[Contribution from Argonne National Laboratory, and the Kedzie Chemical Laboratory, Michigan State College]

Fluorine Exchange Reactions between Hydrogen Fluoride and the Halogen Fluorides

By Max T. Rogers and Joseph J. Katz

The exchange of radioactive F^{18} between hydrogen fluoride and various halogen fluorides has been studied in both the liquid and vapor phase in metal apparatus. Certain related exchange reactions have been investigated, and convenient methods are described for counting radioactive fluorine in the form of gaseous fluorides. The exchange reactions between HF and the liquid interhalogen compounds BrF_3, ClF_3, BrF_5 and IF_5 were found to be essentially complete at room temperature with a contact time of ten minutes. The exchange reactions between HF and gaseous ClF_3, BrF_5 and IF_7 are essentially complete in a contact time of 3 minutes at room temperature and atmospheric pressure, while the exchange between HF and SF_6 or CCl_2F_2 and between ClF_3 and F_2 is essentially zero. The mechanism of the liquid and gas-phase reactions is briefly discussed. Although an atomic mechanism for the gas-phase reactions cannot be excluded, a mechanism involving formation of relatively stable intermediate complexes appears to be more satisfactory.

Introduction

The physical and chemical properties of the interhalogen compounds have recently received considerable attention.[1] Liquid BrF_3 conducts an electric current fairly well; solutions of KF or of SbF_5 in BrF_3 are good conductors, and salts of the type $KBrF_4$ and BrF_2SbF_6 have been isolated. Woolf and Emeléus[2] postulate the following ionic equilibria in BrF_3 solutions

$$2BrF_3 \rightleftarrows BrF_2^+ + BrF_4^- \quad (1)$$

$$KF + BrF_3 \rightleftarrows K^+ + BrF_4^- \quad (2)$$

$$SbF_5 + BrF_3 \rightleftarrows BrF_2^+ + SbF_6^- \quad (3)$$

If this hypothesis is correct, rapid exchange of fluorine should take place between HF and BrF_3 in the liquid phase through the equilibrium

$$HF + BrF_3 \rightleftarrows BrF_2^+ + HF_2^- \quad (4)$$

Similar equilibria are possible with other interhalogen compounds in the liquid phase. However, in the vapor phase it was considered possible that the exchange of fluorine between hydrogen fluoride and interhalogen ion would be slow as was observed for the $HF-F_2$ system by Dodgen and Libby.[3] A rapid homogeneous vapor-phase reaction would probably take place if it occurred by the formation of an intermediate molecular complex as postulated for the $HBr-Br_2$ exchange.[4]

The rates of the exchange reactions between hydrogen fluoride and the interhalogens in the vapor phase should provide information concerning the possible existence and stability of intermediate molecular complexes. Similar data for the liquid-phase reactions would be a check on the hypotheses made by Emeléus concerning the nature of the solutions. No previous data on exchange reactions involving fluorine have been reported except a study of the $HF-F_2$ system in the gas phase by Dodgen and Libby.[3] We have, therefore, investigated a variety of these exchange reactions.

Experimental

Materials.—Anhydrous HF, BrF_3, BrF_5, ClF_3 and SbF_5 were obtained from Harshaw Chemical Co. in steel cylinders. These compounds were purified by distillation before use. SF_6, CCl_2F_2 and BF_3 were obtained from The Matheson Co. in cylinders and were used directly, as was F_2 gas from Pennsylvania Salt Co. Iodine heptafluoride was prepared by the method of Schumb[5] from IF_5 (General Chemical Co.) and F_2.

The 112-min. nuclide F^{18}, which emits a 0.7-mev. positron, was prepared by irradiation of anhydrous liquid hydrogen fluoride in the cyclotron by the reaction $F^{19}(n,2n)F^{18}$, using fast neutrons produced by the bombardment of a lithium target with deuterons; Libby[3] has shown this procedure to yield a pure fluorine activity. Alternatively, F^{18} was prepared by the reaction $F^{19}(\gamma,n)F^{18}$, using the 84-mev. X-rays produced by the University of Chicago betatron. A decay curve taken over four half-lives revealed no contaminating impurities. In both cases, specific activities of the order of 5000–10000 counts/min. were readily obtained.

