$(BX)^{n_1} + k_2(AX)^{m_2}(BX)^{n_2} + \ldots\ldots$ where the conditions in case C are satisfied by the number pairs m_1, n_1; m_2, n_2; etc.

F. Same as A except that $R_1(t) = k_1(AX)^{m_1}\cdot(BX)^{n_1} + k_2(AX)^{m_2}(BX)^{n_2} + \ldots\ldots$ where the conditions in case A or B are satisfied by the number pairs m_1, n_1; m_2, n_2; etc.

G. $v(t) = v$ (constant); $R_1(t) = k(AX)(BX)$; $R_2(t) = k_2(AX)$; $R_3(t) = k_3(BX)$.

Acknowledgment.—We wish to thank Dr. R. D. Fowler of this Laboratory for his interest in this work and for assistance in the present interpretation of Koskoski, Dodson and Fowler's results.[7]

LOS ALAMOS, NEW MEXICO

[CONTRIBUTION FROM THE UNIVERSITY OF NEW MEXICO]

The Kinetics of the Exchange of Antimony between Antimony Trichloride and Antimony Pentachloride in Carbon Tetrachloride[1]

BY FRANKLIN B. BARKER AND MILTON KAHN

RECEIVED OCTOBER 7, 1955

A measurable exchange has been observed between antimony trichloride and antimony pentachloride in carbon tetrachloride. The exchange reaction was investigated over a temperature range from 50.1 to 81.0°; the concentration of antimony trichloride ranged from 0.0153 to 0.115 M and that of antimony pentachloride from 0.0055 to 0.0667 M. The rate law for the exchange reaction is $R = 1 \times 10^6 e^{-19,000/RT}(\mathrm{SbCl_5}) + 4 \times 10^6 e^{-15,000/RT}(\mathrm{SbCl_3})(\mathrm{SbCl_5})^2$ where the units of R are moles × liter^{-1} × sec.$^{-1}$.

Introduction

This paper deals with the kinetics of the exchange of antimony atoms between antimony trichloride and antimony pentachloride in carbon tetrachloride. The exchange reaction was found to proceed through two paths; one path is first order with respect to antimony pentachloride; the other path is first order with respect to antimony trichloride and second order with respect to antimony pentachloride.

Experimental

Radioactivity.—The 60-day Sb^{124}, which was used as tracer in all experiments, was produced by neutron-irradiation of reagent grade antimony trichloride. After allowing at least five weeks for the decay of the 2.8-day Sb^{122}, the irradiated antimony trichloride was distilled twice in a helium atmosphere at a pressure of 50 mm. of mercury.

The radiochemical purity of the tracer was checked by observing the decay of an active solution of antimony. The antimony decayed with a half-life of 60.3 days over a period of four half-lives in satisfactory agreement with the previously reported value.[2] Also, the specific activity of an aliquot of an active antimony trichloride solution was the same as that of an aliquot purified from arsenic, tin, indium, copper, bismuth, cadmium, lead, mercury, iron and chromium carriers.

Chemicals.—Baker C.P. carbon tetrachloride was further purified according to the method of Fieser,[3] treated with chlorine and chlorine dioxide as described by Dickinson and Jeffreys,[4] and finally distilled from phosphorus pentoxide.

Helium and argon, used interchangeably for inert atmospheres, were washed with "Oxorbent" and sulfuric acid, and passed over "Drierite."

U.S.P. boric acid was further purified by recrystallization from water.

Hydrogen sulfide and sulfur dioxide, obtained from the Ohio Chemical and Surgical Supply Company, were used without further purification.

Matheson chlorine was used without further treatment for the purification of carbon tetrachloride.

The chlorine used in the preparation of antimony pentachloride solutions was prepared by the action of hydrochloric acid on manganese dioxide. The liberated chlorine was first passed through a saturated potassium permanganate solution and subsequently through sulfuric acid.

All other chemicals were of reagent grade and were used without further purification.

Procedure.—A stock solution of active antimony trichloride, prepared by dissolving the twice-distilled active antimony trichloride in carbon tetrachloride, was stored under an inert atmsophere. A stock solution of antimony pentachloride was prepared by allowing chlorine to react in carbon tetrachloride with an excess of inactive antimony trichloride. The reaction mixture was contained in a sealed flask under an inert atmosphere and maintained at 50.1° for a period of ten days; under these conditions more than 99% of the chlorine was consumed.

