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·BrF$_3$.

X-Ray investigation of 3NaF·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·BrF$_3$, is formed by the sorption of gaseous bromine trifluoride on sodium fluoride.

Contribution from the Department of Chemistry,
North Carolina State University,
Raleigh, North Carolina 27607

Mechanism of Exchange Reactions Involving Mixed Halides of the Type (CH₃)₃SbClX

By Charles G. Moreland* and Robert J. Beam

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 ^{1}H 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 ^{1}H nmr

(1) J. C. Lockhart, *Chem. Rev.*, **65**, 131 (1965).
(2) K. Moedritzer, "Organometallic Reactions," Wiley-Interscience, New York, N. Y., 1971, pp 4–115.
(3) H. Weingarten and J. R. Van Wazer, *J. Amer. Chem. Soc.*, **88**, 2700 (1966).
(4) C. G. Moreland, M. H. O'Brien, C. E. Douthit, and G. G. Long, *Inorg. Chem.*, **7**, 834 (1968).
(5) H. G. Streim, E. A. Boyce, and J. R. Smith, *Anal. Chem.*, **33**, 85 (1961).
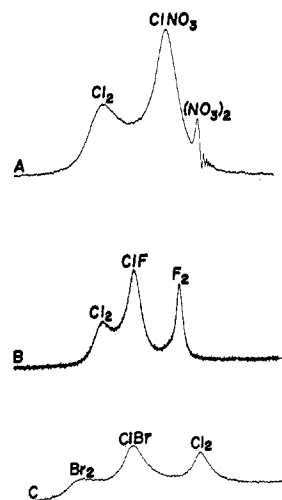

Figure 1.—Methyl proton spectra: (A) nitrobenzene solution of trimethylantimony dichloride–trimethylantimony dinitrate at 45°; (B) equimolar mixture of trimethylantimony difluoride–trimethylantimony dichloride in CDCl$_3$ at 58°; (C) equimolar mixture of trimethylantimony dichloride–trimethylantimony 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.)

signals and its water content was below 30 ppm as measured by a Karl Fischer Titrator (Labindustries, Berkeley, Calif.).

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 ^{1}H 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 ^{1}H 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

(6) G. G. Long, G. O. Doak, and L. D. Freedman, *J. Amer. Chem. Soc.*, **86**, 209 (1964).
(7) R. J. Beam, M.S. Thesis, North Carolina State University, 1970.

sharp signal which did not shift over the temperature range 20–80° (see Figure 1A), meaning that no exchange involving the dinitrate was *observable*. The exchange reaction can thus be treated as a two-site case, and if one assumes the bimolecular mechanism

$$(CH_3)_3SbCl_2 + (CH_3)_3SbClNO_3 \underset{k_1}{\overset{k_1}{\rightleftharpoons}} (CH_3)_3SbClNO_3 +$$
$$(CH_3)_3SbCl_2 \quad (1)$$
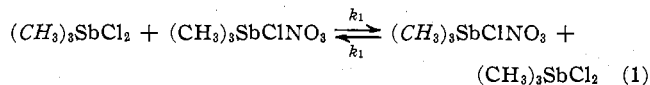
it is possible to define the appropriate exchange lifetimes as

$$\frac{1}{\tau_{Cl_2}} = -\frac{d[Cl_2]}{dt} \Big/ [Cl_2] = k_1[ClNO_3] \quad (2)$$

$$\frac{1}{\tau_{ClNO_3}} = -\frac{d[ClNO_3]}{dt} \Big/ [ClNO_3] = k_1[Cl_2] \quad (3)$$

$$\frac{1}{\tau_{mean}} = \frac{1}{\tau_{Cl_2}} + \frac{1}{\tau_{ClNO_3}} = k_1([Cl_2] + [ClNO_3]) \quad (4)$$

Table I contains data on the rate constant k_1 at different

				$k_1(32°)$, 1. mol^{-1} sec^{-1}	
[ClCl],[b] *M*	[ClNO$_3$],[b] *M*	[NO$_3$NO$_3$],[b] *M*	Eq 2 $(1/\tau_{ClCl})/$ [ClNO$_3$]	Eq 3 $(1/\tau_{ClNO_3})/$ [ClCl]	Eq 4 $(1/\tau_{mean})/$ ([ClCl] + [ClNO$_3$])
0.1163	0.0721	0.0024	117 ± 8	122 ± 12	115 ± 10
0.0987	0.0903	0.0044	111 ± 8	109 ± 7	114 ± 9
0.0782	0.1231	0.0103	117 ± 10	102 ± 10	108 ± 12
0.0493	0.0451	0.0022			109 ± 8

