[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

The Rate of the Chlorate–Bromide Reaction in Acid Solution with Arsenious Acid Present. Arsenic Acid as a Catalyst

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I. Introduction

Skrabal and Schreiner[1a] have studied the rate of reaction of chlorate ion with the halides in acid solution in the presence of arsenious acid.[2] They found the reaction to be autocatalytic with bromide and iodide, but not with chloride ion. Since arsenious acid reacts rapidly with the free halogen,[3] the net reaction is

$$3H_3AsO_3 + ClO_3^- = 3H_3AsO_4 + Cl^- \qquad (A)$$

which may be considered as the sum of

$$ClO_3^- + 9X^- + 6H^+ = 3X_3^- + 3H_2O + Cl^- \qquad (B)$$

and

$$3(H_3AsO_3 + X_3^- + H_2O = H_3AsO_4 + 3X^- + 2H^+) \qquad (C)$$

where X stands for the halogen in question.

In order to account for the autocatalytic effect in the chlorate–bromide case, they proposed the rate law[4]

$$-d(H_3AsO_3)/dt = k_1(ClO_3^-)(Br^-)(H^+)^2 + \lambda(H_3AsO_4) \qquad (1)$$

a relation which is in harmony with their results. Here $k_1(ClO_3^-)(Br^-)(H^+)^2$ is the characteristic term in the chlorate or bromate–halide reaction rate,[5] corresponding to reaction (B).[6,7]

The present investigation was undertaken to test the validity of eq. (1) over a fairly wide range of the concentration parameters, in particular, at moderate arsenic acid concentration in order to establish definitely the role of arsenic acid as catalyst in the chlorate–bromide reaction.[8,9] Thus, it seemed likely that λ should contain any one or all of the concentrations of chlorate, bromide or hydrogen ion. This was borne out by experiment. It is shown below that at low arsenic acid and hydrogen ion concentrations, the rate law is

$$-d(H_3AsO_3)/dt = k_1(ClO_3^-)(Br^-)(H^+)^2 + \kappa(ClO_3^-)(Br^-)(H^+)(H_3AsO_4) \qquad (2)$$

where κ is approximately independent of (H^+) and (H_3AsO_4). It is found that $k_1 = 3 \times 10^{-4}$ while $\kappa = 3 \times 10^{-3}$. Thus, arsenic acid not only acts as a catalyst, but as a good one.

Conventions and Symbols.—Aqueous solutions of arsenic oxide and arsenious oxide are referred to as containing H_3AsO_4 and H_3AsO_3, respectively. Concentration is designated by parentheses around a symbol, and is expressed in moles per liter throughout. The concentrations: (ClO_3^-), (Br^-) and (H_3AsO_3) are taken equal to the concentrations of sodium chlorate, sodium bromide and twice arsenious oxide, respectively. A distinction is made, however, between $(H^+)_{add}$ and (H^+), $(H_3AsO_4)_{add}$ and (H_3AsO_4). $(H^+)_{add}$ is equal to the concentration of perchloric acid added; (H^+) is taken as $(H^+)_{add} + (H_2AsO_4^-)$, where[10] $K = (H^+)(H_2AsO_4^-)/(H_3AsO_4) = 5 \times 10^{-3}$. Similarly, $(H_3AsO_4) = (H_3AsO_4)_{add} - (H_2AsO_4^-)$. A zero subscript signifies the value of the quantity at time equals zero. Time, t, is given in minutes.

II. Experimental Methods

Rate Measurements.—In each experiment, the reaction was started by adding a known volume of sodium bromide solution in water to a known aqueous mixture of the following reagents: sodium chlorate, perchlorate acid, arsenious acid, arsenic acid and sodium perchlorate. All reactants were at 25° at the time of mixing; the temperature was maintained at that value, within 0.1° for the duration of the experiment. Within five minutes, a sample of reaction mixture was withdrawn, treated with excess sodium bicarbonate and titrated with standard iodine. Five or six additional determinations were made at intervals over the course of the reaction (10^4–10^5 minutes). In this way, arsenious acid concentration was established as a function of time.

