

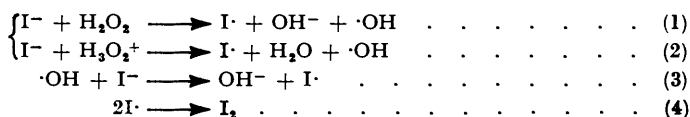
NOTES.

Reactions between Hydrogen Peroxide and Halide Ions.

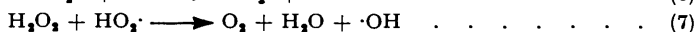
By M. C. R. SYMONS.

[Reprint Order No. 5596.]

Two fundamentally different mechanisms have been proposed recently for the reactions between hydrogen peroxide and halide ions, both mechanisms being satisfactorily in accord with the observed kinetics (see Morgan, *Quart. Reviews*, 1954, **8**, 123, for references) and with the concepts of reaction mechanisms enumerated by Hinshelwood (*J.*, 1947, 694). Weiss (*Ann. Reports*, 1947, **44**, 60) has proposed a radical mechanism with a first stage similar to that of the reaction between hydrogen peroxide and ferrous ion :



Reactions (1) and (2) are thought to be rate-determining, thus giving $-d[I^-]/dt = k_1[H_2O_2][I^-] + k_2[H_2O_2][I^-][H^+]$, concordant with experiment. Weiss does not discuss mechanisms for the similar reactions which occur with bromide and chloride ions, but suggests the following mechanism for the reaction between hydrogen peroxide and iodine in less acidic solution and hence, by a combination of the two schemes, a system for the catalytic decomposition of hydrogen peroxide by iodide :



Hence, Weiss shows that in the stationary state,

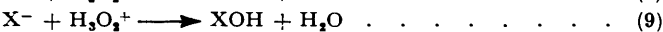
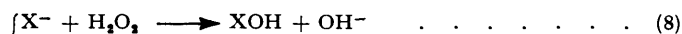
$$d[O_2]/dt = (k_1 k_6 [I_2] [HO_2^-]) / (k_{-5} [I^-] + k_6 [HO_2^-])$$

Abel (*Z. physikal. Chem.*, 1928, **136**, 161) has found

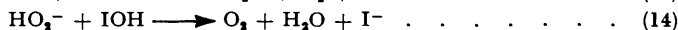
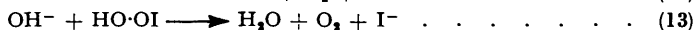
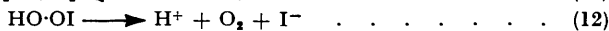
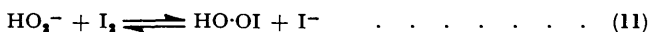
$$\frac{d[O_2]}{dt} = \frac{k[I_2][H_2O_2]}{[I^-][H^+]} + \frac{k'[I_2][H_2O_2]}{([I^-][H^+])^2}$$

and Morgan (*loc. cit.*), who strongly supports Weiss's mechanism, shows that if $k_{-5}[I^-] \gg k_6[HO_2^-]$, the derived expression becomes equivalent to the first experimental term. He suggests that the second term shows that reaction (7) must involve O_2^- as well as HO_2 ; however, it is difficult to see how this could affect the kinetics if reaction (6) is rate-determining.

In an important series of articles, Edwards (*Chem. Reviews*, 1952, **50**, 455; *J. Phys. Chem.*, 1952, **56**, 279; *J. Chem. Educ.*, 1954, **31**, 270; *J. Amer. Chem. Soc.*, 1954, **76**, 1540) has succeeded in correlating a large amount of kinetic data concerning nucleophilic displacement reactions, and has shown that the reactions between hydrogen peroxide and halide ions can be included in this scheme. This correlation provides good circumstantial evidence that these reactions are nucleophilic displacements of the type



Edwards does not discuss the reaction between hydrogen peroxide and iodine, but this reaction may be represented in a similar manner :



Reactions (8) and (9) will be irreversible since XOH would preferentially form XO^- ; reaction (10) may proceed *via* XOH_2^+ ; reaction (11) is postulated as a reversible process; reactions (12) and (13) represent two possible modes for the decomposition of "periodous acid" ($HO\cdot OI$), and the sequence (8)—(14) represents the simplest mechanism for the catalytic formation of oxygen.

