502. *Liquid Hydrogen Bromide and Hydrogen Iodide as Ionizing Solvents.*

By T. C. WADDINGTON and J. A. WHITE.

The conductivities and neutralization reactions of a number of compounds in liquid anhydrous hydrogen bromide have been studied. The following new compounds have been prepared in the solvent: Me_4NBBr_4, Et_4NBBr_4, PH_4BBr_4, $C_5H_5NHBBr_4$; as well as a number of compounds previously prepared by other methods. Tetraphenylarsonium and tetra-n-butylammonium hydrogen dibromide have been prepared as stable solids. The solubilities of compounds in liquid hydrogen bromide are in general less than in liquid hydrogen chloride, and an interesting two-layer effect was observed with solutions of tetramethylammonium bromide. Liquid hydrogen iodide has been used as a solvent in the preparation of the following tetraiodoborates: Me_4NBI_4, Et_4NBI_4, $C_5H_5NHBI_4$.

AFTER studies [1] of the properties of liquid hydrogen chloride as an ionizing solvent and of its use as a solvent in preparative inorganic chemistry, the properties of liquid hydrogen bromide and liquid hydrogen iodide have been investigated. The preparation of tetrabromoborates and tetraiodoborates in their respective hydrogen halides have been briefly reported [2] in preliminary communications and Klanberg and Kohlschutter [3] have studied some reactions and preparations in liquid hydrogen iodide. Apart from this work these solvents have been neglected since the work of Archibald, McIntosh, and Steele [4,5] in the early years of this century. In this paper we report the conductivities and reactions of several organic and inorganic materials which function as bases in liquid hydrogen bromide, and the behaviour of the potential Lewis acids BF_3, BCl_3, BBr_3, $SnBr_4$, $AlBr_3$, and Br_2 in the solvent.

EXPERIMENTAL

Apparatus and Procedures.—The apparatus and experimental procedures employed were very similar to those used in the study of liquid hydrogen chloride,[1] and will be described only where they differ. Hydrogen bromide was prepared by direct union of the elements.[6] This

---

[1] Waddington and Klanberg, *J.*, 1960, 2329, 2332; Peach and Waddington, *J.*, 1961, 1238; 1962, 600, 2680.

[2] Waddington and White, *Proc. Chem. Soc.*, 1960, **85**, 315.

[3] Klanberg and Kohlschutter, *Z. Naturforsch.*, 1961, **166**, 68; *Ber.*, 1961, **94**, 781, 786.

[4] Steele and McIntosh, *Proc. Chem. Soc.*, 1903, **19**, 220; Walker, Archibald, and McIntosh, *Proc. Chem. Soc.*, 1904, **20**, 134; McIntosh and Steele, *Proc. Roy. Soc.*, 1904, **73**, 450; Steele, *Proc. Roy. Soc.*, 1905, **74**, 320; Walker, McIntosh, and Archibald, *J.*, 1904, 1082, 1098; *J. Amer. Chem. Soc.*, 1906, **28**, 588.

[5] Steele, McIntosh, and Archibald, *Phil. Trans.*, 1906, **205**, 99.

[6] Ruhoff, Burnett, Emmet, and Reid, *Org. Synth.*, **2**, 338.

method gives hydrogen bromide contaminated only by a little water and bromine. The water is removed by distillation in the vacuum-line through two traps at −111° (melting carbon disulphide), and the bromine by slow passage twice through a tube containing copper turnings. The most sensitive check on the purity of hydrogen bromide is the conductivity of the liquid. Previous values of the specific conductivity of liquid hydrogen bromide are 0·05 [5] and 0·004 μmho cm.$^{-1}$.[7] In direct preparations where electrical measurements of high accuracy were not required, the solvent was purified by one operation as described above; the specific conductivity of this material was 0·019 μmho cm.$^{-1}$. Four further purifications reduced the specific conductivity of the liquid to 0·00014 μmho cm.$^{-1}$, and this liquid was used for electrical measurements. All the electrical measurements on liquid hydrogen bromide described in this paper were made at −83·6° (melting ethyl acetate). Hydrogen iodide was prepared by the direct union of the elements.[8]

Materials.—All the materials except those referred to below were available as chemicals of reagent or "AnalaR" quality. Tetra-n-butylammonium bromide and tetraphenylarsonium bromide were made by shaking solutions of tetra-n-butylammonium iodide or tetraphenylarsonium chloride in methanol with an excess of silver oxide, filtration, and neutralization with hydrobromic acid. The neutralized solutions were then evaporated to dryness and the solids pumped for 1 hr. at 100°. Phosphine was generated by the action of aqueous sodium carbonate on phosphonium iodide, itself made by a standard method.[9] Phosphorus oxybromide was prepared from phosphorus pentabromide and phosphorus pentoxide by a standard method.[10] The boron tri-iodide was kindly given by Dr. P. Thompson.

