values are of the same order of magnitude as were obtained for the corresponding equilibrium constants determined in the studies of the unsaturated acids.[1f] It is interesting to note that the earlier observation[1e] that the magnitude of K_3/K_4 is much less affected by changes in structure of the unsaturate than are the K_3 and K_4 values is upheld in the present investigation.

The equilibrium constants for the silver complexes of phenol, crotyl alcohol and allyl alcohol reported in Table II agree favorably with those obtained by somewhat different procedures by Winstein and Lucas[2] (2.19, 5.17 and 12, respectively) for solutions of ionic strength equal to 1. The change in ionic strength should have little effect on the equilibrium constants so that the values may be compared directly. Structures of the type previously proposed for silver ion and aromatic compounds would seem appropriate for the silver ion-phenol complex.[2,9] In general the values of K_6 follow the same trends as do the values of K_3. However, the effect of varying substituents at the double bond does not produce as marked an effect on K_6 as on K_3. It is interesting to note that the cuprous complexes are much more stable than the silver complexes as may be seen by comparing the values of K_3 and K_6 given in Table III. As in the case of the cuprous complexes, silver ion complexes vinylacetic acid to about the same extent as it does allyl alcohol. Even with saturated solutions of maleic and fumaric acid no indication of complex formation with silver ion could be obtained. This again would be in agreement with the results obtained with cuprous ion which indicated that the maleic and fumaric acid complexes were much less stable than the vinylacetic acid complex.

Summary

By measurement of the solubility of cuprous chloride or silver bromate in aqueous solutions of unsaturated alcohols, equilibrium constants for the reactions to form the complexes Un·Cu$^+$, Un·CuCl and Un·Ag$^+$ at 25° have been determined. The cuprous ion complexes are considerably more stable than the corresponding silver ion complexes. α,β-Unsaturated alcohols show a somewhat greater tendency for this type of complex formation than do α,β-unsaturated acids. When hydrogen atoms at the double bond are replaced by methyl groups, the tendency for the unsaturated alcohols to undergo cuprous complex formation is reduced.

DAVIS, CALIFORNIA RECEIVED MAY 28, 1949

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[9] Keefer and Andrews, THIS JOURNAL, **71**, 3644 (1949).

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, WASHINGTON UNIVERSITY]

The Exchange Reaction between Antimony(III) and Antimony(V) in Hydrochloric Acid Solutions

BY NORMAN A. BONNER

This paper deals with a preliminary study of the exchange reaction between antimony(III) and antimony(V) in hydrochloric acid solutions. The kinetics of the exchange have been studied in 6 *f* hydrochloric acid, and in addition, the rates of exchange have been measured in 3 *f* and 12 *f* hydrochloric acid. In 6 *f* acid, half-times in the neighborhood of sixty hours were observed and the rate was found to depend critically on the hydrochloric acid concentration.

Experimental

Tracers.—The 60-day Sb^{124} tracer was obtained from the Atomic Energy Commission in the form of 200 mg. of metallic antimony which had been irradiated in the Clinton Pile. The metal was boiled with a small amount of aqua regia, the resulting oxide dissolved in concentrated hydrochloric acid, and the solution boiled to remove chlorine and nitrogen oxides. Stock +3 tracer solutions were made by diluting aliquots of the above solution to about 3 *f* hydrochloric acid and passing hydrogen sulfide into the boiling solution until the antimony sulfide turned black. The sulfide was filtered off, washed, dissolved in 6 *f* hydrochloric acid, boiled to remove hydrogen sulfide and diluted to a known volume with 6 *f* hydrochloric acid.

The +5 tracer solutions were prepared in the same manner except that after the sulfide precipitate had been dissolved and the hydrogen sulfide removed, the 6 *f* hydrochloric acid solution was diluted with an equal volume of distilled water and chlorine gas bubbled through the hot solution for several hours. The solution was then boiled to remove chlorine and bring the hydrochloric acid concentration to 6 *f*. The final, known volume was obtained by dilution with 6 *f* hydrochloric acid.

As a check on the radiochemical purity of the tracer, a sample was sealed in a test-tube and the γ-radiation counted at intervals in a standard geometry with the same brass-wall Geiger–Mueller counter. The counter itself was checked against a similar 5.3-year Co^{60} standard and found to give the same corrected counting rate, within the statistical counting error, at all times.

