[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, HEBREW UNIVERSITY]

The Reaction between Ethyl Alcohol and Bromine[1]

BY L. FARKAS, B. PERLMUTTER AND O. SCHÄCHTER

The present paper deals with the mechanism of the reaction between ethyl alcohol and bromine. The starting point was the work of Bugarszky[2] whose main results are: (1) When 76% alcohol (by weight) and bromine in a molar ratio of two to one react at 25°, ethyl acetate and hydrobromic acid are the sole reaction products. (2) The reaction between alcohol of the above concentration and bromine at a concentration not exceeding 0.1 *N* is of the first order with respect to free bromine. The tribromide ion formed during the reaction does not react with alcohol.

By measuring the rate of the reaction under suitable conditions and by appropriate mathematical analysis of the results, Bugarszky determined the dissociation constant of tribromide into bromine and bromide, *K*, and the rate constant for the oxidation of alcohol by free bromine, *k*. (3) In dilute alcohol, 1–4% by weight, two consecutive reactions take place, *viz.*

$$CH_3CH_2OH + Br_2 \xrightarrow{k_I} CH_3CHO + 2HBr \quad (I)$$

$$CH_3CHO + Br_2 + H_2O \xrightarrow{k_{II}} CH_3COOH + 2HBr \quad (II)$$

As the oxidation proceeds, the rate of (II) increases in comparison with that of (I). In the limit, the two reactions proceed at equal rates, the concentration of aldehyde becomes stationary and equal to the alcohol concentration multiplied by the ratio of k_I/k_{II}. At this stage the rate of decrease of bromine is twice as fast as in the absence of aldehyde.

Experimental

All the experiments were carried out at 25 ± 0.1° in a solution of 41% alcohol (by weight). Accurately weighed quantities of bromine (analytical grade) were sealed in thin-walled ampoules which were broken in the reaction vessel. The initial concentration of bromine varied from 0.005 to 0.6 *N*.

The following analytical methods were used: (a) titration with thiosulfate in the presence of potassium iodide for bromine plus tribromide; (b) Volhard's method for hydrobromic acid; (c) the bisulfite method for acetaldehyde; (d) titration with 0.1 *N* sodium hydroxide, with phenolphthalein as indicator, for acetic acid; (e) determination of the saponification number for ethyl acetate.[3]

All the solutions used were standardized with respect to bromine.[4]

Results

1. The Reaction Products.—The reaction products obtained at varying initial molarities of bromine were determined. The bromine was always quantitatively reduced to hydrobromic acid, and no bromination took place. The concentrations of ethyl acetate, acetic acid and acetaldehyde at the end of the reaction are given in the second and third column of Table I.

TABLE I

DEPENDENCE OF THE OXIDATION PRODUCTS OF ALCOHOL ON THE INITIAL BROMINE CONCENTRATION

Initial concentration of bromine (millimole·l.$^{-1}$)	Ethyl acetate plus acet. acid (millimole·l.$^{-1}$)	Acetaldehyde (millimole·l.$^{-1}$)	Acetaldehyde detrm. from Fig. 2[a] (millimole·l.$^{-1}$)
4.1	0.0	4.1	4.1
5.5	0.0	5.5	5.5
9.9	1.0	8.0	7.9
33.2	7.6	17.9	17.8
67.5	21.1	24.7	24.3
85.5	28.8	26.8	26.4
108.5	...	28.7	28.4
200.0	84.2	31.3	31.3
243.5	105.0	32.1	32.0
327.5	...	32.2	32.2

[a] *Cf.* section 4.

2. Kinetics of the Reaction.—According to Bugarszky's results, the rate equation can be written as

$$-\,dx/dt = ky \qquad (1)$$

where *x* is the molarity of bromine plus tribromide, as determined by titration, *y* the molarity of *free* bromine, and *k* the rate constant in 41% alcohol (the concentration of alcohol being considered constant throughout the experiment).

