2}}$ (sec.)
		Nitrobenzene					*Acetonitrile*		
1	9°	1·32	1·14	4	1	−20°	14·1	5·97	31
					2	−20	7·22	6·48	36
		Chloroform			3	−20	40·1	23·4	9
1	25	5·06	6·96	2280	4	−20	14·2	11·5	20
2	25	10·6	12·1	1200	5	−20	9·4	6·99	37 *
3	20	5·10	6·40	4920	6	−10	8·98	7·06	12
4	0	6·0	7·53	30,000					

* In the dark.

TABLE 2. *Exchange of chlorine between solvents and chloride ions at* 18°.

Solvent	Active chloride	Conditions	Time of separation (min.)	Activity of solvent (counts/min.)	Activity of standard (counts/min.)
$POCl_3$	Et_4NCl	In light	4	392	382
			13	403	
			36	395	
			60	403	
$POCl_3$	Et_4NCl	In dark	10	382	379
			25	386	
			36	383	
			64	392	
$AsCl_3$	Me_4NCl	In light	10	207	216
			22	211	
			40	199	
$AsCl_3$	Me_4NCl	In dark	4	261	260
			15	265	
			40	258	
$SeOCl_2$	NaCl	In light	60	340	330
			120	332	
$SeOCl_2$	KCl	In light	55	295	289
			160	294	

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[15] Wahl and Bonner, " Radioactivity Applied to Chemistry," Chapman and Hall, Ltd., London, 1951, p. 7.

selenium oxychloride was large, as great difficulty was experienced with the rate of dissolution of the active chloride owing to the high viscosity of the solvent.

Complete exchange of added chloride ion with the chlorine-containing solvents does not conclusively prove self-ionisation of the solvent. For phosphorus oxychloride, the kinetic equation, corresponding to an ionisation $POCl_3 \rightleftharpoons [POCl_2]^+ + Cl^-$, would be of the form, Rate $= k_1[POCl_3]$. The most probable alternative mechanisms are: (*a*) Formation of the $[POCl_4]^-$ ion by direct interaction of phosphorus oxychloride and a labelled chloride ion, with dissociation of this ion leading to transfer of the activity to the solvent; then, Rate $= k_2[POCl_3][Cl]^-$. (*b*) The initial rapid formation of the $[POCl_4]^-$ ion and transfer of activity occurring by slow exchange of chloride ion between this ion and a molecule of phosphorus oxychloride, rather than by a dissociation of the complex ion $[POCl_4]^-$, *i.e.*:

$$POCl_3 + {}^*Cl^- \xrightarrow{\text{Rapid}} [POCl_3{}^*Cl]^-$$

$$[POCl_3{}^*Cl]^- + POCl_3 \xrightarrow{\text{Slow}} [POCl_4]^- + POCl_2{}^*Cl$$

$$\text{Rate} = k_3[POCl_3]^2[Cl^-]$$

For the alternative mechanisms to be possible, it is necessary that in the solvated chloride ion, *i.e.*, $[POCl_4]^-$, the chlorine is bonded directly to the phophorus, not to the oxygen as occurs in certain metal chloride–phosphorus oxychloride complexes,[16] and that the structure of the solvated chloride ion involves at least one other chlorine atom in a similar spatial position to the labelled chlorine atom. The $[POCl_4]^-$ ion has been considered to exist in phosphorus oxychloride, although no solid derivative of it has been isolated. The analogous ion $[AsCl_4]^-$ in the case of arsenic trichloride is well established, and since the structure is considered to be a trigonal bipyramid with a lone pair of electrons occupying an equatorial position,[17] there would be equivalence of the chlorine atoms in the ion. In the pure solvents, because of the high rate of reaction, it is not possible to differentiate between these possibilities, and in order to see which is most probable we have investigated the exchange of labelled chloride ion with phosphorus oxychloride in some anhydrous organic solvents.

Exchange Reactions in Organic Solvents.—We have investigated the exchange of phosphorus oxychloride with labelled chloride ion in chloroform, nitrobenzene, and acetonitrile, as this covered a wide range of polarity of the solvents. A unimolecular mechanism is most likely in the solvent of highest polarity, acetonitrile, and we therefore made the most detailed study of acetonitrile solutions. Table 3 contains values of the rate constants calculated on the basis of the three mechanisms postulated above. The constancy of the values of k_2 over the range of concentration indicates that the mechanism of the exchange is of first order with respect to chloride ion and phosphorus oxychloride in both chloroform and acetonitrile. This is in agreement with a mechanism of the form (*a*) postulated above. The variation in the rate constant with temperature gave values of 17·6 and 13·5 kcal. mole^{-1} for the energy of activation in chloroform and acetonitrile respectively.

TABLE 3. *Rate constants for exchange of chlorine between tetraethylammonium chloride and phosphorus oxychloride.*

Temp.	Run no.*	k_1 (sec.$^{-1}$)	k_2 (sec.$^{-1}$ mole^{-1} l.)	k_3 (sec.$^{-1}$ mole^{-2} l.^{2})	Temp.	Run no.*	k_1 (sec.$^{-1}$)	k_2 (sec.$^{-1}$ mole^{-1} l.)	k_3 (sec.$^{-1}$ mole^{-2} l.^{2})
		Acetonitrile					*Chloroform*		
−20°	1	0·030	2·07	346	25°	1	0·00018	0·035	5·04
	2	0·016	2·16	333		2	0·00035	0·037	3·05
	3	0·084	2·09	90					
	4	0·030	2·14	186					
	5	0·017	1·85	264					

* Cf. Table 1.