The calculation of concentration of reactants was made assuming additivity of volumes. This assumption was shown to be correct within 0.1% in expts. 1–6 (Table I). The estimated uncertainty in concentration of a reactant due to errors in volumetric technique was a few tenths % at most.

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(1) (a) Skrabal and Schreiner, *Monatsh.*, **65**, 213 (1934); (b) Kubina, *ibid.*, **43**, 439 (1923); (c) Bowmann, *J. Phys. Chem.*, **11**, 292 (1903); (d) Schilow, *Z. physik. Chem.*, **42**, 641 (1903); (e) Hirade, *Bull. Chem. Soc. Japan*, **10**, 97 (1935).

(2) Compare the results of Bray and Liebhafsky, THIS JOURNAL, **57**, 51 (1935), on the bromate–bromide reaction with those of Bray and Davis, *ibid.*, **52**, 1427 (1930), and Young and Bray, *ibid.*, **54**, 4284 (1932), on the same reaction in the presence of hydrogen peroxide.

(3) This is the leading function of the arsenious acid; possible loss of X_2 by volatilization is eliminated. By the addition of arsenious acid, the net reaction is greatly simplified; bromide or iodide and hydrogen ion concentrations are rendered definite and virtually constant (see below, Section III). If bromine, for example, is allowed to form, bromide concentration is rendered indefinite due to distribution between Br^- and Br_3^-.

(4) Here the symbols of Skrabal and Schreiner have been changed: $k_1 = 3K_1$ (their K_1), $\lambda = k$ (their k).

(5) Skrabal, "Int. Crit. Tables," Vol. VII, 149 (1930).

(6) In the absence of arsenious acid, the rate law is simply $-3d(ClO_3^-)/dt = k_1(ClO_3^-)(Br^-)(H^+)^2$, $k_1 = 1.8 \times 10^{-8}$ at 40°, Hirade.[1e]

(7) A term proportional to $(ClO_3^-)(Cl^-)(H^+)$,^{2} corresponding to reaction (B) with X equals chlorine, should be added to the right-hand side of eq. (1). However, in the expt. which established eq. (1), this term was negligible. Skrabal and Schreiner[1a] found that the rate constants corresponding to the term $(ClO_3^-)(X^-)(H^+)^2$ stand in the ratio 44.4:2.07:1.00 as X is iodine, bromine or chlorine, respectively.

(8) Apparently several of the other halate–halide reactions are *not* catalyzed by arsenic acid. The following pairs have been studied in the presence of arsenious acid and show no indication of arsenic acid catalysis: iodate–iodide,[1b] chlorate–chloride,[1b] bromate–iodide[1c] and bromate–bromide.[1a,1d]

(9) Hirade[1e] gives evidence that the chlorate–bromide reaction is also catalyzed by phosphoric acid and sulfate ion.

(10) Washburn and Strachan, THIS JOURNAL, **35**, 681 (1913); Walden, *Z. physik. Chem.*, **2**, 49 (1888).

TABLE I

EXPERIMENTS WITHOUT ADDED ARSENIC ACID

Expt.	$(ClO_3^-)_i$	(Br^-)	$(H^+)_{add}$	$(H_3AsO_3)_0$	$k_1 \times 10^4$	$\kappa \times 10^{+3b}$ 0.2	0.4	0.6	μ
S.-S.[a]	0.2	0.2	0.2	0.04	3.0	3.1	3.6	3.6	0.4
1	.202	.264	.171	.15	2.7	5.9	5.4	4.9	.76
43	.161	.162	.531	.002	3.0	5.4	5.5	5.8	.85
2	.193	.252	.487	.08	3.6	...	4.1	4.4	1.0
3	.202	.264	.341	.07	3.3	3.4	4.3	4.3	1.0
4	.202	.264	.171	.07	3.3	...	...	...	1.0
5	.202	.132	.511	.08	3.7	3.4	4.1	4.2	1.0
6	.101	.264	.511	.08	3.7	3.1	3.8	4.0	1.0

[a] Skrabal and Schreiner, ref. (1a): 2. *Versuch.* [b] At $(H_3AsO_4)/(H_3AsO_3)_0$ = 0.2, 0.4 and 0.6.

