as it is for aqueous systems at 25° where it is known[13] that electron transfer between $Fe^{2+}(aq)$ and $FeCl^{2+}(aq)$ occurs by both mechanisms although the bridged, inner-sphere mechanism predominates; the effect of introducing a Cl^- ion (probably in place of a solvent molecule) into the activated complex has very much the same effect when the rest of the ligands are DMSO molecules as when they are water molecules. This suggests, but does not prove, that the role of Cl^- in reaction 2 is the same as it is in the aqueous system. Thus, not only are the free energy, enthalpy, and entropy of activation of reaction 1 approximately equal to those for the corresponding reaction between hexaaquo iron ions,[7] but the effect on the free energy of activation in both solvents is essentially the same when Cl^- is added to the activated complex. Some difference for the two solvents is indicated by the fact that k_2/k_1 is approximately 7 in DMSO but 2 in water and that at Cl^- concentrations above 2.00×10^{-3} M the value of k_{app} begins to increase rapidly indicating a third chloride-catalyzed path. Since no indication of a third chloride species was found spectrophotometrically at similar chloride concentrations no formation constant for this species had been determined and the kinetic studies at the higher Cl^- concentrations were discontinued.

Acknowledgment.—The authors wish to gratefully acknowledge the support of A.E.C. Contract No. AT(11-1)-622 and to thank Professor Z Z. Hugus of the Chemistry Department, University of Minnesota, for the computer calculation of the molar extinction coefficients and formation constants.

---

(13) R. J. Campion, T. J. Conocchioli, and N. Sutin, *J. Am. Chem. Soc.*, **86**, 4591 (1964).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
NORTH CAROLINA STATE UNIVERSITY, RALEIGH, NORTH CAROLINA 27607

Nuclear Magnetic Resonance Studies on Exchange Reactions of Trimethylantimony Dihalides

BY G. G. LONG, C. G. MORELAND, G. O. DOAK, AND M. MILLER

Received March 15, 1966

Proton magnetic resonance spectra for the four trimethylantimony dihalides, $(CH_3)_3SbF_2$, $(CH_3)_3SbCl_2$, $(CH_3)_3SbBr_2$, and $(CH_3)_3SbI_2$, show methyl proton signals of considerably different chemical shifts. The spectrum at −32° of a chloroform solution containing any pair of the previously mentioned compounds shows three methyl proton signals, two of which are characteristic of the two parent dihalides, $(CH_3)_3SbX_2$ and $(CH_3)_3SbY_2$, and a third signal which has been identified as the mixed halide, $(CH_3)_3SbXY$. All six of the solutions made by pairwise combinations of the dihalides show a similar temperature dependence. The initial result of increasing the temperature above −32° is the broadening of the three methyl signals. At higher temperatures the signal of the heavier dihalide (X_2) and the mixed halide (XY) coalesce to a broad intermediate signal which is closer to that of the mixed halide. At still higher temperatures the lighter dihalide (Y_2) signal begins to merge with this intermediate signal. Finally, a single, somewhat broadened signal with a chemical shift corresponding to that of the mixed halide is attained for the dibromide–diiodide solution at 70°, dichloride–dibromide at 80°, and difluoride–dichloride at 150°. These results are explained on the basis of a series of exchange equilibria. In addition, ^{19}F chemical shifts are reported for the fluorine-containing species.

For some time we have been interested in trigonal bipyrimidal molecules that have several dissimilar groups attached to the central atom, *e.g.*, MA_3BC and MA_2B_2C. A problem encountered in the study of these compounds is the fact that elemental analysis cannot distinguish between a pure compound and certain mixtures. Thus, materials which have an elemental analysis corresponding to MA_3BC may be either the pure compound or a series of mixtures each containing equimolar quantities of MA_3B_2 and MA_3C_2.