The antimony sample decayed with a 60 ± 1-day half-life over a period of five half-lives in satisfactory agreement with the previously determined value.[1] The antimony had been received from Oak Ridge more than a month before these particular experiments were started and the standard was prepared so the activity of the 2.8-day Sb^{122} (and any short-lived impurities) had decreased to an immeasurably small value.

Reagents.—Analytical reagents were used.

The +3 and +5 antimony carriers were made up in the same manner as the corresponding tracers, but the starting material was an accurately weighed sample of antimony trioxide instead of antimony metal. The trioxide was analyzed by triiodide titration and found to be 99.9% pure.

The carrier, tracer and hydrochloric acid solutions were all analyzed gravimetrically for total chloride by the pre-

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[1] Seaborg and Perlman, *Rev. Modern Phys.*, **20**, 585 (1948), list the half-life as sixty days.

cipitation of silver chloride. The precipitation was carried out in the presence of tartaric acid in the case of the carrier and tracer solutions in order to prevent the precipitation of antimony.

The hydrogen ion and chloride ion concentrations were calculated from the known total antimony and chloride concentration with the assumption that the principal forms of the +3 and +5 complexes in 6 *f* hydrochloric acid are $SbCl_4^-$ and $SbCl_6^-$, respectively. If these formulas are wrong (as is easily possible) the hydrogen ion and chloride ion concentrations will be correspondingly slightly in error.

Reaction mixtures were prepared by adding the proper amounts of carrier, hydrochloric acid and tracer solutions in the order mentioned to a 25-ml. volumetric flask. The time at which the tracer solution was added to the other reagents was taken as the time origin for the exchange reaction. At temperatures other than 25°, the carrier mixture was allowed to come to temperature equilibrium with the thermostat before the tracer was added.

The isopropyl ether used in the separation procedure was freed from peroxides by repeated shakings with ferrous ammonium sulfate solution acidified with sulfuric acid. The ether was stored over an acidified solution of ferrous ammonium sulfate. This purification step was found necessary in order to prevent the oxidation of antimony (III) to antimony(V) by the peroxides. No other purification was carried out.

Separation Procedures.—For the 6 *f* and 12 *f* runs, ether extraction was used as the separation method, the only difference between the two cases being that the aliquots from the 12 *f* run were diluted with an equal volume of water before proceeding.

An aqueous solution 2.14 *f* in magnesium chloride, 6.0 *f* in hydrochloric acid was prepared and saturated with isopropyl ether. An 11.7-ml. portion of this solution was mixed with 16.7 ml. of isopropyl ether. To carry out the separation, 5.0 ml. of the reaction mixture was added to the above two-phase system. The mixture was shaken vigorously for one minute in a centrifuge tube fitted with a ground-glass top, then centrifuged for five minutes. For the 9.8 and 25.0°-runs in 6 *f* hydrochloric acid the time at which centrifugation was started was taken as the time of separation. In the 34.6°-run, the time at which the aliquot was added to the other reagents was taken as the time of separation. In the 12.0 *f* experiment, the time of separation was considered to be the time at which the aliquot was diluted with water. Aliquots of the two phases were pipetted off, weighed to the nearest 0.02 g. and the γ-radiation counted. The total activity in each phase was calculated from the known density and with the assumption that the total volume of each phase did not change when the ether and the hydrochloric acid solutions were mixed. Semi-quantitative experiments indicated that this assumption was justified. It was further justified by the fact that the sum of the activities of the two fractions always equalled, within experimental error, the activity of a standard containing the same total amount of tracer.

Under the above conditions it was found that 98% of the antimony(V) went into the ether phase and 98% of the antimony(III) remained in the aqueous phase. No exchange (0 ± 2%) was observed during the separation.

The separation procedure used in the experiment in 3 *f* hydrochloric acid involved the precipitation of antimony (III) with 8-hydroxyquinoline. The reaction mixture (20 ml.) was added to several ml. of solution containing a total of 1 g. of citric acid. To this was added about 25 ml. of 7 *f* ammonium hydroxide and 4 ml. of a 2% solution of 8-hydroxyquinoline in 2 *f* acetic acid. The resulting mixture was heated on a steam-bath for about one and one-half hours and then filtered. The precipitate was mounted on filter paper and the β-radiation counted under cellophane. The filtrate was acidified and antimony sulfide precipitated with hydrogen sulfide. The precipitate was filtered and the β-radiation counted. Each of the two samples was analyzed for antimony.