[a] Errors are standard deviations for at least five independent measurements. [b] These equilibrium concentrations were first estimated using 20 as the value of the equilibrium constant and then adjusted to give the best fit when experimental and calculated methyl proton line shapes were compared. The equilibrium concentrations changed very little with temperature.

ferent equilibrium concentrations of the dichloride, chloride nitrate, and dinitrate species. Since the k_1 values were calculated by eq 2–4, the data confirm that the exchange reaction is first order in the dichloride and in the chloride nitrate (second order overall) and is consistent with eq 1. The data also show very close agreement among the k_1 values obtained from the three separate calculations.

Table II contains k_1 values at different temperatures.

Temp, °C	k,[a] 1. mol^{-1} sec^{-1}	Temp, °C	k,[a] 1. mol^{-1} sec^{-1}
20	46 ± 3	55	314 ± 41
32	114 ± 9	60	399 ± 51
45	246 ± 32		

[a] Errors are standard deviations from at least 10 values obtained from mean lifetimes and individual lifetimes calculated on three solutions of different concentrations.

The activation parameters obtained from a plot of ln k_1 *vs.* $1/T$ are $\Delta H^{\ddagger} = 10.6 \pm 2.1$ kcal/mol and $\Delta S^{\ddagger} = -16 \pm 6$ cal/mol K at 32°. The negative value of $\Delta S^{\ddagger}$ could indicate either a four-centered activated complex[2,3] or solvent ordering in the transition state. Recent investigations in our laboratory show that $k_1 = 60 \pm 10$ 1. mol^{-1} sec^{-1} at 64° in methylene dichloride, a solvent with a lower dielectric constant than nitrobenzene where $k_1 = 414 \pm 60$ 1. mol^{-1} sec^{-1}

at 60°. This suggests that the formation of solvent-separated ion pairs (*i.e.*, $R_3SbX^+\|Y^-$) occurs in these solutions and indicates that a more detailed solvent study is needed.

Even if one accepts eq 1 as the net exchange reaction for the dichloride–chloride nitrate exchange, it still remains to be explained why no *observable* exchange is shown by the dinitrate. In the mixed species (as shown by eq 1) it is the NO$_3$ group that is involved in the exchange with the dichloride. As shown by the following equation, the methyl proton spectrum could not be used to *observe* exchange of Cl between the dichloride and chloride nitrate

$$(CH_3)_3SbCl_2 + (CH_3)_3SbClNO_3 \rightleftharpoons$$
$$(CH_3)_3SbCl_2 + (CH_3)_3SbClNO_3$$
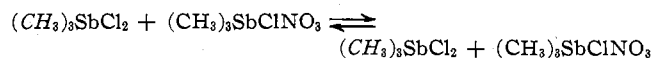
Likewise, exchange of NO$_3$ groups would not be *observable* in the methyl proton spectrum of the dinitrate or chloride nitrate species

$$(CH_3)_3Sb(NO_3)_2 + (CH_3)_3SbClNO_3 \rightleftharpoons$$
$$(CH_3)_3Sb(NO_3)_2 + (CH_3)_3SbClNO_3$$
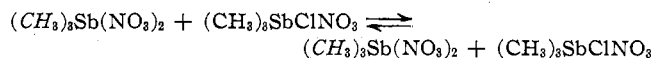
A possible explanation would be that the mixed halide forms a species with a labile NO$_3$ group, $\{(CH_3)_3SbCl^+\|NO_3^-\}$. The exchange involving this labile NO$_3^-$ with the dichloride would be *observable* but not that with the dinitrate. The fact that neither exchanges between dinitrate + chloride nitrate nor dinitrate + dichloride are observed suggests that rate constants for these processes are much smaller than k_1 and possibly that species of the type $\{(CH_3)_3SbNO_3^+\|Cl^-\}$, $\{(CH_3)_3SbCl^+\|Cl^-\}$, and $\{(CH_3)_3SbNO_3^+\|NO_3^-\}$ do not form readily.

