

[CONTRIBUTION FROM THE CHEMISTRY DIVISION, UNIVERSITY OF CALIFORNIA, LAWRENCE RADIATION LABORATORY, LIVERMORE, CALIFORNIA]

Antimony in HCl Solutions. Kinetics of Complex Exchange and Hydrolysis Reactions¹

BY NORMAN A. BONNER AND WATARU GOISHI

RECEIVED APRIL 7, 1960

We have studied the kinetics of the exchange of antimony atoms between Sb(III) and Sb(V) in 7 and 7.7 *f* HCl. The observed exchange curves are complex in general; that is, they consist of two exponential components. The complexity has been shown to be the result of the known slow hydrolysis reaction of Sb(V) in HCl solutions. One slow step is rate-determining in the series of Sb(V) hydrolytic reactions occurring in 3 to 12 *f* HCl. The actual exchange with Sb(III) occurs principally with an Sb(V) species on the less hydrolyzed side of this slow step. The fraction of Sb(V) on the less hydrolyzed side increases from 0.011 to 6.00 *f* HCl to 0.912 in 10.08 *f* HCl. The hydrolysis of Sb(V) was studied spectrophotometrically to aid in the interpretation of the exchange data. The extraction behavior of Sb(V) from HCl solutions into isopropyl ether indicated the presence of two extractable species. The hydrolysis rate and the exchange rate in 7 and 7.7 *f* HCl are of the same order of magnitude, so that both rates are involved in the apparent exchange rates. The exchange rate constant is 1.39 ± 0.07 and $1.07 \pm 0.04 f^{-1} \text{ min.}^{-1}$ in 7.04 and 7.69 *f* HCl, respectively. These values agree very well with the trend of values in 6 to 12 *f* HCl deduced from the data of previous investigators. The experimental activation energies are 17.2 ± 2 kcal./mole for exchange and 21.3 ± 2 kcal./mole for hydrolysis. The ΔH for the hydrolysis reaction is 5.0 ± 0.7 kcal./mole. These values correlate well with the observed activation energies for the over-all exchange reaction in from 6 to 12 *f* HCl.

I. Introduction

The study described in this paper developed because of some curious exchange curves observed by Cheek, *et al.*² He measured the Sb(III)-Sb(V) exchange rate as a function of the HCl concentration. In the region of 7 *f* HCl he obtained complex exchange curves, *i.e.*, the plot of $\log(1 - \text{fraction exchange})$ vs. t was not a straight line. Because complex exchange curves had never been observed before, we decided to make some detailed measurements in 7 *f* HCl. The problem grew (as problems will) and developed into a general treatment of the Sb(III)-Sb(V) exchange in 6 to 12 *f* HCl.

Cheek concluded that the complex nature of the exchange curves was caused by one or more slow steps in the hydrolysis reactions of Sb(V). We were thus led into making a more accurate spectrophotometric study of the Sb(V) hydrolysis.

We have attempted to tie together all of the data on antimony exchange and hydrolysis in all HCl concentrations. We believe we have a fairly complete picture of the reactions occurring, although the exact nature of the ions involved is not entirely clear.

There are several sets of data which must be treated. In the original paper on the exchange reaction in 6 *f* HCl, Bonner³ found that the rate law included the 0.6 power of the Sb(III) concentration. He suggested that this might be due to the existence of Sb(III) as a dimer, with the principal reaction path involving a monomer. There is no good evidence for this mechanism.

Cheek's work, mentioned above, followed. In addition to the exchange studies, he measured the hydrolysis rate of Sb(V) in HCl solutions of differing concentrations. He was thus able to prove that Sb(V) existed in more than one form, with slow rates of interconversion. He also proposed

that the slow reactions between Sb(V) species could explain Bonner's results, but he did not make a quantitative treatment.

At about the same time, Neumann¹² and Neumann and Ramette⁴ had been making independent studies of the Sb(V) hydrolysis reaction.

Neumann and Brown⁵ made a few more exchange measurements, including some very interesting non-equilibrium exchange studies. They correlated the data available at that time, including much of Cheek's unpublished thesis. Their treatment was based on the existence of two non-equivalent Sb(V) species and was more quantitative than Cheek's. The equation for complex exchange (see equation 1 below) had not been developed at that time, so they were unable to treat the complex exchange curves, and their calculations were semi-quantitative. In spite of this limitation, they obtained fairly good agreement between calculated and observed half-times for the exchange experiments.

In our present treatment we have extended the exchange and hydrolysis data and have reinterpreted much of the older data.

II. Experimental

A. Tracers.—The 2.0-year Sb¹²⁵ fission product was obtained from the Oak Ridge National Laboratory. The material had been separated from other fission products and was carrier-free. The label indicated that it was about six months old when shipped.

We purified the antimony further after adding a small amount of carrier. The purification procedure was quite extensive and was known to produce radiochemically pure antimony. The final step in the preparation of the main stock solution involved solution of Sb₂S₃ in HCl followed by evaporation to remove excess H₂S and filtration to remove free S and any insoluble material which might have been introduced during the purification. The stock was thus entirely in the +3 state when first prepared. This solution was never used directly in an exchange experiment but was first diluted as described below.

The Sb(III) tracer solutions were made by simple dilution of the main stock tracer with HCl of the desired concentration. Some of the diluted tracer solutions had low antimony concentrations ($\sim 0.004 f$), and we found them gradually being oxidized to Sb(V). The percentage oxidized was reduced to negligible amounts by keeping the solutions in the

(1) Presented in part at the Symposium on Aqueous Solutions at the 136th meeting of the American Chemical Society in Atlantic City, N. J., September 1959.

(2) C. H. Cheek, N. A. Bonner and A. C. Wahl, *THIS JOURNAL*, **83**, 80 (1961).

(3) N. A. Bonner, *ibid.*, **71**, 3909 (1949). There is an error in Table I of this paper. The heading for the last column should read $k \times 10^{12}$. The same error occurs in the rate laws on pp. 3913 and 3914.

(4) H. M. Neumann and R. W. Ramette, *THIS JOURNAL*, **78**, 1848 (1956).

(5) H. M. Neumann and H. Brown, *ibid.*, **78**, 1843 (1956).

dark and raising the Sb concentration to $\sim 0.03 f$ by the addition of inactive antimony.

The Sb(V) tracer solutions were made by bubbling Cl_2 gas through a portion of the Sb(III) tracer in boiling $\sim 6 f$ HCl. The solution was then boiled to remove excess Cl_2 and the HCl concentration adjusted to the desired value by adding HCl of known concentration. The solutions were stored in the dark.

B. Reagents.—Analytical reagents were used whenever they were available. The Sb(III) and Sb(V) carriers were made by dissolving Baker and Adamson SbCl_3 and Baker SbCl_5 , respectively, in HCl of the appropriate concentration. The Sb(V) solutions contained an extraneous oxidizing agent, presumably Cl_2 , which rapidly oxidized Sb(III) and hence could not be tolerated in the exchange experiments. This became apparent when Sb(III) tracer was added to some of the Sb(V) in $8 f$ HCl and the solution quickly mixed with isopropyl ether. The activity was mostly in the ether phase, showing that the Sb(III) tracer had been oxidized to Sb(V). Sb(III) solution was added to the Sb(V) solution in successive small amounts until the oxidizing agent was all destroyed. After each addition the extraction test, using Sb(III) tracer as just described, was made to test for the presence of the oxidizing agent.

The isopropyl ether used in the extractions (Eastman white label) was purified by treatment with dilute $\text{Na}_2\text{Cr}_2\text{O}_7\text{-H}_2\text{SO}_4$ solution followed by repeated treatments with fresh portions of a 1:1 mixture of $6 f$ NaOH and saturated KMnO_4 . The ether was then washed several times each with water, dilute HCl and again water. It was finally washed once with, and stored over, $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ solution acidified with H_2SO_4 .

C. Analytical Procedures.—The solutions were analyzed for antimony content by bromate titration⁶ and for chloride content by the dichlorofluorescein method.⁷ All antimony stock solutions were kept in flasks painted with black Tygon.

The HCl concentrations of some of the Sb(III) and Sb(V) solutions were adjusted spectrophotometrically as will be described later.

D. Extraction Procedure.—The Sb(III)–Sb(V) separations were made by isopropyl ether extraction from $8 f$ HCl at 23.4° . The Sb(V) is extracted to the largest extent at this HCl concentration and temperature. In the $7 f$ HCl runs, for example, 5.00 ml. of $8.50 f$ HCl and 15.0 ml. of isopropyl ether were placed in a 40 -ml. glass cone. 0.025 ml. of a solution $0.05 f$ in Sb(III), $0.05 f$ in Sb(V) and $7.00 f$ in HCl was added as protection against the possible presence of oxidizing or reducing agents in the extraction mixture. The cone was covered with Parafilm and left in a 23.4° water-bath for at least 5 minutes before use. It was kept in the bath until after the counting samples had been removed. 2.00 ml. of the exchange solution were delivered (with a pipet painted with black Tygon) to the cone while the solution was being stirred with a motor-driven glass paddle. The mixture was stirred for 2 minutes and allowed to settle for at least 4 minutes before sampling each layer. 5.00 ml. of each layer were delivered to 16×100 mm. glass tubes containing 0.50 ml. of acetone. The acetone prevented the separation of the aqueous sample into two phases on warming. The tubes used in each exchange run were matched in external diameter to minimize fluctuations in counting geometry.

E. Counting Procedure.—The extraction samples were gamma counted in a well-type NaI scintillation counter. Interference from the activity of the Te^{125m} daughter was eliminated with the use of a lower discriminator set at 125 kev. No difference could be detected between the counting rate of the same size sample in ether and in HCl.

F. Exchange Procedure.—Exchange mixtures were made in painted 25-ml. volumetric flasks. The solutions were kept in a thermostatted bath regulated to better than $\pm 0.05^\circ$. A mixture of appropriate amounts of tracer solution, carrier of the same oxidation state as the tracer, and HCl was allowed to stand overnight or longer in the bath. To begin the exchange reaction, carrier solution of the other oxidation state was delivered, the flask filled to volume with HCl and the solution mixed thoroughly. The latter two

solutions were also thermostatted beforehand. 2.00 -ml. portions of the exchange solution were removed at appropriate times for the determination of the specific activities of the Sb(III) and Sb(V) fractions as described under "Extraction Procedure" and "Counting Procedure." The time of sampling was taken as the time at which the pipet was half empty. Eleven or 12 such samples were taken in each run. Included in these are one or two samples which were taken when the exchange reaction was essentially completed.

G. Spectrophotometry.—Sb(V) hydrolysis studies were made using a Cary Model-14 Spectrophotometer. Measurements were made between 2200 and 3600 \AA . using 1- and 10-cm. fused silica cells. There were provisions for regulating the cell compartment temperature by the passage of thermostatted water through a water jacket but the temperature could only be regulated at $25 \pm 1^\circ$. With the addition of insulated water jackets on the compartment covers the temperature control was improved to $\pm 0.1^\circ$ for the last few runs. The procedure below gives details of a typical run in which we followed the hydrolysis of Sb(V) when its environment was suddenly changed from 12 to $7.00 f$ HCl.

All the solutions used were allowed to come to hydrolysis equilibrium in a 25° bath before the run was begun. 10λ of $1 f$ Sb(V) solution in $12 f$ HCl was mixed with an amount of HCl such that the final HCl concentration was $7.00 f$ and the final volume 50.0 ml. The spectrum between 2200 and 3500 \AA . was scanned at ten-minute intervals in a 1-cm. cell with $7.00 f$ HCl as the blank. The equilibrium spectrum was taken after ten hydrolysis half-times.