Less than 2% exchange occurred during this separation procedure.

Counting Procedures.—Gamma radiation was counted directly from the solutions by placing a test-tube containing the sample in a standard geometry near a brass-wall Geiger–Mueller counter. The test-tubes were always filled to the same height and were calibrated so that corrections could be made for slight differences in counting rate due to differences in the dimensions of individual tubes. A correction was also applied for the difference in counting rate of the same size sample in ether and in aqueous solution. The counting rate in ether was found to be 2% higher than in the hydrochloric acid–magnesium chloride solution used.

For β-counting the sulfide or 8-hydroxyquinoline precipitates were mounted under cellophane on cards which could be placed in a standard position under an 8 mg./sq. cm. dural window in the side of a brass Geiger–Mueller counter.

No coincidence corrections were applied to either γ- or β-counting rates, since the highest counting rate used was about 2000 c./min. and the usual rate was 1000 or less. The coincidence correction on the counters used amounted to less than 2% at a counting rate of 2000 c./min.

Results

The reaction studied is $\text{Sb}^{\text{III}\prime} + \text{Sb}^{\text{V}} = \text{Sb}^{\text{III}} + \text{Sb}^{\text{V}\prime}$, where the primes indicate radioactive atoms. For this particular reaction, the logarithmic form of the first order exchange law[2] is

$$-\ln(1 - F) = \frac{R[(\text{Sb}^{\text{III}}) + (\text{Sb}^{\text{V}})]t}{(\text{Sb}^{\text{III}})(\text{Sb}^{\text{V}})}$$

where

(Sb^{III}) = total concentration (active + inactive) of Sb^{III}

(Sb^{V}) = total concentration (active + inactive) of Sb^{V}

$F = (\text{Sb}^{\text{V}})'/(\text{Sb}^{\text{V}})'_\infty$ = fraction exchange at time, t, when $(\text{Sb}^{\text{V}})' = 0$ at $t = 0$

$(F = (\text{Sb}^{\text{III}})'/(\text{Sb}^{\text{III}})'_\infty$ if $(\text{Sb}^{\text{III}})' = 0$ at $t = 0)$

$(\text{Sb}^{\text{V}})'_\infty = (\text{Sb}^{\text{V}})'$ at time, $t = \infty$

R = actual rate at which exchange of antimony atoms occurs between Sb^{III} and Sb^{V}. R will be constant during any one experiment, since (Sb^{III}) and (Sb^{V}) are then constant.

According to this equation, a plot of log $(1 - F)$ *vs.* time should give a straight line regardless of the mechanism of the reaction. The only requirements are that the exchange reaction be homogeneous[3] and all conditions (including the concentrations of reactants and products) be kept constant. Further, if one (or both) of the reacting chemical species contains more than one antimony atom, the atoms must be chemically equivalent.

In general, a set of four measurements of F, the fraction exchange, were made at different times for each experiment. In all cases a straight line passing through the origin was obtained when log $(1 - F)$ was plotted *vs.* time. Figure 1 is a typical example of such a plot.

When 50% exchange has occurred, $F = 1/2$, $(1 - F) = 1/2$ and $t = T_{1/2}$ by definition. At this point

$$R = \frac{(\text{Sb}^{\text{III}})(\text{Sb}^{\text{V}}) \ln 2}{[(\text{Sb}^{\text{III}}) + (\text{Sb}^{\text{V}})]T_{1/2}}$$

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[2] Duffield and Calvin, THIS JOURNAL, **68**, 557 (1946), or Friedlander and Kennedy, "Introduction to Radiochemistry," John Wiley and Sons, Inc., New York, N. Y., 1949.

[3] In this situation the meaning of "homogeneous" includes the possibility that the reaction is heterogeneously catalyzed. It is necessary, however, that the reactants and products exist principally in one, homogeneous medium.