TABLE II

EXPERIMENTS WITH ADDED ARSENIC ACID. VARIATION OF THE RATE WITH CHLORATE AND BROMIDE

$(H_3AsO_3)_0 = 0.03$, $\mu = 0.80 \pm 0.02$

Expt.	$(ClO_3^-)_0$	(Br^-)	$(H^+)_{add}$	$(H_3AsO_4)_{add}$	Initial rate $\times 10^6$	$\kappa \times 10^3$	$k_2 \times 10^3$
27	0.101	0.0330	0.356	0.407	3.61	7.20	4.5
28	.101	.330	.356	.407	35.5	7.07	4.3
34	.101	.330	.107	.153	2.95	5.10	4.2
33	.101	.132	.107	.153	1.095	4.72	3.8
29	.0253	.132	.356	.407	3.42	6.80	4.2
30	.253	.132	.356	.407	36.6	7.30	4.4
31	.253	.132	.107	.153	2.96	5.10	4.2
32	.505	.132	.107	.153	6.11	6.29	4.4
42	.0968	.194	.196[a]	.293	0.030	4.72	4.4

[a] Sodium hydroxide added = 0.196.

Ionic strength,[11] μ, was adjusted with sodium perchlorate.

Stock Solutions.—Sodium thiosulfate, iodine, arsenious acid and perchloric acid were standardized in the usual way against once-crystallized potassium iodate. Sodium chlorate was treated with potassium iodide in 6 *M* hydrochloric acid; the resulting iodine was estimated with sodium thiosulfate. Arsenic acid solution was treated with potassium iodide in 4 *M* sulfuric acid and the iodine so formed was titrated with sodium thiosulfate.[12] Excess sodium bicarbonate was then added, and the arsenious acid estimated with iodine. The iodine titers were more consistent than the thiosulfate values; the former were used in computing arsenic acid concentration. Sodium perchlorate solution was made by titrating sodium hydroxide solution with standard perchloric acid, using phenol red as external indicator. Sodium bromide solution was standardized gravimetrically; bromine was weighed as silver bromide. The mean deviation of the analyses was about 0.1% except for the arsenic acid determination where it was about 0.3%.

All the stock solution chemicals were reagent grade; they were used without further purification. The specific resistance of the water was >10^5 ohm cm.

III. Experimental Results

In Table I are presented results of experiments in which no arsenic acid was added to the system, while in Tables II and III results of experiments are shown in which the initial arsenic acid concentration was made between 0.1 and 0.6. The tables contain the initial concentration, in moles per liter, of chlorate, bromide and hydrogen ions, as

TABLE III

EXPERIMENTS WITH ADDED ARSENIC ACID. VARIATION OF THE RATE WITH HYDROGEN ION AND ARSENIC ACID

$(ClO_3^-)_0 = 0.101$, $(Br^-) = 0.132$, $(H_3AsO_3)_0 = 0.03$, $\mu = 0.79 \pm 0.03$. κ and k_2 computed with $K = 5.0 \times 10^{-3}$, $k_1 = 3.0 \times 10^{-4}$, $k_3 = 4.0 \times 10^{-3}$, $k_4 = 3.0 \times 10^{-3}$

Expt.	$(H^+)_{add}$	$(H_3AsO_4)_{add}$	Initial rate $\times 10^6$	$\kappa \times 10^3$	$k_2 \times 10^3$
7	0.511	0.610	35.8	8.33	4.4
8	.511	.407	20.9	7.16	3.9
9	.511	.254	12.5	6.65	3.9
10	.511	.153	7.75	6.49	4.0
39	.559	.102	6.55	7.03	4.5
11	.341	.610	20.9	7.27	4.1
12	.341	.407	12.2	6.34	3.8
13	.341	.254	7.25	5.89	3.8
14	.341	.153	4.38	5.68	3.9
38	.373	.102	3.57	6.02	4.2
23	.249	.610	14.9	7.03	4.2
24	.249	.407	8.82	6.25	4.0
25	.249	.254	5.03	5.65	3.9
26	.249	.153	2.98	5.43	4.0
15	.170	.610	9.89	6.56	4.0
15′	.178	.610	10.0	6.38	3.8
16	.170	.407	5.70	5.80	3.9
45[a]	.178	.407	6.22	6.09	4.2
17	.170	.254	3.29	5.40	4.0
18	.170	.153	1.84	4.98	3.8
37	.178	.102	1.39	5.29	4.3
19	.107	.610	7.37	6.95	4.7
20	.107	.407	4.17	6.36	4.7
21	.107	.254	2.20	5.58	4.4
22	.107	.153	1.10	4.72	3.8
36	.107	.102	0.781	5.08	4.3