In a preliminary experiment we noted that the pmr chemical shifts of the trimethylantimony dihalides, $(CH_3)_3SbF_2$, $(CH_3)_3SbCl_2$, $(CH_3)_3SbBr_2$, and $(CH_3)_3SbI_2$, differ considerably. This suggested that the presence of a mixed halide, $(CH_3)_3SbXY$, could be detected by observation of the methyl proton chemical shift. The synthesis of the pure mixed halide probably would be difficult.[1] However, if disproportionation between two dihalides, $(CH_3)_3SbX_2$ and $(CH_3)_3SbY_2$, occurs readily, the presence of the mixed halide, $(CH_3)_3SbXY$, could be detected by the observation of a pmr signal that does not correspond to that of either of the two starting materials. Also, if one of the dihalides is $(CH_3)_3SbF_2$, we should be able to confirm the disproportionation by observation of different ^{19}F nmr signals for the difluoride and for the mixed derivative. Reported in this paper are the pmr chemical shifts for the trimethylantimony dihalides, the results of experiments to prepare and detect the mixed halides, and some of the interesting equilibria observed in solutions of these compounds.

Experimental Section

The ^1H and ^{19}F nmr studies were carried out using a Varian HA-100 high-resolution spectrometer equipped with a variable-

---

(1) G. O. Doak and G. G. Long, *Trans. N. Y. Acad. Sci.*, **28**, 402 (1966).

temperature probe. The temperature of the sample was regulated to ±0.5° by a Varian variable-temperature controller (V4343) which had been previously calibrated with a thermocouple in place of the sample. The pmr spectra were run on precalibrated chart paper at a 500-cps sweep width with TMS as the internal "lock" reference. The solvent was $CDCl_3$ except in one case at 150° where bromoform was used. The ^{19}F chemical shifts were obtained by the side-band technique with $CFCl_3$ as the internal reference. The samples studied were (a) 0.025 *M* solutions of the four trimethylantimony dihalides and (b) the six solutions obtained by mixing, pairwise, equal volumes of 0.050 *M* solutions of the four dihalides.

All of the trimethylantimony dihalides studied were prepared by the procedures given by Long, Doak, and Freedman.[2]

TABLE I

PMR SPECTRAL PARAMETERS FOR THE TRIMETHYLANTIMONY DIHALIDES

0.050 *M* soln of	δ,[a] ppm downfield from TMS			Multiplicity[b] and J_{FH}, cps (at −32°)
	−32°	30.5°	70°	
$(CH_3)_3SbF_2$	1.75	1.71	1.68	Triplet, 5.0
$(CH_3)_3SbCl_2$	2.38	2.34	2.31	Sharp singlet
$(CH_3)_3SbBr_2$	2.66	2.62	2.60	Sharp singlet
$(CH_3)_3SbI_2$	3.01	2.98	2.96	Sharp singlet

[a] Accuracy of each measurement is ±0.01 ppm. [b] At 30.5 and 70° each peak is a broad singlet.

Results and Discussion

Trimethylantimony Dihalides, $(CH_3)_3SbX_2$.—The proton chemical shift values of 0.025 *M* solutions of the trimethylantimony dihalides are presented in Table I. Measurements are reported at −32, 30.5, and 70°. At −32°, sharp, ringing signals are observed, and in the case of the difluoride, the methyl protons are coupled with the fluorines. At higher temperatures, an intermolecular exchange of halogen must occur since each signal is broadened, and in the case of the difluoride, the coupling between the methyl protons and the fluorines is no longer observed. A 100° change in temperature produces only a slight upfield shift of each dihalide signal.

The observation of a single methyl proton signal, split at −32° by two equivalent fluorines, is consistent with the trigonal bipyramidal geometry suggested by Clark[3] for this molecule on the basis of a study of the infrared spectrum. This also is confirmed by the observation of a single ^{19}F signal at room temperature which is considerably broadened as the temperature is decreased (fluorine coupled with nine equivalent protons).

TABLE II

PMR SPECTRAL PARAMETERS FOR SPECIES IN SOLUTIONS PREPARED BY MIXING EQUAL MOLAR QUANTITIES OF TWO TRIMETHYLANTIMONY DIHALIDES