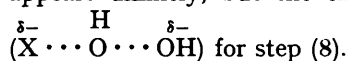
If reactions (8) and (9) are rate-determining, the observed kinetic expression for iodine formation is satisfactorily explained, and if reaction (8) is still rate-determining for the catalytic evolution of oxygen in neutral solution, then $d[O_2]/dt = 2d[I_2]/dt$, as observed experimentally by Brode (*Z. physikal. Chem.*, 1904, **49**, 208). Application of stationary-state kinetics to the sequence (11), (12), (13), treating $HO\cdot OI$ as an unstable intermediate, gives :

$$\frac{d[O_2]}{dt} = \frac{k_{11}k_{12}[HO_2^-][I_2]}{k_{-11}[I^-] + k_{12}} + \frac{k_{11}k_{13}[HO_2^-][I_2][OH^-]}{k_{-11}[I^-] + k_{13}[OH^-]}$$

Provided that $k_{-11}[I^-] \gg k_{12}$ and $k_{-11}[I^-] \gg k_{13}[OH^-]$, this expression approximates to that found experimentally (Abel, *loc. cit.*).

Clearly, both mechanisms require that the evolved oxygen be derived entirely from the hydrogen peroxide, as is found experimentally (Cahill and Taube, *J. Amer. Chem. Soc.*, 1952, **74**, 2312).

Liebhaftsky and Mohammed (*ibid.*, 1933, **55**, 3977) have derived a value of 13,400 cal. for the activation energy of the reaction between hydrogen peroxide and iodide, not catalysed by hydrogen ion. By assuming that the heats of solution of hydroxyl radicals and iodine atoms are similar to the corresponding values for water and molecular iodine respectively (cf. Evans, Hush, and Uri, *Quart. Reviews*, 1952, **6**, 188), the change in heat content for reaction (1) is found to be approximately +19,000 cal. (Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, 1952), and for reaction (8), when X⁻ is iodide, to be approximately -24,000 cal. Thus, since the energies of activation of endothermic steps must be equal to, or greater than, their thermochemical heats of reaction, step (1) appears unlikely, but the experimental figures may well describe the transition state



The intermediates postulated by Weiss, if present, should give rise to certain characteristic induced reactions, and failure of the hydrogen peroxide-iodide system to induce these reactions may be taken as evidence against their presence. Since iodine atoms are known to induce a rapid chain reaction between iodine and oxalate, Taube (*J. Amer. Chem. Soc.*, 1942, **64**, 161) has tested for their presence by adding oxalate to the hydrogen peroxide-iodide-iodine system, and has concluded that they cannot be formed during the reaction. Alternatively, hydroxyl radicals, if present during the reaction, should, in the presence of vinyl monomers, initiate polymerisation (Baxendale, Evans, and Park, *Trans. Faraday Soc.*, 1946, **42**, 155) and, in the presence of benzoic acid, give hydroxylation of the aromatic ring (Bates, Evans, and Uri, *Nature*, 1950, **166**, 869). Extensive tests have been carried out with acrylonitrile, using Thunberg tubes, as described by Drummond and Waters (*J.*, 1953, 2836). The pH was varied by the addition of dilute perchloric acid, and the initial concentration of hydrogen peroxide and sodium halide (chloride, bromide, or iodide) was altered over a wide range in many different experiments, since too high a concentration of radicals may invalidate the test (Dainton, *J.*, 1952, 153). In no instance was polymerisation observed; as a check on the method, it was ascertained that, under similar conditions, the hydrogen peroxide-ferrous sulphate reaction gave instantaneous precipitation of polymer.