For the evaluation of *y*, a knowledge of *K*, the dissociation constant of tribromide, is essential. Following Bugarszky's method for the evaluation of *k* and *K*, we made use of the following facts: (a) When the initial bromine concentration is very small, the tribromide formation is negligible and we have $y = x$; thus *k* can be determined in the usual way. (b) When bromide is added initially in a high concentration, *b*, we may write: $y = x \times K/b$, and

$$-\,dx/dt = kK \times x/b \qquad (2)$$

whence *K* can be determined when *k* is known. In intermediate cases we have

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[1] Abstracted from a thesis by B. Perlmutter, presented to the Senate of the Hebrew University, in partial fulfillment of the requirements for the Ph.D. degree, November, 1947.

[2] Bugarszky, *Z. physik. Chem.*, **38**, 561 (1901); **71**, 705 (1910).

[3] When samples of the alcoholic solution were discharged normally from pipets, erratic titration results were obtained. Therefore, after the solutions had run out, the pipets were always rinsed twice with distilled water. The pipets were standardized for this procedure.

[4] An auxiliary solution of hydrobromic acid was standardized by titrating with thiosulfate the amount of iodine liberated by the acid from an excess of potassium iodide and iodate, and used to standardize the silver nitrate and sodium hydroxide solutions.

$$y = {}^1/_2\{[(2a - 3x + b + K)^2 + 4Kx]^{1/2} - (2a - 3x + b + K)\} \quad (3)$$

a representing the initial molarity of the total bromine. The above limiting expressions for y can be derived by expanding the square root in equation (3) and it is seen that

$$y = x \times K/b \text{ when } b \gg (2a - 3x) \quad (4)$$

and

$$4Kx/(b + K)^2 \ll 1 \quad (5)$$

$$y = x \text{ when } 2(2a - x)/K \ll 1 \quad (6)$$

For practical purposes it is sufficient

$$\text{when } 2a - x/K \leq 0.05 \quad (7)$$

Furthermore, obviously $y \approx x$ at the beginning of the reaction (as long as $(a - x) \ll x$).

Expressions (4), (5) and (6) serve as the basis for choosing the appropriate conditions for the determination of k and K, factors which had not been considered in Bugarszky's treatment.

A preliminary value for k was determined by plotting log ($\zeta \times 10^4$) (ζ designating the normality of bromine) against the time in minutes for various initial bromine concentrations from 2.0 to 8 millimoles per liter as shown in Fig. 1 (top two curves). From the highest value of d log ζ /dt we can infer: $k \geq 0.092$ min.$^{-1}$.

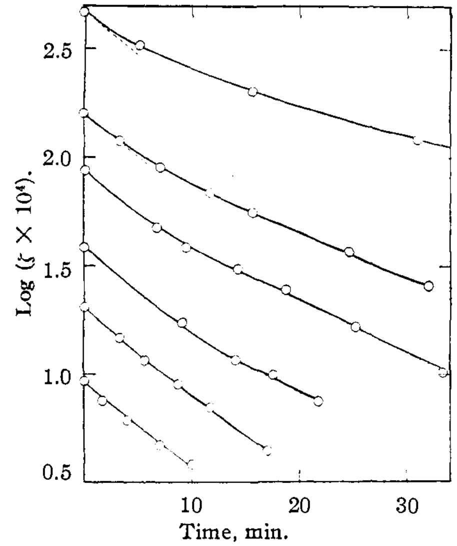

Fig. 1.—Rate of decrease of bromine titer, ζ(log($\zeta \times 10^4$) as a function of time in minutes.).

Experiments were then carried out in the presence of bromide at concentrations 10–100 times the initial molarity of bromine. From the results the value kK was computed by means of equation (2) and was found to equal 0.99 ± 0.03 millimole·min.$^{-1}$ liter^{-1}. Thus, $K \leq 0.0108$ mole·l.$^{-1}$, and from expression (7) it can be seen that $x = y$ at an initial bromine concentration low enough so that $(2a - x) \leq 0.55$ millimole·l.$^{-1}$.

