accounted for by an appropriate combination of field and resonance contributions. Additional work, to appear elsewhere, will extend our analyses to carboranes and polyhedral boranes.

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Sorption of Gaseous Bromine Trifluoride on Sodium Fluoride

BY T. SAKURAI

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The interaction between gaseous bromine trifluoride (BrF_3) and sodium fluoride (NaF) was studied for the following purposes.

(i) In the author's laboratory, a study has been made on the fluoride volatility process for reprocessing of nuclear fuels. Gaseous BrF_3 may be used as the fluorinating reagent, and NaF has been used as the chemical trap to separate uranium and plutonium from the fission products. It is therefore necessary to check the interaction between BrF_3 and NaF.

(ii) BrF_3 seems to be more reactive to uranium compounds than elemental fluorine, though more stable thermodynamically.[1] With gaseous BrF_3, the materials can be fluorinated at lower temperatures and lower concentrations of the reacting gas than with F_2.[2-5] Why this is so, has not been made clear yet; however, it may be due to the adsorption of BrF_3 on the materials. The present study was carried out to obtain information on the reactivity of BrF_3.

Experimental Section

Reagent grade sodium fluoride in powder of purity greater than 99% was used, after outgassing overnight at 350° under vacuum.[6,7] Particle size ranged from 1 to 5 μ, and the surface area as determined by krypton adsorption was 0.2 m^2/g.

Commercial grade bromine trifluoride, from the Matheson Co., was purified by vacuum distillation, as reported previously.[8]

All valves and tubing in the apparatus in contact with bromine trifluoride were made of Monel or Teflon. The weight increase of samples caused by sorption of the BrF_3 was obtained with a thermobalance, details of which were given in the previous work.[5] About 100 mg of the sodium fluoride was placed in the reaction tube. After outgassing the sample powder, the reaction tube was raised to a specific temperature and filled immediately with helium gas at atmospheric pressure. Gaseous BrF_3 of a given partial pressure in helium as the carrier gas was then allowed to pass through the reaction tube at a constant flow rate. A continuous record of the weight change of the sample with the time was obtained with a recording potentiometer.

Results and Discussion

The weight change of sample with the time is shown in Figure 1. In this experiment, gaseous BrF_3 of partial pressure 15 mm was passed over the sample at 110°. The weight increased rapidly in the first 50 min and then very slowly. The shape of sorption curve is similar to that of UF_6 on NaF reported by other workers.[6] About 120 min after the start, the supply of BrF_3 was stopped, and the reaction tube was evacuated (10^{-2} mm) to observe any change in weight. Since no change was caused, the sample was then heated under vacuum. At 140°, the weight started to decrease because of the desorption of BrF_3, returning gradually to its initial weight; unlike a physically adsorbed layer, the sorbed BrF_3 was not removed by reducing the pressure. The weight increase obtained during the 120 min was 57 mg, which was some 10^3 times the amount of BrF_3 expected for its physical or chemical adsorption on the sodium fluoride; it was therefore indicated that the sorbed BrF_3 diffused into the sodium fluoride crystal.

In some experiments, the temperature of sorption was varied, with the BrF_3 partial pressure being kept constant at 15 mm. The results of experiments are shown in Figure 2. The rate of the sorption decreased with increase of the temperature, and no weight increase was observed at temperatures over 180°. The sorption was therefore found to be a nonactivated one.

A fluorine-18-exchange reaction was examined between BrF_3 and NaF. The nuclide ^{18}F was prepared by irradiation of the sodium fluoride in the 20-MeV linear accelerator of Japan Atomic Energy Research Institute by the reaction $^{19}F(\gamma,n)^{18}F$. The radioactive sodium fluoride (NaF*) was then treated with gaseous BrF_3 in the same way as in Figure 1; the BrF_3 desorbed from the NaF* was collected in a counting tube. Consequently, a fluorine-exchange reaction was noticed between sodium fluoride and the sorbed bromine trifluoride; the percentage exchange, calculated by Gens' equation,[9] was 19%. It was considered that fluorine atoms were exchanged through complex formation.[10,11]