Iodide ions should compete with acrylonitrile for hydroxyl radicals, since reaction (3) is strongly exothermic (Evans, Hush, and Uri, *loc. cit.*), but this would be unlikely to suppress polymerisation completely as this is a chain reaction and all experiments were performed with acrylonitrile in large excess. However, a qualitative check on the relative importance of the two competing reactions was devised whereby hydrogen peroxide was added to an acidified, saturated, aqueous solution of acrylonitrile containing iodide ion and a trace of ferrous ion. With small concentrations of iodide, only polymer was formed; with a large excess of iodide only iodine appeared; with intermediate concentrations of iodide both iodine and polymer were produced. Accordingly, it is concluded that when the concentration of acrylonitrile is very much greater than the concentration of iodide, hydroxyl radicals, if present, should give rise to observable polymerisation. A similar exchange occurring during the reaction between hydrogen peroxide and chloride ions would not inhibit polymerisation appreciably, since chlorine atoms are also efficient initiators.

As a further test for the presence of free hydroxide radicals, benzoic acid was treated as above at various temperatures and for various times, but insufficient salicylic acid was formed to give an observable colour with added ferric ion; again, addition of hydrogen peroxide to a solution of benzoic acid containing a trace of ferrous ion gave an immediate purple colour.

It is therefore concluded that free hydroxyl radicals are not formed during these reactions and it is considered that this negative evidence lends further support to the nucleophilic displacement mechanisms proposed by Edwards. These mechanisms are essentially similar to those originally proposed (*e.g.*, by Abel, and by Liebhaftsky and

Mohammed, *loc. cit.*) except in so far as they stress the postulated S_N2 nature of the separate steps. In the absence of compelling evidence in favour of the prior hydrolysis of iodine in its reaction with hydrogen peroxide (see, however, Liebafsky, *Chem. Reviews*, 1935, 17, 89) the sequence (11)—(13) is considered preferable since it is simpler and seems to be more self-consistent.

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Infra-red Absorption Characteristic of Diazonium Cations.

By M. ARONEY, R. J. W. LE FÈVRE, and R. L. WERNER.

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IN connection with other work we desired to know whether the infra-red spectra of diazonium salts display any features which could usefully serve for the recognition of the $(R \cdot N_2)^+$ cation. As the literature appeared to contain no data on the point we have examined 21 substances which (apart from the zwitter-ionic *p*-diazobenzenesulphonic acid) are either diazonium salts with single anions or complex salts containing diazonium cations. The majority were easily prepared by addition of the appropriate metal halide dissolved in hydrochloric acid to a solution containing the requisite diazonium chloride (for references, see Saunders, "The Aromatic Diazo-compounds and their Technical Applications," E. Arnold and Co., 2nd Edn., London, 1949, pp. 74 *et seq.*). Borofluorides or tetrachloroiodites ($R \cdot ICl_4$) were obtained by the procedures described respectively by Le Fèvre and Turner (*J.*, 1930, 1158) and Chattaway, Garton, and Parkes (*J.*, 1924, 125, 1980). Spectra have been recorded for Nujol mulls with a Perkin-Elmer model 12C spectrometer. In every case a strong absorption band has appeared in the region 2230—2310 cm^{-1} (see Table).

Diazonium salt	Strong absorption (cm^{-1})	Diazonium salt	Strong absorption (cm^{-1})
Benzenediazonium ferrichloride	2256	Diphenyl- <i>pp'</i> -bisdiazonium borofluoride	2296
platinichloride	2253	zincichloride	2270
aurichloride	2260	Diazobenzenesulphonic acid	2282
tetrachloroiodite	2257	Naphthalene-1-diazonium borofluoride	2262
borofluoride	2296	zincichloride	2231
<i>o</i> -Chlorobenzenediazonium ferrichloride	2239	mercurichloride	2234
tetrachloroiodite	2250	cadmichloride	2256
Toluene- <i>p</i> -diazonium ferrichloride	2234	Naphthalene-2-diazonium borofluoride	2291
platinichloride	2254	zincichloride	2250
aurichloride	2255	cadmichloride	2250
<i>p</i> -Nitrobenzenediazonium borofluoride	2306		

The figures are centred around 2261 cm^{-1} (with standard deviation, ± 21 cm^{-1}), this is of the order to be expected for a triple linkage and thus provides physical evidence for the modern equivalent of Blomstrand's formulation of diazonium salts (see Sidgwick, Taylor, and Baker, "Organic Chemistry of Nitrogen," Oxford, 1937, p. 413). Moreover, since the spectra near 2260 cm^{-1} are clear of other group effects, the occurrence of such absorption may reasonably be accepted for the purpose mentioned at the outset.

