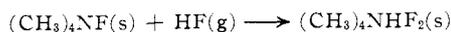


## Strong Hydrogen Bonds. II. The Hydrogen Difluoride Ion

Sir:

There has been much interest in the bond energy of the hydrogen difluoride ion. Current textbooks list values ranging from  $\sim 27$  to  $58$  kcal./mole. The first value is just slightly greater than the experimental heat of reaction of cesium fluoride with hydrogen fluoride, while the latter is due to a value corrected for lattice effects by Waddington.<sup>1</sup> We have now determined an enthalpy of  $-37$  kcal./mole for the reaction



This is the largest experimentally determined hydrogen bond energy reported to date. Further, lattice expansion should be slight for this reaction.<sup>2</sup> Thus the value of  $-37$  kcal./mole should be within 1 to 2 kcal. of the heat of the hydrogen bond in  $\text{HF}_2^-$ .

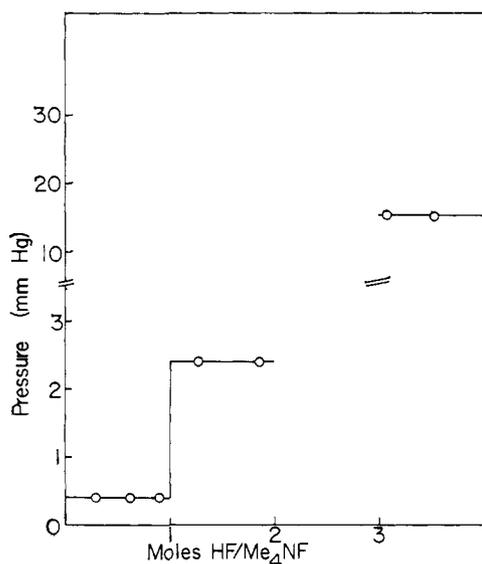


Fig. 1.—Pressure-composition isotherm for the system hydrogen fluoride-tetramethylammonium fluoride at  $90.5^\circ$ .

Tetramethylammonium fluoride was prepared under anhydrous conditions by the method of Tunder and Siegel<sup>3</sup> with slight modification. Anhydrous hydrogen fluoride was prepared by the thermal decomposition of potassium hydrogen difluoride which had been dried according to the method of Kilpatrick.<sup>4</sup> The interaction of hydrogen fluoride with tetramethylammonium fluoride was carried out in a vacuum line constructed of type K copper tubing with all joints silver alloy brazed. The sample tube and valves were constructed of monel. Pressure was measured by means of Wallace and Tierman Model 145 gauges constructed of monel with actuating bellows of Ni-Span-C. The entire copper apparatus, except the gauges, was thermostated at the desired temperatures. The temperatures used were high enough so that the hydrogen fluoride was present as a monomer. The pressure-composition isotherm for this system is shown in Fig. 1, and the variation of

(1) T. C. Waddington, *J. Chem. Soc.*, 1708 (1958).

(2) See Fig. 7 of D. H. McDaniel and R. E. Vallee, *Inorg. Chem.*, **2**, 996 (1963), for the effect of cation size on the heat of reaction of hydrogen halides with tetraalkylammonium halides.

(3) R. Tunder and B. Siegel, *J. Inorg. Nucl. Chem.*, **25**, 1097 (1963).

(4) M. E. Runner, G. Balog, and M. Kilpatrick, *J. Am. Chem. Soc.*, **78**, 5183 (1956).

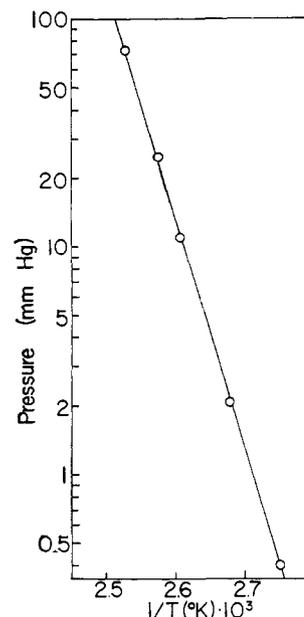


Fig. 2.—Variation of decomposition pressure of tetramethylammonium hydrogen difluoride with temperature.

pressure with temperature, for  $90.5$  to  $122.0^\circ$ , is shown in Fig. 2.

The region of composition between 2 and 3 moles of HF to  $(\text{CH}_3)_4\text{NF}$  was not studied owing to a failure of one of the gauges.

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## The Occurrence of the $\text{Re}_3\text{Br}_9$ Group in Compounds Derived from Rhenium(III) Bromide

Sir:

It has been shown recently<sup>1</sup> that rhenium(III) chloride is built up of  $\text{Re}_3\text{Cl}_9$  groups which contain a triangular  $\text{Re}_3$  metal atom cluster. This result had been anticipated from, and, in turn, provides an explanation for, the fact that numerous compounds prepared directly from rhenium(III) chloride contain the  $\text{Re}_3\text{Cl}_9$  group.<sup>1-5</sup>

We now wish to report evidence that rhenium(III) bromide similarly gives rise to numerous compounds containing the  $\text{Re}_3\text{Br}_9$  group which also contains the triangular  $\text{Re}_3$  metal atom cluster. Several new compounds,<sup>6</sup> the spectra of their solutions, and spectra of solutions of rhenium(III) bromide will be described in support of this statement.