Apparatus.—Experiments were carried out using a vacuum-line apparatus constructed of copper and nickel with silver-soldered or flared connections. Tanks of HF, ClF_3, BrF_5 and He were connected directly to this line. Provision was also made for attaching copper, nickel and fluorothene tubes or reaction vessels. Either Crane bellows valves or Hoke diaphragm valves were used, and pressures were read on Helicoid gages equipped with Monel metal Bourdon tubes. Liquids were stirred by removing the vessel from the vacuum line and shaking; the reaction vessels were provided with valves and a flared joint to facilitate this operation.

Fluorine[18] was counted as hydrogen fluoride (or other gaseous fluoride) in a 600-ml. copper vessel connected to the vacuum line; the counter was a Victoreen 1B85 Aluminum Thyrode. A vacuum-tight seal was made between the thyrode and the copper vessel with a fluorothene gasket and a specially machined compression screw. Lacquer was removed from the counting tube before use, and a thin layer of fluorothene grease placed over the soldered joint; under these conditions a tube would survive continuous use for about a month before failure occurred by corrosion at the solder joint. The counter was protected by a lead shield to permit measurements *in situ*. A standard scale-of-64 scaler was used, and counts were made for two-minute periods.

Measurements on the $HF-ClF_3$ gas-phase system were also made in a fluorothene apparatus. A fluorothene vessel of 800-cc. volume was made by flaring two 400-cc. beakers and compressing the edges together by a metal ring. The top of the vessel was fitted with two teflon stopcocks held in place by teflon nuts. These plug-type stopcocks were made from a solid block of teflon machined with a standard flare joint on top, a male threaded portion at the bottom (for connection to the vessel), and a fluorothene plug carefully machined to fit a tapered hole in the teflon block. When the plug was held in by a compression spring and lubricated by fluorothene grease, the apparatus was sufficiently vacuum-tight for the short periods involved. The outlet plug was connected by a fluorothene flare-fitting to a fluorothene NaF absorption tube, thus eliminating any contact with metal surfaces.

Method.—Liquid-phase exchanges were carried out in nickel or fluorothene tubes. A weighed, outgassed sample of hydrogen fluoride was counted and transferred to the reaction vessel, which contained a weighed sample of the interhalogen compound frozen at −180°. The tube was

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[1] See reviews by A. G. Sharpe, *Quart. Rev. Chem. Soc.* (*London*), **IV**, 115 (1950); V. Gutmann, *Angew. Chem.*, **62**, 312 (1950).

[2] A. A. Woolf and H. J. Emeléus, *J. Chem. Soc.*, 2865 (1949).

[3] H. W. Dodgen and W. F. Libby, *J. Chem. Phys.*, **17**, 951 (1949).

[4] L. C. Liberatore and E. O. Wiig, *ibid.*, **8**, 165, 349 (1940); W. F. Libby, *ibid.*, **8**, 348 (1940).

[5] W. C. Schumb and M. A. Lynch, *Ind. Eng. Chem.*, **42**, 1383 (1950).

warmed by using an appropriate bath; the liquids were mixed and then separated by vacuum distillation. Two or three fractional distillations were carried out using baths of suitable temperatures. The recovered hydrogen fluoride was then transferred to the counter vessel, and a final count taken, after which the recovered HF was weighed. The interhalogen compounds ClF_3 and BrF_5 were also counted in the vapor phase before a final weight was taken; these compounds could not be completely separated from hydrogen fluoride by the distillation procedure used. In these cases, the hydrogen fluoride was absorbed in sodium fluoride and subsequently recovered by heating the pellets of $NaHF_2$ to about 300° in a vacuum. Initial and final counts were corrected for background and coincidence losses; the final counts were also corrected for the decay of F^{18}.

Gas-phase exchange reactions were carried out by mixing weighed, outgassed samples of hydrogen fluoride and the interhalogen compound in one of several large copper reaction vessels (570-, 1140-, 1710-ml. volume). The hydrogen fluoride was first counted, and both gases were counted and weighed after separation. The HF–BrF_3 and HF–F_2 mixtures were separated by passage through several traps held at appropriate temperatures to condense out the hydrogen fluoride. Pressures were maintained close to 1 atm. for both the pure gases and for the mixtures.

Two exchange reactions involving active ClF_3 were carried out. Labeled ClF_3 was prepared by mixing HF* and ClF_3 and removing the HF with NaF, leaving ClF_3*. Active $NaHF_2$*, prepared by absorbing HF* on NaF, was used in several experiments designed to check the exchange of F between ClF_3 (or BrF_5) and $NaHF_2$*. Active NaF* resulted when $NaHF_2$* was heated and was assumed to contain one-half the original activity in the HF* used to make the $NaHF_2$*.