Analytical Methods.—Carbon, hydrogen, and nitrogen were determined by standard micro-combustion methods. Halogen was determined as silver halide. Tin was determined as stannic oxide. Phosphorus was determined spectrophotometrically [11] by comparison with standard solutions. Boron was found not to interfere. Boron was determined acidimetrically as the borate–mannitol complex; this cannot, however, be used in the presence of phosphate. Compounds containing both boron and phosphorus were hydrolysed in a mixture of much methanol and a little water; a trace of concentrated sulphuric acid was added, and the methyl borate distilled into dilute sodium hydroxide. After acidification, the boric acid–mannitol complex was titrated with sodium hydroxide.

RESULTS

Tetra-n-butylammonium and tetraphenylarsonium bromide gave, with liquid hydrogen bromide, hydrogen dibromides. Smaller cations did not lead to hydrogen dibromides. About 0·25 g. of the material was dissolved in liquid hydrogen bromide, the solvent was then removed, and the solid product evacuated at −83·6°, then allowed to warm to room temperature. Analysis confirmed the composition of *tetra-n-butylammonium hydrogen dibromide* (Found: Br, 39·4, and in two separate estimations, 1·05 and 1·00 mole per mole of acid. $C_{16}H_{37}Br_2N$ requires Br, 39·6%, and 1·00 mole per mole of acid). That of *tetraphenylarsonium hydrogen dibromide* was also confirmed by analysis (Found: Br, 29·4, and 1·05 mole per mole of acid. $C_{24}H_{21}AsBr_2$ requires Br, 29·4%, and 1·00 mole per mole of acid).

TABLE 1.

Specific and molar conductivities of compounds in liquid hydrogen bromide.

Compound	Concn. (mole/l.)	Specific conductance (10^{-6} ohm^{-1} cm.$^{-1}$)	Molar conductance ohm^{-1} cm.$^{-1}$ mole^{-1})	Compound	Concn. (mole/l.)	Specific conductance (10^{-6} ohm^{-1} cm.$^{-1}$)	Molar conductance (ohm^{-1} cm.$^{-1}$ mole^{-1})
PBr_5	0·012	0·10	—	Acetyl bromide	0·016	0·0023	0·00014
PBr_5	0·022	0·12	—	$POBr_3$	0·061	0·34—0·95	0·005—0·016
Me_4NBr	0·023	9·8	0·432	PH_4Br	Satd.	0·70	—
Me_4NBr	0·050	24·3	0·489	$SnBr_4$	0·064	0·024	0·00038
Et_4NBr	Satd.	0·075	—	Al_2Br_6	Satd.	0·073	—
Pyridine ...	0·024	1·07	0·046				

---

[7] Smythe and Hitchcock, *J. Amer. Chem. Soc.*, 1933, **55**, 1833.

[8] Cayley and Burfood, *Inorg. Synth.*, **1**, 189.

[9] Work, *Inorg. Synth.*, **2**, 141.

[10] Booth and Seaguiller, *Inorg. Synth.*, **2**, 151.

[11] Allen, *J. Biochem.*, 1940, **34**, 358.