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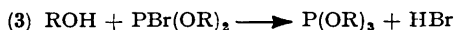
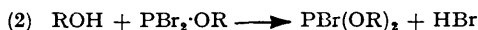
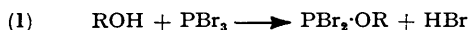
Reactions in Alcohol-Phosphorus Tribromide Systems.

By W. GERRARD and H. HERBST.

[Reprint Order No. 5716.]

ALKYL PHOSPHORODICHLORIDITES, $\text{PCl}_2\cdot\text{OR}$, and chloridites, $\text{PCl}(\text{OR})_2$, are quickly formed during the addition of an alcohol such as butan-1-ol to phosphorus trichloride (Gerrard, Isaacs, Machell, Smith, and Wyvill, *J.*, 1953, 1920; Gerrard and Shepherd, *J.*, 1953, 2069), and their properties are of significance in the description of alcohol-phosphorus trichloride systems. It was therefore necessary to examine the corresponding dibromidite and bromidite, in order to describe phosphorus tribromide systems. Already a general resemblance between the two systems was apparent (Gerrard, *J.*, 1945, 848; Gerrard and Whitbread, *J.*, 1952, 914); but the more vigorous dealkylating power of hydrogen bromide, compared with hydrogen chloride, made it difficult to follow the sequence of reactions which occur when such an alcohol is added to phosphorus tribromide.

By carefully removing hydrogen bromide before distillation, *n*-butyl phosphorodibromidite was prepared from butan-1-ol (1 mol.) and the tribromide (1 mol.) (reaction 1); but alkyl bromide, the tribromide, and undistillable material were also isolated, for, as is clear from the trichloride system, reactions (2) and (3) probably occurred concurrently, and dealkylation of the esters produced gives alkyl bromide. The dibromidite was stable at 100° (2 hr.), but slowly decomposed at 160°, giving alkyl bromide, undistillable



products, and, unexpectedly, phosphorus tribromide. This decomposition was to some extent facilitated by pyridine hydrobromide. An alkyl bromide and phosphorus tribromide were also slowly formed when the dibromidite reacted with hydrogen bromide at 22°. The slowness of the dealkylation is in accord with the mechanism previously discussed (Gerrard and Whitbread, *loc. cit.*); but the formation of phosphorus trihalide by the two procedures was not observed in the trichloride system, probably owing to experimental factors and the slowness of the reactions.

Di-*n*-butyl phosphorobromidite could not be obtained by using more alcohol [reaction (2)], but was prepared by the addition of a mixture of alcohol and pyridine to the dibromidite. It decomposed on being stored at 15°, and at 100° afforded alkyl bromide in 90% yield in 2 hr. When the ester was dealkylated by hydrogen bromide, alkyl bromide (1 mol.) was formed in 4-5 hr. at 25°.

Experiments with *sec.*-butyl and *isobutyl* esters afforded similar results, except that *isobutyl* bromide was accompanied by *tert.*-butyl bromide when obtained by thermal decomposition of the dibromidite.

Experimental.—Reagents were rigorously purified. Specimens of alkyl bromides were characterised by b. p., n_D , and bromine content. They were always withdrawn from reaction mixture at low pressure, and trapped.

Preparation of the dibromidites. The alcohol (1 mol.) was added dropwise to phosphorus tribromide (1 mol.) at -15° , hydrogen bromide being swept away by a stream of dry carbon dioxide. It is imperative to remove hydrogen bromide before distillation. Alkyl bromide and phosphorus tribromide were isolated, and there was always an undistillable residue. Results are recorded in Table 1.