In the experiments, it was found that the repeated sorption and desorption of BrF_3 on sodium fluoride increases the rate of sorption. In Figure 3, curve I is the sorption curve for the original NaF at 110° and BrF_3 partial pressure 15 mm. The sorbed BrF_3 was then desorbed from the material by heating to 150° under vacuum. The sodium fluoride obtained was treated again with gaseous BrF_3 under the same conditions as in the first sorption. Curve II shows the second sorption, which proceeds much more rapidly up to a point (P) which corresponds to the final point in the first sorption; it then proceeds slowly. In the third treatment, the sorption rate is further increased, as shown in the figure. These results indicate that an irreversible change in the sample occurred in the course of the sorption and desorption process. Micro-

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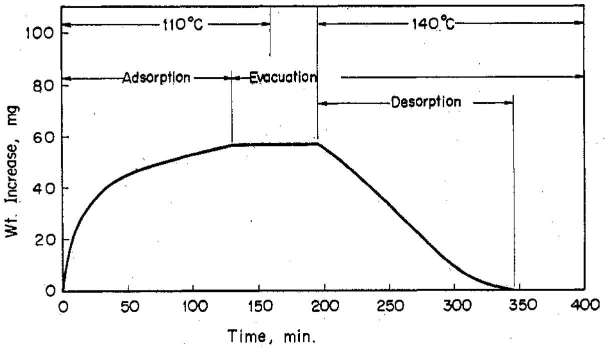

Figure 1.—A sorption and desorption curve. The BrF_3 of partial pressure 15 mm was admitted to the sample NaF at 110° for 120 min.

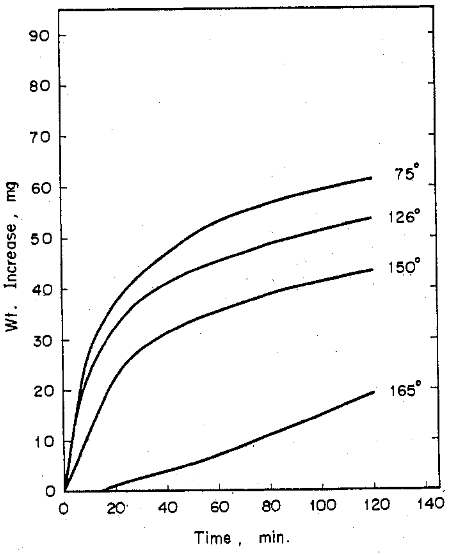

Figure 2.—Temperature dependence of the sorption rate. BrF_3 partial pressure 15 mm; carrier gas helium, 15 l./hr; initial weight of the sample 100 mg.

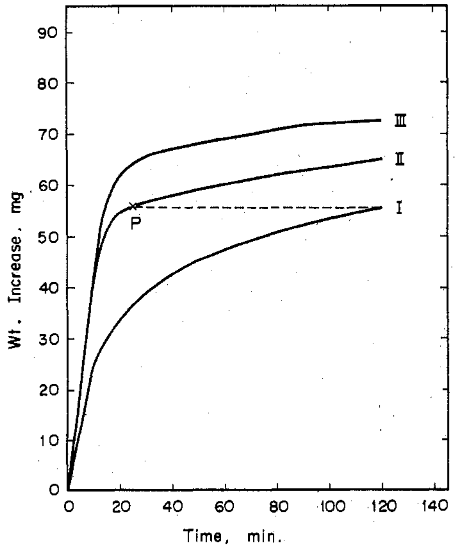

Figure 3.—Increase of the sorption rate resulting from the repeated sorption–desorption of BrF_3. BrF_3 partial pressure 15 mm; sorption temperature 101°; initial weight of sample NaF 101.0 mg. Curve I is the sorption curve in the first treatment, curve II is in the second treatment, and curve III is in the third treatment of the NaF with BrF_3.

