[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE JOHNS HOPKINS UNIVERSITY]

Kinetics of Bromide–Alpha-Bromopropionic Acid Exchange in Aqueous Solution

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Introduction

Exchange reactions in organic halides have been studied to demonstrate the mechanism of the Walden inversion,[4] Friedel–Crafts reaction,[5] certain ionization mechanisms[6] and to a limited extent they have been investigated simply from the standpoint of the kinetics of chemical change.[7] It is to this latter point of interest that this paper is confined. The kinetics of the exchange of bromide ions with α-bromopropionic acid has been studied in acetone solution[8] at room temperature, and it has been shown that the rate of exchange is identical with the rate of racemization to within experimental error. It is of some interest to study the corresponding exchange in aqueous solution and to investigate the temperature dependence of the rate. Here the situation is somewhat complicated by the presence of hydrolysis; however, it has been found that this effect can readily be separated from the exchange process.

Experimental Part

Materials.—The α-bromopropionic acid (Eastman Kodak Co.) was carefully purified by vacuum distillation. The radioactive bromine was obtained by bombardment of butyl bromide with neutrons from the deuteron–deuteron disintegration apparatus in this Laboratory. The butyl bromide was distilled and the fraction boiling between 101–102° was used for irradiation. After irradiation the organic halide was shaken vigorously with water containing a little sodium bromide to act as a carrier. The active bromide was concentrated and the droplets of organic material were removed by boiling down the solution to a small volume. The resulting solution was then permitted to stand for forty-eight hours or longer, so that only the thirty-four hour activity remained in appreciable amount. The solution was then made up to approximately the desired bromide ion concentration and standardized. The α-bromopropionic acid was dissolved in water and enough sulfuric acid was added to make the final solution 1 *N* with respect to sulfuric acid. This solution was standardized with respect to α-bromopropionic acid by hydrolyzing a measured amount with sodium hydroxide solution and then titrating the resulting bromide ions by the Volhard method. Preliminary experiments showed that this method was suitable for determining the concentration of the organic acid.

Procedure.—Except in preliminary experiments all of the reactions were carried on in Y-shaped sealed vessels. The α-bromopropionic acid solution was placed in one arm and the sodium bromide solution in the other, and they were then heated and when the desired temperature was reached the vessel was inverted, thoroughly mixed and the time was noted. After a measured time the vessel was cooled rapidly by plunging it into an ice mixture. Previous experiments showed that the amount of exchange at the temperature of the ice mixture was negligibly small. The organic acid was separated from the inorganic bromide by four extractions with diethyl ether. The aqueous solution was then acidified with nitric acid, precipitated with an excess of standard silver nitrate solution, and then the silver nitrate was back titrated with potassium thiocyanate solution. The ether portion was extracted with 0.1 *N* sodium hydroxide solution, which was then boiled to hydrolyze the α-bromopropionic acid, and the resulting solution was analyzed for bromide ions in the same manner as the corresponding aqueous sample. Preliminary experiments showed that these methods of extraction of the organic acid from the aqueous and ethereal solutions were satisfactory for our purpose. The precipitates were then collected on one-inch filter papers in a Hirsch funnel, washed with water, acetone, dried, mounted and examined for activity. The activities were measured with a ball-point counter having a flat mica window, 1-$^1/_8$ inches in diameter and with a thickness of 2.9 mg./cm.^{2}. The filter papers were mounted on flat glass plates which could be placed about $^3/_{16}$ inch below the mica window in an exactly reproducible position. The counter was surrounded with about 2 inches of lead on all sides and gave a background count of about twelve counts per minute. A high speed scale-of-eight circuit of the type described by Lifschutz[9] was used with the counter. During long runs the background count was periodically taken, and the counter sensitivity was checked for constancy with a standard uranium source. The sensitivity remained constant and the background count did not vary by more than two counts per minute through the course of the day. The decay curves were followed up for three or four days and then were all extrapolated to a common time. These measurements had to be corrected for the difference in the absorption between silver bromide and silver thiocyanate. We were able to obtain this correction from a preliminary experiment in which we used a constant amount of radioactive bromine but varied the amount of silver bromide and silver thiocyanate. This correction was not large and in extreme cases amounted to about 6%. However, we ap-

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(1) This work constitutes a portion of a thesis to be submitted by W. Koskoski in partial fulfillment of the requirements for the degree of Doctor of Philosophy in The Johns Hopkins University.

(2) American Can Company Fellow 1936–1940.[3]

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(4) E. D. Hughes, F. Juliusburger, S. Masterman, B. Topley and J. Weiss, *J. Chem. Soc.*, 1535 (1935).