Preparation of the bromidites. The alcohol (1 mol.) and pyridine (1 mol.) in ether (20 mols.) were added to the dibromidite (1 mol.) in ether (20 mols.) at -15° . Base hydrobromide (100%) was immediately precipitated, and from the filtrate, the *bromidite* (see Table 2) was obtained with some difficulty, owing to its instability. The bromidites decomposed on being stored at 15°, and on being heated at 100° for 2 hr., gave the alkyl bromide (Bu^n , 0.90; Bu^s , 0.83; Bu^t , 0.62 mol.).

Dealkylation of the bromidites. Hydrogen bromide was passed into the bromidite (1 mol.) for the time and at the temperature stated. Alkyl bromide was withdrawn at 15 mm., and the residue was always undistillable. The *n*-butyl ester (7.35 g.) gave, at 25°, butyl bromide (3.9 g., 1 mol., after 4.5 hr.; 4.6 g., 1.2 mol., after 24 hr.) and a residue (4.1 g.). The

TABLE 1.

ROH		Phosphorodibromidites						Residue,
R	g.	Yield (%)	B. p./mm.	n_D^{20}	d_4^{20}	Br (%) *	P (%) *	g.
Bu ^a	2.9	57	38°/0.01	1.5441	—	60.7	11.2	0.9
Bu ^l	5.95	56	64°/5	1.5391	1.768	60.4	11.5	3.0
Bu ^s	6.7	35	38°/0.1	1.5409	1.798	61.1	11.2	4.1

* C₄H₉OBr₂P requires Br, 60.6; P, 11.7%.

isobutyl ester (5.5 g.) gave, at 21°, alkyl bromide (2.1 g., 0.71 mol., after 20 hr.) and a residue (4.0 g.). The *sec*-butyl ester (6.95 g.) gave, at 21°, the alkyl bromide (3.7 g., 1 mol., after 7 hr.; 4.0 g., 1.08 mol., after 24 hr.) and a residue (3.5 g.).

Thermal stability and dealkylation of the dibromidites. The *n*-butyl ester (8.03 g.) was slowly heated to 100° (2 hr.), but the liquid remained colourless, and no alkyl bromide could be withdrawn at low pressure. At 160°, decomposition was obvious; after 2 hr. *n*-butyl bromide (1.25 g., 30%), phosphorus tribromide (3.45 g.), b. p. 23°/0.01 mm. (Found: Br, 86.0. Calc. for PBr₃: Br, 88.5%), butyl dibromidite (2.06 g.), b. p. 38°/0.01 mm. (Found: Br, 60.9%), and a residue (0.23 g.) were obtained. Similarly, the *isobutyl ester* (4.05 g.) gave a mixture

TABLE 2.

PBr ₃ -OR		Phosphorobromidites			
R	g.	Yield (%)	B. p./mm.	n_D^{20}	Br (%) *
Bu ^a	5.71	42	50°/0.05	1.4690	31.1
Bu ^l	4.22	45	64°/0.4	1.4535	30.9
Bu ^s	4.50	40	32—34°/0.05	1.4598	31.9

* C₈H₁₈O₂BrP requires Br, 31.1%.

(0.71 g., 34%) of *isobutyl bromide* (40%) and *tert*-butyl bromide (60%), as well as phosphorus tribromide (0.9 g.), b. p. 24°/0.02 mm. (Found: Br, 85.7%), butyl dibromidite (1.08 g.), b. p. 32°/0.2 mm. (Found: Br, 60.9%), and a residue (0.9 g.). The *sec*-butyl ester (4.61 g.) decomposed about 118°, and after 3 hr. gave *sec*-butyl bromide (1.08 g., 45%), phosphorus tribromide (1.01 g.), b. p. 23°/0.01 mm. (Found: Br, 87.0%), butyl dibromidite (1.2 g.), b. p. 38°/0.1 mm. (Found: Br, 61.0%), and a residue (0.9 g.).

