

calculated values of  $\Delta H$ . The  $\Delta H$  obtained at this wave length is  $-3.9 \pm 0.2$  kcal./mole.

(2) The complex maxima occurs around  $460 \text{ m}\mu$ . Since these bands appear to decrease at the maxima and increase in the wing areas with temperature increase, there should be points on either side of the maxima where  $\epsilon$  does not change with temperature. The constancy of the enthalpy values reported in Table II in the  $430$  to  $450 \text{ m}\mu$  region and the agreement of these enthalpies with that obtained at  $550 \text{ m}\mu$  indicates that any changes in molar absorptivity with temperature in this region are minor. It is also seen that the percentage change in  $\epsilon_C - \epsilon_I$  at  $460 \text{ m}\mu$  is not as great as that at  $520 \text{ m}\mu$ . The enthalpy calculated at  $460 \text{ m}\mu$  assuming no change (Table II) is not as large as that at  $520 \text{ m}\mu$ . This is in part due to the larger value of  $\epsilon_C - \epsilon_I$  at  $460 \text{ m}\mu$ .

The changes noted in both  $\epsilon_C$  and  $\epsilon_I$  with temperature are in accord with reported behavior and changes expected theoretically. Reportedly the band intensity at the maximum decreases, the absorbance in the wing areas increases and the band area remains constant when the temperature is raised. The arguments presented are in agreement with theoretical prediction and explain both the variation in  $\Delta H$  with wave length when spectral changes are ignored and the changing wave length for the isobestic point with temperature increase. The following set of thermodynamic data best describes this system<sup>10</sup>

$$-\Delta F_{298} = 0.79 \pm 0.02 \text{ kcal. mole}^{-1}$$

$$-\Delta H = 4.0 \pm 0.2 \text{ kcal. mole}^{-1}$$

$$-\Delta S = 10.7 \pm 0.7 \text{ e.u.}$$

At  $520 \text{ m}\mu$  and  $25^\circ$  a value of  $686 \pm 16$  is obtained for  $\epsilon_C - \epsilon_I$ .

The structure of the complex was examined by infrared and ultraviolet spectroscopy. The infrared spectrum indicated a shift of the carbonyl stretching vibration in the adduct to lower wave numbers than that in the free amide. This is evidence for oxygen coordination.<sup>11</sup>

When the heat of association or  $\log K$  for the DMB adduct is plotted *versus*  $\sigma^*$  and compared with the plot for a series of aliphatic amides,<sup>12</sup> the DMB value does not fall on the line.

Since the  $\sigma^*$  value employed for these plots is that for a non-conjugated ring, the lack of correlation suggests that the phenyl ring is conjugated with the amide group resulting in a large equilibrium constant and heat of formation for the DMB adduct.

**Acknowledgment.**—The authors would like to thank the Chemistry Branch of the Atomic Energy Commission for their generous support of this research through Contract No. AT (11-1)758.

(10) Error limits are imposed at the 90% confidence level.

(11) C. D. Schmulbach and R. S. Drago, *J. Am. Chem. Soc.*, **82**, 4484 (1960).

(12) R. S. Drago, R. L. Carlson and D. A. Wenz, *ibid.*, **84**, 1106 (1962).

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## The Kinetics of the Oxidation of Ethanol and of Acetaldehyde by Bromine in Aqueous Solution. Influence of pH

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At low and moderate values of pH—at least up to 7.5—the reaction between bromine and acetaldehyde in aqueous solution consists purely in oxidation. The kinetics of the reaction in bromine water show that in the pH range investigated molecular bromine, and *not* hypobromous acid, is the reactive species in the oxidation of acetaldehyde and of ethanol. The reaction rates increase with increasing pH in a way which agrees quantitatively with the assumption that the anions of alcohol and of acetaldehyde (hydrate) are oxidized much more rapidly than the undissociated molecules—in analogy with the oxidation of formic acid and of D-glucose.

### Introduction

The reactions of acetaldehyde<sup>1</sup> and of ethanol<sup>2,3</sup> in bromine water, in the absence of added buffer, consist purely in oxidation. In dilute solution, both reactions are first order with respect to the two reactants.<sup>1,2</sup> In the case of ethanol the situation is somewhat complicated by the presence of two consecutive reactions, the oxidation of ethanol to acetaldehyde, and of acetaldehyde to acetic acid.<sup>2,3</sup> The conditions under which the intermediate, acetaldehyde, reaches a practically constant concentration have been worked out in detail.<sup>3</sup> More recently Kaplan,<sup>4</sup> utilizing the isotope effect, showed that rupture of a C-H linkage is involved in the rate determining step. The suggestion that the hydrogen should be abstracted by the bromine in

the form of a hydride ion<sup>3,4</sup> is supported by a comparison between the kinetic isotope effect in the reaction of bromine water with 2-propan-2-*d*-ol. and with 1-fluoro-2-propan-2-*d*-ol.<sup>5</sup>

In buffer solution it was found<sup>3</sup> that at pH  $\sim 2.6$  the rate started to increase with increasing pH. The pH effect was not investigated in detail and remained without explanation at the time except that it is *not* due to the increase in the relative concentration of hypobromous acid.