The stock solutions were analyzed for antimony(III) by titration with standard potassium bromate,[5] for antimony(V) by iodometric titration,[6] and for chloride by the Volhard method.[7]

Because all solutions were prepared at room temperature it was necessary to correct the analytically determined concentrations for the volume change of the reaction mixtures at the higher temperatures. These corrections were calculated from the expression for the cubical coefficient of expansion for carbon tetrachloride.[8]

A reaction mixture was prepared from appropriate amounts of the stock solutions and carbon tetrachloride, and 10-ml. portions of this mixture were sealed in ampoules containing an inert atmosphere. The ampoules were wrapped in aluminum foil to exclude light and then placed in a constant temperature (±0.1°) water-bath. All operations from the mixing of the solutions to the wrapping of the ampoules were carried out in a dark room illuminated by a photographer's red safe-light.

At suitable time intervals the reaction was quenched by cooling an ampoule under the tap; the reactants were separated and the radioactivity in each fraction determined.

Separation Procedure.—Five to 10 ml. of the reaction mixture was added to a solution which contained 22.5 ml. of absolute ethanol, 1.5 ml. of concentrated hydrochloric acid and 1.0 ml. of 48% hydrofluoric acid. Approximately 1 ml. of a 1% solution of "Aerosol OT" in absolute alcohol was added and hydrogen sulfide was passed into the solu-

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(1) This communication is based on work done under the auspices of the Los Alamos Scientific Laboratory and the Atomic Energy Commission and submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the University of New Mexico, June, 1954, by Franklin B. Barker. Presented before the Physical and Inorganic Division of the American Chemical Society in Minneapolis, September, 1955.

(2) J. J. Livingood and G. T. Seaborg, *Phys. Rev.*, **55**, 414 (1939).

(3) L. F. Fieser, "Experiments in Organic Chemistry," 2nd Ed., D. C. Heath and Co., New York, N. Y., 1941, p. 365.

(4) R. G. Dickinson and C. E. P. Jeffreys, THIS JOURNAL, **52**, 4288 (1930).

(5) W. W. Scott, "Scott's Standard Methods of Chemical Analysis," 5th Edition, Vol. I, Edited by N. H. Furman, D. Van Nostrand Co., New York, N. Y., 1939, p. 74.

(6) Ref. 5, p. 75.

(7) Ref. 5, p. 271.

(8) N. A. Lange, Editor, "Handbook of Chemistry," 7th Ed., Handbook Publishers, Inc., Sandusky, Ohio, 1949, p. 1639.

tion for two minutes in order to precipitate the antimony(III). The mixture was centrifuged and the supernatant liquid, which contained the antimony(V)-fluoride complex was added to 25 ml. of 2 *N* hydrochloric acid saturated with boric acid. The carbon tetrachloride was removed by gentle boiling; the solution was cooled to 50° or below and subsequently treated with hydrogen sulfide. The precipitate was dissolved in about 5 ml. of hot concentrated hydrochloric acid, the hydrogen sulfide was boiled off, and the resulting solution saturated with sulfur dioxide in order to assure complete reduction of antimony (V). The activity and antimony in the solution were determined after the excess sulfur dioxide was boiled off.

Measurement of Radioactivity.—The γ-radiation associated with the decay of Sb^{124} was detected with a scintillation counter employing a #5819 R.C.A. phototube and a thallium activated sodium iodide crystal. Liquid samples were prepared according to the procedure of Keneshea and Kahn.[9]

Results and Discussion

The reaction investigated is

$$Sb^{*}Cl_3 + SbCl_5 = SbCl_3 + Sb^{*}Cl_5$$

where the asterisks indicate radioactive atoms. The logarithmic form of the isotopic exponential exchange law[10] for this reaction is

$$-\ln(1 - F) = \frac{R[(SbCl_3) + (SbCl_5)]t}{(SbCl_3)(SbCl_5)} \qquad (1)$$

where $(SbCl_3)$ = total concentration of antimony trichloride (active + inactive) in moles per liter; $(SbCl_5)$ = total concentration of antimony pentachloride (active + inactive) in moles per liter; F = fraction exchange at time t; R = constant rate of exchange of antimony atoms between antimony trichloride and antimony pentachloride.

Because the concentrations of the antimony species are known in any one experiment, it is possible to evaluate R, the rate of exchange, for that experiment from the half-time of exchange $t_{1/2}$, as determined from a plot of log $(1 - F)$ *vs.* t. According to equation 1 this plot should give a straight line passing through the origin. In all instances these straight line plots, determined from the data by the method of least squares, did not pass through the origin. These curves indicated an apparent zero-time exchange of about 5% which may have been the result of incomplete precipitation of Sb(III) or separation-induced exchange, or both.[11]

Dependence on Antimony Trichloride and Antimony Pentachloride.—The dependence of R, the rate of exchange, on the concentration of antimony trichloride and antimony pentachloride was found to be

$$R = k_1(SbCl_5) + k_2(SbCl_3)(SbCl_5)^2 \qquad (2)$$

where k_1 and k_2 are specific rate constants. According to equation 2, a plot of $R/(SbCl_5)$ against $(SbCl_3)(SbCl_5)$ should yield a straight line of slope k_2 and intercept k_1. The rate constants k_1 and k_2 were evaluated from such plots of the data in Table I by the method of least squares[12] and are listed in Table II.