To determine the actual rate of reaction in a solvent of low dielectric constant, it is

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[16] Groeneveld, *Rec. Trav. chim.*, 1956, **75**, 594.

[17] Lindqvist, *Acta Chem. Scand.*, 1955, **9**, 73.

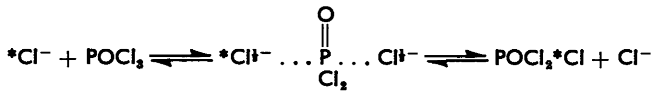
necessary to allow for the incomplete dissociation of the electrolyte in the solvent. Evans and Sugden [18] discuss the exchange of bromide with alkyl bromides in acetone and show that the true rate constant is related to the observed rate constant by the relation αk (true) = k (obs.), where α is the degree of dissociation. Therefore the slow rate of exchange observed in chloroform may be attributed to a low concentration of free chloride ions. In calculating the rate constant, it is necessary to assume that the degree of dissociation of the ionic chloride does not vary markedly over the concentration range considered. The magnitude of the activation energy depends on the rate of change of the degree of dissociation with temperature and the value for chloroform solutions was calculated on the basis that this was zero. The results in chloroform are, therefore, considered more tentative than those in acetonitrile. Since, however, the mechanism in acetonitrile is bimolecular, a bimolecular mechanism would be expected in chloroform, as a transition from a bimolecular mechanism to a unimolecular mechanism normally occurs with increase in polarity of the solvent.

In nitrobenzene it was not possible to vary the concentration sufficiently to give the chloride ion dependence and only one value for the exchange has been included in the Table. The observed half-lives of the reactions considered were in agreement with a bimolecular mechanism of the type that was occurring in acetonitrile. Thus, when the data on the variation of the rate constant with temperature were used, the calculated half-life of the exchange in acetonitrile for the concentrations cited in Table 1 for nitrobenzene was 14 sec. at 9°. After allowance for the incomplete dissociation of the tetraethylammonium chloride in nitrobenzene calculated from the dissociation constant $K = 1{\cdot}3 \times 10^{-2}$, this half-life is increased to 15 sec. The observed half-life of the reaction at 9° was of the order of 4 sec., and this is considered to be significantly different from the calculated half-life for the reaction in acetonitrile. This increase in the half-life is consistent with previous observations on the variation of the rate of a bimolecular reaction of this type on increasing the polarity of the solvent.[19]

In all the solvents considered, the exchange between chloride ion and phosphorus oxychloride may thus be considered to be of the first order in chloride ion and phosphorus oxychloride. The rapid exchange of chloride ion with phosphorus oxychloride in the pure solvent is probably a bimolecular process. It may be considered to occur either by direct addition of chloride ion to the phosphorus oxychloride, utilising an empty *d*-orbital at the phosphorus atom :

$$\mathrm{POCl_3 + {}^*Cl^- \rightleftharpoons [POCl_3{}^*Cl]^- \rightleftharpoons POCl_2{}^*Cl + Cl^-}$$

or by a mechanism analogous to the S_N2 mechanism for halide ion exchange with alkyl halides : †



$$\mathrm{{}^*Cl^- + POCl_3 \rightleftharpoons {}^*Cl^{\frac{1}{2}-} \ldots \underset{Cl_2}{\overset{\overset{O}{\|}}{P}} \ldots Cl^{\frac{1}{2}-} \rightleftharpoons POCl_2{}^*Cl + Cl^-}$$

The transfer of the activity to the solvent does not proceed through a self-dissociation of the solvent. These mechanisms are similar to that proposed to explain the exchange of labelled sulphite ion and the solvent in liquid sulphur dioxide; Johnson, Norris, and Huston [20] suggested an oxygen ion transfer between a sulphur dioxide molecule and a sulphite ion in order to explain the rapid exchange in preference to a self-ionisation of the sulphur dioxide involving a sulphite ion.

For the exchange of chloride with arsenic trichloride, the ready formation and stability of the tetrachloroarsenite ion makes a bimolecular process of a similar type to that

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† The authors are indebted to one of the referees for suggesting this alternative mechanism.

[18] Evans and Sugden, *J.*, 1949, 270.

[19] Ingold, " Structure and Mechanism in Organic Chemistry," Bell and Sons, Ltd, London, 1953, pp. 345 *et seq.*

[20] Johnson, Norris and Huston, *J. Amer. Chem. Soc.*, 1951, **73**, 3052.

postulated for phosphorus oxychloride very probable. The above conclusions do not disprove a self-ionisation in these solvents, but establish the existence of the $POCl_4^-$ ion in phosphorus oxychloride. Since there was no induced exchange in these reactions, it follows that the concentration of free chloride ion, in solutions of phosphorus oxychloride in the organic solvents considered, is low. One of the differences between protonic solvents and chlorine-containing solvents of the type of phosphorus oxychloride and arsenic trichloride is that in the latter solvation of anions and in the former solvation of cations occurs. We would therefore expect that the analogous exchange in protonic systems would occur by a bimolecular mechanism involving the hydrogen ion and a solvent molecule (*i.e.*, for water by the formation of the well-established ion H_3O^+).

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