Species in solution resulting from equal molar mixtures of	δ,[a] ppm downfield from TMS (at −32°)	Multiplicity and J_{FH}, cps
$(CH_3)_3SbF_2 + (CH_3)_3SbCl_2 =$		
$(CH_3)_3SbF_2$	1.76	Triplet, 5.0
$(CH_3)_3SbFCl$	2.07	Doublet, 4.3
$(CH_3)_3SbCl_2$	2.38	Sharp singlet
$(CH_3)_3SbF_2 + (CH_3)_3SbBr_2 =$		
$(CH_3)_3SbF_2$	1.76	Triplet, 5.0
$(CH_3)_3SbFBr$	2.23	Doublet, 4.1
$(CH_3)_3SbBr_2$	2.66	Sharp singlet
$(CH_3)_3SbF_2 + (CH_3)_3SbI_2 =$		
$(CH_3)_3SbF_2$	1.76	Triplet, 5.0
$(CH_3)_3SbFI$	2.45	Doublet, 3.5
$(CH_3)_3SbI_2$	3.00	Sharp singlet
$(CH_3)_3SbCl_2 + (CH_3)_3SbBr_2 =$		
$(CH_3)_3SbCl_2$	2.37	Sharp singlet
$(CH_3)_3SbClBr$	2.52	Sharp singlet
$(CH_3)_3SbBr_2$	2.65	Sharp singlet
$(CH_3)_3SbCl_2 + (CH_3)_3SbI_2 =$		
$(CH_3)_3SbCl_2$	2.38	Sharp singlet
$(CH_3)_3SbClI$	2.73	Sharp singlet
$(CH_3)_3SbI_2$	3.01	Sharp singlet
$(CH_3)_3SbBr_2 + (CH_3)_3SbI_2 =$		
$(CH_3)_3SbBr_2$	2.65	Sharp singlet
$(CH_3)_3SbBrI$	2.84	Sharp singlet
$(CH_3)_3SbI_2$	2.00	Sharp singlet

[a] Values for no observable exchange as confirmed by the sharpness of the signals and the observed coupling between the fluorines and the methyl protons. Accuracy of each measurement is ±0.01 ppm.

Mixed Trimethylantimony Halides, $(CH_3)_3SbXY$.—When equal volumes of 0.050 *M* $(CH_3)_3SbX_2$ and 0.050 *M* $(CH_3)_3SbY_2$ are mixed together, the pmr spectra at −32° show three signals. Table II contains the pmr data for the species in each of the six solutions that are obtained by the pairwise mixing of equal volumes of the four 0.050 *M* dihalide solutions. By comparison of these data with the chemical shift values in Table I, the highest and lowest field signals were identified as belonging to the two dihalides, $(CH_3)_3SbX_2$ and $(CH_3)_3SbY_2$, used to prepare the mixture. The middle signal was assigned to the mixed halide, $(CH_3)_3SbXY$. In cases where one of the halogens is fluorine, this middle signal is observed as a well-resolved doublet. Since a triplet is observed in the case of the difluoride (methyl protons coupled to two fluorines), the splitting of the middle signal by fluorine (methyl protons coupled to a single fluorine) confirms the assignment of this signal to the mixed halides, $(CH_3)_3SbXY$. It also should be noted that in each case the signal due to the mixed halide falls very nearly midway between the signals from the two parent dihalides. This would suggest that all of these compounds, dihalides and mixed halides, have the same trigonal bipyramidal geometry as was reported by Wells for the dichloride, dibromide, and diiodide.[4]

The pmr spectra of all six of the above solutions show similar temperature dependence. The initial result of increasing the temperature above −32° is to broaden these signals and to obscure the coupling of the methyl protons with the fluorine(s) in the case of the fluorine-containing species. At higher temperatures, the signals of the heavier dihalide and the mixed halide coalesce to a broad intermediate signal which is closer to that of the mixed halide. At still higher temperatures, the lighter dihalide signal begins to merge with this intermediate signal. Finally, a single, somewhat broadened signal with a chemical

---

[2] G. G. Long, G. O. Doak, and L. D. Freedman, *J. Am. Chem. Soc.*, **86**, 209 (1964).

[3] H. C. Clark, private communication.

[4] A. F. Wells, *Z. Krist.*, **99A**, 367 (1938).