Table 1 lists the conductivities of compounds studied in liquid hydrogen bromide. The conductivities of pyridine and tetramethylammonium bromide were studied as a function of concentration. The molar conductivity of pyridine is plotted against the square root of the concentration in Fig. 1, and shows a straight-line relation from concentrations of ~0·1 to ~1·0 mole l.$^{-1}$. Such a straight-line relationship at higher concentrations is predicted by the theory of Fuoss and Kraus.[12] Deviations from linearity at concentrations above 1·0 mole l.$^{-1}$ probably reflect changes in activity coefficients. Tetramethylammonium bromide showed some most unusual features in the solvent. Solutions more concentrated than about 0·06M divided into two liquid layers. The lower layer was colourless and clear. The upper was pale yellow and opalescent and its amount increased with increase of tetramethylammonium bromide concentration. No solution could be prepared which consisted of the upper layer only and the solubility of tetramethylammonium bromide was below 1·27 moles l.$^{-1}$. The upper, opalescent, layer was much more highly conducting than the bottom layer, as was found by preparing solutions in which the electrodes were totally immersed in one or other of the layers. These results are summarized in Table 2. In conductivity titrations with tetramethylammonium bromide it was necessary to use solutions sufficiently dilute to avoid two-phase formation. The result of such a conductivity titration with boron tribromide is shown in Fig. 2. The titration curve shows a sharp break at a ratio of 1 : 1. The resulting *tetramethylammonium tetrabromoborate* was soluble in liquid hydrogen bromide, but could be isolated as a solid when

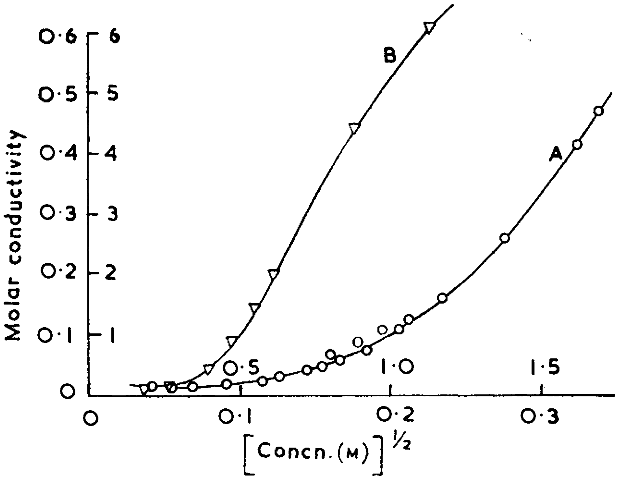

FIG. 1. Molar conductivity (ohm^{-1} cm.$^{-1}$ mole^{-1}) of pyridine plotted against the square root of the concentration. Outer figures on axes refer to curve A and inner figures to curve B.

TABLE 2.

Specific and molar conductivities of tetramethylammonium bromide.

Concn. (mole/l.)	No. of layers	Layer surrounding plates	Specific conductance (10^{-6} ohm^{-1} cm.$^{-1}$)	Molar conductance (ohm^{-1} cm.$^{-1}$ mole^{-1})
0·023	1	—	9·8	0·43
0·050	1	—	24·3	0·49
0·115	2	Lower only	24·5	—
0·195	2	Both	1630	—
0·416	2	Lower only	658	—
0·519	2	Upper only	7530	—
0·605	2	Both	6770	—
0·740	2	Both	8290	—
1·27	2		Incomplete solution	

---

[12] Kraus and Fuoss, *J. Amer. Chem. Soc.*, 1933, **55**, 21; Fuoss and Kraus, *ibid.*, p. 2387.

the solvent is evaporated (Found: C, 12·6; H, 3·0; B, 2·5; Br, 80·7; N, 3·4. $C_4H_{12}BBr_4N$ requires C, 11·9; H, 2·9; B, 2·7; Br, 79·0; N, 3·5%).

The insolubility of tetraethylammonium bromide in the solvent made it unsuitable for conductometric titrations, but a suspension could be used to afford *tetraethylammonium tetrabromoborate* in good yield (Found: C, 20·5; H, 5·5; B, 2·0; Br, 66·6; N, 3·0. $C_8H_{20}BBr_4N$ requires C, 20·9; H, 4·4; B, 2·35; Br, 69·4; N, 3·0%). It seems necessary that the solvent should be present, the boron tribromide reacting with the small quantity of base which dissolves. Analysis confirmed the composition Et_4NBBr_4.

Pyridinium tetrabromoborate has been prepared by Lappert [13] by another method. When pyridinium bromide was titrated against boron tribromide in the solvent a white precipitate of the salt appeared at the first addition of boron tribromide. The conductivity plot, however, still shows a break at the 1 : 1 point (Fig. 2). Removal of the solvent and of the excess boron tribromide left the bromoborate (Found: C, 15·0; H, 1·97; B, 2·6; Br, 77·1; N, 3·1. Calc. for $C_5H_6BBr_4N$: C, 14·6; H, 1·5; B, 2·6; Br, 77·8; N, 3·1%).