The presence of the  $\text{Re}_3\text{Br}_9$  group has been conclusively demonstrated in  $\text{M}_2\text{Re}_3\text{Br}_{15}$ , where M represents quinolinium, pyridinium, or tetraethylammonium

(1) F. A. Cotton and J. T. Mague, *Proc. Chem. Soc.*, 233 (1964); *Inorg. Chem.*, **3**, 1402 (1964).

(2) F. A. Cotton, *et al.*, *Science*, 1305 (1964).

(3) F. A. Cotton and J. T. Mague, *Inorg. Chem.*, **3**, 1094 (1964).

(4) J. A. Bertrand, F. A. Cotton, and W. A. Dollase, *ibid.*, **2**, 1166 (1963); B. H. Robinson, J. E. Fergusson, and B. R. Penfold, *Proc. Chem. Soc.*, 116 (1963).

(5) J. E. Fergusson, B. R. Penfold, and W. T. Robinson, *Nature*, **201**, 181 (1964).

(6) Elemental analyses have been carried out on all new compounds mentioned and agree satisfactorily with the proposed formulas.

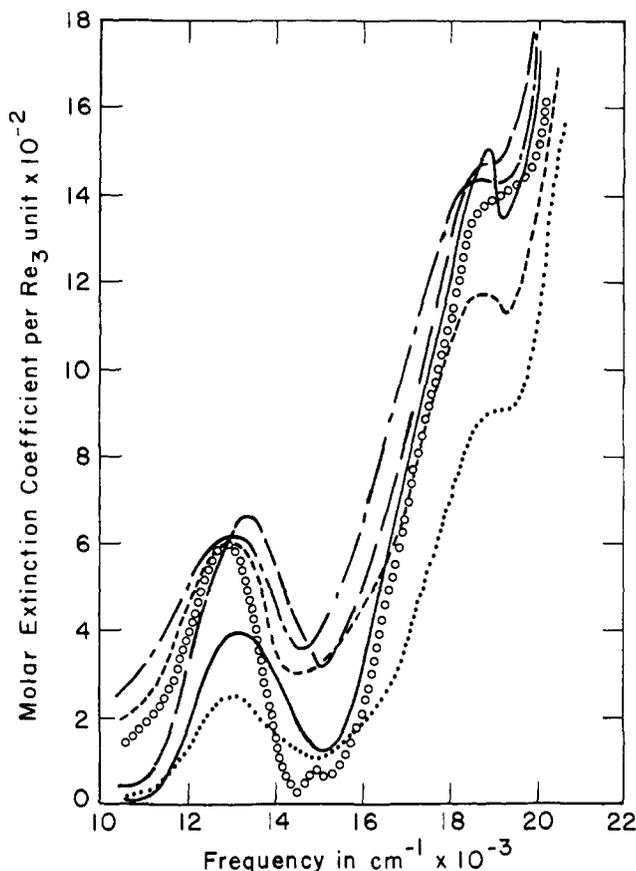


Fig. 1.—Visible spectra of rhenium(III) bromide and some derivatives.  $(\text{ReBr}_3)_n$  in 48% aq. HBr (—);  $(\text{ReBr}_3)_n$  in acetone (---);  $(\text{C}_5\text{H}_5\text{N})_2\text{Re}_4\text{Br}_{15}$  in acetone (OOOOO);  $(\text{C}_9\text{H}_5\text{N})_2\text{Re}_3\text{Br}_{11}$  in aq. HBr (— · —);  $[\text{ReBr}_3(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5\text{P}]_3$  in  $\text{CHCl}_3$  (.....);  $[\text{ReBr}_3(\text{C}_6\text{H}_5)_3\text{As}]_3$  in acetone (.....).

ion, by a single crystal X-ray study,<sup>7</sup> and in  $\text{Re}_3\text{Br}_9[(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5\text{P}]_3$ , because the latter compound is isomorphous with  $\text{Re}_3\text{Cl}_9[(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5\text{P}]_3$ , the structure of which has been determined.<sup>8</sup> The compounds  $[\text{ReBr}_3(\text{C}_6\text{H}_5)_3\text{As}]_n$  and  $(\text{C}_9\text{H}_5\text{N})_2\text{Re}_3\text{Br}_{11}$ , which have now been prepared from rhenium(III) bromide as well as solutions of rhenium(III) bromide in aqueous HBr and acetone, have visible spectra which are all very similar to one another and to the spectra of  $(\text{C}_5\text{H}_5\text{N})_2\text{Re}_4\text{Br}_{15}$  and  $\text{Re}_3\text{Br}_9[(\text{C}_2\text{H}_5)_2\text{C}_6\text{H}_5\text{P}]_3$ . These are shown in Fig. 1.