[a] μ = 0.44.

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(11) Lewis and Randall definition, $\frac{1}{2}\Sigma C_i Z_i^2$.

(12) The equilibrium constant for reaction (C) is about 1.6 × 10^{-1} and 3 × 10^{+16} as X is iodine or bromine, *cf.*, Latimer, "Oxidation Potentials," Prentice-Hall, New York, N. Y., 1938. In the rate experiments described below, even where $(H_3AsO_4)_{add}$, $(H^+)_{add}$ and (Br^-) are several tenths, the equilibrium concentration of arsenious acid and bromine is vanishingly small.

well as arsenic acid and arsenious acid. The ionic strength μ is given. The initial rate of arsenious acid disappearance is also listed in Tables II and III under the heading "initial rate $\times\ 10^6$" and is equal to the decrease in moles of +3 arsenic per liter per minute at time equals zero. For the sake of brevity, the experimental results in Table I are represented by derived quantities. The units of k_1, k_2 and κ are mole^{-3} liter^{+3} min.$^{-1}$, of k_3 and k_4, mole^{-4} liter^{+4} min.$^{-1}$.

In the experiments of Table II and III, where both the initial arsenic acid and chlorate ion concentrations are large compared to the initial arsenious acid concentration (in general, about five to one), a plot of arsenious acid concentration against time gives very nearly a straight line; the reaction rate essentially is constant. Even in experiments 29 (Table II) or expts. 39, 38, etc. (Table III), where either the chlorate or arsenic acid concentration is of the same order of magnitude as initial arsenious acid, the arsenious acid concentration *vs.* time plot shows only slight deviation from linearity. On the other hand, the rate increases significantly with time in the experiments of Table I, where initial arsenic acid concentration is zero.

For the experiments of Tables II and III, then, the initial rate is readily found; in most cases it is simply the slope of the arsenious acid concentration–time straight line. For the experiments of Table I, the initial rate was obtained by graphical extrapolation to zero time of the arsenious acid–time slopes at small times.

These results are consistent with eq. (2). It may be noted that the stoichiometric relation (A) certifies the constancy of bromide ion concentration in all cases and the virtual constancy of hydrogen ion in most cases (increase in arsenic acid with time leads to a second order increase in hydrogen ion).

In cases where the term $\kappa(\mathrm{ClO_3^-})(\mathrm{Br^-})(\mathrm{H^+})\cdot(\mathrm{H_3AsO_4})$ dominates $k_1(\mathrm{ClO_3^-})(\mathrm{Br^-})(\mathrm{H^+})^2$ strongly (eq. (2)), *i. e.*, most of the experiments of Tables II and III (recall $\kappa \simeq 10k_1$; even in experiment 39, the κ term is twice the k_1 term), the acceleration of the reaction is approximately $\kappa(\mathrm{Br^-})(\mathrm{H^+})((\mathrm{ClO_3^-})\mathrm{d}(\mathrm{H_3AsO_4})/\mathrm{d}t + (\mathrm{H_3AsO_4})\mathrm{d}(\mathrm{ClO_3^-})/\mathrm{d}t)$. Since $\mathrm{d}(\mathrm{H_3AsO_4})/\mathrm{d}t = -3\mathrm{d}(\mathrm{ClO_3^-})/\mathrm{d}t$, it follows that for an experiment in which initial chlorate ion concentration is one-third the initial arsenic acid concentration the reaction rate is essentially constant. Moreover, in all cases, the decrease in rate due to the disappearance of chlorate ion is opposed by an increase in rate due to the formation of arsenic acid.