TABLE I

RESULTS OF EXCHANGE EXPERIMENTS

Expt.	Tracer	Sb(III) concn., f	Sb(V) concn., f	(Cl^-), f	(H^+), f	$T_{1/2}$, hr.	R^a × 10^5	R'^b × 10^{14}	k^c × 10^{11}
1	III	0.0219	0.0198	5.700	5.742	97.2	7.40	1.073	7.99
2	III	.0219	.0198	5.452	5.494	178.5	4.04	1.041	7.74
3	III	.0219	.0198	5.543	4.750	261	2.76	1.100	8.18[d]
4	III	.0219	.0198	5.786	5.494	97.0	7.43	1.120	8.33[e]
5	V	.0039	.0022	3.0	3.0	~1400			[f]
6	III	.0235	.0198	12.0	12.0	0.604			
7	V	.0211	.00082	6.046	6.068	90.5	0.605	0.0414	10.41
8	III	.0219	.00792	6.016	6.045	75.5	5.34	0.388	7.89
9	III	.0217	.0196	5.950	5.992	55.5	12.88	1.068	8.04
10	III	.0219	.0396	5.836	5.898	40.2	24.3	2.55	8.85
11	III	.00082	.0198	6.048	6.069	20.8	2.62	0.1783	9.50
12	III	.00924	.0198	6.008	6.037	41.0	10.63	0.785	9.80
13	III	.0227	.0198	5.910	5.952	53.0	13.82	1.252	9.10
14	III	.0430	.0396	5.736	5.819	47.5	30.03	3.90	9.01
15	III	.0211	.0198	5.983	6.024	49.0	14.47	1.119	8.54[g]
16	V	.0211	.0214	5.881	5.923	60.5	12.17	1.172	8.19[h]
17	V	.0209	.0204	5.935	5.977	49.5	14.46	1.241	9.16
18	III	.00925	.00791	6.076	6.093	74.8	3.95	0.254	8.70
19	V	.00842	.00874	6.061	6.078	62.0	4.79	0.559	10.32
20	V	.0211	.0214	5.881	5.923	61.5	11.97	1.153	8.06
21	V	.0211	.0214	5.881	5.923	708	1.040	0.1011	0.706[i]
22	V	.0211	.0214	5.881	5.923	14.2	51.9	5.01	35.0[j]

[a] $R = (Sb^{III})(Sb^{V})\ 0.693/[(Sb^{III}) + (Sb^{V})]T_{1/2}$. [b] $R' = R/(H^+)^4(Cl^-)^9$. [c] $k = R'/(Sb^{III})^{0.6}(Sb^{V})^{1.1}$. [d] The solution also contained 0.834 mole/l. of Na^+. [e] The solution also contained 0.3336 mole/l. of Na^+. [f] Only one point obtained on the exchange curve. [g] Low activity. β-counting used. [h] Flask packed with glass beads. [i] 9.8°. [j] 34.6°.

In any given experiment the antimony(III) and antimony(V) concentrations are known, and $T_{1/2}$ can be obtained from the plot of log $(1 - F)$ vs. t. It is then possible to calculate the value of R, the rate of exchange, for each experiment.

Effect of Hydrochloric Acid Concentration.—The hydrochloric acid concentration varied from one experiment to the next as the antimony concentrations were changed, so it was necessary to determine the effect of this variation. In addition, the dependence of the rate of exchange on the hydrochloric acid concentration is of interest in itself.

By a process of trial and error, with the first approximations based on experiments 1–4 (see Table I in which the data for all experiments are summarized) it was found that the best values of the dependences on hydrogen ion and chloride ion concentrations were 4.0 ± 0.5 and 9.0 ± 0.5, respectively. In other words, in a series of experiments in which the antimony concentrations are kept constant and the hydrogen ion and chloride ion concentrations are varied, the expression $R/[(H^+)^4(Cl^-)^9]$ is essentially constant. R is the measured rate of the reaction. Any other values of the exponents give a less constant result.

The total variation in the hydrogen ion concentration was from 4.7 f to 6.1 f, and the chloride ion concentration varied from 5.4 f to 6.1 f. In experiments 3 and 4 Na^+ was added, as sodium chloride solution, to allow independent variation of (H^+) and (Cl^-).

The actual numbers 4 and 9 have no fundamental significance under these circumstances since the activity coefficients of hydrogen ion, chloride ion and the antimony ions undoubtedly suffer large changes with small changes in the hydrochloric acid concentration.

The function $R' = R/[(H^+)^4(Cl^-)^9]$ is thus an empirical expression which corrects the measured rates for changes in the concentrations of hydrogen ion and chloride ion. Furthermore, it corrects the rate for variations in the activity coefficients of hydrogen ion, chloride ion and the antimony ions resulting from changes in the hydrochloric acid concentration.