(5) F. Fairbrother, *ibid.*, 503 (1937).

(6) T. P. Nevell, E. de Salas and C. L. Wilson, *ibid.*, 1188 (1939).

(7) L. J. LeRoux and S. Sugden, *ibid.*, 1279 (1939).

(8) W. A. Cowdrey, E. D. Hughes, T. P. Nevell and C. L. Wilson, *ibid.*, 209 (1938).

(9) H. Lifschutz, *Rev. Sci. Instruments*, **10**, 21 (1939).

plied this correction to all of our results, reducing the count to that which would have been obtained if equivalent amounts of silver bromide and silver thiocyanate had been present.

Treatment of Results

In order to obtain a mathematical expression that will describe the course of the exchange reaction we may consider the following reactions

$$\mathrm{RBr} + \mathrm{Br}^{*-} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{RBr}^* + \mathrm{Br}^- \qquad (1)$$

$$\mathrm{RBr}^* + 2\mathrm{H_2O} \xrightarrow{k_3} \mathrm{ROH} + \mathrm{H_3O^+} + \mathrm{Br}^{*-} \qquad (2)$$

$$\mathrm{RBr} + 2\mathrm{H_2O} \longrightarrow \mathrm{ROH} + \mathrm{H_3O^+} + \mathrm{Br}^- \qquad (3)$$

Reaction (1) is considered as a bimolecular reversible reaction; (2) and (3) are treated as first order non-reversible reactions. The reasonableness of these considerations is apparent from the work of Ingold and his co-workers.[10] The total rate of appearance of activity in the organic material will be

$$\mathrm{d}[\mathrm{RBr}^*]/\mathrm{d}t = k_1[\mathrm{RBr}][\mathrm{Br}^{*-}] - k_2[\mathrm{RBr}^*][\mathrm{Br}^-] - \lambda[\mathrm{RBr}^*] - k_3[\mathrm{RBr}^*] \qquad (4)$$

Now if a is the initial concentration of the organic halide, c the initial concentration of Br^{*-}, x the concentration of RBr^* and b the initial concentration of Br^- we have

$$\mathrm{d}x/\mathrm{d}t = k_1[ae^{-k_3t}][ce^{-\lambda t} - x] - k_1x[b + a(1 - e^{-k_3t})] - \lambda x - k_3x \qquad (5)$$

where $k_1 = k_2 =$ exchange constant and λ and k_3 are the decay and hydrolysis constants, respectively. Integrating, solving for the exchange constant and noting that $ae^{-k_3t} =$ RBr we get

$$k_1 = -\frac{1}{a+b}\ln\left[1 - r\frac{(a+b)}{[\mathrm{RBr}]}\right] \qquad (6)$$

where r is the ratio of the activity found in the organic halide to the total activity.

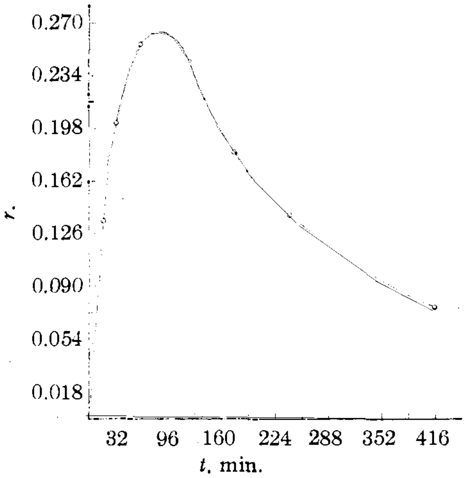

Fig. 1.

Discussion of Results

Examination of the several reactions going on shows that we have essentially two competing reactions, (1) the exchange tending to increase the number of radio organic halide molecules and (2) the hydrolysis which tends to decrease the number of radio organic halide molecules. We would as a result of this consideration expect that if the exchange was faster than the hydrolysis the radioactivity of the organic halide would increase to a maximum and then decrease almost exponentially to zero. In order to study the course of the reaction and determine the position of the maximum, we made a series of preliminary investigations in which the reaction was permitted to go on for a comparatively long time. Table I is a typical example of the results of such experiments made at 100°, and Fig. 1 gives the graphic picture of the course of the reaction.