For the experiments of Table I, in which no arsenic acid was added, the acceleration is equal approximately to $\kappa(\mathrm{Br^-})(\mathrm{H^+})(\mathrm{ClO_3^-})\mathrm{d}(\mathrm{H_3AsO_4})/\mathrm{d}t$ for small values of the time. k_1 was simply determined from the results of expts. in Table I since the initial rate is equal to $k_1(\mathrm{ClO_3^-})_0(\mathrm{Br^-})(\mathrm{H^+})^2$ when no arsenic acid is added to the system. Integration of eq. (1) yields $\lambda(\mathrm{H_3AsO_4})/k_1(\mathrm{ClO_3^-})_0(\mathrm{Br^-})(\mathrm{H^+})^2 = -1 + \exp \lambda t$ if $(\mathrm{ClO_3^-})$ is regarded as constant and equal to $(\mathrm{ClO_3^-})_0$. From this approximation, λ was computed at values of the ratio $(\mathrm{H_3AsO_4})/(\mathrm{H_3AsO_3})_0 = 0.2$, 0.4 and 0.6, and thence, κ from the definition $\lambda = \kappa(\mathrm{ClO_3^-})(\mathrm{Br^-})(\mathrm{H^+})$. Skrabal and Schreiner used a different method of calculation. They computed $k_1 = 2.97 \times 10^{-4}$ and $k_2 = 3.94 \times 10^{-3}$.

IV. Discussion

The experiments of Table I were performed to check the findings of Skrabal and Schreiner concerning the autocatalytic effect as well as the numerical value of k_1. As may be seen by inspection of Table I, the results of this investigation are in fair agreement with the experiment of Skrabal and Schreiner. The quantity k_1 is satisfactorily constant; there is some evidence that k_1 increases slightly with ionic strength between $\mu = 0.8$ and 1.0. In making the calculations for Tables II and III, where $\mu = 0.8$, k_1 has been taken as 3.0×10^{-4}.

Inspection of experiments 1, 2 and 43 shows clearly that the reaction rate is not an explicit function of$(\mathrm{H_3AsO_3})$. In this investigation, however, no attempt has been made to discover whether the magnitude of the rate constants is the same in the presence or absence of arsenious acid.[2]

The values of κ lie between about 3 and 5×10^{-3}; this fact may be taken as weak evidence in favor of the rate law eq. (2). It may be seen that the κ values more nearly coincide and approach a value in the neighborhood of 4×10^{-3} as $(\mathrm{H_3AsO_4})/(\mathrm{H_3AsO_3})_0$ increases. This is doubtless due to the fact that the term $\kappa(\mathrm{ClO_3^-})(\mathrm{Br^-})(\mathrm{H^+})(\mathrm{H_3AsO_4})$ makes an unimportant contribution to the rate of reaction at small times. In experiments 2–6 (Table I), for example, when $(\mathrm{H_3AsO_4})/(\mathrm{H_3AsO_3})_0 = 0.6$, the terms $k_1(\mathrm{ClO_3^-})(\mathrm{Br^-})(\mathrm{H^+})^2$ and $\kappa(\mathrm{ClO_3^-})(\mathrm{Br^-})(\mathrm{H^+})(\mathrm{H_3AsO_4})$ are approximately equal.

The essential experiments of this investigation are those of Tables II and III, in which arsenic acid was added. Using $k_1 = 3 \times 10^{-4}$, it is found that the term $k_1(\mathrm{ClO_3^-})(\mathrm{Br^-})(\mathrm{H^+})^2$ is only about 10% of the initial rate observed for the experiments of Table II. Skrabal and Schreiner assumed that the quantity "initial rate-$k_1(\mathrm{ClO_3^-})_0(\mathrm{Br^-})(\mathrm{H^+})^2$" contains $(\mathrm{H_3AsO_4})$ as a factor, and called the proportionality constant λ. It is readily apparent from Table II that λ also contains $(\mathrm{ClO_3^-})$ and $(\mathrm{Br^-})$ as factors. Thus, in experiments 27 and 28 where $(\mathrm{Br^-})$ is varied tenfold and the concentrations of the other reactants are the same in both cases, the rate is found to vary about tenfold. The values of κ in experiments 27 and 28 differ by only about 2%. Similarly, there are three other pairs of experiments in Table II in which $(\mathrm{ClO_3^-})$ or $(\mathrm{Br^-})$ alone is varied; and for each pair κ differs by 8% at most.