Under these conditions it was found that $k = 0.094$ min.$^{-1}$ (*cf.* Fig. 1 curve VI). Hence

$$K = 0.0106 \text{ mole·l.}^{-1}.$$

This value fits well between the values of K = 0.059 mole·l.$^{-1}$ in aqueous solution[5] and K = 0.0044 mole·l.$^{-1}$ in 76% alcohol.[2] For a final evaluation of k, the experiments at higher bromine concentrations were also taken into account, since the determination of very low bromine concentrations in alcoholic solution is not very accurate. For this purpose, Bugarszky's integrated form of equation (1) was transformed into

$$k = 1/(t - t_0)\{1/3 \ln 100\, y_0 - (2a/K + 2/3)[\ln (1 + w_0) - w_0/(1 + w_0)] - 1/3 \ln 100\, y + (2a/K + 2/3)[\ln(1 + w) - w/(1 + w)]\}$$

where $w_0 = K/3\, y_0$ and $w = K/3\, y$ with y defined by equation (3).

The average value for the experiments shown in Fig. 1 and several others carried out in the same range of concentrations was

$$k = 0.0942 \pm 0.0006 \text{ min.}^{-1}.^{6}$$

3. The Influence of the *p*H on the Reaction Rate and the Rôle of Hypobromous Acid.—The fact that k is constant during the experiment and is the same for various initial bromine concentrations, shows that the hydrogen ions which are formed during the process have no influence on the rate of reaction. That the rate is independent of the presence of strong acids was confirmed by direct experiments carried out in presence of dilute nitric and sulfuric acid. Thus, the assumption that in strongly acid solution hypobromous acid is involved in a rate-determining step seems to be ruled out. Moreover, it was shown that concentrations and temperatures being equal, the reaction with pure hypobromous acid proceeds at a rate commensurate with that of the oxidation by bromine. (In order to prevent formation of elementary bromine, silver nitrate was added.)[7]

On the other hand, in solutions above *p*H 3, the rate was found to increase markedly with increasing *p*H. We shall deal with this reaction in a separate paper.

4. The Intermediate Formation of Aldehyde.—The differential equations which govern the rate of the two consecutive reactions I and II are

$$\mathrm{d[CH_3CHO]}/\mathrm{d}t = y(k_\mathrm{I} - k_\mathrm{II}[\mathrm{CH_3CHO}]_t) \quad (8)$$

and

$$-\,\mathrm{d}x/\mathrm{d}t = y(k_\mathrm{I} + k_\mathrm{II}[\mathrm{CH_3CHO}]_t) \quad (9)$$

This system was solved by Bugarszky[2]; the result, as given by this author, is extremely unwieldy and the only conclusions which he drew from it are quoted in the last paragraph of our intro-

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[5] Griffith, McKeown and Winn, *Trans. Faraday Soc.*, **28**, 101 (1932).

[6] According to Bugarszky, k = 0.105 min.$^{-1}$ in. 76% alcohol.

[7] Further experiments on this reaction are in progress in our Laboratories. At concentrations of hypobromous acid not exceeding 0.04 *M*, the reaction products are bromide ion and acetaldehyde. The kinetic behavior of the reaction is complex and silver ion acts as a catalyst.

duction. These, however, can be inferred directly from the rate equations (8) and (9).[8]

By the following method the systems I and II can be treated conveniently. Solving the equation

$$-\,\mathrm{d}x/\mathrm{d}[\mathrm{CH_3CHO}] = (k_{\mathrm{I}} + k_{\mathrm{II}}[\mathrm{CH_3CHO}]_t)/(k_{\mathrm{I}} - k_{\mathrm{II}}\,\mathrm{CH_3CHO}_t) \quad (10)$$

and introducing $p = (a - x)k_{\mathrm{II}}/k_{\mathrm{I}}$ and $q = [\mathrm{CH_3.CHO}]_t k_{\mathrm{II}}/k_{\mathrm{I}} = [\mathrm{CH_3CHO}]_t/[\mathrm{CH_3CHO}]_s$ (the subscript s referring to the stationary concentration), we obtain $p = -q - 2 \ln (1 - q)$, an expression valid for any system of the type I and II, and independent of the numerical value of the constants involved.