Whenever more accurate optical density values were desired at specific wave lengths, the Cary was run at constant wave length for ~ 20 sec. at each of the desired wave lengths. This was necessary in many cases because of the rapid change of optical density with wave length. Constant wave length runs were also necessary for the determination of the shorter hydrolysis half-times.

In those runs for which the total change in the spectrum was small, the precision of the $D - D_{eq}$ values was markedly improved by making some equilibrium solution beforehand and placing it (instead of plain HCl) in the blank and reference cells. This procedure largely compensates for errors in optical density due to wave length and temperature fluctuations.

The HCl, Sb(III) and Sb(V) carrier solutions used for making up exchange mixtures had to be matched accurately so that no shift in the hydrolysis equilibrium of Sb(V) occurred when the solutions were mixed. This was especially important when Sb(V) carrier solution was added to the exchange mixture to begin a run. The spectrophotometer was used in making the matches. For example, solutions used in the $7.69 f$ HCl exchange were adjusted as follows: 1.00 ml. of the Sb(V) solution was diluted to 50 ml. with $7.69 f$ HCl and the optical density at 3500 \AA . was followed in a 10-cm. cell. It was found to decrease with time, showing that the HCl concentration of the Sb(V) solution needed to be lowered. This adjustment was made and the test was repeated after the Sb(V) solution had reached equilibrium. This process was continued until the optical density no longer changed with time upon dilution with $7.69 f$ HCl.

The acidity of the Sb(III) solution was then adjusted to $7.69 f$ in a similar manner, using Sb(V) as an indicator. 10.00 ml. of the Sb(III) solution and 1.00 ml. of the Sb(V) solution were mixed and allowed to reach hydrolysis equilibrium. The solution was then diluted to 50 ml. volume with $7.69 f$ HCl and the optical density was followed as before.

The acidity of the Sb(V) solution for the $7.0 f$ HCl runs was adjusted after some of the runs had been made. The Sb(III) solution in $\sim 7 f$ HCl was not adjusted but its acidity was determined so that corrections for acid concentration could be made.

III. Development of Exchange Equations

In order to develop the equation for the fraction exchange as a function of time, we must make some assumptions about the number of species present and the reactions between them. The validity of the assumptions will be discussed with the results of the experiments.

We assume first that under the conditions of our experiments the exchange system can be repre-

(6) I. M. Kolthoff and R. Belcher, "Volumetric Analysis," Vol. III, Interscience Publishers, Inc., New York, N. Y., 1957, pp. 507, 513 and 515.

(7) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The MacMillan Company, New York, N. Y., 1943, p. 571.

sented by the diagram

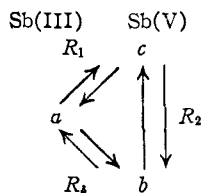


Fig. 1.—Three component exchange system.

In this diagram a represents Sb(III) and b and c represent two forms of Sb(V) in different stages of hydrolysis, c being the less hydrolyzed form.⁸ The equilibrium between b and c is established slowly. R_1 , R_2 and R_3 are the rates of the indicated reactions. The forward and reverse reaction rates are equal because the system is at equilibrium.

The solution of the differential equations for systems of this type has been published.⁹ The exchange equation in its general form is

$$1 - F_a = Q_1 e^{-(q+p)t} + Q_2 e^{-(q-p)t} \quad (1)$$

where F_a is the fraction of a exchanged in time, t , and q , p , Q_1 and Q_2 are functions of the rates and concentrations

$$2q = \left(\frac{A+C}{AC}\right) R_1 + \left(\frac{B+C}{BC}\right) R_2 + \left(\frac{A+B}{AB}\right) R_3$$

$$p_2 = q^2 - r$$

$$r = (R_1 R_2 + R_1 R_3 + R_2 R_3) \left(\frac{A+B+C}{ABC}\right)$$

$$Q_1 = \frac{1}{2pA} \left[-A(q-p) + \frac{(R_1 + R_3)S_a^0 - R_1 S_c^0 - R_3 S_b^0}{S_a^0 - S_a^\infty} \right] \quad (2)$$

$$Q_2 = 1 - Q_1$$

A, B, C = concentrations of a, b, c , respectively
 S_a^0, S_b^0, S_c^0 = specific activities of a, b, c , respectively, at $t = 0$

S_a^∞ = specific activity of a at equilibrium

If the experimental curve can be resolved into its two components, four quantities are measured by each experiment, namely, two intercepts and two slopes. However, because of the relationship $Q_1 + Q_2 = 1$, only three independent quantities can be determined. For example, if the three concentrations, A, B and C are known, one experiment will give values for all three rates.

In an exchange run we know the total concentration of Sb(V) rather than the individual values of B and C . For convenience we have called the total Sb(V) concentration E and have defined the quantity ϕ as the fraction of Sb(V) in the c form, i.e., $E = B + C$, $\phi = C/E$, and $1 - \phi = B/E$.

If we now assume the rate laws to be

$$R_1 = k_1 AC = k_1 A \phi E$$

$$R_2 = k_2 C = k_2 B = k_2 \phi E = k_2 (1 - \phi) E \quad (3)$$

$$R_3 = k_3 AB = k_3 A (1 - \phi) E$$

we can express the quantities of eq. 1 in terms of

(8) We are assuming that if c is composed of two or more species in equilibrium with each other, these equilibria are established rapidly compared with R_1 and R_2 , the reactions involving c . Analogous assumptions are made for a and b .

(9) D. F. Abell, N. A. Bonner and W. Goishi, *J. Chem. Phys.*, **27**, 658 (1957).

ϕ , k_1, k_2, k_3 and the concentrations of Sb(III) and Sb(V).

$$2q = A(k_1 + k_3) + E[\phi k_1 + (1 - \phi)k_3] + k_1/\phi$$

$$r = (A + E) \left\{ A k_1 k_3 + \frac{k_1}{\phi} [\phi k_1 + (1 - \phi)k_3] \right\} \quad (4)$$

$$Q_1 = \frac{1}{2p} \{ -(q - p) + (A + E) [\phi k_1 + (1 - \phi)k_3] \}$$

These expressions also assume that $S_b^0 = S_c^0$, which was true for all of our exchange runs except No. 35.

It should be noted that eq. 1 is written in terms of F_a , the fraction exchange of species a . In a system of this type F_a, F_b and F_c are usually not equal. Our extraction procedure separates Sb(III) from Sb(V), with only minor separation of the b and c forms. The specific activities of the Sb(III) fraction and of the Sb(V) fraction are the quantities most easily obtained. Treatment of the data as described below allows calculation of the fraction exchange of Sb(III) and of Sb(V) as a whole. Since these two quantities are equal, they will be referred to simply as the fraction exchange, F .

In terms of experimental quantities, F has the forms:

Case I.—The activity is initially all in Sb(III)

$$F = \frac{S_{b+c}}{S_\infty} = \frac{\frac{\alpha}{\alpha - \beta} - \left(\frac{1 - \alpha}{\alpha - \beta}\right) R \frac{A_a}{A_e}}{R \frac{A_a}{A_e} + 1} \left(\frac{A + E}{E}\right)$$

S_{b+c} is the specific activity of Sb(V) ($b + c$)

S_∞ is the equilibrium specific activity

α and β are the fractions of radioactive Sb(III) and Sb(V), respectively, in the aqueous phase

R is the ratio of aqueous to ether volume after mixing
 A_a and A_e are the counting rates of equal volumes of the aqueous and ether phases, respectively.

Case II.—The activity is initially all in Sb(V)

$$F = \frac{S_a}{S_\infty} = \frac{\left(\frac{1 - \beta}{\alpha - \beta}\right) R \frac{A_a}{A_e} - \frac{\beta}{\alpha - \beta}}{R \frac{A_a}{A_e} + 1} \left(\frac{A + E}{A}\right)$$

S_a is the specific activity of Sb(III).

The quantity β requires special mention because it is not constant during an experiment. It changes because the two species b and c have different extraction coefficients and their specific activities are not equal during the exchange run. The calculation of β for any experimental point thus requires a knowledge of the three reaction rates as well as the values of the extraction coefficients of b and c . Fortunately, the use of an average value of β causes an error of less than 0.004 in the value of F . We were thus able to calculate approximate values of the rate constants using a constant β , then use these rate constants to calculate β properly for each point. These values of β could then be used to calculate correct values of F . With very few exceptions the net effect of this correction was to change the values of the rate constants 5% or less.

IV. Results

A. Exchange Experiments.

1. General.—This exchange system is rather difficult to work with. The necessity of resolving

TABLE I
SUMMARY OF EXCHANGE DATA FOR 7.04 AND 7.69 *f* HCl
(24.95° except where otherwise specified)

Run no.	Sb(III) × 10 ² <i>f</i>	Sb(V) × 10 ² <i>f</i>	1st component <i>t</i> _{1/2} , min.	2nd component <i>t</i> _{1/2} , min.	<i>Q</i> ₂	<i>Q</i> ₁ + <i>Q</i> ₂	Equil. (HCl) <i>f</i>	Initial (HCl) of Sb(V), <i>f</i>	<i>k</i> ₁ <i>f</i> ⁻¹ min. ⁻¹	<i>k</i> _f × 10 ³ min. ⁻¹	ϕ
27	0.01235 ^c	2.148	...	200.0	0.9920	...	7.04	7.04	1.55
28	0.02470 ^c	2.148	...	209.0	.9867	...	7.04	7.04	1.50
31	2.113 ^c	2.148	16.05	351.9	.8651	1.0000	7.07	7.18	1.44	1.30	0.107
32	2.092	2.150 ^c	16.80	346.6	.8960	0.9989	7.07	7.05	1.29	1.42	.108
33	2.092	0.0231 ^c	17.97	717.6	.9443	.9923	7.04	7.00	1.31	1.35	.114
34	2.113 ^c	2.148	14.73	342.6	.8728	.9983	7.07	7.18	1.58	1.33	.100
35	...	2.149 ^c	55.01	7.04	7.04	...	1.33	..
36	2.112 ^c	2.148	16.09	341.8	.8951	1.0013	7.07	7.05	1.35	1.43	.108
37	0.1042 ^c	2.094	58.20	251.6	.9605	1.0000	7.00	7.00	1.41
38	4.205 ^c	4.188	9.45	295.1	.8770	1.0001	7.07	7.00	1.32	1.47	.102
39	2.092	0.1062 ^c	17.79	686.6	.9399	0.9927	7.04	7.00	1.33	1.34	.116
40	2.092	0.5250 ^c	16.92	591.9	.9354	.9973	7.04	7.00	1.37	1.34	.108
41	2.113 ^c	4.188	13.98	261.9	.8646	.9986	7.04	7.00	1.50	1.39	.098
42	0.5435 ^c	2.094	28.67	303.7	.9259	.9995	7.01	7.00	1.46
43	4.205 ^c	2.094	9.16	378.2	.9091	1.0038	7.07	7.00	1.41	1.47	.098
44	2.113 ^c	2.094	15.47	375.3	.9085	0.9998	7.04	7.00	1.39	1.41	.101
45 ^a	2.113 ^c	4.188	5.47	68.10	.8511	1.0028	7.04	7.00	3.40 ^d	6.03	.129
48 ^a	2.113 ^c	2.094	5.62	97.19	.8983	0.9999	7.04	7.00	3.53	5.92	.128
46 ^b	2.113 ^c	2.094	70.11	2854	.9220	.9972	7.04	7.00	0.342	0.167	.069
47 ^b	2.113 ^c	4.188	75.46	2039	.8758	.9970	7.04	7.00	0.303	0.164	.075
49	2.050 ^c	2.112	16.54	125.96	.8230	1.0006	7.69	7.69	1.08	5.15	.267
50	2.050 ^c	4.224	15.41	93.27	.7144	0.9987	7.69	7.69	1.06	5.02	.273

^a 34.96°. ^b 11.34°. ^c Indicates traced species. ^d Values of constants for runs 45 through 48 are not corrected for HCl concentration.

two-component exchange curves requires higher than usual precision, but the necessary precision is more than usually difficult to achieve. The HCl concentration is extremely critical, the separation procedure must be carefully controlled because of the two Sb(V) species, and a photochemical reaction further complicates matters. The experiments presented here were done after many earlier ones were found to contain unexpectedly large errors as the result of lack of control of the above factors.