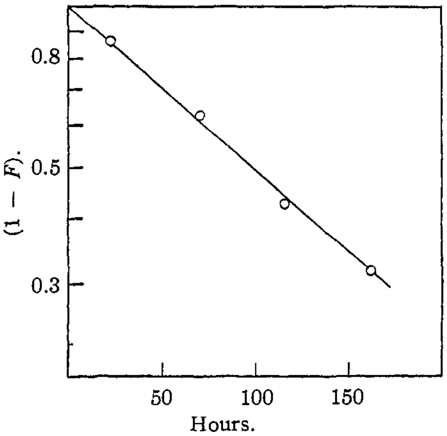

Fig. 1.—Semi-logarithmic plot of (1-fraction exchange) vs. time for run 1: $T_{1/2}$ = 97.2 hr.

In addition to the series of experiments in 6 f hydrochloric acid, one experiment was carried out in 3 f and one in 12 f hydrochloric acid. Both experiments were done at 25.0°.

In the 3 f experiment (No. 5), only one point was measured on the exchange curve. At 191.5 hours, exchange was 9.3% complete with antimony(III) and antimony(V) concentrations of 0.0039 f and 0.0022 f, respectively. The half-time is thus approximately 1400 hours. The 8-hydroxyquinoline precipitation method was used for the separation.

In 12.0 f hydrochloric acid with antimony(III) and antimony(V) concentrations of 0.0235 f and 0.0198 f, respectively, the half-time was 36.2 min. (Expt. no. 6). A plot of the values of log (1 − F) *vs.* t for the four points obtained gave a straight line passing through the origin.

Effect of Antimony Concentrations.—Figure 2 is a plot of log $R' = R/(\mathrm{Cl}^-)^9(\mathrm{H}^+)^4]$ *vs.* log $(\mathrm{Sb}^{\mathrm{V}})$ with the antimony(III) concentration held at 0.0219 f (Experiments 7–10). In two cases the concentrations were slightly different from 0.0219 and the rates were adjusted according to the correction discussed in the next paragraph. The slope of the line, and therefore the dependence of the rate on the antimony(V) concentration, is 1.1 ± 0.1.

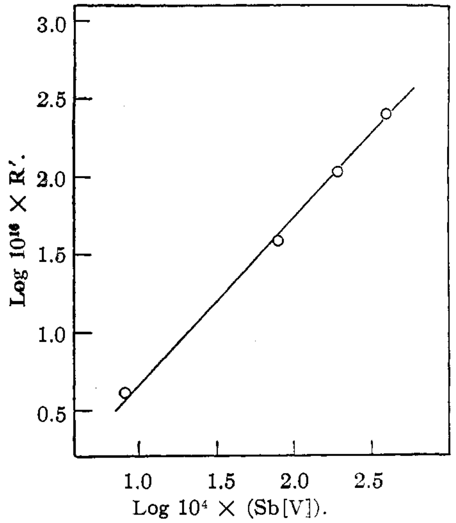

Fig. 2.—Dependence of rate of exchange on antimony(V) concentration: antimony(III) concentration = 0.0219 f; slope = 1.1 ± 0.1.

Figure 3 is a similar plot of log R' *vs.* log $(\mathrm{Sb}^{\mathrm{III}})$, the antimony(V) concentration being 0.0198 f. Also included is a point corresponding to an antimony(V) concentration of 0.0396 f which has been corrected to 0.0198 f (Experiments 11–14). The slope of the line is 0.60 ± 0.05.

An inspection of Table I shows that the rates are the same within experimental error regardless of whether the tracer is added in the form of antimony(III) or antimony(V).

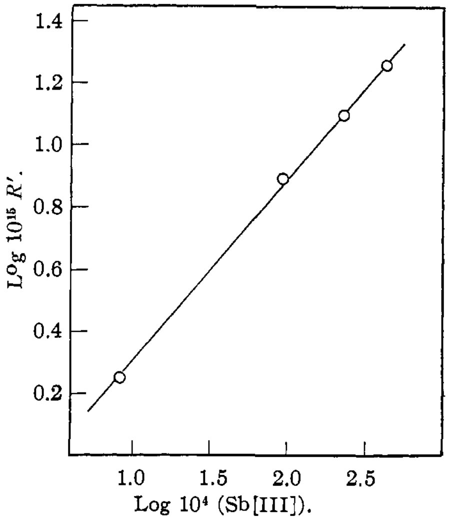

Fig. 3.—Dependence of rate of exchange on antimony(III) concentration: antimony(V) concentration = 0.0198 f; slope = 0.6 ± 0.05.