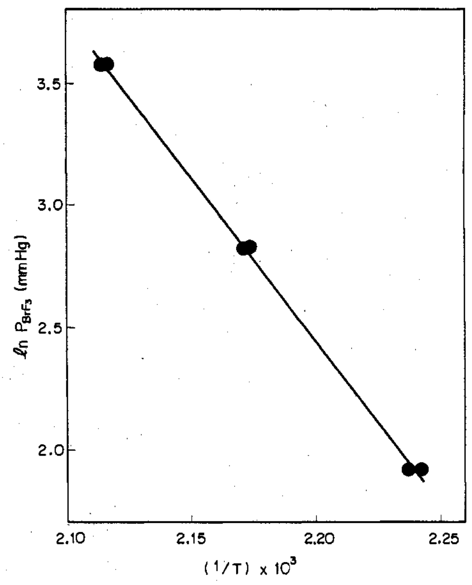

Figure 4.—Decomposition temperature curve of $3NaF \cdot BrF_3$.

photographs showed that sodium fluoride crystal is pulverized by the sorption–desorption of BrF_3; the increase in sorption rate by the repeated sorption–desorption is therefore attributed to the increase in surface area of the sample caused by the pulverization. The pulverization was considered to be due to the formation and decomposition of a complex between NaF and BrF_3.

All of the experimental results described above suggest that a complex may be formed by the sorption of BrF_3 on NaF. Therefore, experiments were further continued to see the ultimate amount of BrF_3 sorbed on NaF. In two experiments, the BrF_3 of partial pressure 26 mm was passed over the sample at 110°, until the weight change was no longer observable. Consequently, it was found that the weight increase was no longer detected, being far less than 1 mg/hr, after about 25 hr. The results are shown in Table I;

TABLE I

THE QUANTITY OF BrF_3 SORBED ON NaF[a]

Wt of NaF, mg	Time treated with BrF_3, hr	Wt increase, mg	Mole ratio NaF/BrF_3
100.7	32	105	3.1
52.7	27	50	3.4

the final mole ratio of NaF/BrF_3 was 3. The sorption is therefore expressed as

$$3NaF + BrF_3 \longrightarrow 3NaF \cdot BrF_3$$

$3NaF \cdot BrF_3$ is not stable, being decomposed rapidly with moisture.

The decomposition temperature of $3NaF \cdot BrF_3$ was examined as follows. $3NaF \cdot BrF_3$, produced as above, was heated carefully in the reaction tube, through which helium gas containing a specific partial pressure of BrF_3 was passed. And the temperature at which the weight decrease began was determined. The temperatures of decomposition are plotted in Figure 4, *vs.* the partial pressures of BrF_3; a straight line is given by means of the least-squares method. The equation for the line is

$$\ln P_{\mathrm{mm}} = 3.76 - {}^{4}/_{3} \times 10^{4}T$$

where *T* is in degrees Kelvin. By X-ray study and the chemical analysis described elsewhere,[8] it was confirmed that NaF and BrF_3 are reproduced by the decomposition of $3NaF \cdot BrF_3$.

X-Ray investigation of $3NaF \cdot BrF_3$ was also attempted, after sealing in a glass capillary in a drybox. However, it was unsuccessful, because the material reacts with glass. Though the crystal structure remains undetermined, present work indicates that a complex, $3NaF \cdot BrF_3$, is formed by the sorption of gaseous bromine trifluoride on sodium fluoride.

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Mechanism of Exchange Reactions Involving Mixed Halides of the Type $(CH_3)_3SbClX$

By Charles G. Moreland* and Robert J. Beam

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Although considerable quantitative data have been reported on the thermodynamics of redistribution reactions of organometallic compounds of group V elements, there is very little information on the kinetics and mechanisms of such reactions.[1-4] This is mainly due to the complexities involved in the interpretation of physical data for multiple-exchange reactions. Kinetic studies are especially difficult in those cases where reactions are random or nearly random because a single reaction usually cannot be studied independently of the other reactions in the series.