Closer inspection of Table II reveals that in the first eight experiments there are only two $(\mathrm{H^+})_{\mathrm{add}}$-

$(H_3AsO_4)_{add}$ pairs, namely, $(H^+)_{add} = 0.356$, $(H_3AsO_4)_{add} = 0.407$ and $(H^+)_{add} = 0.107$, $(H_3AsO_4)_{add} = 0.153$. For the first pair κ is about 7×10^{-3}; for the second pair κ is only about 5×10^{-3}. On the basis of experiments 27–34, then, it seems fair to state that the quantity "initial rate-$k_1(ClO_3^-)(Br^-)(H^+)^2$" is satisfactorily proportional to chlorate ion concentration up to 0.5 and bromide concentration up to 0.3 and is roughly proportional to hydrogen ion and arsenic acid concentration. These experiments indicate that κ is an increasing function of (H^+) and/or (H_3AsO_4). In order to test this point, the experiments recorded in Table III were performed.

In these experiments chlorate and bromide ion concentrations, as well as ionic strength (except experiment 45), were fixed throughout. $(H^+)_{add}$ and $(H_3AsO_4)_{add}$ were varied over the range 0.1 to 0.5 or 0.6. In general, κ increases measurably both with (H^+) and (H_3AsO_4).[13]

Thus, when κ is plotted against $(H_3AsO_4)_{add}$ at constant $(H^+)_{add}$ for each of the $(H^+)_{add}$ values in Table III, the points can be connected in a reasonable way by a family of parallel straight lines of slope $3 \times 10^{-3} = \partial\kappa/\partial(H_3AsO_4)_{add}$. To a fair approximation $\partial\kappa/\partial(H_3AsO_4)_{add} = \partial\kappa/\partial(H_3AsO_4)$ and hence κ = function of $(H^+) + k_4(H_3AsO_4)$ with $k_4 = 3 \times 10^{-3}$. Similarly, when κ is plotted against $(H^+)_{add}$ at constant $(H_3AsO_4)_{add}$ for each of the $(H_3AsO_4)_{add}$ values in Table III, the points, once more, can be connected in a reasonable way by a family of parallel straight lines of slope 4×10^{-3}. Then κ = function $(H_3AsO_4) + k_3(H^+)$ and in view of the above relation for κ, it appears that $\kappa = k_2 + k_3(H^+) + k_4(H_3AsO_4)$. Substitution of this relation into eq. (2) yields a rate law which represents the experimental results considerably better than eq. (2), namely

$$-d(H_3AsO_3)/dt = k_1(ClO_3^-)(Br^-)(H^+)^2 + (ClO_3^-)(Br^-)(H^+)(H_3AsO_4)(k_2 + k_3(H^+) + k_4(H_3AsO_4)) \quad (3)$$

It may be noted that in only eleven of the experiments in Table III does the sum of the two fifth order terms in eq. (3) equal more than one-half the term $k_2(ClO_3^-)(Br^-)(H^+)(H_3AsO_4)$; thus the fifth order terms constitute minor corrections. They need not be regarded as evidence of fifth order rate determining steps. Doubtless, many other formulations would represent the results equally well; the principal justification of eq. (3) lies in the simplicity with which it represents the experimental results in terms of concentration parameters easily calculated from the stoichiometric concentrations.