The results of our exchange experiments are summarized in Table I. The fraction exchange *vs.* time data were fitted to eq. 1 by the method of least squares. The points were weighted equally, that is, a given size error in $1 - F$ was assumed to be equally probable for all the points. The two slopes are represented by half-times in the table. The column headed $Q_1 + Q_2$ is included to show the absence of separation-induced exchange and as an indication of the reproducibility of the separation and analytical techniques. The samples which were taken when the exchange reaction was complete gave $1 - F$ values which on the average deviated from zero by ± 0.004 but never more than 0.009.

Figure 2 is an example of the type of exchange curve seen with this system in 7 *f* HCl. This is not a typical curve; usually the short-lived component is present to a smaller extent. We picked this one because the two components show up better. The precision is typical of our later experiments. The points are the experimental values and the curve is the least squares fit to the points. The two components of the least squares fit are also shown.

The values of k_1 , k_f and ϕ were calculated from each individual experiment using relations 4 and

with the further assumption that $k_3 = 0$. This assumption is based on the results of plotting $r/(A + E)$ *vs.* A . The value of r can be calculated from each experiment with no assumptions beyond those used in deriving the basic eq. 1; it is the product of the slopes of the two components. The data scatter rather badly when plotted this way, but an upper limit to the slope can be established. This corresponds to a value of $k_3 \leq 0.004 f^{-1}$ min.⁻¹. The effect of a k_3 value of this size is a little hard to estimate, but the best approach is probably to compare ϕk_1 with $(1 - \phi)k_3$, since these two expressions are proportional to the rates of the two exchange reactions. If k_3 is 0.004, then $(1 - \phi)k_3$ is less than 3% of ϕk_1 , so the effect of k_3 on the exchange is probably negligible.

After many of these experiments had been completed, we found that the HCl concentrations of all the stock solutions were not identical. Some differences were greater than 1%. The values of k_1 , k_f and ϕ in the table are all corrected to an HCl concentration of 7.04 *f*. The actual HCl concentration in each run is listed in column 8 and the HCl concentration of the Sb(V) solution before the run is given in column 9. The corrections were made empirically, using the values of the constants obtained in 7.7 *f* HCl as a measure of the variation with HCl concentration. The relations used were: k_1 proportional to (HCl)^{-2.58}, k_f proportional to (HCl)^{14.77} and $\phi/(1 - \phi)$ proportional to (HCl)^{12.64}. In the case of ϕ , the HCl concentration of the run was taken to be the mean of the values in columns 8 and 9. The reason for this is that ϕ changes during a run if the HCl concentration of the Sb(V) stock solution is not the same as the final HCl concentration of the exchange mixture.

The corrections for acid concentration were, in

general, small. For k_1 the corrections were about 1%, for k_f they were a few per cent. with some as large as 8%. For ϕ they averaged about 5%, with two experiments requiring 15% corrections.

As the best values of the constants we took the average from all the runs from 31 to 44 except 35. The average values and mean deviations of the constants in 7.04 *f* HCl are:

$$\begin{aligned} k_1 &= 1.39 \pm 0.07 \text{ } f^{-1} \text{ min.}^{-1} \\ k_f &= (1.39 \pm 0.05) \times 10^{-3} \text{ min.}^{-1} \\ \phi &= 0.105 \pm 0.005 \\ k_3 &\leq 0.004 \text{ } f^{-1} \text{ min.}^{-1} \end{aligned}$$

The data in Table I show that the same results are obtained using either Sb(III) or Sb(V) as the tracer.

The consistency of the values of the constants is a good indication that the proposed rate laws (eqs. 3) are correct. As a further check, we made a somewhat different type of calculation. Our basic assumption here was that Sb(V) exists in the *b* and *c* forms and that we can measure the concentrations of *b* and *c* spectrophotometrically. With a spectrophotometric value of ϕ for each experiment, we could then calculate R_1 , R_2 and R_3 from equations 2.

Without making corrections for differences in acid concentration between experiments, we found that the average deviation of the values of $R_1/AE\phi$ ($\cong k_1$) and $R_2/E\phi$ ($\cong k_h$) from their respective means were 5% and 15%. The value of R_3 was sometimes positive and sometimes negative, indicating that the value of k_3 is close to zero.

These calculations are a further indication that the rate laws 3 are correct.

2. Exchange Experiments Requiring Special Treatment.—Experiments 27 and 28, the ones with the lowest Sb(III) concentrations, gave exchange curves which appear to have only a single component. As a result, only one quantity could be calculated from them. The simplest quantity to get from these two experiments is ϕk_1 . In the approximation that Ak_1 is small compared to $E\phi k_1$, the relation is $\frac{\ln 2}{t_{1/2}} = E\phi k_1 - \frac{Ak_1(E\phi k_1 - k_f)}{(k_f/\phi) - E\phi k_1}$.

For experiments 27 and 28 the second term in the equation is about 1% of $E\phi k_1$, so the correction is almost negligible. However, the proper value of $t_{1/2}$ to use is not the observed half-time, but the true half-time of the long component. To get this value the following procedure was used:

Using the average values of the constants obtained from the other experiments, we calculated the expected contribution of the short component to the value of $(1 - F)$ for each experimental point. These contributions were subtracted from the experimental $(1 - F)$ values and the resulting numbers were fitted by least squares to a single half-time. This new half-time was found to be different from the uncorrected one by about 1%.

The values of k_1 listed in the table for these two experiments were obtained by dividing the corrected values of ϕk_1 by the average value of ϕ obtained from the rest of the experiments.

The exchange curves for experiments 37 and 42 were resolvable but only the long-lived component could be evaluated with useable precision. As in

experiments 27 and 28, only ϕk_1 was obtained from these runs. When all three constants were calculated from each experiment, very poor results were obtained. This was in spite of the fact that the experimental $1 - F$ values differed by less than 4% from the $1 - F$ values calculated from the average values of the constants.

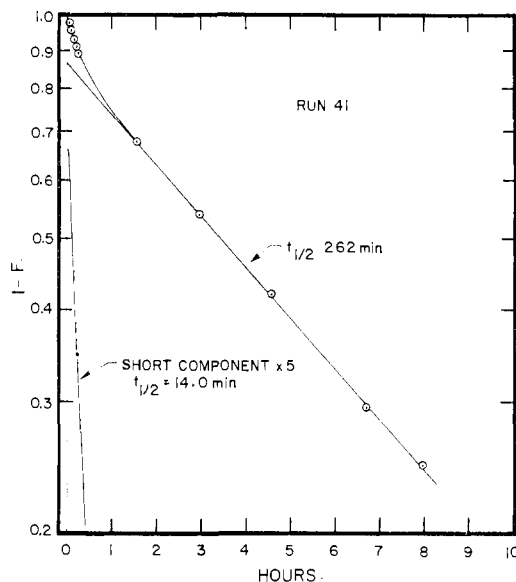


Fig. 2.—Example of complex exchange curve.

Experiment 35 was an unusual one in that no Sb(III) was used. Our purpose was to make a direct measurement of the exchange between the *b* and *c* forms of Sb(V). This is, of course, equivalent to measuring the hydrolysis rate of Sb(V) under equilibrium conditions.

The experiment was started by adding a small amount of Sb(V) tracer in the *c* form (in concd. HCl) to Sb(V) in equilibrium with 7.04 *f* HCl. The amount of Sb in the tracer was too small to disturb the equilibrium appreciably. The experimental procedure was the same as for an ordinary exchange run. Because the *b* and *c* forms have different extraction coefficients, enough separation occurred to allow calculation of the fraction exchange.

This is an exchange system with only two components, so the exchange curve is a simple one. As would be expected, the observed half-time was the same, within experimental error, as the spectrophotometrically determined half-time of the hydrolysis reaction at the same HCl concentration.

3. Temperature Dependence.—The temperature dependence of each of the three constants was determined by running pairs of exchange experiments at $11.34 \pm 0.01^\circ$ and $34.96 \pm 0.05^\circ$ in addition to the usual $24.95 \pm 0.02^\circ$ experiments.

The experiments in this set are numbers 41 and 44 through 48. The data are plotted in Fig. 3.

The experimental activation energies, E_{exp} , for k_1 and k_f are 17.2 ± 2 and 26.3 ± 2 kcal./mole, respectively. The ΔH for $\phi/(1 - \phi)$ is 5.0 ± 0.7 kcal./mole.

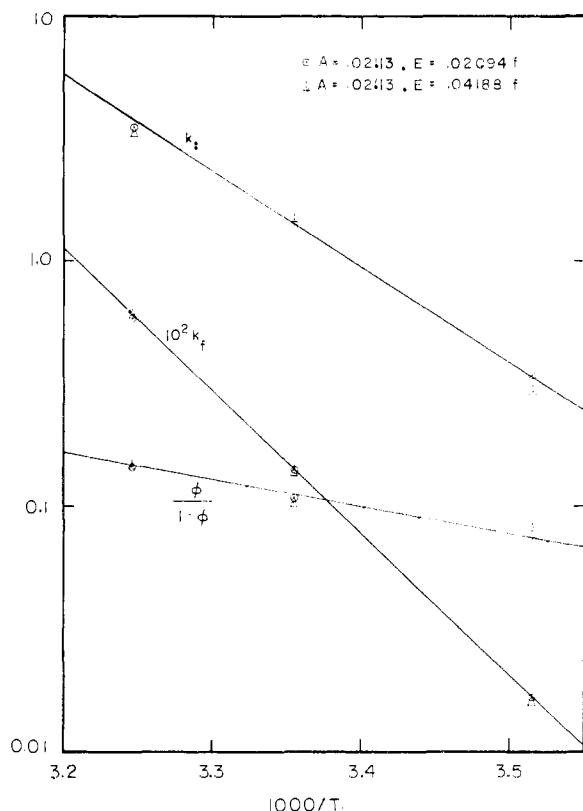


Fig. 3.—Temperature dependence of k_1 , k_f and $\phi/(1 - \phi)$.

Using Eyring's absolute rate theory,¹⁰ the entropies of activation can be calculated from the equation

$$k = \frac{ekT}{h} e^{-E_{\text{exp}}/RT} e^{\Delta S^*/R}$$

where k is the Boltzmann constant and all other symbols have their usual meaning.

For k_1 , $\Delta S^* = -10.3$ e.u. and for k_f , $\Delta S^* = 6.52$ e.u.