The dibromidites were heated at 100° for 2.5 hr. in the presence of pyridine hydrobromide (1 mol.), which was unchanged at the end (Found: Br, 49.5. Calc.: Br, 50.0%). The *n*-butyl ester (7.88 g.) gave *n*-butyl bromide (1.46 g., 35.7%), phosphorus tribromide (2.2 g.), b. p. 23°/0.01 mm. (Found: Br, 87.5%), and butyl dibromidite (2.81 g.), b. p. 38°/0.01 mm. (Found: Br, 60.0%). The *isobutyl ester* (4.71 g.) gave a mixture of *isobutyl* (0.28 g.) and *tert*-butyl (0.42 g.) bromide, phosphorus tribromide (1.01 g.), b. p. 22°/0.01 mm., and butyl dibromidite (2.20 g.) (Found: Br, 60.8%).

Dry hydrogen bromide was passed into the ester at 22°, and effluent gas was passed through a trap at -40°. The rate of production of alkyl bromide was followed by withdrawing volatile matter. The *n*-butyl ester (3.47 g.) gave after 8 hr. *n*-butyl bromide (1.6 g., 89%), and phosphorus tribromide (2.1 g.), b. p. 23°/0.02 mm. (Found: Br, 87.0%). The *isobutyl ester* (4.74 g.) gave, after 23.5 hr., *isobutyl bromide* (1.96 g., 79.5%), phosphorus tribromide (0.9 g.) (Found: Br, 87.4%), butyl dibromidite (0.97 g.) (Found: Br, 60.0%), and a residue (1.55 g.). The *sec*-butyl ester (4.7 g.), after 24 hr., gave *sec*-butyl bromide (2.2 g., 89.5%), phosphorus tribromide (2.5 g.), b. p. 23°/0.01 mm. (Found: Br, 86.0%), and a residue (1.01 g.).

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The Electrical Conductivities of Phosphorus and Antimony Trifluorides.

By A. A. WOOLF.

[Reprint Order No. 5742.]

THE conductivities of phosphorus and antimony trifluorides have been measured during an investigation of Group v double fluorides. To determine whether Ruff and Plato's antimony trifluoride-antimony pentafluoride compounds (*Ber.*, 1904, **37**, 673) were ionic, the conductivities of antimony trifluoride in the pentafluoride and of the pentafluoride in the trifluoride were required. Antimony trifluoride appeared to be insoluble in the pentafluoride and failed to increase its conductivity. This is in agreement with other observations which show that the pentafluoride is not an ionizing solvent. The conductivity of the trifluoride was then measured and is of the same order as that of fused zinc chloride (*ca.* 10^{-2} mho). The values obtained were approximate, because of experimental difficulties, so that measurements with quinquevalent antimony solutions were not attempted. The high conductivity of antimony trifluoride is of interest because it demonstrates again that the conductivity of a melt is not necessarily related to that of the solid structure. Both aluminium trichloride, which has a two-dimensional ionic lattice (Ketelaar, MacGillavry, and Renes, *Rec. Trav. chim.*, 1947, **66**, 501), and phosphorus pentachloride with a three-dimensional ionic lattice (Clark, Powell, and Wells, *J.*, 1942, **642**) possess negligible conductivities in their melts (Biltz, Klemm, and Voigt, *Z. anorg. Chem.*, 1923, **126**, 39; 1924, **133**, 277), whereas the molecular lattices of antimony trifluoride (Bystrom and Westgren, Gmelin's "Handbuch," 8th edn., 1949, Vol. XVIII, *B*, p. 395) and di-iodine hexachloride (Boswigg and Wiebenga, *Acta Cryst.*, 1954, **7**, 417) give highly conducting melts (Greenwood and Emel us, *J.*, 1950, 987).