TABLE I

RESULTS OF EXCHANGE EXPERIMENTS

Temp., °C.	$(SbCl_5)$, *f*	$(SbCl_3)$, *f*	$t_{1/2}$, hr.	$R \times 10^4$, mole l.$^{-1}$ hr.$^{-1}$
50.1	0.00562	0.1145	765	0.0488
	.0103	.0958	433	.149
	.0193	.0620	416	.245
	.0284	.0786	220	.658
	.0386	.0310	232	.513
	.0386	.0310	235	.507
	.0496	.0586	146	1.27
	.0500	.0577	140	1.33
	.0588	.0297	149	0.917
	.0662	.0440	125	1.46
	.0667	.0435	124	1.47
68.4	.00549	.1016	169	0.213
	.0143	.0832	108	0.805
	.0254	.0603	79	1.57
	.0302	.0699	70	2.06
	.0482	.0153	41	1.96
	.0508	.0404	43	3.63
	.0533	.0343	40	3.61
81.0	.0374	.0164	19.5	4.05
	.0374	.0567	22.1	7.06
	.0661	.0178	10.6	9.17

TABLE II

SPECIFIC RATE CONSTANTS AT VARIOUS TEMPERATURES

Temp., °C.	First-order constant, k_1, sec.$^{-1}$	Third order constant, k_2, l.^{2} moles^{-2} sec.$^{-1}$
50.1	$(1.6 \pm 0.3) \times 10^{-7}$	$(1.8 \pm 0.2) \times 10^{-4}$
68.4	$(7.5 \pm 1.5) \times 10^{-7}$	$(6.0 \pm 0.6) \times 10^{-4}$
81.0	$(2.1 \pm 0.4) \times 10^{-6}$	$(1.5 \pm 0.2) \times 10^{-3}$

Effect of Light on the Rate of Exchange.—The results of an experiment carried out at room temperature and in room light (daylight + fluorescent lighting) indicate that light has a marked accelerating effect on the rate of the exchange reaction.

Effect of Glass Surface on the Rate of Exchange.—No variation of the rate of exchange was detected at 50.1° when the surface in contact with the reaction mixture was increased approximately five times with glass beads.

Activation Energies.—The curves shown in Fig. 1 are semilogarithmic plots of 1000 × k_1 and k_2 against the reciprocal of the absolute temperature. The experimental activation energies determined from these plots are 19,000 ± 200 cal. for the first-order path and 15,000 ± 100 cal. for the third-order path.

The Rate Law.—From the foregoing discussion it appears that the exchange reaction is homogeneous and proceeds through two paths. One path is first order with respect to antimony pentachloride; the other path is first order with respect to antimony trichloride and second order with respect to antimony pentachloride. The experimental data, obtained over a temperature range from 50.1 to 81.0°, an antimony trichloride concentration range from 0.0153 to 0.115 *M* and an antimony pentachloride concentration range from 0.0055 to 0.0667 *M*, are well represented by the rate law

$$R = 1 \times 10^6 e^{-19{,}000/RT}(SbCl_5) + 4 \times 10^6 e^{-15{,}000/RT}(SbCl_3)(SbCl_5)^2$$

where the units of R are moles × liter^{-1} × sec.$^{-1}$.

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[10] G. Friedlander and J. W. Kennedy, "Introduction to Radiochemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 285 ff.

[11] O. E. Myers and R. J. Prestwood, "Radioactivity Applied to Chemistry," Edited by A. C. Wahl and N. A. Bonner, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 16.

[12] A. G. Worthing and J. Geffner, "Treatment of Experimental Data," John Wiley and Sons, Inc., New York, N. Y., 1943, p. 238.