4. 7.7 *f* HCl.—To determine the HCl dependences of the constants, two exchange experiments were done at 7.69 *f* HCl. By the time we did these experiments we had eliminated most of the sources of error. All of the necessary separation conditions were properly controlled and the Sb solutions were spectrophotometrically matched in HCl concentration. As a result, the two experiments gave good agreement in the values of the three constants.

$$\begin{aligned} k_1 &= 1.07 \pm 0.01 \text{ f}^{-1} \text{ min.}^{-1} \\ k_f &= (5.08 \pm 0.06) \times 10^{-3} \text{ min.}^{-1} \\ \phi &= 0.270 \pm 0.003. \end{aligned}$$

The errors given here are merely half of the difference between the numbers from the two experiments. The true uncertainty is probably 3–5%.

B. Extraction Studies

In the calculation of the fraction exchange it is necessary to know the extraction behavior of the various Sb species.

1. Effect of Temperature.—A series of extraction experiments were carried out at various temperatures. Sb(V) carrier-tracer mixture in equilibrium with 7.0 *f* HCl at 25° was extracted as described in the Experimental section under "Extraction Procedure." The extraction mixture was at

(10) S. Glasstone, K. Laidler, H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 199.

the temperature given in Table II, but the Sb(V) which was added to the mixture was always at 25°. D , the extraction coefficient, is the ratio of the concentration of Sb(V) in the ether phase to the concentration in the aqueous phase.

TABLE II

EFFECT OF TEMPERATURE ON THE EXTRACTION OF Sb(V)

t , °C.	D
10.0	2.8
15.8	9.3
20.5	20
25.0	22
30.5	18

D has a maximum value at about 24°. The exchange run extractions were carried out at 23.4°.

2. Effect of HCl Concentration.—Two series of experiments were carried out using a variety of HCl concentrations in the extraction mixture. In the first series the extractions were done in the same way as the above set except that the extraction temperature was held constant at 23.4° and the acid concentration of the extraction mixture was varied. Again the Sb(V) solution was in equilibrium with 7.0 *f* HCl at 25°. The data are summarized in Table III.

TABLE III

EXTRACTION COEFFICIENT OF Sb(V) AS A FUNCTION OF THE HCl CONCENTRATION OF THE SEPARATION MIXTURE

Initial (HCl)	Final (HCl)	D
7.9	7.7	21
8.2	7.9	22
8.5	8.1	22
8.8	8.3	20

The first column lists the HCl concentration of the aqueous solution added to the ether to prepare the separation mixture. The second column is the HCl concentration the aqueous phase would have had if no ether had been added. The true equilibrium value is considerably less.

On the basis of these experiments, 8.5 *f* HCl was used in the separation mixture for the 7 *f* exchange runs.

In the second series of experiments (Table IV) the extractions were carried out on solutions in which the Sb was in hydrolysis equilibrium. Equal volumes of aqueous solution and ether were used in these experiments.

TABLE IV

EXTRACTION COEFFICIENTS FOR Sb(V) IN HYDROLYSIS EQUILIBRIUM

(HCl)	D
6.0	0.63
7.0	6.4
8.0	27
9.0	8.2

3. Volume Ratio.—Using 7.00 ml. of 8.1 *f* HCl and 15.0 ml. of isopropyl ether we found the equilibrium volume ratio at 23.4° to be 0.536 (aqueous/ether).

4. Extraction Coefficients of the b and c Forms of Sb(V).—An Sb(V) carrier-tracer mixture was prepared in 5.0 *f* HCl at 25° as a source of the pure b form. Using the normal extraction procedure (23.4°, final HCl concentration 8.1 *f*, volume ratio 0.536) the extraction coefficient was found to be 19.5 ± 0.5 .

A few experiments in which the ratio of volumes of HCl and ether was changed showed that the value of D was not independent of the ratio. This was probably due to the fact that ether saturated with water was used in the extractions. As a result, the equilibrium HCl concentration would be different for different ratios of ether to HCl.

Similar experiments using Sb(V) in conc. HCl as a source of the pure c form gave a distribution coefficient of ≥ 250 . One good value was obtained from run 35 by extrapolating a plot of $\ln(A_b^\infty - A_b)$ to zero time. This gave a value of 300.

D_b , D_c and D_v , the extraction coefficients of the b form, the c form and of an equilibrium mixture of the b and c forms in the proportion $(1 - \phi):\phi$, respectively, should satisfy the equality

$$\frac{1}{D_v + R} = \frac{1 - \phi}{D_b + R} + \frac{\phi}{D_c + R}$$

where R is the equilibrium aqueous to ether volume ratio. D_b and D_c were given above as 19.5 and 300. The exchange experiments gave $\phi = 0.105$ in 7.0 f HCl. These values make $D_v = 21.7$ for $R = 0.536$. The directly measured value, $D_v = 22.4$, is in reasonable agreement.

A lower limit to ϕ in 12 f HCl can be deduced from the above extraction data. If one assumes that there still is some b form present in 12 f HCl, the D value of 300 is to be interpreted as due to a mixture of the b and c forms with D values of 19.5 and > 300 , respectively. By taking D_c to be infinite one obtains a lower limit of 0.93 for ϕ .

5. Extraction of Sb(III).—Sb(III) solutions extracted under the usual conditions gave an extraction coefficient of 0.0087.

On several occasions Sb(III) tracer was inadvertently oxidized and quickly extracted into isopropyl ether. This occurred when Sb(V) solution containing an extraneous oxidizing agent was mixed with the tracer or when impure ether was used. The extraction coefficient was > 200 , showing that the Sb(III) was oxidized principally to the c form. This phenomenon has been observed by others with a variety of oxidizing agents.¹¹

C. Photochemical Reaction

An early set of experiments had been done in normal laboratory lighting (fluorescent lamps plus daylight). This set, which is not reported here, gave apparently consistent results except for the one experiment at the lowest Sb(III) concentration (0.0004 f). In this experiment the value of k_t was about four times the average value for the rest of the set, and both ϕ and k_f were abnormally low. After considering a number of hypotheses involving strange rate laws, we decided to test for the effect of light. A similar experiment in the dark gave normal values for the constants. This observation was very surprising, because Cheek² had tested for the existence of a photochemical effect in 9.3 f HCl and found none. This point was explained when we compared the results of all of the experiments done in the dark with all of those in the light. Apparently the effect shows up only when the Sb(III) concentration is low (10^{-3} f or less). (It is also possible that the effect appears only in systems where the ratio of Sb(V) to Sb(III) is high, since our experiments do not distinguish between the two possibilities.) Cheek's test was made in solutions in which the concentrations of Sb(III) and Sb(V) were each 0.02 f . Our interpretation of his data (see Discussion section) indicates that he did have a photochemical effect in a few of his experiments.

Rather than start a study of the photochemical reaction, we solved the problem by avoiding it. All of the experiments reported here were done in flasks painted black and were sampled with black painted pipets. No precautions were taken to eliminate light during the extraction procedure.

D. Spectrophotometric Results

1. Sb(V).—Consider the system



where c and b signify the two groups of Sb(V) species. The species within each group are assumed to be in rapid equilibrium with each other but the two groups are connected by a slow re-

action step. This step is characterized by the pseudo-first order rate constants k_h and k_f .

Since the absorption spectra of b and c are different, the rate of the reaction can be followed spectrophotometrically. For determining the rate in 7 f HCl, for example, two independent measurements can be made. In one case, the optical density, D , is followed as a function of time for a solution in which Sb(V) at equilibrium in 12 f HCl is suddenly diluted to 7 f HCl. In the other case, the same measurement is made on a solution in which the HCl concentration is suddenly changed from 4 f to 7 f . Runs of this kind will be referred to as "12 $f \rightarrow 7 f$ run," "4 $f \rightarrow 7 f$ run," etc.

For each of the two experiments, $\ln |D - D_{eq}|$ should be a linear function of time with the same slope equal to $k_{eq} = k_h + k_f$. D_{eq} is the D value when the Sb(V) has reached hydrolysis equilibrium. The experimental curves are indeed straight lines and the slopes for the two types of runs are the same and do not depend on the wave length. These facts are good evidence that there is only one slow step in the hydrolysis reactions. They also verify the pseudo-first order rate law assumed in equation 3.

In the determination of k_{eq} , the relative amounts of b and c present in the 12 f and 4 f HCl solutions are immaterial. If, however, we know the relative amounts in the two acid concentrations, a combination of the two types of runs described above allows an unambiguous determination of ϕ . If $\phi = 1$ in 12 f HCl and $\phi = 0$ in 4 f HCl, then D_0 , the optical density extrapolated to zero time for the 12 $f \rightarrow 7 f$ run, is the optical density of pure c in 7 f HCl. Similarly, D_0' , the optical density of the pure b form in 7 f HCl, is obtained by extrapolating the 4 $f \rightarrow 7 f$ run to zero time. If the extrapolations are carried out at a series of wave lengths, the spectra of the b and c forms in 7 f HCl can be obtained. Fig. 4 shows the results obtained from this procedure. The equilibrium spectrum is included for comparison. It can be seen that ϕ can be determined from the relation

$$\phi = \frac{D_{eq} - D_0'}{D_0 - D_0'}$$

where all optical densities are, of course, for the same Sb(V) concentration and the same wave length. Once ϕ has been determined, the individual values of k_f and k_h can be calculated from the value of k_{eq} and the relation $\phi k_h = (1 - \phi)k_f$.

This method of calculating ϕ requires only two assumptions, namely, that Sb(V) is entirely in the c form in 12 f HCl and entirely in the b form in 4 f HCl. It seems unlikely that these assumptions lead to appreciable error. Cheek's exchange data in 4 f HCl (see Discussion section) show that $\phi \leq 10^{-5}$ at that acid concentration. In 12 f HCl the extraction data show that $\phi \geq 0.93$. The fact that the equilibrium spectrum in 13 f HCl is nearly identical with that in 12 f HCl is further evidence that ϕ is close to unity in 12 f HCl. In addition, the agreement between the ϕ values determined from exchange and from spectrophotometry in 7 and 7.7 f HCl is good evidence that both assumptions are correct.

(11) R. W. Ramette and E. B. Sandell, *Anal. Chim. Acta*, **13**, 455 (1955).

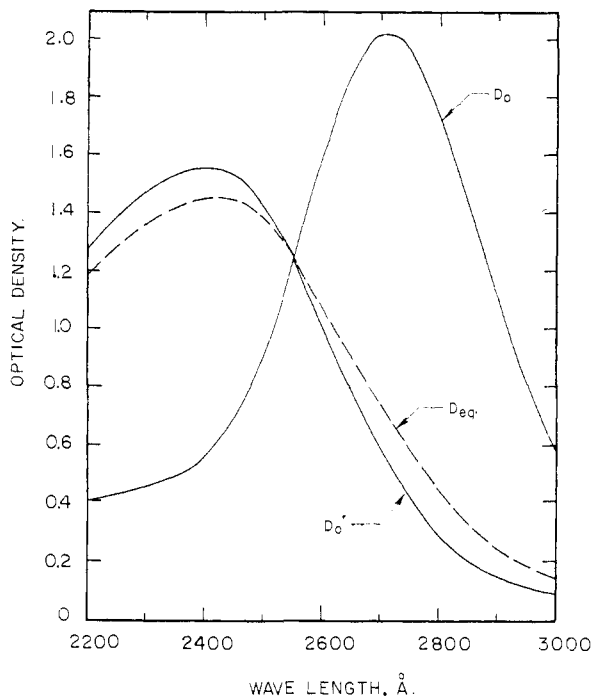


Fig. 4.—Sb(V) Spectra in 7.00 *f* HCl, 2.2×10^{-4} *f* Sb(V), 1-cm. cells. D_0 -spectrum of *c* form; D_0' -spectrum of *b* form; D_{eq} -spectrum of equilibrium mixture.

Our values of k_f , k_h and ϕ are summarized in Table V.