It should be emphasized at this point that the values 0.6 and 1.1 for the antimony(III) and antimony(V) concentration dependences are much less arbitrary than are the values for the hydrogen ion and chloride ion concentration dependences. The corrected rate, R', includes empirical corrections for changes in the activity coefficients of the antimony ions caused by changes in the hydrochloric acid concentration.

As a result, the values 0.6 and 1.1 are probably very nearly the correct ones. It seems likely that the true values are 0.5 and 1.0.

One effect has not been allowed for, however. No corrections have been made for variations in the activity coefficients of the antimony ions resulting from changes in their own concentrations. At an ionic strength of about 6, one might expect these particular changes to be small.[4] Since no accurate method is known for making corrections of this type, it has been assumed for the present that the effect is small.

Effects of β-Radiation.—In order to eliminate the possibility that β-radiation was affecting the rate of exchange a run was made in which the amount of active antimony was approximately $^1/_{80}$ of the maximum amount used. In this experiment the separation was carried out by ether extraction as usual, but the antimony in the samples was precipitated as sulfide and β-counted. The value of the rate constant for this run (no. 15) was, within experimental error, the same as the average value. Therefore, any effect of radiation is negligible.

Effect of Surface Area of the Reaction Vessel.—A run was made in a 100-ml. volumetric

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(4) Nachtrieb and Fryxell, THIS JOURNAL, **70**, 3552 (1948), in studies of the distribution of iron(III) between ether and hydrochloric acid solutions have found effects which can be explained by assuming that a change in the (small) iron concentration causes an appreciable change in the activity coefficient in spite of the fact that the hydrochloric acid concentration is kept constan .

flask packed with soft glass beads instead of in the usual 25-ml. flask. The flask was rotated in the thermostat in such a way that the solution was continuously flowing over the beads. The rate constant for this run (no. 16) was the same as the average, within experimental error.

The Rate Law.—From the foregoing discussion, it appears that the empirical rate law for the antimony(III)–antimony(V) exchange reaction at 25.0° is

$$R = (8.8 \pm 0.9) \times 10^{-11} (\mathrm{Sb^{III}})^{0.6}(\mathrm{Sb^{V}})^{1.1}(\mathrm{H^+})^4(\mathrm{Cl^-})^9$$

where all concentrations are uncorrected formal concentrations, and the units of R are moles × liters^{-1} × hr.$^{-1}$.

The chloride ion concentrations were calculated by analyzing for total chloride and subtracting the amount of chloride complexed with antimony, assuming the formulas $SbCl_4^-$ and $SbCl_6^-$ for the +3 and +5 states, respectively. The hydrogen ion concentrations are then the sum of the chloride ion and the total antimony concentrations. (Except in the case where Na^+ was present, when in addition an analysis of the added sodium chloride solution was necessary.)

This rate law is valid in the ranges of concentration $(H^+) = 4.7\,f$ to $6.1\,f$, $(Cl^-) = 5.4\,f$ to $6.1\,f$, antimony(III) = $0.0008\,f$ to $0.040\,f$ antimony(V) = $0.0008\,f$ to $0.040\,f$, and $(Na^+) = 0.0\,f$ to $0.8\,f$.

Most of the variation in the value of the rate constant is probably due to slight uncertainties in the hydrochloric acid concentration. A difference of 1% in the hydrochloric acid concentration would lead to a difference of almost 15% in the rate.

The Activation Energy.—Three experiments were carried out at temperatures of 9.8, 25.0 and 34.6°, respectively (Expts. 20–22). The solutions were all made up at the same time, using the same pipets in order that differences in the concentrations of the various ions be minimized.

The experimental activation energy calculated from this set of data is 27 ± 2 kcal./mole.

Discussion of Results

At the present time there appears to be a considerable lack of knowledge concerning the nature of the ions existing in solutions of antimony in hydrochloric acid. There is a large amount of experimental information on the behavior of antimony solutions,[5] but it is mostly not applicable to a determination of the true nature of the ions in $6\,f$ hydrochloric acid.

