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Hydrogen Chloride Catalyzed Exchange between Antimony(III) and Antimony(V) Chlorides in Carbon Tetrachloride[1]

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The effect of hydrogen chloride on the electron-exchange reaction between antimony(III) and antimony(V) chlorides in carbon tetrachloride has been studied. The exchange rates are fitted to the rate law $R = 1.6 \times 10^{-7}[SbCl_5] + 1.8 \times 10^{-4}[SbCl_3][SbCl_5]^2 + 2.1 \times 10^{-5}[SbCl_3][HSbCl_6]$. In the presence of $[HCl] > [SbCl_5]$, the rate is given by the third term alone. A mechanism is proposed for this new (third) path which involves an activated complex consisting of two $SbCl_6$ octahedra sharing a common face.

The electron-transfer between antimony(III) and -(IV) in a variety of media has been the subject of a number of papers[2-9] in recent years. In the presence of strong HCl Neumann and co-workers[4,5] proposed a chloro-bridged intermediate. Barker and Kahn[6] studied the exchange in carbon tetrachloride and found two paths, one involving dissociation of $SbCl_5$ and one having an intermediate (or activated complex) containing one $SbCl_3$ and two $SbCl_5$ molecules. In this work the effect of anhydrous HCl on the exchange between $SbCl_3$ and $SbCl_5$ in carbon tetrachloride has been examined.

Experimental

Reagents.—Anhydrous antimony trichloride labeled with ^{125}Sb (2.6-year) was prepared by the method of Michael and Murphy[10] as modified by Epperson, *et al.*[11] The antimony oxide required for the synthesis was obtained by hydrolysis of a 6 *M* hydrochloric acid solution of antimony(III) containing the tracer. Enough carrier and tracer was used to yield 1 g. of antimony trichloride with a total activity of 50 μcuries. The ^{125}Sb tracer was a high-purity, carrier-free material obtained from Oak Ridge National Laboratory as a hydrochloric acid solution. The unlabeled antimony trichloride was reagent grade from the Fisher Scientific Co. Baker and Adamson reagent grade antimony pentachloride was distilled under vacuum and a middle fraction collected for use. C.P. carbon tetrachloride was further purified according to the method of Fieser,[12] treated with chlorine as described by Dickinson and Jeffreys,[13] and given a final drying, before use, by distilling from phosphorus pentoxide under an atmosphere of dry nitrogen. A.R. grade potassium bromate was obtained from Matheson Coleman and Bell. Arsenic(III) oxide, used for standardization of potassium bromate solutions, was primary standard from Fisher Scientific Co. C.P. nitrogen was used as an inert atmosphere after it was dried by passage through towers containing concentrated sulfuric acid, calcium sulfate, and magnesium perchlorate, in that order. Hydrogen chloride (Matheson) was passed over magnesium perchlorate. Hydrogen sulfide, sulfur dioxide, and chlorine (Matheson) were used without further purification. All other chemicals were reagent grade and used without further purification.

Procedure.—A stock solution of antimony trichloride was prepared by dissolving unlabeled antimony trichloride in carbon tetrachloride, followed by addition of labeled antimony trichloride that had been previously dissolved in carbon tetrachloride. The specific activity of the final solution was of the order of 2 μcuries/mg.-atom of Sb. Antimony pentachloride stock solutions were prepared by adding carbon tetrachloride to the purified material in the container into which it had been distilled. For a given kinetic run, 100 ml. of antimony trichloride solution and 100 ml. of antimony pentachloride solution were prepared in separate containers by dilution of aliquots of the stock solutions to the approximate concentration desired. These were then treated with hydrogen chloride gas under a dry, nitrogen atmosphere and stored until needed.

Exchange was initiated by mixing the antimony tri- and pentachlorides and pipetting 10.0-ml. aliquots of the resulting solution into twenty separate ampoules. The ampoules were sealed, wrapped in metal foil to exclude light, and placed in a constant temperature bath at 50.0 ± 0.1°. The entire operation from the mixing of the solutions to the wrapping of the ampoules was carried out in the dark except for a small indirect incandescent lamp required to level the pipet meniscus to the mark. A given experiment consisted of a set of twelve ampoules: three for chemical analysis, nine as the samples for determination of rate. The reactions were followed for about three half-lives.

At intervals of approximately 24 hr., ampoules were removed from the bath and the antimony(III) and -(V) were separated essentially as described by Barker and Kahn.[6] Ampoules were cooled to quench the exchange and were opened and poured into a solution of 22.5 parts of ethanol, 1 part of 37% hydrofluoric acid, 1.5 parts of concentrated hydrochloric acid, and a trace of Aerosol OT. The mixture was saturated with hydrogen sulfide. The antimony(III) sulfide fraction was discarded; antimony(V) sulfide was precipitated and then was dissolved with heating in 6 ml. of 6 *M* hydrochloric acid. The solution was filtered to remove elemental sulfur and undissolved sulfide and 4.0 ml. was pipetted into a 1-dram vial for γ-scintillation counting. After counting, the contents of the vials were transferred quantitatively to flasks for titration, treated with sulfur dioxide to reduce all the antimony to the 3+ oxidation state, boiled to remove the excess sulfur dioxide, and then analyzed for antimony.