As a test of eq. (3), k_2 has been computed for each of the experiments in Tables II and III using $k_1 = 3.0 \times 10^{-4}$, $k_3 = 4.0 \times 10^{-3}$ and $k_4 = 3.0 \times 10^{-3}$ and $K = 5.0 \times 10^{-3}$. The k_2 values for twenty-two of the thirty-four expts. in Tables II and III lie within 5% of 4.0×10^{-3}. Several values are distinctly high, as anticipated above.[13] The high k_2 values are found, in general, in those experiments where either (H^+) is much greater than (H_3AsO_4) or (H_3AsO_4) is much greater than (H^+) as in experiments 39, 19 and 20.

The high values of k_2 observed when (H^+) is much greater than (H_3AsO_4) and where the term $k_1(ClO_3^-)(Br^-)(H^+)^2$ makes its most important contribution to the reaction rate, can be brought into line if k_1 is taken as 3.5×10^{-4} (the average of experiments 2–6) instead of 3.0×10^{-4}.

In computing κ and k_2, the dissociation of arsenic acid has been taken into account in computing (H^+) and (H_3AsO_4). The high values of k_2 obtained where (H_3AsO_4) is much larger than (H^+), and where the variation in k_2 with K is significant, are considerably improved if

$$K = (5.0 + 12(H_3AsO_4)) \times 10^{-3} \quad (4)$$

instead of 5.0×10^{-3} is used in the calculation. The justification of eq. (4) comes from experiments (not reported here) in which no hydrogen ion other than that furnished by arsenic acid was added. For these experiments, K was computed so as to make $k_2 = 4.0 \times 10^{-3}$. The values of K found in this way show a fairly regular increase with (H_3AsO_4) over the interval $0.1 < (H_3AsO_4) < 1.0$, which is adequately represented by eq. (4).

Using eq. (4) and $k_1 = 3.5 \times 10^{-4}$, "corrected" values of k_2 (not presented in Tables II or III) are obtained, virtually all of which lie within 5% of $k_2 = 4.0 \times 10^{-3}$.

An attempt was made to determine whether or not the rate depends on $(H_2AsO_4^-)$ at low (H^+). In experiment 42 (Table II), $(H_2AsO_4^-)$ was made about 0.2 by the addition of sodium hydroxide; (H_3AsO_4) was about 0.1. To a fair degree of approximation $(H^+) = K((H_3AsO_4)_{add} - (NaOH)_{add})/(NaOH)_{add}$; hence, the calculated value of k_2 in this case is approximately inversely proportional to K. Using 6.2×10^{-3} (eq. (4)), $k_2 = 4.4 \times 10^{-3}$ in this experiment. Therefore, it appears unlikely that the reaction rate could be properly represented as a function of $(H_2AsO_4^-)$.

It should be noted that in the present experiments, chloride ion does not directly influence the reaction rate. Thus, k_5 of the term[1a] $k_5(ClO_3^-)(Cl^-)(H^+)^2$ is only about 1.5×10^{-4}. This term makes its most important contribution in experiment 1 (Table I), where it amounts to only 5% of the total rate at $(H_3AsO_4)/(H_3AsO_3)_0 = 0.5$. Moreover, the chlorate–chloride reaction is not measurably catalyzed by arsenic acid.

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[13] Apparent exceptions to this rule may be found, however, by comparing experiment 10 with 39, 14 with 38, 18 with 37, 22 with 36, as well as 15 or 15′ with 19, 16 with 20 and so on, for each of the equi-(H_3AsO_4)add pairs in the two series 15 to 37 and 19 to 36, inclusive. These complications may be due to experimental error since experiments 7–26, 15′ and 36 to 39, inclusive, were performed with separate and independently standardized sets of stock solutions. This seems unlikely since the values of κ from experiments 15 and 15′ agree within about 3%. Nevertheless, in the first approximation to a rate law more adequate than eq. (2), it is convenient to regard κ as a monotonically increasing function of (H^+) and (H_3AsO_4) and to disregard the deviations from this rule which are outlined above.

Comparison of experiments 16 and 45 indicates that k_2 does not vary significantly with μ over the interval 0.4 to 0.8.

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Summary

1. The rate of the chlorate–bromide reaction in the presence of arsenious acid has been investigated at high ionic strength at 25°. In the absence of arsenic acid, the rate (initial) is given by $k_1(ClO_3^-)(Br^-)(H^+)^2$ with $k_1 = 3.0 \times 10^{-4}$.