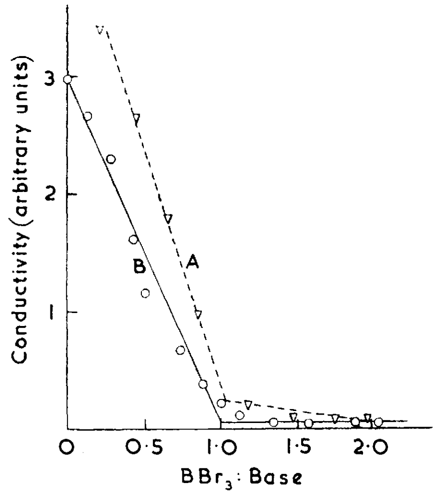

FIG. 2. Conductometric titrations of (A) Me_4NBr and (B) pyHBr against BBr_3.

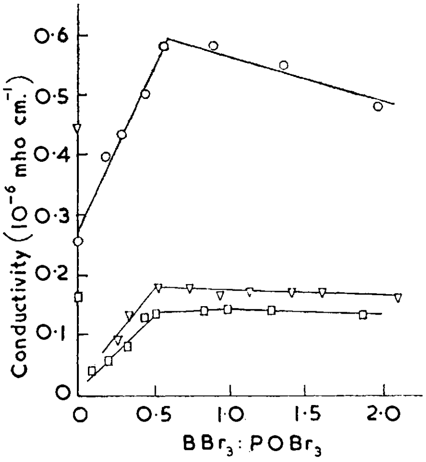

FIG. 3. Conductometric titration of $POBr_3$ against BBr_3.

Tetrabromophosphonium tetrabromoborate, $PBr_4^+BBr_4^-$, has been prepared by another method.[14] The insolubility of phosphorus pentabromide precluded a conductometric titration; however, it was possible to use a suspension in the solvent to prepare the tetrabromoborate in good yield (Found: B, 1·6; Br, 93·9; P, 4·5. Calc. for BBr_8P: B, 1·6; Br, 93·9; P, 4·55%).

Phosphonium tetrabromoborate, $PH_4^+BBr_4^-$, was prepared by treating a suspension of phosphonium bromide in the solvent with boron tribromide (Found: Br, 85·2. H_4BBr_4P requires Br, 87·3%). Again the base was too insoluble for a conductometric titration to be carried out. Analysis confirmed the composition.

The variability in the conductivities of phosphorus oxybromide in the solvent indicated that a titration with boron tribromide might present difficulties. It was found, however, that after the first addition of boron tribromide a fairly consistent titration curve could be obtained. The titration curves (Fig. 3) shows a sharp break at the 2 : 1 point, indicating the formation of the compound $(POBr_3)_2BBr_3$ in solution. The conditions of preparation and titration, *i.e.*, excess of boron tribromide, were such as to favour the isolation of the known 1 : 1 compound,[15] $POBr_3,BBr_3$, on removal of the solvent. Analysis of the white powder confirmed the composition (Found: B, 2·0; Br, 88·2; P, 5·8. Calc. for BBr_6PO: B, 2·0; Br, 89·6; P, 5·8%).

---

[13] Lappert, *Proc. Chem. Soc.*, 1957, 21.

[14] Tarible and Moissan, *Compt. rend.*, 1893, **116**, 1521.

[15] Frazer, Gerrard, and Patel, *J.*, 1960, 726.

Ammonium bromotrichloroborate has been reported together with analytical data;[16] we investigated the reactions of boron trichloride in liquid hydrogen bromide with tetramethylammonium bromide. After treatment of tetramethylammonium bromide with an excess of boron trichloride and removal of the solvent and excess of boron halide, analysis of the residue showed that it was tetramethylammonium tetrabromoborate (Found: C, 12·7; H, 3·1; Br, 78·2%).

In view of the successful preparation of chlorotrifluoroborates in liquid hydrogen chloride the reactions of boron trifluoride in the solvent were investigated. When tetramethylammonium bromide was treated with an excess of boron trifluoride in the solvent, evaporation gave tetramethylammonium bromide (Found: C, 29·6; H, 7·6; N, 9·1. Calc. for $C_4H_{12}BrN$: C, 31·6; H, 7·8; N, 9·1%). A similar experiment with tetraethylammonium bromide indicated that no stable compound was left at room temperature, the bromide being recovered (Found: C, 46·2; H, 10·2; N, 6·9. Calc. for $C_8H_{20}BrN$: C, 45·7; H, 9·6; N, 6·7%). The conductometric titration of pyridine against boron trifluoride was investigated to see if interaction took place in the solution; though addition of boron trifluoride was accompanied by a marked drop in conductivity no definite break in the titration curve could be identified (Fig. 4).