For the present case, Table I shows that $k_{\mathrm{I}}/k_{\mathrm{II}} = [\mathrm{CH_3CHO}]_s = 32.3$ millimole·l.$^{-1}$.[9]

From an inspection of a plot of p against q (Fig. 2) the following important conclusions can be drawn:

For $p \geqslant 8$, ($a \geqslant 0.25$ M) the final concentration of aldehyde is practically equal to $[\mathrm{CH_3CHO}]_s$. This is in accordance with Table I.

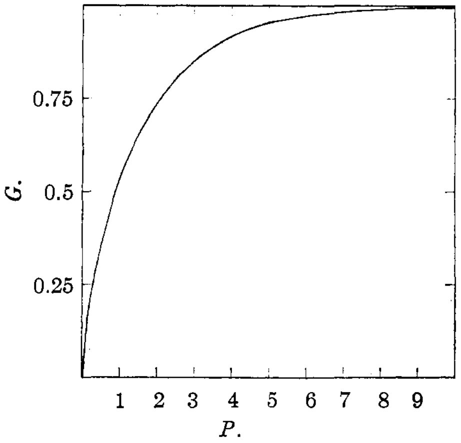

Fig. 2.—The concentration of aldehyde as a function of the amount of bromine consumed.

On the other hand, when $p \leqslant 0.25$ (($a - x) \leqslant 8$ millimole·l.$^{-1}$) acetaldehyde is the sole product. Thus, the value of k cited above is now seen to be identical with k_{I}. Incidentally, k_{II}, the rate constant for the oxidation of aldehyde in the presence of 41% alcohol, can now be calculated: $k_{\mathrm{II}} = 2.9$ l.·mole^{-1}·min.$^{-1}$.

Furthermore, the final concentration of aldehyde for any initial concentration of bromine can be evaluated. The calculated values are given in the last column of Table I and are seen to correspond with the experimental ones (column 3).

When aldehyde is added initially at a concentration [CH$_3$CHO], we have approximately $k = k_{\mathrm{I}} + k_{\mathrm{II}}\,[\mathrm{CH_3CHO}] = k_{\mathrm{I}}(1 + q)$. In Fig. 3, k has been plotted against [CH$_3$CHO] by drawing a straight line through the points corresponding to [CH$_3$CHO] = 0 and $[\mathrm{CH_3CHO}]_s$. The experimental values of k coincide with this line within the limit of experimental error.

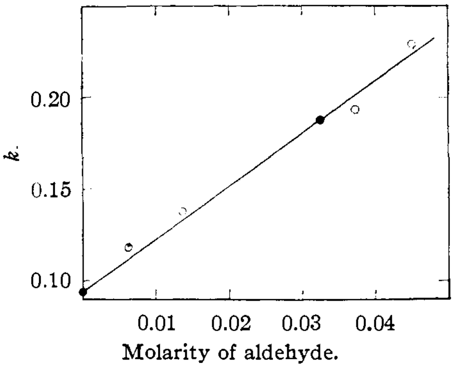

Fig. 3.—The rate constant, k, as a function of aldehyde concentration: ●, calculated from the rate constant in the absence of aldehyde; ○, experimental.

Lastly, the value of $k_{\mathrm{I}} + k_{\mathrm{II}}[\mathrm{CH_3CHO}]$ can be calculated for any amount of consumed oxidizing agent and compared with the experimental value of k, obtained at initial bromine concentrations above 8 millimole·l.$^{-1}$.

In Fig. 4, k is plotted against $a - x$. The points corresponding to several experiments follow the course of the theoretical line (full curve).

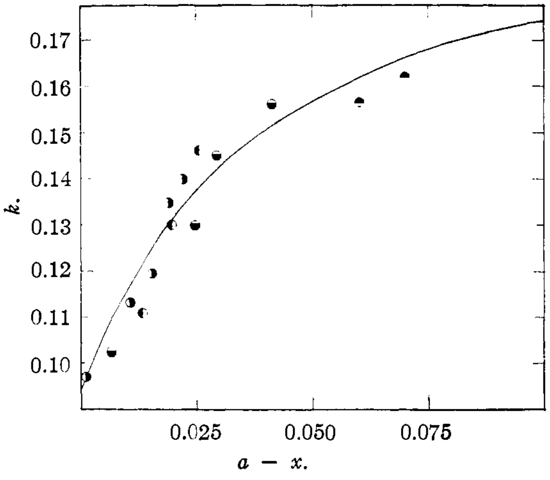

Fig. 4.—The rate constant, k, as a function of the decrease of bromine titer. $a - x$, for four independent experiments, indicated by ◓, ◒, ◐ and ◑, respectively.