Probable Errors.—The usual errors inherent in counting are increased here because of the relatively short half-life and also as a result of the high background arising from exchange of HF with the AlF_3 on the surface of the counter and the CuF_2 on the surface of the counting vessel. Several experiments were made to determine whether any activity was introduced into the interhalogen compound by exchange with active fluorides on the surface of the apparatus; results indicated the error from this source was small (< 1%).

Some loss (≃3%) of both HF and interhalogen compound always occurred in handling because of the great reactivity of these compounds. Since the degree of polymerization of hydrogen fluoride changes rapidly with temperature and pressure, the same sample may not always give the same count when present in the counter at the same pressure (as is assumed in the method used here) in the absence of very close temperature control. It is also assumed here that the radioactive F atoms would give the same count whatever gaseous fluoride they were present in.

The percentage exchange calculated has a probable error of about ±10% as a result of these uncertainties, and individual runs may have larger errors. For these reasons the exchange is assumed to be complete or not to occur to any appreciable extent if the percentage exchange is >90% or < 10%, respectively. Measurements were made at room temperature, 27 ± 3°, unless otherwise stated. Time of contact was usually the minimum for the apparatus and technique used (3 ± 1 minutes for gas phase reactions and 10 ± 3 minutes for liquid phase reactions).

The final count to be expected for complete exchange is calculated in each case on the assumption that all fluorine atoms in the system were capable of undergoing exchange. From this and the count expected if no exchange occurred, a percentage exchange was calculated. In a typical experiment, 0.18 mole HF gas, which gave a count of 10,200 c./min. in the gas counter, was mixed with 0.073 mole ClF_3 gas; after separation 0.18 mole of HF gave a final count of 4564 c./min. (4580 calculated for complete exchange) and 0.073 mole of ClF_3 gave a final count of 5710 c./min. (5620 observed for complete exchange), leading to two independent calculations of the percentage exchange of 100.3 and 101.6%, respectively.

Results and Discussion

Liquid-phase Reactions.—The exchange of fluorine atoms was essentially complete in 10 minutes at 27° for all of the reactions examined in the liquid phase (Table I). This behavior is readily explained by the hypothesis that ionic equilibria of the following types exist in the solutions

$$IF_5 + HF \rightleftharpoons IF_4^+ + HF_2^-$$

$$HF + SbF_5 \rightleftharpoons H^+ + SbF_6^-$$

as well as equilibria shown in equations (1) and (4). This is in agreement with the conclusions of Emeléus based on other experiments. The exchange reaction between ClF_3 and BrF_3 may proceed through the equilibrium

$$ClF_3 + BrF_3 \rightleftharpoons ClF_2^+ + BrF_4^-$$

and agrees with other observations that chlorine trifluoride acts as a base in bromine trifluoride solution.

All of the observations made in solution are consistent with the hypothesis that exchange proceeds through common ions. A non-ionic intermediate complex would also account for the results, but it does not appear necessary to use this explanation at this time.

Gas-phase Exchange Reactions.—The rapid gas-phase exchange reactions are rather more surprising, especially if they prove to be true homogeneous gas reactions. These reactions may, however, be heterogeneous and occur either on the walls of the metal apparatus or on the surface of the sodium fluoride used to absorb the hydrogen fluoride from the mixture. To determine whether catalysis by $NaHF_2$ or NaF occurs in the separation step, radioactive $NaHF_2$* and NaF* were prepared, and ClF_3 was passed over each under conditions as nearly similar as possible to those prevailing in the separation step; a small percentage exchange is observed in each case (Table I). Although the exchange might conceivably be more rapid when the HF–ClF_3 mixture is passed over sodium fluoride than when ClF_3 itself is passed over the solid, it scarcely seems likely from