2. Arsenic acid catalyzes the reaction. Arsenious acid and arsenate ion do not.

3. At low (H^+) and (H_3AsO_4), the catalytic action of arsenic acid can be represented fairly well by the term $k_2(ClO_3^-)(Br^-)(H^+)(H_3AsO_4)$ where $k_2 = 4.0 \times 10^{-3}$.

4. At moderate (H^+) and (H_3AsO_4), the rate of reaction is significantly higher than computed from the sum of the (fourth order) k_1 and k_2 terms. These deviations can be accounted for by adding to the rate law two more terms (fifth order), namely, $k_3(ClO_3^-)(Br^-)(H^+)^2(H_3AsO_4)$ and $k_4(ClO_3^-)(Br^-)(H^+)(H_3AsO_4)^2$, where $k_3 = 4.0 \times 10^{-3}$ and $k_4 = 3.0 \times 10^{-3}$.

5. The values of the rate constants listed above appertain to high ionic strengths. The numerical values of the constants do not vary significantly for ionic strengths in the neighborhood of 0.8.

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[CONTRIBUTION FROM THE METCALF RESEARCH LABORATORY OF BROWN UNIVERSITY]

Properties of Electrolytic Solutions. XXXIV. Conductance of Some Long Chain Electrolytes in Methanol–Water Mixtures at 25°[1]

BY E. CHARLES EVERS[2] AND CHARLES A. KRAUS

I. Introduction

The present paper is the first of a series of articles reporting the results of investigations of the conductance and some other properties of long chain electrolytes in aqueous solution, as well as in mixtures of water and methanol and other solvents. Specifically, in the present investigation, conductance measurements were carried out with mixtures of methanol and water, as well as with the pure solvents, for the purpose of determining how the form of the conductance function changes on going from an aqueous solution, which exhibits the characteristic breakpoint phenomenon, to a solution in a non-aqueous solvent in which no anomalies appear.[3]

During the course of the present investigation, Ward[3] reported the results of studies on the conductance of sodium dodecylsulfate in ethanol–water mixtures. More recently, Ralston and Hoerr[3] have examined the conductance of dodecylammonium chloride in the same solvent mixtures. Our results with *n*-hexadecylpyridonium bromide and *n*-octadecyltrimethylammonium nitrate in methanol–water mixtures are similar to those of Ralston and Hoerr. However, we have found that with *n*-octadecylpyridonium chloride, a maximum occurs in the Λ–$\sqrt{C}$ curves in certain mixtures of methanol and water at concentrations where a breakpoint might normally be expected. Since none of the other salts yielded a maximum, the result with the chloride is highly significant in that it indicates the importance of the gegenion in determining the state of the solution, a factor which has not been stressed in previous discussions of solutions of long chain electrolytes. In this connection, it may be noted that recent investigations in this Laboratory have disclosed that with certain combinations of long chain ions and inorganic gegenions, for example, *n*-octadecylpyridonium iodate, a maximum occurs in the conductance curve for solutions in pure water.[4] Recently, Ralston, Eggenberger and Du Brow[5] have found maxima for aqueous solutions of quaternary ammonium chlorides having two long chain alkyl groups in the cation.

II. Experimental

A. Apparatus and Procedure.—Mixed solvents were made up by the weight method and their methanol content is reported in weight per cent. of methanol. In making

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(3) Ward, *J. Chem. Soc.*, I, 522 (1939); *Proc. Roy. Soc.* (London), **176A**, 512 (1940); Ralston and Hoerr, THIS JOURNAL, **68**, 2460 (1946); Thompson and Kraus, *ibid.*, **69**, 1016 (1946); Weaver and Kraus, *ibid.*, **70**, 1707 (1948).

(4) Brown, Grieger, Evers and Kraus, *ibid.*, **69**, 1835 (1947); G. L. Brown, Thesis, Brown University, 1947.

(5) Ralston, Eggenberger and Du Brow, *ibid.*, **70**, 977 (1948).