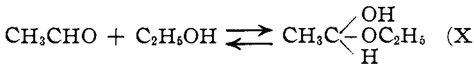
The simultaneous formation of ethyl acetate and acetic acid can be explained on the assumption that hemiacetal is formed according to the equilibrium reaction



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

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 *p*H 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 ($pH \geq 2.2$).

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).

Table I

The Concentration of Acetaldehyde in the Reaction Products for Varying Initial Concentrations of the Oxidizing Agents

Initial normality			
Bromine	Bromate	Total oxidizing agent	$[CH_3CHO]_\infty$ mole liter^{-1}
0.007	0.0898	0.0905	0.020
.108	.196	.304	.030
.129	.196	.325	.031
.055	.347	.402	.031

of the oxidation of 41% alcohol to that of the oxidation of aldehyde,[1] it follows that this ratio is independent of the presence of bromate.

II. Investigation of the Kinetics of the Reaction.—Assuming that the rate equation is the same as that of the oxidation of alcohol by bromine alone, we have

$$-d\zeta/dt = 2ky = 2y(k_I + k_{II}[CH_3CHO]_t) \quad (1)$$

ζ denoting the normality of the total oxidizing agent present (bromine + tribromide + bromate) and y the concentration of free bromine in mole l.$^{-1}$.

In Fig. 1, T, the total bromine titer (bromine + tribromide) is plotted against $\zeta_0 - \zeta$. The fact that the titer decreases during the reaction shows that the hydrobromic acid formed generates somewhat less than the equivalent amount of bromine. The hydrogen ion concentration is: $[H^+]_t = T_0 - T_t$, T_0 being the initial bromine titer.

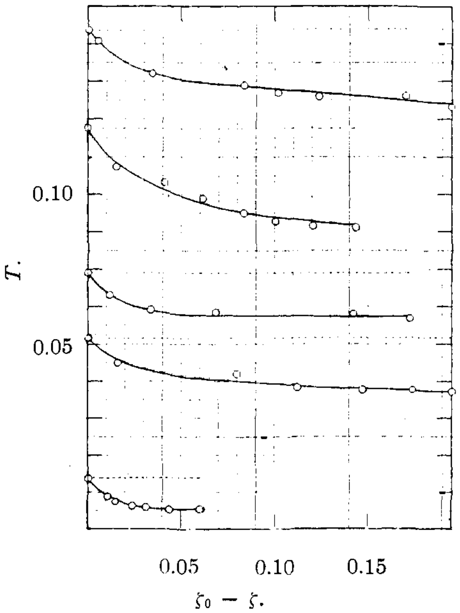

Fig. 1.—The bromide titer, T, as a function of the decrease of the normality of total oxidizing agent, $\zeta_0 - \zeta$, for five different initial bromine titers. The uppermost curve represents an experiment carried out in the presence of potassium bromide.

The validity of the above relations is shown by Fig. 2.

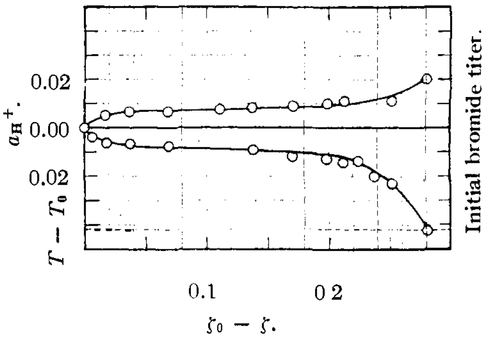

Fig. 2.—The hydrogen ion activity, a_{H^+}, and the change in bromine titer, $T - T_0$, as functions of the decrease of the normality of total oxidizing agent, $\zeta_0 - \zeta$. The discrepancy between a_{H^+} and $T_0 - T$, which appears toward the end of the reaction cannot be explained. It is not due to the formation of organic bromide.

From free energy data, the equilibrium constant of reaction II in aqueous solution at 25° is 6×10^{33}. Under the conditions of our experiments, this would correspond to a pH of 4.2 – 4.9. The pH actually measured is about 2. Thus, unless the equilibrium is fundamentally changed by the presence of alcohol, reaction II does not reach its equilibrium position, and the amount of bromine liberated is determined by the relative rates of reactions I and II.

Table II

Rate of Oxidation of Ethanol

Time, min.	Normality of total oxidizing agent	Bromine titer, mole/l.	Free bromine, mole/l.	k, min.^{1}	$k_{theor.}$
			A		
0.0	0.398	0.0515	0.0515		0.094
12.4	.382	.0450	.0349		
32.5	.318	.0427	.0217	0.112	0.132
47.1	.286	.0383	.0168	.114	.155
64.5	.251	.0382	.0134	.133	.163
78.5	.225	.0382	.0109	.153	.169
103.5	.180	.0375	.0089	.182	.174
130.0	.141	.0375	.0079	.175	.179
151.5	.111	.0374	.0072	.168	.181
173.5	.087	.0373	.0068	.162	.182
185.0	.073	.0343	.0057	.179	.183
195.0	.064	.0340	.0055	.198	.184
			B		
0.0	0.304	0.108	0.108		0.094
1.5	.290	.098	.080	0.099	.102
4.8	.266	.094	.065	.103	.120
7.5	.249	.090	.055	.105	.137
12.5	.221	.085	.040	.120	.145
15.7	.204	.083	.035	.142	.152
19.8	.184	.082	.031	.147	.157
24.6	.161	.082	.021	.162	.164