TABLE I

t, min.	Br^-	RBr	r
0	0.0346	0.0270	0
17	.0366	.0246	0.135
32	.0390	.0232	.202
60	.0419	.0202	.256
120	.0470	.0150	.244
183	.0521	.0111	.182
240	.0536	.00769	.139
415	.0571	.00406	.0761

An examination of the figures, graph and expression (6) indicates that accurate values of the exchange constant can be obtained from the first part of the reaction up to a time of about one hour, for it is in this region that the exchange is an important reaction whereas on the other side of the maximum the hydrolysis is all important. The logarithmic part of our equation involves an expression which is the difference between unity and a fraction. As we pass the maximum this fraction approaches unity and differs from unity by an amount which is smaller than our experimental error, making useless any attempts to determine the exchange constant from this part of the curve. We therefore limited our studies at 100° to times of no longer than one hour. Table II gives the results of a run made with 0.0376 N sodium bromide solution and 0.0318 N α-bromopropionic acid in 1.014 N sulfuric acid solution at 100°. The concentrations in all of the

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[10] W. A. Cowdrey, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 1208 (1937).

work have been corrected for expansion and the constant is given in liters mole^{-1} sec.$^{-1}$.

TABLE II

t, min.	Br^-	RBr	r	$k_1 \times 10^3$
10	0.0397	0.0301	0.101	6.4
20	.0411	.0287	.167	6.2
30	.0419	.0272	.216	6.4
40	.0430	.0260	.241	6.2
50	.0438	.0254	.262	6.0
60	.0453	.0241	.282	6.7

It is apparent that the exchange constant is constant to within our experimental error, and these results indicate that our equation adequately describes the course of the reaction under the conditions that we have imposed.

The rate constants of some racemization and exchange reactions have been shown[11] to drift with the halide ion concentration, indicating that the reaction was not exactly proportional to the first power of the bromide ion concentration but to some power less than one. To test for any possible drifts in the rate constants, we made a run with a very small concentration of bromide. Table III gives the results of this experiment at 100°. The initial concentration of sodium bromide was 0.00244 N, the α-bromopropionic acid was 0.0292 N and sulfuric acid was 1.014 N.

TABLE III

t, min.	Br^-	RBr	r	$k_1 \times 10^3$
15	0.00406	0.0270	0.141	6.3
30	.00669	.0253	.236	6.2
45	.00776	.0232	.294	6.0
60	.00900	.0220	.366	6.5

The data of Table III give an average exchange constant which is the same to within experimental error as the previously determined value for concentrations over ten-fold greater, indicating that the reaction at very small bromide ion concentration is still exactly proportional to the bromide ion concentration.

The sole purpose of the sulfuric acid in these experiments was to suppress the ionization of the organic acid and thus ensure that the main reaction was that of the undissociated molecule. In order to determine whether the sulfuric acid concentration affected the rate of exchange in any way we made a run similar to the above runs but with half the amount of sulfuric acid. The solution was 0.0389 N with respect to sodium bromide, 0.0306 N with respect to α-bromopropionic acid and 0.507 N with respect to the sulfuric acid.

The temperature was 100°, and the data are given in Table IV.

TABLE IV

t, min.	Br^-	RBr	r	$k_1 \times 10^3$
10.5	0.0407	0.0285	0.107	6.9
20	.0430	.0272	.164	6.5
30	.0452	.0253	.190	6.0
40	.0452	.0242	.226	6.3
50	.0471	.0225	.236	6.3
60	.0484	.0210	.244	6.6

Table IV shows that the rate of hydrolysis has increased, but the exchange rate constant remains the same within the limits of experimental error.

The rate of bromine racemization[10] in optically active α-bromopropionic acid has been determined indirectly under conditions similar to ours and its value is given as 0.008 liter mole^{-1} sec.$^{-1}$, a value which is somewhat different from our exchange value. The reason for this apparent difference cannot be given without more detailed work.

Tables V, VI and VII give the results of the determinations of the rate constants at 60, 70 and 80°, respectively. The sulfuric acid concentration in all cases was 1.014 N. The plot of log k against $1/T$ is given in Fig. 2, and the activation energy calculated from the slope of this curve is 20.9 kcal.

TABLE V

t, min.	Br^-	RBr	r	$k_1 \times 10^4$
0	0.0843	0.217		
60	.0850	.216	0.150	2.17
120	.0856	.215	.246	1.96
180	.0873	.213	.343	2.03
240	.0890	.212	.415	2.05
305	.0900	.210	.454	1.90

TABLE VI

t, min.	Br^-	RBr	r	$k_1 \times 10^4$
0	0.0399	0.0412		
60	.0400	.0410	0.070	5.1
120	.0408	.0405	.127	5.0
181	.0413	.0397	.180	5.2
242	.0419	.0390	.210	4.9

TABLE VII

t, min.	Br^-	RBr	r	$k_1 \times 10^3$
0	0.0401	0.0290		
40	.0408	.0288	0.074	1.18
60	.0411	.0285	.099	1.10
80	.0413	.0282	.127	1.15
100	.0419	.0278	.157	1.20
117	.0426	.0266	.173	1.22

With the values of the rate constants and the

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(11) E. D. Hughes, F. Juliusberger, S. Masterman, B. Topley and J. Weiss, *J. Chem. Soc.*, 1525 (1935).