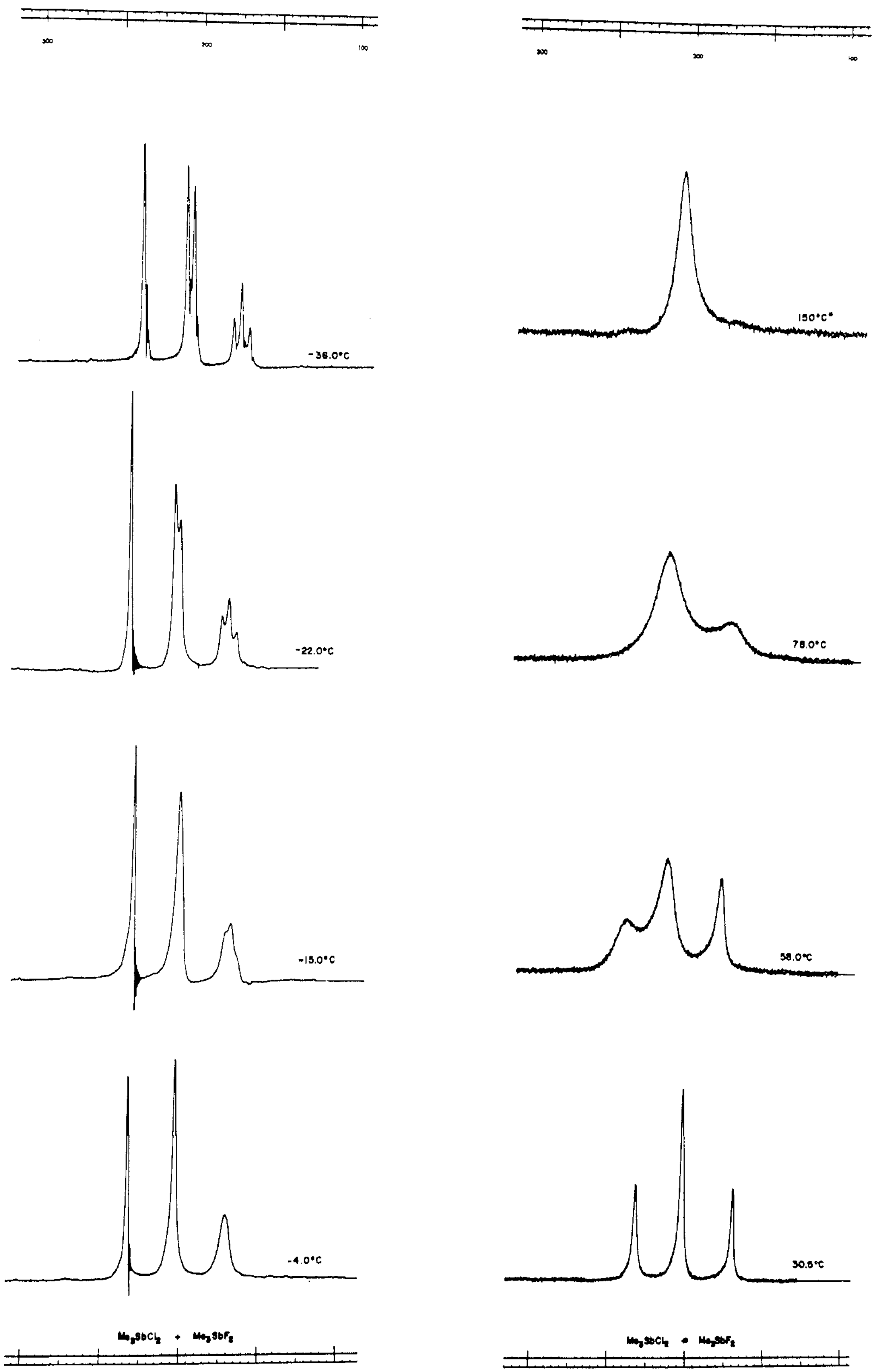

Figure 1.—Temperature-dependent pmr spectra for the $(CH_3)_3SbF_2$–$(CH_3)_3SbCl_2$ solution.

shift corresponding to that of the mixed halide was attained for the dibromide–diiodide solution at 70°, dichloride–dibromide at 80°, and difluoride–dichloride at 150°. The other three solutions, difluoride–dibromide, difluoride–diiodide, and dichloride–diiodide, would undoubtedly show similar behavior if carried to a sufficiently high temperature. Figure 1, which consists of the photographs of the pmr spectra of the difluoride–dichloride solution at several temperatures between −32 and 150°, is a typical example of the temperature-dependent spectra obtained on the mixed dihalide solutions.