TABLE V
SPECTROPHOTOMETRIC RESULTS

(HCl), <i>f</i>	k_h , min. ⁻¹	k_f , min. ⁻¹	$\phi_{exp.}$	$\phi_{calcd.}$
1.2	0.0022			
3.0	.0034			
6.00	.0084	0.000094	0.011	0.011
7.00	.0125	.00131	.095	.093
7.69	.0146	.00506	.258	.261
9.34	.0255	.0936	.786	.786
10.08	.0300	.311	.912	.906

The method outlined above for determining ϕ differs from the equilibrium measurements made by Neumann¹² in one important respect. His method requires the assumption that the *c* form is a single species whose spectrum does not change with acid concentration. Figure 5 compares the D_0 spectrum in 7 *f* HCl with the equilibrium spectrum in 12 *f* HCl. The difference is appreciable, so a value of ϕ calculated from Neumann's data would be in error. Either there is a fairly large solvent effect or the *c* form contains two (or more) species. If there are two species their spectra must be quite similar because the D_0 spectra are very similar in solutions 1.2, 3.0, 6.00, 7.00 and 7.69 *f* in HCl. The relative amounts of the two species would almost certainly change by a large factor over this range of acid concentration.

The present method also differs from the kinetic measurements of Neumann and Ramette.⁴ In that method the initial slope of a plot of $\log |D - D_b|$ was determined. Their value of D_b , the optical density of the mixture of *b* species, was

(12) H. M. Neumann, THIS JOURNAL, **76**, 2611 (1954).

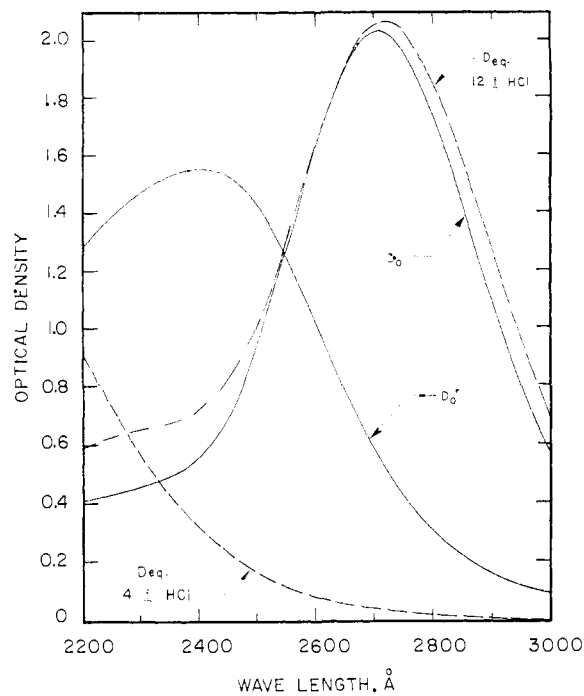
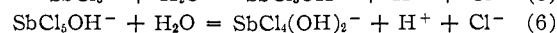
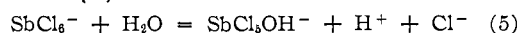


Fig. 5.—Dependence of spectra of *b* and *c* forms of Sb(V) on HCl concentration; 2.2×10^{-4} *f* Sb(V), 1-cm. cells. D_0 and D_0' are the same as in Fig. 4.

based on Neumann's estimation of the spectra of the individual Sb(V) species based on the equilibrium spectra at different HCl concentrations.

Neumann postulated that the first two hydrolysis steps of Sb(V) are



He obtained a value of 4.5×10^4 for K_1 , the equilibrium constant for the first reaction, and a value of 2.7×10^3 for K_2 , the equilibrium constant for the second reaction. Neumann and Ramette obtained a value of 2.2×10^4 for K_1 using the kinetic method.

If we assume that these reactions are the correct ones, we can calculate values of K_1 and K_2 from our values of ϕ at various HCl concentrations. The *c* form is assumed to be SbCl_6^- . A least squares fit of K_1 and K_2 to the values of ϕ summarized in Table V gives $K_1 = 2.34 \times 10^4$ and $K_2 = 4.44 \times 10^3$. These results are in reasonably good agreement with Neumann's equilibrium values, and K_1 agrees remarkably well with Neumann and Ramette's value of K_1 obtained by the kinetic method. The HCl activities used were those summarized by Robinson and Stokes,¹³ and the water activity values were taken from Akerlof and Teare.¹⁴ The activity coefficients of the Sb(V) species were assumed to be equal.

The last column in Table V gives the values of ϕ calculated from the two equilibrium constants. The agreement obtained lends a great deal of credence to Neumann's proposed reactions.

There is no doubt that the *b* form sometimes

(13) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths Scientific Publications, London, 1955, p. 489.

(14) C. Akerlof and J. W. Teare, THIS JOURNAL, **59**, 1855 (1937).

consists of more than one species. The equilibrium constant calculations indicate that above 8 *f* HCl it is probably almost entirely $\text{SbCl}_5\text{OH}_2^-$, but that in the 6 *f*–8 *f* region there are at least two species, probably SbCl_5OH^- and $\text{SbCl}_4(\text{OH})_2^-$. In 4 *f* HCl still other species become important as indicated by the great difference between the equilibrium 4 *f* spectrum and the D_0 spectrum for the 4 *f* → 7 *f* run (see Fig. 5).

The existence of isosbestic points in the 3, 6, 7 and 7.7 *f* HCl runs supports the other evidence that the reactions among the *b* species are fast compared to the *b*–*c* interconversion. The 1.2 *f* run did not show an isosbestic point, but it probably occurs below 2200 Å., which was the shortest wave length at which we made measurements. In the 9.34 *f* and 10.08 *f* runs we did not look for isosbestic points because of the inconveniently short half-times.

There is at least one measurably slow reaction among the *b* species, but it is fast enough to make very little difference to our measurement of ϕ and k_h . Cheek¹⁵ made a 3 *f* → 7 *f* hydrolysis run at 3500 Å. and obtained a two component curve. The half-time of the short component was about $\frac{1}{2}$ of that of the usually observed longer component.

We had been obtaining only one reading for each wave length during the first 10 minutes of any of the 6 or 7 *f* hydrolysis runs, and so we could have easily missed the short-lived component that Cheek observed. We therefore made a 4 *f* → 6 *f* HCl run in which the optical density at 3000 Å. was followed continuously from $t = 4.5$ minutes. There was indeed a well-defined 1.9-minute component in addition to the previously observed ~80-minute line. An analogous 12 *f* → 6 *f* HCl run showed no short component. This shows that the second measurable step involves a *b* subspecies whose equilibrium concentration in 6 *f* HCl is negligible. The second step should therefore cause no trouble in exchange runs in 6 *f* or higher HCl.

In the 7.69 *f* and higher HCl hydrolysis runs data were obtained early enough so that any component of reasonable size and with a half-time of ~1 minute or longer would have been detected. None, however, was found. The half-time of the short-lived component is probably much less than 1 minute at these higher acidities.

An estimate of the effect of the second measurable hydrolysis step on the experimental values of the hydrolysis constants can be made. Lowry and John¹⁶ have solved the differential equations for a pair of consecutive, unimolecular, and reversible reactions, which is what is involved here. Both the extrapolated value and slope of the longer-lived component are affected by the existence of a second measurable step. By considering all situations consistent with what was known about the concentrations and extinction coefficients of the species involved as well as the values of the rate constants, it was concluded that the effect of the second slow step was to cause an error in ϕ and k_t of no more than 3% and an error in k_h of no more than 1%.

(15) C. H. Cheek, private communication.

(16) T. M. Lowry and W. T. John, *J. Chem. Soc.*, **97**, 2634 (1919).

From Cheek's data on the second slow hydrolysis step in 7 *f* HCl we can conclude that it causes about the same errors in the hydrolysis constants in 7 *f* HCl as in 6 *f* HCl. It is possible that the hydrolysis data at higher HCl concentrations are affected by the same effect.

2. Sb(III) Spectrophotometry.—The absorption spectrum of Sb(III) was measured in HCl solutions from 6 *f* to 12 *f*. The shape of the spectrum is very similar to that of Sb(V) in conc. HCl, but the wave length of maximum absorption is at about 2300 Å. The spectrum appears identical at all HCl concentrations except for a slight shift along the wave length scale.

It thus seems likely that the principal Sb(III) species remains unchanged throughout the region from 6 to 12 *f* HCl.

It is interesting to note that if the absorption were to be measured at wave lengths far from the peak, one might conclude that the nature of the Sb(III) species was changing with HCl concentration. A shift of only 15 Å in the position of the peak (with no change in peak absorption) in changing from 12 *f* to 8 *f* HCl causes a 20% change in optical density at 3400 Å.

E. Interaction Absorption Experiments

Semi-quantitative experiments were done to compare the interaction absorption color¹⁷ with exchange and hydrolysis rates.

1.0 ml. of 1 *f* Sb(V) in conc. HCl was added to 9.0-ml. portions of 0.1 *f* Sb(III) in HCl of different concentrations. Three experiments were done in which the final HCl concentrations were 3.9, 6.6 and 12 *f*. The yellow colors were compared visually, and all three appeared to be nearly the same, with the 6.6 *f* solution being perhaps a little darker than the other two. The color of the 3.9 *f* solution faded rapidly, with a half-time of a few minutes. When equilibrium had been established, the 3.9 *f* solution was colorless, the 6.6 *f* solution was just perceptibly yellow and the 12 *f* solution was apparently unchanged.

These observations show that it is the *c* form of Sb(V) which is responsible for the interaction absorption.

V. Discussion and Interpretation

A. General.—In spite of the apparent complexity of the Sb(III)–Sb(V) exchange system in HCl, we can represent the kinetics of the reactions fairly simply. We have already shown how the diagram of Fig. 1 can be used to explain the data in 7.0 and 7.7 *f* HCl. The rate laws are those of equations 3 with the simplification that $k_3 \cong 0$.

The data in this region are extremely helpful in explaining the results at other acid concentrations. Here the true nature of the complexity is most obvious. The exchange experiments measure not only the Sb(III)–Sb(V) exchange rate but also the Sb(V) hydrolysis rate constant and the relative amounts of Sb(V) in the two hydrolysis states. These latter two quantities, k_h and ϕ , can be measured independently spectrophotometrically. The agreement between the values obtained by the two methods is probably the best existing evidence for the proposed rate laws.

We are now in a position to show how the general picture of the reactions in the 7 *f* HCl region fits the entire concentration range from 6 to 12 *f* HCl quantitatively.

(17) See discussion section for a description of the interaction absorption phenomenon.

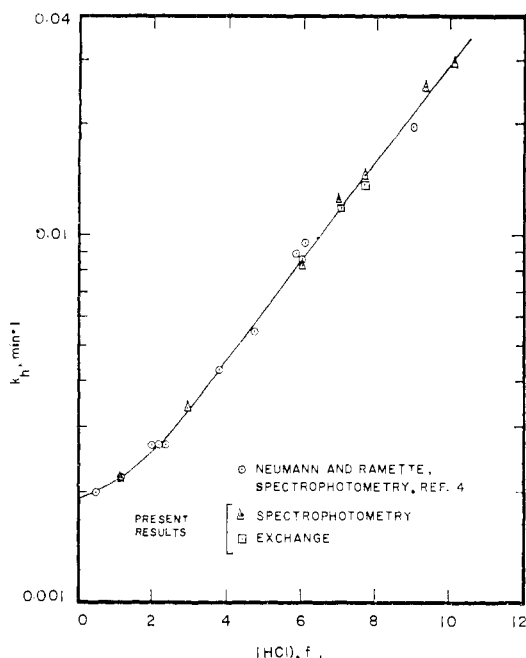


Fig. 6.—Summary of values of k_h as function of HCl concentration.