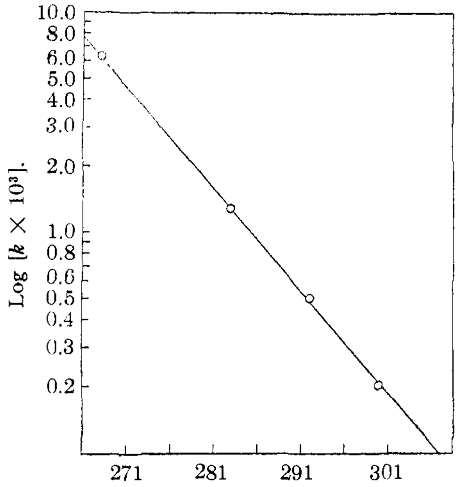

Fig. 2.

activation energy the parameter A of the modified Arrhenius equation

$$\log \frac{k}{\sqrt{T}} = A - \frac{E}{4.57T}$$

may be evaluated and in turn the effective collision diameter can be calculated from

$$\log \frac{k}{\sqrt{T}} = \log\,[6.06 \times 10^{20}\,\sigma^2\,(8\pi R/M)^{1/2}] - \frac{E}{4.57T}$$

The value found for A is 8.8 and σ = 1.3 Å. The value found for the activation energy and the effective collision diameter are in accord with those found by Elliott and Sugden[12] in their studies of bromide exchanges in a series of alkyl bromides.

Acknowledgment.—The apparatus used in this research was built with the aid of a grant from the Research Corporation.

Summary

The exchange of bromide ions with α-bromopropionic acid was studied in aqueous solution and the activation energy was determined. The reaction obeyed the Arrhenius equation to within experimental error and the value of the effective collision diameter was found to be about what would be expected from simple collision theory. The values of the activation energy and collision diameter are in accord with other similar work.

(12) G. A. Elliott and S. Sugden, *J. Chem. Soc.*, 1836 (1939).

BALTIMORE, MARYLAND RECEIVED MAY 19, 1941

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

Rates of Reaction of Excited Mercury with Oxygen, Hydrogen Sulfide and Nitrous Oxide, and their Relation to Effective Collision Diameters

BY JAMES E. CLINE AND GEORGE S. FORBES

Introduction.—This investigation was undertaken to correlate the quantitative dependence of reaction rate on pressure with effective collision diameters in reactions involving mercury excited by resonance radiation. Effective collision diameters have been estimated through studies of the quenching of mercury fluorescence by various gases. Of numerous papers a few may be cited.[1–4] Zemansky[3,4] corrected his results for reabsorption of fluorescence radiation. Frank[5] concluded that reaction rate is proportional to intensity of resonance radiation (λ = 2537 Å.) and that radiation of wave length less than 2000 Å. is without influence upon the reaction. His further conclusions are discussed below. Leipunski and Sagulin[6] had shown that this resonance radiation is necessary for the reaction, but Noyes[7] had stated that participation of shorter wave lengths also was required for explanation of his results.

With new methods of correction for experimental complications, we have reinvestigated the reaction of oxygen with excited mercury, and have studied hydrogen sulfide and nitrous oxide as well. Our theoretical interpretation takes into consideration the mean lifetime of excited mercury, the quenching efficiency of foreign gas and the reabsorption of fluorescence radiation by mercury. In this way the effects of pressure, temperature and geometry of reaction vessel can be explained.

The well-known Stern–Volmer equation for quenching of fluorescence radiation can be obtained starting from

$$0 = \frac{d[\mathrm{Hg}^*]}{dt} = kI - k_2[\mathrm{Hg}^*]p - k_3[\mathrm{Hg}^*] \qquad (1)$$

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(1) Stern and Volmer, *Physik. Z.*, **20**, 183 (1919).

(2) Stuart, *Z. Physik*, **32**, 262 (1925).

(3) Zemansky, *Phys. Rev.*, **31**, 812 (1928).

(4) Zemansky, *ibid.*, **36**, 919 (1930).

(5) Frank, *Acta Physicochim.* (U. S. R. R.), **1**, 833 (1934).

(6) Leipunski and Sagulin, *Z. physik. Chem.*, **B1**, 362 (1928).

(7) Noyes, THIS JOURNAL, **49**, 3100 (1927).