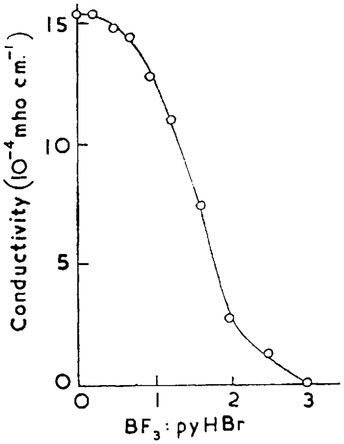

FIG. 4. Conductometric titration of pyHBr against BF_3.

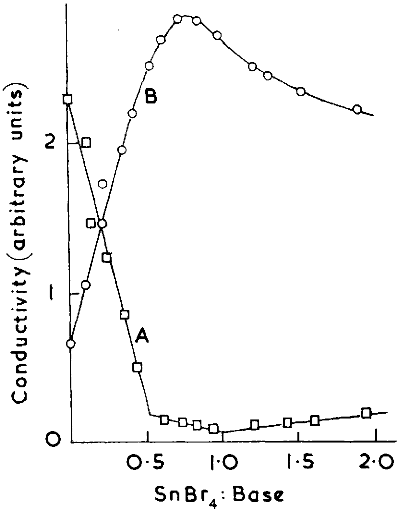

FIG. 5. Conductometric titrations of (A) pyHBr and (B) $POBr_3$ against $SnBr_4$.

The reactions of stannic bromide as an acid in the solvent were studied in titrations against pyridine and phosphorus oxybromide. The conductometric titration of stannic bromide against pyridine is shown in Fig. 5. At the first addition of stannic bromide to the pyridine solution a precipitate appeared. This did not prevent a satisfactory conductivity curve from being obtained which showed a sharp break at an acid : base ratio of 1 : 2 and a less distinct one at a ratio of 1 : 1, corresponding to the compounds $(pyH)_2SnBr_6$ and perhaps $pyHSnBr_5$. However, though the 1 : 1 salt may exist in solution at −83·6°, removal of the solvent and pumping to remove the excess of stannic bromide left *dipyridinium hexabromostannate* (Found: C, 15·3; H, 1·4; Br, 64·3; N, 3·75; Sn, 15·1. $C_{10}H_{12}Br_6N_2Sn$ requires C,·15·8; H, 1·6; Br, 63 2; N, 3·7; Sn, 15·6%).

Phase studies have shown that no compound exists between phosphorus oxybromide and stannic bromide at room temperature.[17] The curve for the conductometric titration of stannic bromide against phosphorus oxybromide is shown in Fig. 5; there is no end-point of definite stoicheiometry discernible, but it is difficult to explain the general rise and fall in conductivity except in terms of ionization.

A conductometric titration of pyridinium bromide with bromine was attempted in the hope

---

[16] Kynaston, Larcombe, and Turner, *J.*, 1960, 1772.

[17] Sheldon and Tyree, *J. Amer. Chem. Soc.*, 1958, **80**.

of showing the existence of one or more salts $pyHBr_n$. No appreciable change of conductivity on addition of bromine was found and it is clear that bromine does not act as a Lewis acid in liquid hydrogen bromide.

Work in liquid hydrogen iodide was restricted to the preparation of tetraiodoborates. Tetramethylammonium iodide (0·260 g.) was introduced into a reaction cell and pumped for a short time at 100° to remove any residual water; 5 ml. of the solvent were then frozen upon it. Sufficient boron tri-iodide to give the 1 : 1 salt was then distilled into the cell. The mixture was melted and the solvent evaporated. A fine powder was left, coloured very pale yellow with iodine. It was generally found to be impossible to obtain products from liquid hydrogen iodide completely free from iodine. This has been confirmed by other workers.[3] Analysis showed that the compound was *tetramethylammonium tetraiodoborate* (Found: C, 8·3; H, 2·1; B, 1·7; I, 86·8; N, 2·65. $C_4H_{12}BI_4N$ requires C, 8·1; H, 2·0; B, 1·8; I, 89·7; N, 2·35%). Tetraethylammonium bromide was treated in the same way as the tetramethylammonium salt except that a 3-fold excess of boron tri-iodide was used. After the solvent was removed, the residual nearly pure tetraethylammonium tetraiodoborate was kept in a vacuum for an hour to remove the excess of boron tri-iodide (Found: B, 1·7; I, 80·4. Calc. for $C_8H_{20}BI_4N$: B, 1·65; I, 78·3%).