In 76% alcohol, too, acetaldehyde is formed as an intermediate—a fact apparently overlooked by Burgarszky. The stationary concentration is similar to that in 41% alcohol, and at high initial bromine concentrations, k was found to increase during the reaction.

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[8] The second term in (8) is zero at $t = 0$ and increases until it becomes equal to k_{I} when $\mathrm{d}[\mathrm{CH_3CHO}]/\mathrm{d}t = 0$, and $[\mathrm{CH_3CHO}]_s = k_{\mathrm{I}}/k_{\mathrm{II}}$. Inserting $[\mathrm{CH_3CHO}]_s$ into (9), it is seen that $-\mathrm{d}y/\mathrm{d}t = 2k_{\mathrm{I}}x$.

[9] The ratio $k_{\mathrm{I}}/k_{\mathrm{II}}$ is not dimensionless, since k_{I} contains the concentration of alcohol!

5. The Oxidation of Acetaldehyde.—When bromate is added to supply bromine, the kinetics of reactions I and II remain unchanged[10] and the acidity is so low that catalysis of the reaction

$$C_2H_5OH + CH_3COOH = CH_3COOC_2H_5 + H_2O \quad (III)$$

is negligible. Bromate was therefore added to find out whether acetic acid and ethyl acetate were both primary oxidation products, which seemed likely because both ester and acid are always found near the beginning of the reaction. The results of an experiment in presence of bromate are given in Table II.

TABLE II

THE OXIDATION PRODUCTS IN PRESENCE OF BROMATE

Time, min.	Amount of oxidizing agent consumed[a]	Molarity of aldehyde[b]	Ethyl acetate plus acetic acid[c]	Acetic acid[d]	$\frac{CH_3COOC_2H_5}{CH_3COOH}$
24	0.071	0.025	0.023	0.008	1.9
95	.294	.032	.131	.040	2.3
217	.412	.032	.190	.059	2.2
317	.611	.032	.289	.079	2.6

[a] Expressed in moles of bromine per liter. [b] From Fig. 2. [c] Calculated from columns 2 and 3. [d] Titrated.

Since the ratios in the last column of this table differ considerably from 0.87, the equilibrium value for 41% alcohol established in a blank experiment, the conclusion is that ester and acid are produced simultaneously by oxidation. Similarly, when methyl alcohol was present in the reaction mixture under conditions when the rate of oxidation of methanol by bromine, as well as the rates of esterification and *trans*esterification are negligibly small, methyl acetate was found to be one of the reaction products (the analysis being carried out by efficient fractionation).

Discussion

Although the above results greatly restrict the reaction mechanisms, a number of schemes seem to be possible.

(a) The first step, which must be the rate-determining one, can be assumed to be an alcoholysis of bromine

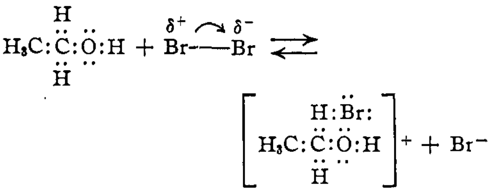
$$C_2H_5OH + Br_2 \rightleftharpoons C_2H_5OBr + HBr \quad (IV)$$

In a second step, the ethyl hypobromite breaks up according to

$$C_2H_5OBr = C_2H_4O + HBr \quad (V)$$

This mechanism seems to be supported by the facts that alkyl hypochlorites exist and break up into aldehyde and hydrochloric acid[11] and ethyl hypochlorite is claimed to be an intermediate in the formation of chloral from ethanol and chlorine.[12]