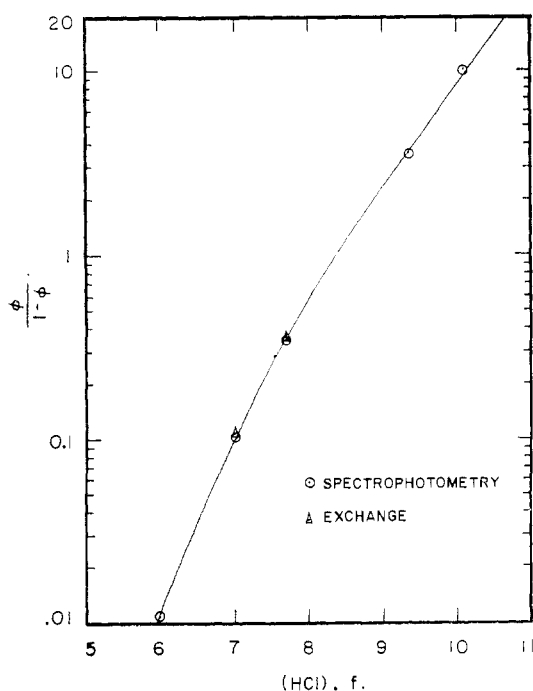


Fig. 7.—Summary of values of $\phi/(1 - \phi)$ as function of HCl concentration.

To calculate the exchange behavior, the four quantities k_1 , k_3 , k_h and ϕ are needed. These are all functions of the HCl concentration, so it is necessary to obtain values of each constant at any HCl concentration of interest. In some cases the photochemical reaction and the Sb(III) catalysis of the Sb(V) hydrolysis must be considered, but they will be discussed only where necessary.

For most HCl concentrations the best values of k_h and ϕ are determined spectrophotometrically.

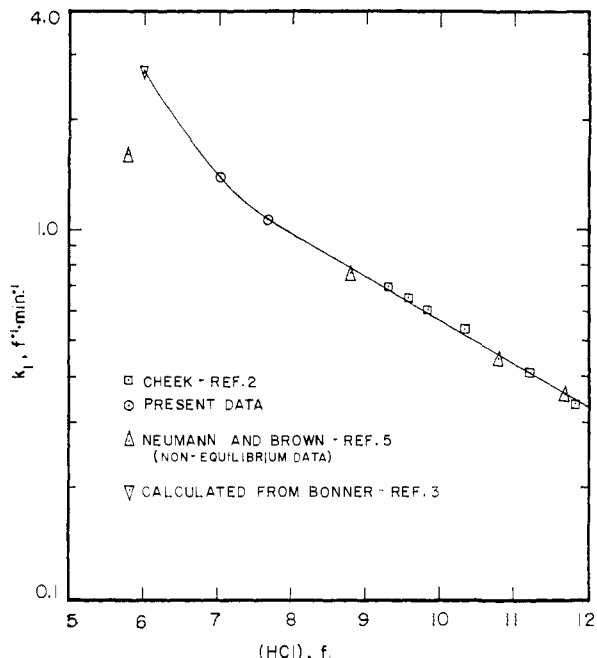


Fig. 8.—Summary of values of k_1 as function of HCl concentration.

Figure 6 summarizes the available data for k_h . This includes spectrophotometric data from this paper and from Neumann and Ramette⁴ and also the two values at 7.04 and 7.69 f HCl obtained from the exchange measurements. All of our data are consistent with the generally accepted pseudo-molecular hydrolysis rate law, $R = k_h \phi E$.

Figure 7 summarizes our data for ϕ from spectrophotometric and exchange measurements. The quantity $\phi/(1 - \phi)$ [$= k_1/k_h$] is presented to make the curve closer to a straight line and thus make interpolation easier. The curve shown was calculated on the assumption that reactions 5 and 6 were the equilibria involved. Our values for the equilibrium constants were used.

The values of k_1 and k_3 must be determined from exchange experiments, of course. We will discuss the exchange behavior along with the determination of k_1 in the various concentration regions studied. The k_1 values are summarized in Figure 8. The value of k_3 appears to be too small to have any effect above 6 f HCl.

B. 9.5–12 f HCl.—In this region the situation is fairly simple. The hydrolysis rate is fast enough for Sb(V) to act as a single species toward the exchange reaction. The rate law is simply $R = k_1 A C = k_1 A \phi E$, so the exchange experiments yield values of ϕk_1 . We have used the spectrophotometric values of ϕ to calculate the values of k_1 in Fig. 8 in this concentration region.

In concd. HCl ϕ is unity, so k_1 is determined directly from the exchange experiments. In 11.8 f HCl, Cheek² got a value of 0.34 $f^{-1} \text{ min.}^{-1}$, and Neumann and Brown⁵ got 0.36 in 11.7 f HCl.

The exchange rate increases with decreasing HCl concentration because k_1 increases faster than ϕ decreases.

C. 9.3 f HCl.—When Cheek² measured the exchange rate as a function of HCl concentration,

he found a maximum at about 9.3 *f* HCl. This seemed to be an interesting point at which to determine the dependence of the rate on the Sb(III) and Sb(V) concentrations. He found first order dependence on Sb(V) but apparently 0.9 order dependence on Sb(III). This appeared reasonable, being intermediate between the 0.6 order found in 6 *f* HCl and the first order found in 12 *f* HCl. Furthermore, one might expect complications to show up at the point where the slope of the rate curve changes sign.

However, our present calculations indicate that the 0.9 order dependence is due principally to the photochemical reaction. Our calculations were done as follows:

All of Cheek's exchange curves in this region appeared to have only a single component. As a first approximation we assumed that the hydrolysis reaction was fast enough to have no effect on the exchange rate. In other words, the rate law was the same as in the region of more concentrated HCl. This is the same condition Cheek used in calculating his values of the bimolecular rate constant, *k*, listed in Table III of the accompanying paper. Hence Cheek's values of *k* are assumed to be approximately equal to ϕk_1 in the present nomenclature. The average of these values divided by the spectrophotometric value of ϕ then gave us an approximate value of *k*₁.

By combining this with the spectrophotometric values of *k*_h and ϕ we could calculate the slopes and intercepts to be expected for these experiments from eq. 1 using relations 3 for the rate laws. *k*₃ was assumed to be zero. This calculation showed that a few of the exchange curves should have had two components. However one would not expect to be able to resolve them because the shorter component was always present to a fairly small extent and the two half-times were not very different.

To compare our calculations with the experiments, we assumed that the observed half-time would be equal to the time at which the calculated value of $(1 - F)$ was equal to 0.5. This is probably a very good assumption for most of these experiments.

When we made the comparison it became obvious that the agreement was good for most of the experiments but poor for the five with the lowest concentrations of Sb(III). After consideration of various possible mechanisms we finally convinced ourselves that the high values of *k*₁ at low Sb(III) concentration were the result of the photochemical reaction. The effects we had observed in 7 *f* HCl were qualitatively the same and quantitatively similar; both laboratories were lighted with similar types of fluorescent lamps.

We then discarded the five anomalous results and determined the best value of *k*₁ for the remainder. We did this by trial and error. For each value of *k*₁ and for each experiment we computed the value of $(1 - F)$ at the experimentally observed half-time, then calculated the root mean square value of $(1 - F) - 0.5$ for the set of experiments. The value which gave the minimum root mean square deviation is *k*₁ = 0.705 *f*⁻¹

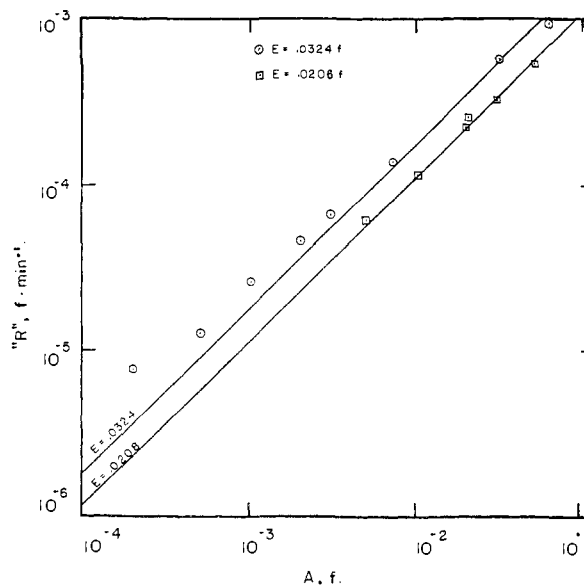


Fig. 9.—Exchange rate vs. Sb(III) concentration in 9.3 *f* HCl. Comparison of experiments with calculations. Points are Cheek's experimental data, lines are values of $[AE/(A + E)] \times (\ln 2/T)$ where *T* = time at which calculated value of $1 - F = 0.5$ when *k*₁ = 0.705 *f*⁻¹ min.⁻¹, *k*_h = 0.0255 min.⁻¹, $\phi = 0.786$.

min.⁻¹. The values of *k*_h and ϕ used were 0.0255 min.⁻¹ and 0.786, respectively. The root mean square deviation was 5%.

The calculations are compared with the relevant experiments in Fig. 9. The points are Cheek's values of the "rate," $R = \frac{AE \ln 2}{(A + E)t_{1/2}}$. The lines are the same function, but the experimental half-time has been replaced by the calculated time at which $(1 - F) = 0.5$. The five anomalous experimental values are included in Fig. 9 to show their deviations. The two points in Fig. 9 with the highest Sb(III) concentrations are the ones which theoretically have the largest amount of a shorter component (6 and 15%). It is not too surprising that these two points deviate from the curve.

The theoretical curves are very nearly straight lines with slopes of 1.0. It is easy to see how the photochemical effect, combined with the two-component curves at high Sb concentrations, made the apparent slope less than unity.

Thus at 9.3 *f* HCl, and with the antimony concentrations used, the hydrolysis reaction is becoming important, but the over-all rate is still determined principally by the rate of the exchange reaction. The curve of exchange rate vs. (HCl) is bending over at this point because ϕ is decreasing faster than *k*₁ is increasing as the HCl concentration decreases.

D. 7.0 and 7.7 *f* HCl.—The values of *k*₁, *k*_h and ϕ obtained from our exchange experiments are included in Figs. 6, 7 and 8. They have been discussed in the Experimental Results section.

It should be noted that in this region the exchange rate and the hydrolysis rate are of nearly equal importance to the over-all exchange reaction.

E. 6 *f* HCl.—The 6 *f* data³ are the most difficult to treat. A very good value can be obtained for k_h by spectrophotometry, but ϕ is so small that the precision in its measurement is probably not better than 10%. In addition, R_3 probably cannot be neglected in this region. Although k_3 is small compared to k_1 , ϕ is also small, and the quantities to be compared are ϕk_1 and $(1 - \phi)k_3$. The latter is about 5% of the former. Furthermore, Neumann and Ramette⁴ showed that Sb(III) catalyzes the Sb(V) hydrolysis reaction appreciably in 6 *f* HCl. As the last straw in the camel's eye, the quantities which must be determined from the experiments are the exchange rate constants, k_1 and k_3 , but the rate is controlled principally by the hydrolysis reaction.