Phosphorus trifluoride had the expected low conductivity in the liquid state (10^{-9} mho). The liquid had a negative temperature coefficient of conductivity and obeyed Ohm's law. Thus the conductivities of the trifluorides so far measured increase from phosphorus to arsenic (10^{-5} mho) to antimony and it would be surprising if the ionic bismuth trifluoride did not continue in this sequence. The relation between the conductivities of fluorides and the rates of complex formation with alkali fluorides—that only liquid fluorides with conductivities of $\leq 10^{-5}$ mho react at an appreciable rate—holds for the other Group v fluorides subsequently examined (Woolf and Greenwood, *J.*, 1950, 2200). When an excess of antimony trifluoride was melted with potassium fluoride for a few minutes and then frozen and the antimony trifluoride was sublimed off *in vacuo*, a solid residue $\text{KF} \cdot 0.36\text{SbF}_3$ was obtained, probably a potassium fluoride-potassium tetrafluorometa-antimonite mixture. Potassium fluoride failed to combine with phosphorus trifluoride at room temperatures during three months. Lange and Stein (unpublished work reported in Simon's "Fluorine Chemistry," Academic Press Inc., New York, 1950, Vol. I, p. 139) found that hot potassium fluoride absorbed phosphorus trifluoride, but we found no combination when phosphorus trifluoride was passed over potassium fluoride *in vacuo* at temperatures up to 240° . At atmospheric pressure and temperatures above 200° an apparent combination occurred but the red product indicated that some phosphorus trifluoride had disproportionated to phosphorus. The concomitant phosphorus pentafluoride can combine with alkali fluorides at these temperatures.

Ruff and Schiller (*Z. anorg. Chem.*, 1911, **72**, 329) have already shown that liquid niobium and tantalum pentafluorides combine with potassium fluoride at an appreciable rate in conformity with the conductivities of these liquids (Fairbrother, Frith, and Woolf, *J.*, 1954, 1031). It is unlikely that the product was the heptafluoro-salt as they suggest, because an excess of pentafluoride was used. The product with even 2 : 1 ratios of alkali fluoride to niobium pentafluoride in anhydrous hydrogen fluoride or bromine trifluoride is exclusively the hexafluoronio-bate (Laubengayer and Polzer, *J. Amer. Chem. Soc.*, 1941, **63**, 3264; Gutmann and Emel us, *J.*, 1950, 1046).

The only Group v fluoride for which it is difficult to predict the conductivity is vanadium pentafluoride. This value may be higher than the position of vanadium in the Group would indicate, since the pentafluoride combines readily with potassium fluoride.

Experimental.—Conductivity of antimony trifluoride. The trifluoride was recrystallised from methanol, to remove oxide and oxyfluoride (Bak and Hillebert, *Acta Chem. Scand.*, 1953, **7**, 236). The purified trifluoride, contained in an aluminium cup surrounded by an external furnace, was sublimed *in vacuo* on to a water-cooled copper condenser. The choice of electrode insulators for the metal cells proved difficult. Fluorides are unsuitable because of possible combination with antimony trifluoride, and oxides may be converted into fluorides. A cemented asbestos was used in these experiments. In one type of conductivity cell constructed of copper, a pair of brass cylinder electrodes was used. These were not absolutely inert. In another type of cell a pointed nickel electrode, whose position could be adjusted from outside the furnace by means of a micrometer head, was placed centrally in a platinum bottle by means of the asbestos insulator. The bottle served as the other electrode. Contact of the rod electrode with the electrolyte could be detected by completing a circuit, after which the electrode was lowered to a fixed position by the micrometer head. With both cells attack on the insulator was severe enough to invalidate any but the initial few readings. A value of 0.065 mho at 300° obtained in the copper cell was close to that in the platinum cell (0.067 mho at 316°). The solid trifluoride appeared to conduct well in the solid state. Even 100° below the m. p. the conductivity was about 10^{-6} mho.

Conductivity of phosphorus trifluoride. The trifluoride was prepared by halogen exchange between phosphorus trichloride and antimony trifluoride (Booth and Bozarth, *J. Amer. Chem. Soc.*, 1939, **61**, 2927) and purified by vacuum-fractionation. The purity of the trifluoride was shown by the absence of any chlorine-containing products. A Pyrex-glass conductivity cell (constant 0.118), the platinum electrodes of which were joined to the Pyrex glass by graded seals, was connected to a gas bulb and final purification train. The conductivity was measured with direct current after Ohm's law had been established in the liquid. The slope of the voltage-current curve gave a value of 0.42×10^{-9} mho at 113°.

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