Lingane[6] presents some polarographic evidence that the formula of the antimony(V) ion in $6\,f$ hydrochloric acid is $SbCl_6^-$. In addition, the acid $HSbCl_6$ and its salts have been prepared.[7] The evidence is admittedly far from conclusive, but since there appears to be no particular reason to doubt this formula, it is the generally accepted one.

The case of the antimony(III) ion (or ions) is even more uncertain. Either of the formulas $SbCl_4^-$ or $SbCl_6^{=}$ is generally assumed,[8] but formulas such as $SbOCl_2^-$ are not necessarily excluded.[9] In the case of solutions in hydrobromic acid there is even a small amount of evidence for the ion $Sb_3Br_{11}^{=}$.[10]

Probably the most interesting result of the exchange experiments is that the rate of exchange does not depend on the first power of the antimony(III) concentration. If the activated complex for the exchange is an ion such as $Sb_2Cl_{12}^{-4}$ ($SbCl_6^{=} + SbCl_6^-$) in which the two antimony atoms are equivalent, one would expect the rate to be first order with respect to the concentrations of antimony(III) and of antimony(V). Since the rate actually depends on the ~1/2 power of the antimony(III) concentration, it is possible that an ion such as $Sb_2Cl_n^{-(n-6)}$ might be the principal antimony(III) ion in solution and be in equilibrium with $SbCl_6^{=}$.

There is some evidence for the existence of the antimony(III)–antimony(V) complex $Sb_2Cl_{12}^{-4}$. The salts of the type Rb_2SbCl_6 are diamagnetic,[11] indicating that the antimony atoms are alternately in the (+3) and (+5) oxidation state, and not in the (+4) state. In addition Whitney and Davidson[12] have obtained spectrophotometric evidence for a +3–+5 complex ion in $11.3\,f$ hydrochloric acid. The concentration of the complex, however, is proportional to the first power of each of the antimony oxidation states.

Furthermore, the experiment in $12.0\,f$ hydrochloric acid (No. 6) would be expected to indicate extremely rapid exchange if the complex observed by Whitney and Davidson were the activated complex. The half-time at 25° was actually 36.2 minutes.

It thus appears that the complex observed by Whitney and Davidson is not the activated complex of the exchange reaction.

Whitney, *et al.*,[13] have found the same effect in the case of the tin(II)–tin(IV) system in hydrochloric acid. A colored complex is formed, but the exchange reaction is relatively slow. Their tentative explanation is that either the slow step in the reaction is the exchange of tin atoms between two different complexes of tin in the same oxidation state (the complex which is

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(5) For example, Thorneycroft, Vol. VI, part V of Friend's "Textbook of Inorganic Chemistry," Charles Griffin and Co., Ltd., London, 1936.

(6) Lingane, This Journal, **69**, 530 (1947).

(7) Weiland and Feige, *Ber.*, **36**, 244 (1903); and Weiland and Schmid, *Z. anorg. Chem.*, **44**, 37 (1905).

(8) See, for example, Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," Prentice Hall, Inc., New York, N. Y., 1938, p. 111.

(9) A few qualitative transference experiments done by the author of this paper show definitely that the antimony ions are negatively charged in $6\,f$ hydrochloric acid.

(10) Vournasos, *Z. anorg. allgem. Chem.*, **192**, 369 (1930).

(11) Elliott, *J. Chem. Phys.*, **2**, 298 (1934).

(12) Whitney and Davidson, This Journal, **69**, 2076 (1947).

(13) Whitney, Browne, McConnell and Davidson, *Brookhaven Conference Report*, **BNL-C-8**, p. 196, December 1–3, 1948.

responsible for the optical interaction and the exchange reaction is then assumed to be present at very low concentration), or the colored complex is not the activated complex for the exchange.

As a result of the lack of accurate knowledge concerning the nature of the ions in solution, it seems rather futile to attempt to decide definitely on the mechanism of the exchange reaction at present.

Further experiments designed to obtain more information about the nature of the antimony ions are planned.

Summary

1. A method has been developed for the separation of antimony(V) from antimony(III) by means of an ether extraction from hydrochloric acid solution.