The first step in the calculation was to correct all of the experimental half-times to 6.00 *f* HCl. We used Bonner's³ empirical observation that $R = k(H^+)^4(Cl^-)^9$, which is essentially the variation of the hydrolysis rate with HCl concentration. The only exception was experiment No. 11 (Bonner's number). In this experiment, the exchange reaction is the principal rate controlling step, so we corrected the half-time using the relation $R = k(HCl)^{-3}$. This is approximately the way k_1 varies with HCl concentration in 7 *f* HCl. The correction was quite small in any case.

After all the half-times had been corrected, we computed $(1 - F)$ for these times and compared the values with 0.5 in the same way that we carried out the 9.3 *f* calculations. The rate laws used were the usual ones of equations 3, with a change in R_2 to account for the Sb(III) catalysis of the Sb(V) hydrolysis reaction. We used Neumann and Ramette's⁴ rate law, $R_2 = [k_h + k_h'(Sb^{III})]\phi(Sb^V)$, and their value of $k_h' = 0.0486 f^{-1} \text{ min.}^{-1}$. The other constants used were our spectrophotometric values of $k_h = 0.00845 \text{ min.}^{-1}$ and $\phi = 0.011$.

We ran calculations with different values of k_1 and k_3 until a pair was found which gave the minimum root mean square value of $(1 - F)_{1/2} - 0.5$ for the set of experiments. The best values are $k_1 = 2.7 f^{-1} \text{ min.}^{-1}$ and $k_3 = 0.0014 f^{-1} \text{ min.}^{-1}$. The root mean square deviation is 7.4%. This is quite reasonable, since the experimental error on the individual half-times is estimated to be 10%.

We then did an extensive set of calculations in which other pairs of values of k_h and ϕ were used. The object was to find out whether there was a true minimum in the root mean square deviation when all four quantities, k_1 , k_3 , k_h and ϕ were allowed to vary. There is a true minimum of 5.6% for $k_h = 0.00755$, $\phi = 0.007$, $k_1 = 5.65$ and $k_3 = 0.0030$. We do not believe, however, that the accuracy of the data warrant determining four parameters in this way. We believe that the k_1 and k_3 values obtained by using the spectrophotometric values of k_h and ϕ are much better.

Our best estimate of the value of k_1 is thus $k_1 = 2.7 \pm 0.3 f^{-1} \text{ min.}^{-1}$. The error in k_3 is difficult to estimate. In fact, the experimental errors are such that it is possible for k_3 to be zero. However, our opinion is that k_3 is real, with a value of $0.0014 f^{-1} \text{ min.}^{-1}$. The uncertainty is somewhere around 30%.

Since the 6 *f* experiments were done in the light, the question of the photochemical reaction arises. None of our calculations give any evidence for such an effect. The most probable reason for this is that the experiments were done in a laboratory lighted with incandescent lamps instead of fluorescent lamps. Also, the experiments took several days to run, so that about half of the running time was at night in the dark.

Table VI summarizes the experimental data and compares them with the calculations.

TABLE VI

EXCHANGE IN 6.00 *f* HCl, COMPARISON OF EXPERIMENT WITH CALCULATION

Experimental data from references 3; values of constants used in calculations are: $k_1 = 2.7 f^{-1} \text{ min.}^{-1}$, $k_3 = 0.0014 f^{-1} \text{ min.}^{-1}$, $k_h = 0.00845 \text{ min.}^{-1}$, $k_h' = 0.0486 f^{-1} \text{ min.}^{-1}$, $\phi = 0.011$.

Exp. no.	(SbIII) $\times 10^2$ <i>f</i>	(SbV) $\times 10^2$ <i>f</i>	Corrected	
			exp. $t_{1/2}$ min.	Δ^a (%)
1	2.19	1.98	3084	+ 3.2
7	2.11	0.082	6072	+ 6.9
8	2.19	0.792	4770	+10.2
9	2.17	1.96	3078	+ 2.7
10	2.19	3.96	1764	- 7.9
11	0.082	1.98	1206	- 6.7
12	0.924	1.98	2560	+ 0.7
13	2.27	1.98	2688	- 6.2
14	4.30	3.96	1680	-14.9
15	2.11	1.98	2911	- 0.6
16	2.11	2.14	2880	+ 1.3
17	2.09	2.04	2646	- 6.0
18	0.925	0.791	5340	+15.1
19	0.842	0.874	4290	+ 3.6
20	2.11	2.14	2928	+ 2.4

(RMS = 7.4)

$$^a \Delta = \frac{[(1 - F)_{1/2} - 0.5] \times 100}{0.5}$$

F. 4 *f* HCl.—Cheek² tried to measure the exchange rate in 4 *f* HCl but found the half-times to be in the range of years. As a result the errors were very large and the apparent 0.8 ± 0.2 power dependence on Sb(III) is not very significant.

The hydrolysis half-time in 4 *f* HCl is about 2.5 hr. With Sb(III) present the rate is even faster. The exchange reaction is thus rate controlling, and the dependence on Sb(III) is almost certainly unity. (There is always the possibility that there is another, extremely slow hydrolysis reaction in the low acid region, but the spectrophotometric data show no sign of it.)

The slow exchange compared to the fast Sb(III) catalyzed hydrolysis shows that hydrolysis catalysis does not cause exchange.

Cheek's experiments give an approximate value for the exchange rate constant, $k = (4 \pm 1) \times 10^{-5} f^{-1} \text{ min.}^{-1}$.

This rate constant is the sum of the terms for both exchange paths, *i.e.*, $k = \phi k_1 + (1 - \phi)k_3$.

Unfortunately, there are no good data available for calculating any of the constants. Some useful limits can be calculated, however. Any reasonable extrapolation of k_1 gives a value greater than 5. If it is assumed that the only exchange path is the one involving the *c* form of Sb(V), $k = \phi k_1$, and an upper limit of 10^{-5} can be set for

ϕ . There is no good way of extrapolating the data of Fig. 7 to 4 *f* HCl, but a value of 10^{-5} is not inconsistent with the other data.

It is thus possible that k_3 is zero in this region and that exchange goes by the same path as in concentrated HCl.

If k_1 is not greater than 10 and ϕ is less than 10^{-6} , then the second term $(1 - \phi)k_3$ could be important. Since $(1 - \phi) = 1$, $k_3 \leq 4 \times 10^{-5}$. This is not a very useful conclusion, however, because k_3 includes a term γ , which is analogous to ϕ . It is the fraction of Sb(V) which exists in the form involved in the k_3 reaction path. Since γ could well be 0.01 or less, the true rate constant, $k_3' = k_3/\gamma$, could be about 10^{-3} . This is the same order of magnitude as k_3 in 6 *f* HCl, so the path cannot be ruled out entirely.

The only definite conclusion that one can draw is that k_3 does not become very large at low acid concentrations.

One very useful bit of information has come out of this, however. In the spectrophotometric determination of ϕ we had to assume that ϕ was small compared to 10^{-2} in 4 *f* HCl. The upper limit of 10^{-5} from the exchange experiments is adequate proof of the correctness of this assumption.

G. Activation Energies.—The experimental activation energies of the exchange and hydrolysis constants which were determined in 7 *f* HCl can be correlated with values at other acidities. Bonner³ obtained 27 ± 2 kcal./mole for the activation energy for the rate constant of the apparently simple exchange reaction in 6 *f* HCl. His value is based on exchange runs in which the concentrations of both Sb(III) and Sb(V) were ~ 0.02 *f*. For these concentrations and this acidity, the hydrolysis is the rate determining step. Since the hydrolysis rate is given by $R_h = k_h\phi E = k_f(1 - \phi)E$, the observed activation energy should be that of $k_h\phi$ or $k_f(1 - \phi)$. In 6 *f* HCl $(1 - \phi)$ is nearly unity and changes very little with temperature. Hence, in 6 *f* HCl the observed activation energy should be that of k_f . Our value of 26.3 kcal./mole for k_f is in good agreement.

Cheek² obtained 18.4 and 17.2 kcal./mole in 9.3 *f* and 11.8 *f* HCl, respectively. It has already been shown that in 11.8 *f* HCl the exchange step determines the exchange rate. The activation energy should thus be that for ϕk_1 . ϕ , however, is 1 and most likely changes very slowly with temperature. The observed activation energy should be, and is, the same as we observed for k_1 , namely, 17.2 kcal./mole.

In 9.3 *f* HCl the exchange step is still rate-determining but the hydrolysis rate is not overwhelmingly faster. Also, the slight temperature dependence of ϕ will increase the experimental activation energy. The activation energy to be expected in 9.3 *f* HCl was calculated by evaluating $q - p$, the slope of the longer-lived component, at 35.1° and 0.6°, the temperatures of Cheek's experiments. This was done by correcting the 25° values of the constants at 9.3 *f* HCl to the indicated temperatures by using the activation energies determined in 7.0 *f* HCl and substituting into eq. 4. *A* and *E* were both taken to be 0.02 *f*

to duplicate Cheek's experiments. The calculated value was 19 kcal./mole, again in reasonable agreement with Cheek's value of 18.4.

The "activation energy" for $q - p$ in 7 *f* HCl is 25 kcal./mole for *A* = 0.02 *f* and *E* = 0.02 and 0.04 *f*. This serves to point out the smooth change in apparent activation energy as we go from 6 *f* to 11.8 *f* HCl and the rate-determining step switches from the hydrolysis step to the exchange step.

H. Interaction Absorption.—When a solution contains an element in two different oxidation states, the color is sometimes abnormally intense. Whitney and Davidson¹⁸ have given a brief review of this effect. They measured the intensity of this "interaction absorption" for solutions of antimony in concd. HCl. The intensity of the color is proportional to the product of the Sb(III) and Sb(V) concentrations.

The interaction absorption complex would appear to be a good candidate for the reaction intermediate for exchange. Cheek¹⁹ and Edwards, Voigt and Diehl²⁰ measured the interaction absorption as a function of HCl concentration and found a maximum at about 10 *f* HCl. Furthermore, the shape of the curve was qualitatively similar to the curve of exchange rate *vs.* HCl measured by Cheek.

Surprisingly, however, there seems to be no direct relation between the interaction complex and either the exchange rate or the Sb(III)-catalyzed hydrolysis of Sb(V). For one thing, the maxima in the two curves mentioned above do not come at the same HCl concentration. Even more convincing evidence comes from our qualitative observations on the interaction absorption in non-equilibrium solutions. When Sb(III) was mixed with the *c* form of Sb(V) in solutions 3.9 *f*, 6.6 *f* and 12 *f* in HCl, the colors were nearly identical. If the interaction complex were the exchange intermediate, one would then expect k_1 to be nearly independent of HCl concentration. It is actually at least 10 times larger in 4 *f* HCl than in concd. HCl. The interaction complex therefore cannot be the principal exchange intermediate.

Similar reasoning shows that the Sb(III)-catalyzed hydrolysis reaction is independent of the interaction complex. The 3.9 *f* and 6.6 *f* HCl solutions were initially very similar in color, but the 3.9 *f* hydrolyzed at least 10 times faster than the 6.6 *f* solution.

The maximum in the interaction absorption at 10 *f* HCl can be explained fairly easily. Since the effect is dependent on the concentration of the *c* form, it would be expected to decrease rapidly below 10 *f* HCl because ϕ is decreasing rapidly. The increase in going from 12 *f* to 10 *f* HCl is probably a slight solvent effect related to the effect observed on the Sb(III) spectrum.

I. Discussion of Extraction Data.—We have noted that at room temperature the extraction co-

(18) J. E. Whitney and N. Davidson, *THIS JOURNAL*, **71**, 3809 (1949).

(19) C. H. Cheek, Ph.D. Thesis, Washington University, St. Louis, Mo. (1953).