The formation of ethyl hypobromite may be envisaged as proceeding through an intermediate positive complex (the conjugate acid of ethyl hypobromite) according to



$$H_3C{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{\underset{H}{\overset{H}{C}}}}{:}\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}{:}H + \overset{\delta^+}{Br}\!\frown\!\!-\!\!\overset{\delta^-}{Br} \rightleftharpoons \left[\begin{array}{c} H{:}\overset{\cdot\cdot}{Br}{:} \\ H_3C{:}\overset{\cdot\cdot}{C}{:}\overset{\cdot\cdot}{O}{:}H \\ \overset{\cdot\cdot}{H} \end{array}\right]^+ + Br^- \quad (VI)$$

which is similar to the first step of the mechanism for the addition of bromine to double bonds. The inactivity of the tribromide ion may be due to the fact that it cannot attack the negative center at the hydroxyl group.

Incidentally, this complex is equivalent to a solvated positive bromine ion. Although the equilibrium concentration of Br^+ is extremely small[13] under the present experimental conditions, this ion may well appear as an unstable intermediate, as suggested by Hinshelwood[14] in the hydrolysis of bromine.

(b) Alternatively, the oxidation of ethanol to acetaldehyde may take place according to

$$CH_3CH_2OH + Br_2 \longrightarrow [CH_3CHOH]^+ + Br_2H^- \quad (VII)$$

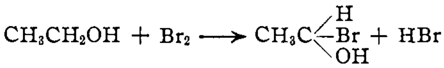
$$[CH_3CHOH]^+ = CH_3CHO + H^+ \quad (VIII)$$

$$Br_2H^- = H^+ + 2Br^- \quad (IX)$$

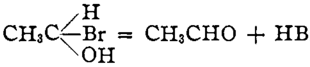
(VII) being the rate-determining step.

The special character of this mechanism is the single-step oxidation of alcohol to form aldehyde by the simultaneous loss of an electron and a hydrogen atom, whereas in general bivalent oxidation (and reduction) reactions proceed in univalent steps. Reactions of this type have been proposed for Friedel–Crafts and inter- and intra-molecular Cannizzaro reactions.[15]

(c) A third reaction scheme also in accordance with the experimental facts is



$$CH_3CH_2OH + Br_2 \longrightarrow CH_3C\begin{cases} H \\ Br \\ OH \end{cases} + HBr \quad (X)$$



$$CH_3C\begin{cases} H \\ Br \\ OH \end{cases} = CH_3CHO + HBr \quad (XI)$$

Here again the first step must be the rate-determining one and the α-bromoethanol appears as an intermediate instead of the carbonium ion of equation (VI). It is, however, difficult to find a process analogous to (X) in which hydrogen is replaced by bromine in a reaction of the second order and at room temperature. Thus, scheme (c) seems the least probable of the three.

If we assume that acetaldehyde reacts in its hydrated form its oxidation can be envisaged to proceed in analogy to any of the above mechanisms.

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(10) Farkas, Perlmutter and Schächter, THIS JOURNAL, **71**, 2833 (1949).

(11) Chattaway and Backeberg, *J. Chem. Soc.*, **123**, 3000 (1923).

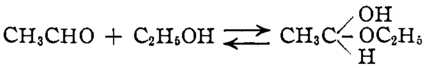
(12) Chattaway and Backeberg, *ibid.*, **125**, 1097 (1924).

(13) Bartlett and Tarbell, THIS JOURNAL, **58**, 466 (1936).

(14) Presidential Address, *J. Chem. Soc.*, 694 (1947).

(15) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., New York, N. Y., 1940, pp. 309, 388.

The simultaneous formation of ethyl acetate and acetic acid can be explained on the assumption that hemiacetal is formed according to the equilibrium reaction



$$CH_3CHO + C_2H_5OH \rightleftarrows CH_3C\begin{cases}OH\\OC_2H_5\\H\end{cases} \quad (XII)$$

and reacts with bromine in the same way as does hydrated aldehyde. The formation of hemiacetal in mixtures of alcohol and aldehyde was ascertained by light absorption and refractive index measurements, and these compounds have been suggested as intermediates in the oxidation of higher alcohols.[16]

This assumption would also explain the fact that k_{II}, the rate constant of the aldehyde oxidation in alcoholic solution, differs from that in aqueous solution, k_a.[17]

The formation of methyl acetate can be readily explained on the basis of a similar assumption.