TABLE I

EXCHANGE REACTIONS OF FLUORINE BETWEEN PAIRS OF FLUORIDES AT 27°

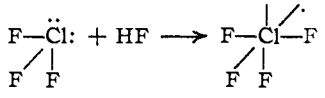
Reaction system	Components	Exchange[a]
Liquid phase[b]	HF* with BrF_3, ClF_3, BrF_5, IF_5, or SbF_5	++
	ClF_3*–BrF_3	++
Vapor phase[c]	HF* with ClF_3, BrF_3 BrF_5, or IF_7	++
	ClF_3*–BF_3	++
	HF*–SF_6	–[d]
	HF*–CCl_2F_2	–[e]
	HF*–F_2	–
	ClF_3*–F_2	–
Vapor–solid[c]	HF*–NaF	++
	ClF_3–$NaHF_2$*	+[f]
	ClF_3–NaF*	+[g]
	BrF_5–$NaHF_2$*	+[h]
	F_2–NaF*	–

[a] ++, complete exchange. *i.e.*, > 90%; +, slow, measurable exchange; –, no exchange, *i.e.*, <10% exchange. [b] Reaction time, 10 min. [c] Reaction time, 3 min. [d] 45 min. Exchange does not increase with time. [e] 30 min. Exchange does not increase with time. [f] 14% exchange. [g] 3–20% exchange. [h] 16% exchange.

these results that the observed complete exchange can be attributed to exchange in this step. To test the second possibility, namely, catalysis by metal fluorides, an apparatus was built which enabled the gases to be mixed and the hydrogen fluoride separated without coming in contact with metal—all parts were fluorothene or teflon, lubricated where necessary with fluorothene grease. Although such surfaces should be much less active catalytically than the interior of metal vessels, complete exchange was again observed between hydrogen fluoride and ClF_3. Hence, if the exchange is heterogeneous, it must be catalyzed by both CuF_2 and fluorothene surfaces or, alternatively, be catalyzed by the sodium fluoride surface under conditions not duplicated in the gas–solid exchange reactions investigated here. It appears likely, therefore, that these gas-phase reactions are homogeneous.

If, as appears reasonable on the basis of the present evidence, the gas-phase reactions are rapid and homogeneous, the question arises whether the exchange proceeds by an atomic mechanism or through the formation of intermediate molecular complexes. Dodgen and Libby[3] concluded from a straightforward calculation that the observed $HF–F_2$ exchange rate could be accounted for by an atomic mechanism if the heat of dissociation of fluorine were less than 38 kcal./mole. A similar calculation indicates that to account for the rate of exchange we observe for ClF_3–HF the Cl–F bond energy would have to be less than 40 kcal./mole. The most recent experimental value of the dissociation energy of fluorine[6] is 38.9 kcal./mole and the probable value for the Cl–F bond energy is about 42 kcal./mole, calculated using the data of Doescher and of Schmitz and Schumaker.[7] An atomic mechanism for these reactions cannot, then, be immediately excluded. However, the $ClF_3–F_2$ exchange is slow (or zero) at room temperature and, since it should proceed at least as readily by an atomic mechanism as the $HF–F_2$ or HF–ClF_3 exchanges, an atomic mechanism seems unlikely. We are led, therefore, to prefer a mechanism involving intermediate complexes for the homogeneous reactions we have studied.

The observed rate for the ClF_3–HF exchange is at least 0.2 l./mole-sec. and would be accounted for if the free energy of activation is less than about 11 kcal./mole. It is difficult to estimate the free energy of activation of a complex between ClF_3 and HF; using the Hirschfelder rule[8] and a Cl–F bond energy of 42 kcal./mole, a very rough approximation would be about 40 kcal./mole. However, such a complex may be stabilized to a large extent by formation of extra covalent bonds, or likely, by hydrogen bonds. The structure of ClF_3 is known[9] to be pyramidal with ∢FClF = 86.5°; IF_5 has a configuration approximating an octahedron with one corner occupied by an unshared pair of electrons and the angles ∢FIF lying between 80 and 90°. If regular covalent bonds were formed, the reaction



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would be exothermic by about 10.5 kcal./mole, and no great change in bond angles would be involved in its formulation. Hence it seems possible that an intermediate complex I with a similar structure might have a sufficiently small activation free energy of formation. Similar remarks apply to the $HF–BrF_5$ exchange, with the activated complex $HBrF_6$ having an IF_7-like configuration. IF_7 itself would not be expected to form such a complex since 9 stable orbitals are required, but rapid exchange is still observed.

Since carbon and sulfur do not form more than 4 or 6 stable bonds, similar complexes in the systems $HF–CCl_2F_2$ and $HF–SF_6$ would have very large free energies of activation and the exchange rates should be very slow, in agreement with our observations.

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