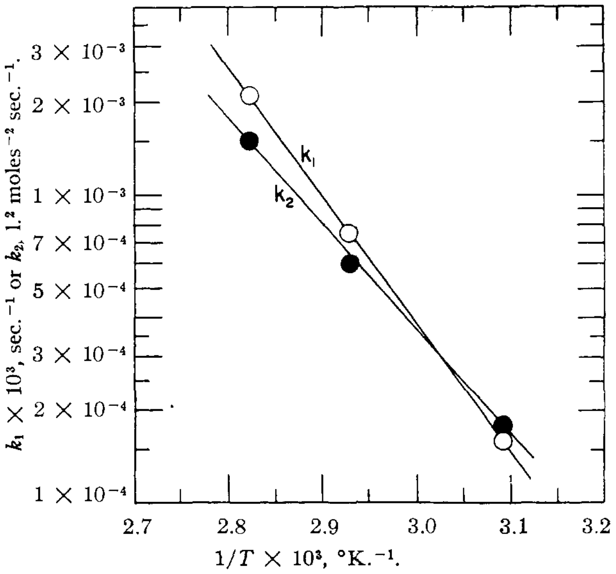

Fig. 1.—The temperature dependence of the specific rate constants.

The Mechanisms.—A mechanism which is consistent with the observed first-order path is represented by the slow equilibrium

$$SbCl_5 = SbCl_3 + Cl_2 \qquad (3)$$

The third-order path is consistent with the mechanism represented by equations 4, 5 and 6

$$2SbCl_5 = Sb_2Cl_{10} \text{ (rapid equilibrium)} \qquad (4)$$

$$Sb_2Cl_{10} + Sb^*Cl_3 = Sb^*Sb_2Cl_{13} \text{ (rapid equilibrium, activated complex)} \qquad (5)$$

$$Sb^*Sb_2Cl_{13} \longrightarrow SbCl_3 + Sb^*SbCl_{10} \text{ (rate-determining step)} \qquad (6)$$

The dimerization of antimony pentachloride is a reasonable possibility in light of the evidence for the existence of compounds of the type $SbCl_5 \cdot MCl_5$, where M may be either phosphorus or arsenic.[13] A possible structure for the activated complex is shown in Fig. 2 wherein the three antimony atoms occupy identical positions.

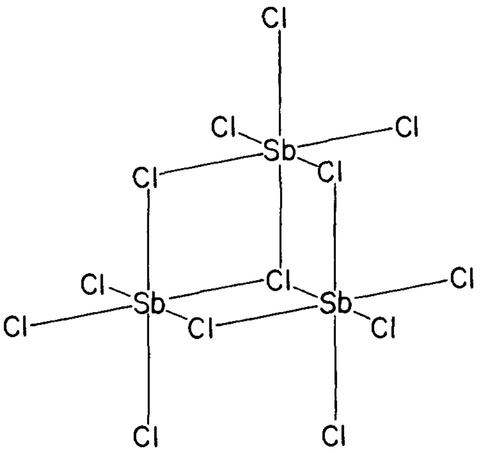

Fig. 2.—Proposed structure for termolecular activated complex.

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ALBUQUERQUE, N. MEX.

[CONTRIBUTION OF THE DEPARTMENT OF CHEMISTRY OF CLARK UNIVERSITY]

Thermodynamics of Metal Chelate Formation. V. Nitrilotriacetic Acid[1]

BY VINCENT L. HUGHES AND ARTHUR E. MARTELL[2]

RECEIVED OCTOBER 5, 1955

Potentials of cells consisting of hydrogen and silver–silver chloride electrodes have been measured in buffer solutions containing acid salts of nitrilotriacetic acid at various ionic strengths. The e.m.f. data obtained were extrapolated to infinite dilution with the aid of the Debye–Hückel activity coefficient relationship, and the thermodynamic acid dissociation constants were evaluated. Similar measurements made in the presence of Mn(II), Mg(II), Ca(II) and Ba(II) ions were used for the determination of the corresponding thermodynamic metal chelate stability constants. The standard free energy changes for the reactions at 0, 10, 20 and 30° were calculated, and the corresponding values of $\Delta H°$ and $\Delta S°$ applying over this temperature range are reported. The results are interpreted on the basis of recent theories of metal chelate formation in aqueous solution.

In order to provide more data for testing the significance of the entropy effect as a factor in the stability of metal chelate compounds,[3] the thermodynamic measurements reported previously for ethylenediaminetetraacetate chelates[4] have been extended in the present research to metal chelate compounds of nitrilotriacetic acid. Although the latter ligand provides fewer coördinating groups than does the anion of ethylenediaminetetraacetic acid, it nevertheless has a remarkable affinity for even the more basic divalent ions. Therefore it seems quite probable that relatively large entropy effects would contribute to the stability of metal–nitrilotriacetate chelates, as has been found to be

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[3] (a) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, p. 151; (b) G. Schwarzenbach, *Helv. Chim. Acta*, **35**, 2345 (1952).

[4] (a) F. F. Carini and A. E. Martell, THIS JOURNAL, **75**, 4810 (1953); (b) **76**, 2153 (1954).