The difference between the various reaction schemes lies in the fact that in (a) the place of attack for the oxidizing agent is the hydrogen of the hydroxyl group, whereas in (b) and (c) it is one of the α-hydrogens.

Summary

The reaction of bromine with aqueous alcohol was investigated at 25° in a 41% solution. Previous results that the reaction consists in an oxidation of alcohol and is of the first order with respect to free bromine, have been confirmed.

The rate constant of the reaction, and the dissociation constant of tribromide in 41% alcohol, have been measured. The reaction takes place in two consecutive steps, the first being the oxidation of alcohol to form aldehyde, and the second the oxidation of aldehyde. A method for the treatment of the kinetics of these consecutive reactions has been developed.

It has been shown that the oxidation of aldehyde leads to the simultaneous formation of ethyl acetate and acetic acid.

Various mechanisms compatible with the kinetics of the reaction are discussed.

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[16] *Cf.* Leo Schulz, "Ann. Rept. Essent. Oils, Synthetic Perfumes, etc.," Schimmel & Co., 1938; p. 119, where previous literature is quoted.

[17] k_a = 1.2 mole·min.$^{-1}$ (Bugarszky *Z. physik. Chem.*, **48**, 61 (1904)). Assuming (according to Table II) that ethyl acetate and acetic acid are formed in a ratio of $k_h h/k_a(f - h) = 2.3$ (where h is the concentration of hemiacetal, f the concentration of aldehyde plus hemiacetal and k_h the rate constant of the oxidation of hemiacetal), we obtain k_h = 7.5 mole^{-1}·min.$^{-1}$ for the rate constant of the oxidation of hemiacetal, which seems to be a reasonable figure.

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY, HEBREW UNIVERSITY]

The Oxidation of Ethyl Alcohol in the Presence of Bromate and Bromine

BY L. FARKAS, B. PERLMUTTER AND O. SCHÄCHTER

The oxidation of ethyl alcohol by bromine[1] takes place mainly according to the stoichiometric equation.

$$2CH_3CH_2OH + 2Br_2 = CH_3COOC_2H_5 + 4H^+ + 4Br^- \quad (I)$$

In presence of bromate the bromide ion formed is reoxidized according to

$$BrO_3^- + 6H^+ + 5Br^- = 3Br_2 + 3H_2O \quad (II)$$

and the bromine re-enters into reaction (I).

In the present paper, the kinetics of the above reactions is dealt with.

Experimental

All the experiments were carried out at 25° in a solution containing 38.6 g. of alcohol per 100 ml. (corresponding to 41.2% by weight).

The experimental procedure and the substances and standard solutions employed have been described in a previous paper.[1]

Since the arsenite method for the determination of the sum of bromine and tribromide is not suitable for alcoholic solutions, the iodine liberated immediately after a sample was pipetted into a solution of potassium iodide, was titrated with thiosulfate. This method was tested with weakly acid solutions of bromine and bromate and found to be satisfactory. The normality of bromate was estimated in the usual way.

The pH was measured with an accuracy of ± 0.02 by means of a glass electrode immersed in a closed vessel.

Results

I. The Products of the Reaction.—In a blank test the reaction between bromate and alcohol—in the absence of bromine—was shown to proceed at a negligibly small rate in moderately acid solutions (pH ≥ 2.2).

The reaction products in the presence of bromate are identical with those found in the reaction with bromine alone, *viz.*, bromide ion, acetaldehyde, ethyl acetate and acetic acid. No bromination takes place. In Table I, $[CH_3CHO]_\infty$ for various initial concentrations of bromine and bromate is given. It is identical with the amount formed in the absence of bromate at a normality of bromine equal to that given in column 3.

Since the concentration of aldehyde is determined by k_I/k_{II}, the ratio of the rate constants

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[1] Farkas, Perlmutter and Schächter, THIS JOURNAL, **71**, 2829 (1949).