A comparison of our earlier results on the $(CH_3)_3SbCl_2 + (CH_3)_3SbF_2$[8] and the $(CH_3)_3SbCl_2 + (CH_3)_3SbBr_2$[7] systems with the $(CH_3)_3SbCl_2 + (CH_3)_3Sb(NO_3)_2$ system reveals a general trend for exchange involving the mixed-halide species. As shown in Figure 1A and eq 1, the dichloride–chloride nitrate exchange represents one extreme in which the chloride nitrate is observed to exchange with the dichloride, but not with the dinitrate. As noted earlier this means that it is the NO$_3$ group, not the Cl, that is the labile species in $(CH_3)_3SbClNO_3$. Even at temperatures above 150° there were no changes in the methyl proton signal of the dinitrate that could be interpreted as resulting from Cl exchange. Therefore, one can only conclude that no Cl exchange is occurring over the available temperature range.

In Figure 1B, the methyl signal of the chloride fluoride is seen to coalesce with the dichloride when exchange broadening of the methyl signal commences. This indicates that the F is the labile species in the exchanges involving the chloride fluoride. The fact that the triplet structure has collapsed to a singlet in the methyl signal of the difluoride means that F exchange is also observed by the difluoride. However, since the chemical shift of the difluoride has only started to average with the fluoride chloride, Cl exchange between the two sites has only begun to be observed. The conclusion is that the F is the more labile species in the mixed halide $(CH_3)_3SbFCl$ but the Cl exchange occurs at higher temperatures. Finally, the conclusion that can be drawn from Figure 1C is that exchange

(8) G. G. Long, C. G. Moreland, G. O. Doak, and M. Miller, *Inorg. Chem.*, **5**, 1358 (1966).

of the chloride bromide with the dichloride is only slightly favored over exchange with the dibromide. This indicates that in $(CH_3)_3SbClBr$ that Cl is only slightly more labile than Br.

In conclusion, it appears that in exchanges involving the mixed halides $(CH_3)_3SbClNO_3$, $(CH_3)_3SbClF$, and $(CH_3)_3SbClBr$, the more electronegative moiety is the more labile and the difference in activity is greater when the electronegative difference is larger.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, U. S. NAVAL ACADEMY, ANNAPOLIS, MARYLAND 21402

Derivatives of the Undecatungstogallate(III) Anion. I.
Cobalto(II)undecatungstogallate(III).
Preparation, Properties, Structure, and Salts

BY ORVILLE W. ROLLINS

In 1966 Baker and others[1] reported an investigation in depth, centered on five complexes, which established unequivocally a large, new, and general structural category of heteropoly anions, formulated $[H_hM^{m+}-O_6X^{x+}O_4W_{11}O_{30}]^{(14-m-x-h)-}$. It was indicated that a wide variety of metal ions might function as octahedrally coordinated M^{m+}, and a wide variety of nonmetals and transition metals, as well as H_2^{2+}, could function as X^{x+}.

The structure of this new series of undecatungsto complexes was shown[1-3] to be a modification of the well-known "Keggin" structure. As indicated in the general formula above, octahedrally coordinated M^{m+} replaces just one of the 12 octahedral W atoms of the conventional Keggin structure, and X^{x+} occupies the central tetrahedral cavity.

Subsequently, various authors[4-7] have reported preparation of a large number of undecatungsto and undecamolybdo complexes, with various M's and X's, which they formulated according to the above.

When the undecatungstogallate(III) anion, which is one of the five complexes mentioned above, was reported[1,3] we were not certain of the Ga(III) coordination within it. The results of some recent nuclear magnetic resonance (nmr) studies by us and others[8] suggests that there may be two forms or modifications of this anion, one with the Ga(III) ions in octahedral coordination and the other with them in tetrahedral

coordination with oxygen atoms. A recent and extensive single crystal X-ray study[9] supports the latter and thus the following formulation for the undecatungstogallate(III) double salt which was used in that study, $(NH_4)_7Na_2[H_2GaO_4W_{11}O_{36}]\cdot15H_2O$.