The concentration of free bromine can be shown to be equal to

$$y = 1/2\{\sqrt{[1/6(\zeta_0 - \zeta) + 5/6\,(T_0 - T) - T/2 + K + b]^2 + 2KT} - [1/6\,(\zeta_0 - \zeta) + 5/6\,(T_0 - T) - T/2 + K + b]\} \quad (2)$$

K being the dissociation constant of tribromide and b the initial normality of bromide. This value of y may be inserted into the rate equation (1), but it is impossible to carry out the integration without a knowledge of the functional relation between any two of the three variables $(T_0 - T)$, $(\zeta_0 - \zeta)$ and t.

If we combine the rate equation for the liberation of bromine from bromate and bromide[2] with equation (1), we obtain

$$\mathrm{d}[\mathrm{H}^+]/\mathrm{d}t = -\mathrm{d}T/\mathrm{d}t = 2ky - 2k_4[\mathrm{Br}^-][\mathrm{H}^+]^2[\mathrm{BrO}_3^-] \quad (3)$$

where k_4 is the rate constant of the forward reaction II in alcoholic solution.

Figures 1 and 2 show that T and $[\mathrm{H}^+]$ behave in qualitative accordance with this equation, both changing rapidly in the beginning, when the concentration of hydrogen ion is very low, and tending to an almost constant value when the two terms on the right hand become commensurate.

The quantitative estimation of $\mathrm{d}T/\mathrm{d}t$, however, cannot be carried out since k_4 has not been determined, and in any case would be rather involved. Therefore, the rate constant was evaluated from the expression

$$-\frac{\Delta\zeta}{\Delta t} \times \frac{1}{2y} = k \quad (1a)$$

using the values of y calculated by equation (2).

Several experiments were carried out at a bromine titer ranging from 0.013 to 0.13 and a normality of total oxidizing agent of 0.3 to 0.4. Experiments with bromide added initially were also carried out. The results of two typical experiments are shown in Tables II, A and B.

The average value of k as defined by eqn. (1) between each two values of ζ has been estimated by the method indicated in our previous communication[1] and is shown as $k_{\mathrm{theor.}}$ in the last column of Tables II, A and B, using $k_{\mathrm{I}} = 0.094$. The deviations between k and $k_{\mathrm{theor.}}$ are not larger than the experimental error and the inaccuracy introduced by using the interpolations of equation (1a).

It can be concluded that the oxidation of alcohol by a mixture of bromine and bromate proceeds according to the same rate equation as the oxidation with bromine alone.

Summary

The oxidation of alcohol by a mixture of bromine and bromate has been investigated.

The ratio of aldehyde to acetate in the reaction product is identical with the ratio found in the case of the oxidation by bromine alone.

The reaction in the presence of bromate proceeds according to the same rate equation as the reaction with bromine alone. The two reactions are fundamentally identical, the bromate merely supplying the free bromine necessary for the reaction to proceed.

The rate of formation of hydrobromic acid in the course of the oxidation of alcohol is faster than, but commensurate with, the rate of liberation of bromine from bromate and hydrobromic acid. Thus, the concentration of hydrobromic acid increases, and the bromine titer decreases during the reaction.

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[2] Sclar and Riesch, THIS JOURNAL, **57**, 667 (1936) (*cf.* also literature quoted in that paper.)

[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, METCALF RESEARCH LABORATORY, BROWN UNIVERSITY]

The High Field Conductance of Some Paraffin Chain Electrolytes[1]

BY WILLIS A. ADCOCK[2] AND ROBERT H. COLE

1. Introduction

To complement the researches which have been carried out in this Laboratory on colloidal electrolytes, an apparatus has been constructed to measure the high field conductance of these electrolytes. The apparatus is described below and preliminary data are given for the high field conductance of hexadecylpyridonium iodate and octadecylpyridonium iodate.

The high field conductance of hexadecylpyridonium chloride was first reported by Malsch and Hartley.[3] These investigators employed the barretter bridge method developed by Wien.[4]

In the barretter bridge method, a damped sine wave voltage pulse is applied to a bridge network and the currents which pass in each side of the bridge are averaged by means of the barretter elements. This method measures the average conductance during the duration of the pulse. Other investigators[5,6] have utilized oscilloscopic recorders to investigate the effect of

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[1] This paper is based on a portion of a thesis presented by Willis A. Adcock in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Brown University.

[2] Present address: Stanolind Oil and Gas Co., Tulsa, Okla.

[3] J. Malsch and G. S. Hartley, *Z. physik. Chem.*, **A170**, 321 (1934).

[4] H. C. Eckstrom and C. Schmelzer, *Chem. Rev.*, **24**, 367 (1939).

[5] W. Fuchs, *Ann. Physik*, **12**, 306 (1932).

[6] W. Hüter, *ibid.*, **24**, 253 (1935).