Thus, when any two of the trimethylantimony dihalide solutions are mixed together at room temperature, a chemical reaction takes place (eq 1) which results in partial conversion of the dihalides to a mixed halide.

$$(CH_3)_3SbX_2 + (CH_3)_3SbY_2 \rightleftharpoons 2(CH_3)_3SbXY \qquad (1)$$

The two dihalides and the mixed halide in the solution are all involved in several halogen-exchange equilibria. These equilibria are slowed down sufficiently, so that at −32° they are not observed in the pmr spectra. Increasing the temperature slightly above −32° results in the observation of exchange. Above room temperature, an equilibrium between the higher molecular weight dihalide and the mixed halide (eq 2) occurs rapidly which is responsible for coalescing these two pmr signals. At higher temperatures, additional equilibria (eq 3 and 4) involving the lower molecular weight dihalide also become important.

$$(CH_3)_3SbXY + (CH_3)_3Sb'X_2 \rightleftharpoons (CH_3)_3SbX_2 + (CH_3)_3Sb'XY \qquad (2)$$

$$(CH_3)_3SbX_2 + (CH_3)_3Sb'Y_2 \rightleftharpoons (CH_3)_3SbXY + (CH_3)_3Sb'XY \qquad (3)$$

$$(CH_3)_3SbXY + (CH_3)_3Sb'Y_2 \rightleftharpoons (CH_3)_3SbY_2 + (CH_3)_3Sb'XY \qquad (4)$$

This results in the observation of a single pmr signal which has a chemical shift corresponding to that of the mixed halide since each methyl group has the same average chemical environment. These results suggest that attempts to synthesize pure trimethylantimony mixed halides will be complicated by equilibria which will result in formation of some of each of the two possible dihalides whenever the mixed halide species is in solution. Synthesis might be effected by carrying out all operations at very low temperatures or by finding a solvent which does not allow these equilibria to be established. The former approach was at least partially successful in the case of triphenylantimony chloride iodide since we were able to prepare a reasonably pure sample by keeping the temperatures of the reaction of triphenylstibine with iodine monochloride at −78° and not recrystallizing the product.[1]

TABLE III

^{19}F CHEMICAL SHIFTS FOR $(CH_3)_3SbF_2$ AND FOR THE THREE $(CH_3)_3SbFX$ SPECIES IN SOLUTION

Fluorine-containing species in solution	ϕ, ppm upfield from $CFCl_3$ (at 30.5°)
$(CH_3)_3SbF_2$	106.1
$(CH_3)_3SbF_2 + (CH_3)_3SbCl_2 =$	
$(CH_3)_3SbF_2$	105.9
$(CH_3)_3SbFCl$	110.9
$(CH_3)_3SbF_2 + (CH_3)_3SbBr_2 =$	
$(CH_3)_3SbF_2$	105.9
$(CH_3)_3SbFBr$	113.7
$(CH_3)_3SbF_2 + (CH_3)_3SbI_2 =$	
$(CH_3)_3SbF_2$	106.2
$(CH_3)_3SbIF$	117.4

Table III lists the ^{19}F chemical shift values for the fluorine-containing species in the three solutions obtained by mixing equal molar quantities of the dichloride, dibromide, or diiodide with the difluoride. These data are reported at 30.5° since all fluorine signals are markedly broadened at lower temperature owing to coupling of the fluorine with nine equivalent protons.

In each case the signal from the difluoride is observed near 106 ppm upfield from $CFCl_3$. The observation of a second signal is consistent with the existence of the respective mixed halides in these solutions.

The fluorine chemical shifts for these species are approximately a linear function of electronegativity[5] of the corresponding halogen. The negative slope of the curve, −10 ppm/unit of electronegativity (increasing ^{19}F chemical shift with decreasing electronegativity of the halogen Y), indicates, according to the theory of Saika and Slichter,[6] an increase in ionic character of the antimony–fluorine bond in the series $F < Cl < Br < I$. A negative slope would also be predicted on the basis of decreasing inductive effect of the halogen, Y.

---

[5] M. L. Huggins, *J. Am. Chem. Soc.*, **75**, 4123 (1953).

[6] A. Saika and C. P. Slichter, *J. Chem. Phys.*, **22**, 26 (1954).