Not only are all of the spectra shown in Fig. 1 similar to one another, but they are quite similar to the characteristic spectrum of compounds containing the  $\text{Re}_3\text{Cl}_9$  group.<sup>1,3</sup> The main difference is that in the bromo compounds strong ultraviolet absorption, presumably of  $\text{Br} \rightarrow \text{Re}$  charge-transfer type, sets in at lower frequencies, and this tends to obscure the absorption band around  $19,000 \text{ cm}^{-1}$ . However, the characteristic pattern of absorption is clearly the same in both the  $\text{Re}_3\text{Cl}_9$  compounds and the rhenium(III) bromide derivatives, and is presumably characteristic of the  $\text{Re}_3$  cluster itself.

The appearance of this characteristic spectrum in the HBr and acetone solutions of rhenium(III) bromide suggests that it consists of  $\text{Re}_3\text{Br}_9$  units, though these may not be connected in the same way as in the chloride

(7) F. A. Cotton and S. J. Lippard, *Inorg. Chem.*, in press. The compound consists of equal numbers of  $\text{Re}_3\text{Br}_9$  groups and  $\text{ReBr}_3^{2-}$  groups. The  $\text{Re}_3\text{Br}_9$  group has essentially the same structure as the  $\text{Re}_3\text{Cl}_9$  groups occurring in other compounds. Its virtual symmetry is  $D_{2h}$ ; the Re-Re bonds are  $2.46 \pm 0.01 \text{ \AA}$  long.

since the two compounds are not isomorphous.<sup>8</sup> A complete structure determination<sup>8</sup> of rhenium(III) bromide should soon provide a conclusive answer on this point.

The compound  $\text{Re}_3\text{Br}_9[(\text{C}_6\text{H}_5)_3\text{P}]_3$  has also been prepared, but since no satisfactory solvent has been found, its spectrum in solution has not been recorded. However, it is isomorphous with the corresponding chloro compound whose trinuclear structure has been substantiated by spectral studies,<sup>1</sup> and, in addition, these  $(\text{C}_6\text{H}_5)_3\text{P}$  compounds are isomorphous with  $\text{Re}_3\text{Br}_9[(\text{C}_6\text{H}_5)_3\text{As}]_3$ .

Finally, it may be noted that the compound  $(\text{C}_9\text{H}_5\text{N})_2\text{Re}_3\text{Br}_{11}$  is to be compared with  $\text{CsRe}_3\text{Br}_{10}$ , recently reported.<sup>9</sup> The greater size of the quinolinium ion is perhaps responsible for stabilizing  $[\text{Re}_3\text{Br}_{11}]^{-2}$ . A complete report on these and other compounds as well as analogs in the rhenium(III) chloride system is in preparation.<sup>10</sup>

(8) F. A. Cotton and S. J. Lippard, unpublished work, still in progress.

(9) J. E. Fergusson and B. H. Robinson, *Proc. Chem. Soc.*, 189 (1964).

(10) This work is being supported by the U. S. Atomic Energy Commission.

(11) N.S.F. Predoctoral Fellow 1962-1965; Woodrow Wilson Fellow (Honorary), 1962-1963.

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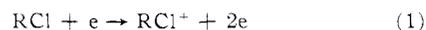
S. J. LIPPARD<sup>11</sup>

RECEIVED AUGUST 10, 1964

#### Appearance Potentials of the Lower Chloroalkanes

Sir:

In the mass spectrum of chloroalkanes of four or more carbon atoms, the abundance of the parent ion is almost invariably less than 1% relative to the most abundant peak.<sup>1</sup> It is not surprising, therefore, that electron impact estimates of the appearance potentials (A.P.) for the process



are still unknown for the chlorobutanes.<sup>2</sup> Such measurements are reported here even for *t*-butyl chloride, whose parent peak has a relative abundance of 0.01%. We also record an unexpected disagreement between some of our values of A.P. and those obtained by photoionization techniques.

Our A.P. were obtained on an A.E.I. Model MS 9 mass spectrometer. The chlorides were admitted to the electron source through an unheated inlet line. Acetylene and iodomethane with A.P. of 11.41 and 9.55 e.v. were primary standards of the voltage scale<sup>2</sup> although other secondary standards were used as checks.<sup>3</sup> Conventional semilogarithmic plots of ion current against ionization voltage<sup>4</sup> of chloroalkane and the standard substance were compared. The peak height was usually set at 100% at 50 v., although normalizations at 14-20 v. were occasionally advantageous. In the case of *t*-butyl chloride, the ionization efficiency curves showed substantial tailing and it was necessary to compare these directly with those of the standards. Similar measurements could not be made

(1) F. W. McLafferty, *Anal. Chem.*, **34**, 2 (1962).

(2) R. W. Kiser, "Tables of Ionization Potentials," T111-6142 Report, Kansas State University, 1960, 1962.

(3) M. Baldwin, A. Maccoll, and S. I. Miller in "Advances in Mass Spectrometry," Vol. 3, to be published by Pergamon Press, London, on the proceedings of a conference held in Paris, Sept., 1964.

(4) F. P. Lossing, K. U. Ingold, and I. H. Henderson, *J. Chem. Phys.*, **22**, 1489 (1954).