2. A study of the rate of the exchange reaction between antimony(III) and antimony(V) shows that the rate law at 25.0°, with hydrogen ion concentrations from 4.7 *f* to 6.1 *f*, chloride ion concentration from 5.4 *f* to 6.1 *f*, antimony(III) concentrations from 0.0008 *f* to 0.040 *f*, antimony (V) concentrations from 0.0008 *f* to 0.0040 *f* and Na^+ concentrations from 0.0 *f* to 0.8 *f* is $R = (8.8 \pm 0.9) \times 10^{-11} (Sb(III))^{0.6} (Sb(V))^{1.1} (H^+)^4 (Cl^-)^9$ mole × liter^{-1} × hr.$^{-1}$.

3. In the same ranges of concentrations the experimental activation energy is 27 ± 2 kcal./mole (measurement made at 9.8, 25.0 and 34.6°).

4. In 12.0 *f* hydrochloric acid at 25.0° the half-time for exchange is 36.2 minutes with an antimony(III) concentration of 0.0235 *f* and an antimony(V) concentration of 0.0198 *f*.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE STATE COLLEGE OF WASHINGTON]

Polarography of Calcium, Strontium and Barium in Liquid Ammonia

BY C. J. NYMAN

The polarographic characteristics of several ions in liquid ammonia have been previously reported.[1] The present paper deals with the reduction of calcium, strontium and barium salts in this solvent.

Experimental

The electrolysis cells and apparatus for preparing the anhydrous liquid ammonia solutions have been described previously.[1] The cell with the internal reference electrode was used in all cases.

The dropping mercury electrode had the following characteristics in a saturated solution (0.021 *M*) of tetraethylammonium iodide in liquid ammonia at −36°. At a pressure of 20 cm., the drop time *t* was 5.1 sec. (open circuit) and the mass of mercury *m* flowing through the capillary was 1.184 mg./sec.

A Fisher Elecdropode, calibrated in the usual manner, was used in this investigation. All applied potentials were checked by means of a student type potentiometer.

The ammonia, barium nitrate and strontium nitrate were C. P. materials of commerce. Calcium iodide was prepared in the following way: 3 g. of calcium hydroxide was made into a slurry with 100 cc. of water, and then ammonium iodide was added until all the calcium hydroxide dissolved. The solution was filtered, and an additional 15 g. of ammonium iodide was added. The solution was evaporated almost to dryness on a hot-plate, and the resulting paste was transferred to porcelain boats. These were placed in a Pyrex combustion tube and heated by means of a tube furnace. A stream of dry hydrogen was used to sweep the water vapor and excess ammonium iodide from the region of the boats. The temperature was raised slowly to about 150° and held for two hours, when it was increased to 400° for two hours. The material was allowed to cool with the stream of hydrogen still passing through the tube. On analysis, the calcium iodide contained less than 0.5% impurity. The purification of the tetraalkylammonium salts has been described previously.[1]

Data and Discussion

Figure 1 shows typical polarograms obtained on electrolysis of calcium iodide solutions when using tetraethylammonium iodide as indifferent electrolyte. A maximum was observed even with low concentrations of calcium ion, and it was only partially suppressed by traces of methyl red. Higher concentrations of methyl red did not completely eliminate the maximum. A similar behavior was exhibited by the strontium ion (see Fig. 2), but the barium ion did not show a maximum when using tetraethylammonium iodide as the indifferent electrolyte (see curve II, Fig. 3). With tetrapropylammonium iodide, barium exhibits a maximum which is not suppressed by either methyl red or methyl cellulose (see curve I, Fig. 3).

TABLE I

DIFFUSION CURRENTS OF CALCIUM, STRONTIUM AND BARIUM IN LIQUID AMMONIA AT −36°

Ion	*C*	*D*	$m^{2/3}t^{1/6}$	i_d, microamp. Calcd.	i_d, microamp. Obs.	% Δ
Ca	0.38	1.91×10^{-5}	1.019	2.05	2.0	−2.5
Ca	.82		1.019	4.4	4.5	+2
Sr	.37	1.94×10^{-5}	1.180	2.32	2.39	+3
Sr	.52		1.180	3.28	3.27	...
Sr	.78		1.185	4.94	5.21	+6
Ba	.43	1.77×10^{-5}	1.249	2.72	2.65	−3
Ba	.63		1.249	4.00	3.90	−3

The diffusion currents for various concentrations of the alkaline earth metal ions, as measured in liquid ammonia at −36°, are recorded in Table I. Tetraethylammonium iodide served

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[1] For previous papers, see H. A. Laitinen and C. J. Nyman, THIS JOURNAL, **70**, 2241, 3002 (1948).