Herein is reported an example where it has been possible using ^1H nmr to obtain some quantitative kinetic data on a nearly random equilibrium, $(CH_3)_3SbCl_2 + (CH_3)_3Sb(NO_3)_2 \rightleftharpoons 2(CH_3)_3SbCl(NO_3)$. In this system one exchange process, namely, $(CH_3)_3SbCl_2 + (CH_3)_3SbClNO_3$, occurs at a faster rate than the others and therefore could be studied independently. Qualitative data on two similar systems, $(CH_3)_3SbF_2 + (CH_3)_3SbCl_2$ and $(CH_3)_3SbBr_2 + (CH_3)_3SbCl_2$, are also presented.

Experimental Section

The nitrobenzene used as a solvent was refluxed for 24 hr over Linde 4A molecular sieves and distilled. The middle fraction was passed through a column of molecular sieves and then was finally dried more thoroughly by the procedure of Streim, *et al.*[5] The solvent purified in this manner was free of extraneous ^1H nmr signals and its water content was below 30 ppm as measured by a Karl Fischer Titrator (Labindustries, Berkeley, Calif.).

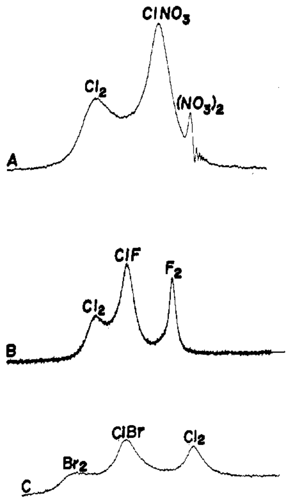

Figure 1.—Methyl proton spectra: (A) nitrobenzene solution of trimethylantimony dichloride–trimethylantimony dinitrate at 45°; (B) equimolar mixture of trimethylantimony difluoride–trimethylantimony dichloride in $CDCl_3$ at 58°; (C) equimolar mixture of trimethylantimony dichloride–trimethylantimony dibromide in nitrobenzene at 80°. (The solution for (A) was not equimolar in dichloride and dinitrate because additional dinitrate produced more chloride nitrate which averaged with the dichloride and would not allow individual methyl proton signals to be observed at temperatures above the freezing point of the solution. In all cases the methyl proton signal of the dinitrate was a sharp unshifted signal.)

The trimethylantimony dichloride and the trimethylantimony dinitrate were prepared by previously reported procedures.[6] All solutions were prepared in a glove bag under a dry nitrogen atmosphere. A portion of the solution was transferred to a Pyrex precision nmr tube which had been sealed to a vacuum stopcock. The sample was then degassed on a vacuum line and sealed. Samples prepared in this way gave reproducible results and did not change with time. The ^1H nmr spectra of the methyl signals were obtained on a Varian HA-100 high-resolution spectrometer with variable-temperature capabilities. At least five spectral traces of the sample were obtained at each temperature.

Two Fortran IV programs were used to calculate nmr line shapes as a function of T_2, frequency, relative chemical shifts, number of sites, site population, and exchange lifetimes (τ). One program was used to calculate the individual lifetime for each site by employing a matrix formulation to solve a set of linear differential equations and the second program was used to obtain the mean lifetimes by solving an integrated line shape equation.[7] Both programs employed an iterative method in which the value of τ was varied until the difference between calculated and experimental intensities was at a minimum.

Results and Discussion

The ^1H nmr spectrum of a nitrobenzene solution of trimethylantimony dichloride and trimethylantimony dinitrate (Figure 1A) shows that the following redistribution reaction occurs

$$(CH_3)_3SbCl_2 + (CH_3)_3Sb(NO_3)_2 \rightleftharpoons 2(CH_3)_3SbClNO_3$$

Integration of the three methyl resonances permits calculation of the equilibrium constant—approximately 20 at 32°. The precision of the value was limited because exchange between $(CH_3)_3SbCl_2$ and $(CH_3)_3SbClNO_3$ broadened these signals so that they overlapped. The methyl resonance for the dinitrate species in all of the nitrobenzene solutions investigated was a

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