In preparing the pyridinium salt, boron tri-iodide (1·20 g.) was distilled into the cell and treated with the solvent (5 ml.) so as to observe the solubility. The compound was largely but not completely soluble. The stoicheiometric quantity of pyridine (0·245 g.), to give the pyridinium salt, was then added. On removal of the solvent the product was a homogeneous, white, solid which became yellow in a few hours. Since the product might possibly have been the pyridine–boron tri-iodide adduct,[18] py,BI_3, a complete elemental analysis was performed which confirmed the expectation that the product was *pyridinium tetraiodoborate* (Found: C, 10·1; H, 1·4; B, 1·0; I, 84·4; N, 2·5. $C_5H_6BI_4N$ requires C, 10·1; H, 1·0; B, 1·3; I, 84·8; N, 2·4%).

DISCUSSION

The general conclusion from this work is the great similarity in solvent properties between liquid hydrogen bromide and liquid hydrogen chloride. As with hydrogen chloride, the ionization equilibrium is best represented by the equation

$$3HHal \rightleftharpoons H_2Hal^+ + HHal_2^- \qquad (1)$$

and it is possible to stabilize the hydrogen dibromide ion in crystal lattices provided that the cation is large enough. As with hydrogen chloride, either halide ion or proton transfer can be regarded as the primary step in equation (1). Thus both pyridine, a proton acceptor, and phosphorus pentabromide, a bromide-ion donor, are strong bases in the solvent. However, hydrogen bromide is a more strongly acid solvent than hydrogen chloride. In hydrogen chloride, boron trifluoride is a sufficiently powerful Lewis acid for the equilibrium

$$HHal_2^- + BF_3 \rightleftharpoons HHal + BHalF_3^- \qquad (2)$$

to lie heavily to the right, whereas in liquid hydrogen bromide the conductometric titrations presented in this paper indicate that the equilibrium lies further to the left. The lower dielectric constant (ε 7·0) of liquid hydrogen bromide means that fewer substances are soluble in it than in liquid hydrogen chloride (ε 10·6). This makes the performance of conductometric titrations more difficult in liquid hydrogen bromide, though the general pattern of conductivities and the way in which they change with dilution is the same in liquid hydrogen bromide and hydrogen chloride. Conductivities in both solvents behave as predicted by the Fuoss and Kraus[12] theory on change of concentration. In spite of the limited range of materials readily soluble in liquid hydrogen bromide, the solvent offers many possibilities as a preparative medium, as does liquid hydrogen iodide, for many materials though incompletely soluble will react completely.

The formation of two liquid layers beyond a certain concentration of tetramethylammonium bromide in liquid hydrogen bromide is very unusual; the only other system

---

[18] Muetterties, *J. Inorg. Nuclear Chem.*, 1960, **15**, 102.

in the liquid hydrogen halides to do this is the, by no means analogous, uranium hexafluoride–liquid hydrogen fluoride system.[19] Two-layer liquid systems have been discussed in detail by Belyaev.[20] For systems of the type AX_m–BX_n, he concludes that two liquid phases are probable if one component is of a salt-like character, and the other is largely covalent containing a formal cation of high charge density. Such a system is KCl–$AlCl_3$. The system Me_4NBr–HBr can, by a stretch of the imagination, be admitted to this category, since the proton has a high charge density. The more highly conducting layer in Me_4NBr–HBr solutions has a conductivity comparable with that of solutions of tetramethylammonium chloride in liquid hydrogen chloride.

One of us (J. A. W.) acknowledges a D.S.I.R. grant.

University Chemical Laboratory, Cambridge. [*Received, September* 24*th*, 1962.]

---

[19] Rutledge, Jarrvand, and Davis, *J. Phys. Chem.*, 1953, **57**, 541.
[20] Belyaev, *Russian Chem. Rev.*, 1960, **29**, 428.