The undecatungstogallate(III) anion reacts in solution, at room temperature, with certain hydrated cations, for example, Co(II), Cu(II), Ni(II), and Mn(II), to form very stable derivatives. The Co(II) derivative was prepared in order to determine the coordination geometry for both the Co(II) and Ga(III) ions in that anion.

By comparison of spectra, we have shown that the Co(II) ions are octahedrally coordinated in the new heteropoly anion, and since the other 11 octahedral positions of the Keggin-type structure are surely occupied by W(VI) atoms, this places the Ga(III) ions in the center of the anion.

Also, to be reported in this article are other studies which were performed with the sodium and ammonium–sodium salts of this new heteropoly anion. These include cryoscopy in saturated sodium sulfate solution, potentiometric titrations, X-ray crystallography, and optical microscopy.

Studies with the Cu(II), Mn(II),[10] and Ni(II) derivatives mentioned above, and others, will serve as the basis for future articles.

Experimental Section

Preparation of Sodium Cobalto(II)undecatungstogallate(III).— A sample of $Na_2WO_4\cdot2H_2O$ (J. T. Baker's Analyzed Reagent) weighing 52.00 g was dissolved in approximately 75 ml of water. To this solution, at room temperature, 10.00 ml of a gallium nitrate solution (prepared by dissolving 25.02110 g of the metal, 99.999% pure, obtained from AIAG, in a minimum of concentrated nitric acid and diluting to 250 ml) was added and the pH of the solution was brought to a value of 6.5 with 6 M nitric acid. These amounts of reagents correspond to an atomic W/Ga ratio of 11.0:1.0. The resulting solution was heated on a steam bath until all of the precipitated gallium hydroxide had dissolved, indicating that the undecatungstogallate(III) complex had completely formed. The solution was allowed to cool to 65° and then 15 ml of solution containing 4.175 g of $Co(NO_3)_2\cdot6H_2O$ (Mallinchrodt's AR Grade) was added dropwise with constant stirring. This gave an atomic Ga/Co ratio of 1.0:1.0. After this solution was allowed to cool to room temperature it was treated with approximately its volume of acetone whereupon the product separated as a heavy oil. The acetone–water solution was decanted and the oil layer was washed several times with acetone until it became very viscous and tacky. The product was taken up with water and then the acetone treatments were repeated until the product was free of nitrates (brown ring test). The product was dried in a vacuum oven at 75° for 3 hr, ground to a powder, allowed to equilibrate (hydrate) with the ambient atmosphere, and then sealed in a vial. The product (Preparation A) weighed 36.1 g for a yield of 79% based on the W taken.[11]

Another sample of this new substance was prepared by the procedure given above with the exception that a different amount of $Na_2WO_4\cdot2H_2O$, 47.25 g, was used. This caused the atomic W/Ga and W/Co ratios to be 10.0:1.0, and it was done in order to test the preparative method. The product (preparation B) weighed 37.9 g for a yield of 80% based on the W taken.

Analysis of $Na_{6.8}[H_{0.2}(H_2O)Co^{2+}O_5GaO_4W_{11}O_{30}]\cdot xH_2O$.[12,13]—

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(6) C. Tourné, *C. R. Acad. Sci., Ser. C*, **266**, 702 (1968).
(7) C. Tourné and G. Tourné, *ibid.*, **266**, 1363 (1968); *Bull. Soc. Chim. Fr.*, 1124 (1969).
(8) L. C. W. Baker, Private Communication.

(9) H. T. Evans, *Perspect. Struct. Chem.*, **4**, 20 (1971).
(10) O. W. Rollins and C. R. Skolds, paper in preparation.
(11) O. W. Rollins, *J. Inorg. Nucl. Chem.*, **33**, 75 (1971).
(12) This formula is in accord with a more general formulation for the undecatungsto (or molybdo) heteropoly complexes recently proposed by Baker and Figgis,[13] namely, $[(Y^{y-})M^{m+}O_5X^{x+}O_4(W \text{ or } Mo)_{11}O_{30}]^{(12-m-x+y)-}$ wherein Y^{y-} is a monodentate ligand which occupies the one unshared coordination position of the octahedral heteroatom M^{m+}. The authors report that Y may be a constitutional water molecule, an oxide ion, or some other monofunctional ligand.
(13) L. C. W. Baker and J. S. Figgis, *J. Amer. Chem. Soc.*, **92**, 3794 (1970).