(20) F. C. Edwards, A. F. Voigt and H. Diehl, *Proc. Iowa Acad. Sci.*, **55**, 247 (1948).

efficient of Sb(V) varies considerably between 6 f and 9 f HCl (see Table IV). This is in disagreement with Edwards and Voigt,²¹ who report that the extraction coefficient of Sb(V) is greater than 200 from 6.5 to 8.5 f HCl . Their higher values undoubtedly stem from the fact that their measurements were made on Sb(V) solutions which were in 11.6 f HCl until just before the extraction. The species being extracted was the c form except for any hydrolysis to the b form in the interval between dilution with water and addition of ether.

The same authors found that in the presence of 0.0625 f Sb(III) , the extraction coefficient of Sb(V) dropped markedly as the HCl concentration was reduced from 6 to 3 f . In the absence of Sb(III) they found that the Sb(V) was extracted very well down to 3 f HCl . This apparent inconsistency also arises from hydrolysis. Neumann and Ramette⁴ found that the hydrolysis of Sb(V) is catalyzed by Sb(III) in 2 to 6 f HCl , the catalysis increasing rapidly with decrease in acid concentration. In 3 f HCl , for example, the hydrolysis half-time in the presence of 0.0625 f Sb(III) is about 3 min. compared to more than 3 hr. when Sb(III) is absent. Apparently, in the presence of Sb(III) , the well-extracted c form hydrolyzed appreciably to the poorly extracting b form before the separation was finished. The data of van Aman, *et al.*,²² show that the c form is extracted almost completely into isopropyl ether from 3 to 8.5 f HCl .

J. Nature of the Antimony Species.—At this stage it appears that we have a good understanding of the kinetics of the reactions among the various antimony species. However, the formulas of the species are still not certain.

Antimony(III) seems to be fairly simple. Haight²³ has presented polarographic data which suggest that Sb(III) may be SbCl_4^- in 1 f to 6 f HCl . The spectrophotometric data indicate that there is probably no change in the nature of the species in the 6 f to 12 f region. The most likely formula of the principal Sb(III) ion is thus SbCl_4^- , or $\text{Sb(H}_2\text{O)}_2\text{Cl}_4^-$ if it is assumed to be hexacoordinated. The formula SbCl_6^{3-} is not ruled out, but Haight's data make the species with four chlorides appear somewhat more likely.

There is no evidence for any slow reactions occurring among Sb(III) species in HCl solutions.

The situation with regard to the Sb(V) species is somewhat more complicated. The data of Neumann¹² and Neumann and Ramette⁴ indicate that the c form is probably SbCl_6^- and that the slow hydrolysis step is reaction 5.

In solutions of constant ionic strength 9 f in Cl^- , they found that the hydrolysis rate constant obeyed the relation $k_h = a + b[\text{H}^+]$. This seems to indicate the presence of two hydrolysis paths, one independent of $[\text{H}^+]$ and one dependent on $[\text{H}^+]$. Their assumption is that the two paths involve SbCl_6^- and HSbCl_6 , respectively. The form of the relation between k_h and $[\text{H}^+]$ requires

that HSbCl_6 be present in small amount relative to SbCl_6^- and that the two be in rapid equilibrium.

All of the hydrolysis data are consistent with this picture, but unfortunately some of Cheek's exchange data are not. He did a set of exchange experiments at constant ionic strength with the chloride concentration held at 9.5 f . The exchange rate under these conditions yields values of ϕk_1 . If we use Neumann and Ramette's equilibrium constant of 2.2×10^4 for the hydrolysis reaction, we can calculate ϕ , and thus get values for k_1 . The variation of k_1 with $[\text{H}^+]$ turns out to be of the form $k_1 = a' + b'/[\text{H}^+]$.

If one applies the same reasoning to this relation as to the one for the hydrolysis rate constant, the conclusion is reached that HSbCl_6 is the major constituent rather than SbCl_6^- . If this is the case, it might appear that the calculation of ϕ is not valid. However, the hydrolysis reaction can then be written



This equilibrium constant has exactly the same form relative to $[\text{HCl}]$ and $[\text{H}_2\text{O}]$ as does reaction 5 so the calculation of ϕ is unchanged. The values of ϕ do not cover a very large range within the set of exchange experiments, so small errors in the calculation make very little difference.

The most likely explanation for the difference between the two sets of observations is that the Sb(V) species are those proposed by Neumann and Ramette and that the dependence of k_1 on $[\text{H}^+]$ is the result of a change in concentration of a minor Sb(III) species. Another possibility is that either Cheek's or Neumann and Ramette's observations are the result of a specific ion effect caused by the substitution of Li^+ for H^+ . It thus seems fairly certain that the predominant c form is SbCl_6^- , with a slight possibility that it is HSbCl_6 .

The first hydrolyzed species is most likely SbCl_5OH^- as assumed by Neumann and Ramette, but again there is the possibility that it is $\text{SbCl}_5\text{H}_2\text{O}$. Similarly, the second hydrolyzed species is probably $\text{SbCl}_4(\text{OH})_2^-$.

The nature of the activated complexes for the various reactions are, of course, less certain than the principal ions in solution. We can, however, put some restrictions on their structure. An analysis of the data leads to the surprising conclusion that there are at least three different activated complexes formed between Sb(III) and Sb(V) . There is one for exchange, one for the Sb(III) -catalyzed hydrolysis of Sb(V) and the interaction absorption complex.

We have already discussed the evidence that shows that the interaction absorption complex is essentially independent of the exchange and catalyzed hydrolysis reactions. We have also pointed out that Cheek's exchange experiments in 4 f HCl show that the catalyzed hydrolysis reaction does not cause exchange. Neumann and Brown⁵ came to the same conclusion from their non-equilibrium exchange experiments.

The exchange data in 6 f HCl prove the converse, namely that exchange does not cause hydrolysis. If it did, the exchange half-time could never be

(21) F. C. Edwards and A. F. Voigt, *Anal. Chem.*, **21**, 1204 (1949).

(22) R. E. van Aman, F. D. Hollibaugh and J. H. Kanzelmeyer, *ibid.*, **31**, 1783 (1959).

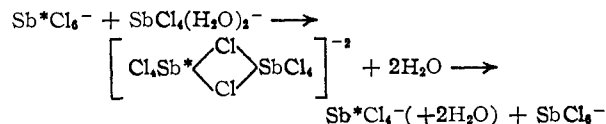
(23) G. P. Haight, Jr., *This Journal*, **75**, 3848 (1953).

shorter than the hydrolysis half-time, as it is in most of the 6 *f* experiments.

These observations show that neither the interaction absorption complex nor the activated complex for catalyzed hydrolysis is symmetrical. If they were symmetrical, exchange would accompany these reactions.

If the *c* form of Sb(V) has six chlorides attached to it, the activated complex for exchange has only a limited number of possible structures. Since hydrolysis does not accompany exchange, the Sb atom which was originally in the +3 state must have six chlorides attached to it in the activated complex, as indicated in the example.

If the Sb(III) atom still had H₂O attached while it was in the activated complex, the Sb(V) result-



ing from the exchange would have the H₂O attached to it and would thus be hydrolyzed. It is not necessary that the exchange activated complex be symmetrical, but it seems reasonable that it should be.

Acknowledgments.—We gratefully acknowledge the assistance of Mrs. Georgia M. Stephas who performed most of the antimony and acid analyses. We also wish to thank Jack Matthews, Thomas N. Haratani and Karl O. Malmquist for the numerous machine computations they made for us.

[CONTRIBUTION FROM THE MONSANTO CHEMICAL COMPANY, RESEARCH AND ENGINEERING DIVISION, RESEARCH DEPARTMENT, DAYTON, OHIO]

Sodium Imidodiphosphate. Synthesis, Identification and Hydrolytic Degradation

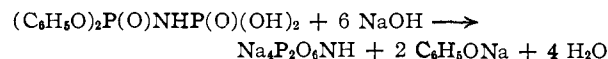
BY MORRIS L. NIELSEN, RALPH R. FERGUSON AND WILLIAM S. COAKLEY

RECEIVED JUNE 16, 1960

Sodium imidodiphosphate was obtained in 95% yield from saponification of diphenyl imidodiphosphoric acid at 135°. Its identification and assay for purity were made by X-ray diffraction and nuclear magnetic resonance methods. Hydrolytic stability was determined in solutions of 20% concentration and the thermodynamic constants calculated.

Sodium imidodiphosphate, Na₄P₂O₆NH, has been prepared by the condensation of disodium phosphoramidate, Na₂PO₃NH₂, at 210° by Klement and Biberacher.¹ The product is ordinarily contaminated with impurities of orthophosphate and pyrophosphate, as well as unreacted phosphoramidate, so that a tedious fractional crystallization must be employed to effect a separation. Furthermore, the condensation is quite slow, so that a reaction time of about a week has been recommended. It has now been found that the presence of a fluxing material greatly accelerates the reaction and reduces the formation of undesirable by-products. For this purpose, either potassium formate or potassium phenoxide has proved suitable.

A simple and direct synthesis of sodium imidodiphosphate consists in the saponification of diphenyl imidodiphosphoric acid, the latter compound having been described by Kirsanov and



Zhmurova.² Unexpectedly, under conditions which readily yield the sodium phosphoramidate or phosphorodiamidate from their phenyl esters,^{1,3} there was obtained the monophenyl derivative, (C₆H₅O)(NaO)P(O)NHP(O)(ONa)₂. However, when the reaction temperature was raised to 135–150°, either by the addition of sodium phenoxide or by maintaining about 30 lb./sq.in. pressure, the reaction proceeded quickly to yield the tetrasodium

salt. The same process, with potassium hydroxide substituted for sodium hydroxide, has yielded the tetrapotassium salt. While the tetraphenyl ester² can also be saponified under similar conditions, its preparation is not as simple as that of the diphenyl imidodiphosphoric acid.

The identification of sodium imidodiphosphate, as well as its assay in mixtures, has been done by paper chromatography,^{1,4} but the application of X-ray diffraction and nuclear magnetic resonance has resulted in two new simple, rapid methods. The X-ray diffraction (x.r.d.) technique requires the preparation of crystalline silver salts of imidodiphosphate and possible impurities, in this case phosphoramidate, ortho- and pyrophosphates. Very finely divided amorphous precipitates, typically formed with silver nitrate, are avoided by starting the precipitation slowly with solid silver acetate. Identification of the various phosphorus compounds by nuclear magnetic resonance (n.m.r.), based on the appearance of their characteristic resonance peaks,⁵ depends on the assumption of non-interference of peaks due to other phosphorus compounds or ionic species.

The hydrolytic degradation of imidodiphosphate has been reported⁴ for 0.02 *M* solutions at 60°. In the present work 20% solutions at 60 and 98° were used, and the activation energy for the process is recorded.

Experimental

Preparation of Na₄P₂O₆NH·10H₂O. A. Condensation of Sodium Phosphoramidate in the Presence of a Flux.—

(1) R. Klement and G. Biberacher, *Z. anorg. allgem. Chem.*, **288** 246 (1956).

(2) A. V. Kirsanov and I. N. Zhmurova, *Zhur. Obshchei Khim.*, **28**, 2437 (1958); *C. A.*, **53**, 3118i (1959).

(3) H. N. Stokes, *Am. Chem. J.*, **15**, 198 (1893); **16**, 123 (1894).

(4) O. T. Quimby, A. Narath and F. H. Lohman, *THIS JOURNAL*, **82**, 1099 (1960).

(5) J. R. Van Wazer, C. F. Callis, J. N. Shoolery and R. C. Jones, *ibid.*, **78**, 5715 (1956).