Analytical.—Antimony(III) was determined by titration with standard potassium bromate with methyl orange as an irreversible indicator.[14] Antimony(V) was determined in the

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same way after reduction to antimony(III) with sulfur dioxide. Chloride was determined gravimetrically as silver chloride. The chloride was precipitated from a tartrate medium, the tartrate being required to keep antimony in solution. Analysis of the reaction mixture was made by selection of a minimum of three ampoules each for chloride and antimony determinations. Since analyses were done at room temperature, the analytically-determined concentrations were corrected for the volume change of the reaction mixtures at the higher temperature by use of the cubical coefficient[15] of expansion for carbon tetrachloride.

Radioactivity Measurements.—Since the tracer employed was of high radiochemical purity, all activities were determined by integral scintillation counting using a NaI(Tl) well-type crystal.

Results and Discussion

The results of the exchange studies and the experimental conditions are given in Table I. Rates are seen to increase with increasing hydrogen chloride concentrations. Graphs of log $(1 - F)$ *vs.* t were good straight lines. Standard deviations in the slopes ranged from 5 to 10% of the slope.

TABLE I

EXPERIMENTAL CONDITIONS AND OBSERVED AND CALCULATED EXCHANGE RATES[a] AT 50.0 ± 0.1° IN CCl_4

$[SbCl_3]$, $M \times 10^2$	$[SbCl_5]$,[b] $M \times 10^2$	[HCl],[b] $M \times 10^2$	$R \times 10^8$, M sec.$^{-1}$ (obsd.)	$R \times 10^8$, M sec.$^{-1}$ (calcd.)
4.320	0.6811	2.862	0.55	0.61
4.356	4.856	0.9163	2.7	2.7
4.482	4.727	0.8247	2.4	2.6
4.279	4.690	0.5733	2.5	2.5
4.632	2.272	1.118	1.2	1.5
3.151	2.110	4.650	1.35	1.4
4.301	3.476	1.129	1.9	1.8
4.416	3.989	3.496	3.0	3.3
1.589	4.349	4.406	1.8	1.4
2.101	4.380	5.326	2.2	1.9
2.771	4.550	3.581	2.5	2.3

[a] Rate of exchange, R, calculated from $R = 2.303(\Delta \log (1 - F)/\Delta t)([SbCl_3][SbCl_5]/([SbCl_3] + [SbCl_5]))$. [b] Values given in table are stoichiometric concentrations of antimony(V) chloride and hydrogen chloride.

In the absence of hydrogen chloride, Barker and Kahn[6] found that the exchange rate law at 50° was

$$R = 1.6 \times 10^{-7}[SbCl_5] + 1.8 \times 10^{-4}[SbCl_3][SbCl_5]^2$$

This law suggests a dissociative path

$$SbCl_5 = SbCl_3 + Cl_2$$

and a path involving a complex, Sb_3Cl_{13}, formed from one molecule of antimony(III) chloride and two of antimony(V) chloride.

In the presence of hydrogen chloride we have been able to fit our data to the Barker and Kahn rate law plus an additional term

$$k_3[SbCl_3][HSbCl_6]$$

assuming that the formation of $HSbCl_6$ is essentially complete, *i.e.*, that the formation constant

$$\frac{[HSbCl_6]}{[SbCl_5][HCl]} = \beta$$

is very large. It is further assumed that there is a negligible amount of $HSbCl_4$ under the experimental conditions.

The value of $k_3 = 2.07 \pm 0.23 \times 10^{-5}\ M^{-1}$ sec.$^{-1}$ was determined by the method of least squares and the equation

$$\frac{R - 1.6 \times 10^{-7}[SbCl_5] - 1.8 \times 10^{-4}[SbCl_3][SbCl_5]^2}{[SbCl_3]} = k_3[HSbCl_6]$$

With 0.02 M antimony(III) and -(V) chlorides, in the absence of HCl the predicted rate of exchange is $R = 4.6 \times 10^{-9}\ M$ sec.$^{-1}$. Under the same conditions but with added $[HCl] = 0.02\ M$, $R = 8.3 \times 10^{-9}\ M$ sec.$^{-1}$. Thus, under typical experimental conditions the $HSbCl_6$ path is about twice as fast as the combined paths of the Barker and Kahn rate law. When $[HCl] = [SbCl_5]$, that is when essentially all the antimony(V) is present as $HSbCl_6$, the exchange is described simply as

$$R = k_3[SbCl_3][HSbCl_6]$$

One can then postulate that the active complex is much like that proposed by Neumann[4,5] and Bonner and Goishi[16] for the exchange in aqueous hydrochloric acid. It can be represented as two $SbCl_6$ octahedra sharing a common face.

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