A similar behavior in the case of formic acid<sup>6,7</sup> and of D-glucose<sup>8</sup> was quantitatively explained on the assumption that the corresponding anions are oxidized at a much higher specific rate than the molecules

(5) C. G. Swain, R. A. Wiles and R. F. W. Bader, *ibid.*, **83**, 1945 (1961).

(6) D. L. Hammick, W. K. Hutchison and F. R. Snell, *J. Chem. Soc.*, **127**, 2715 (1925).

(7) L. Binoun and B. Perlmutter-Hayman, *Bull. Research Council Israel*, **5**, 52 (1955).

(8) B. Perlmutter-Hayman and A. Persky, *J. Am. Chem. Soc.*, **82**, 276, 3809 (1960).

(1) S. Bugarszky, *Z. physik. Chem.*, **48**, 63 (1904).

(2) S. Bugarszky, *ibid.*, **38**, 561 (1901); **71**, 705 (1910).

(3) L. Farkas, B. Perlmutter and O. Schächter, *J. Am. Chem. Soc.*, **71**, 2829 (1949).

(4) L. Kaplan, *ibid.*, **76**, 4645 (1954); **80**, 2639 (1958).

themselves.<sup>6-8</sup> The results are again not compatible with the suggestion<sup>9</sup> that hypobromous acid is a faster oxidizing agent than bromine. A rapid pre-equilibrium involving an organic hypobromite has recently been suggested in order to explain the observed pH-dependence in the case of glucose.<sup>10</sup> Such an assumption is however quantitatively contradicted by the way the reaction rate depends on bromide concentration.<sup>4,8</sup>

It seemed interesting to find out whether the reaction between bromine water and ethanol is in line with the analogous formic acid and glucose reactions. Since acetaldehyde appears as an intermediate, its oxidation was also investigated.

### Experimental

Most of the procedure has been described before.<sup>8</sup>

Alcohol solutions (10 M) were prepared by accurate weighing of absolute alcohol (Hopkin and Williams) and were checked by measuring the density.

Solutions of acetaldehyde (0.1 M) were similarly prepared, using May and Baker's Laboratory Grade acetaldehyde. The stability of these solutions was checked by carrying out two identical kinetic experiments, one with a freshly prepared solution and one with a solution which had been kept for two months. Within the limit of experimental error, the solutions were found to be stable over that period.

The acetaldehyde in the reaction product was determined by the method described by Stein and Weiss,<sup>11</sup> the above solutions serving for calibration.

The occurrence of substitution was determined by titrating the bromide formed and comparing the result with that of an experiment carried out with *exactly* the same initial bromine concentration, but at low pH where we know substitution to be absent. (This latter point was checked by comparing the initial bromine concentration and the final bromide concentration.) In order not to give the reaction products time to decompose,<sup>12</sup> the analysis was carried out not more than one or 2 hr. after the beginning of the reaction, the unreacted bromine being reduced by sodium bisulfite.

The initial concentrations were 0.01 M for acetaldehyde, 2 M for ethanol and  $\sim 0.006$  M for bromine, unless otherwise stated.

The temperature was 0°. An ordinary "thermos" flask containing a mixture of ice and water, and provided with a lid, served as a constant temperature bath.

Preliminary experiments carried out in a transparent glass thermostat had shown that the rate of reaction is influenced by broad daylight. Parallel runs were therefore carried out in which ordinary and "Low Actinic" Erlenmeyer flasks were inserted in the "thermos" flask; identical kinetic results were obtained. This shows that the "thermos" flask provides sufficient protection against the influence of light.

In preliminary experiments carried out at 25° and an alcohol concentration of 0.167 M, the reaction at pH above 6.4 was accompanied by bromate formation. (The rate of the latter reaction increases<sup>13</sup> strongly with increasing pH, reaching a maximum at pH 7.3. Since bromate does not react with alcohol, the rate constants in this range had to be suitably corrected.) The experimental conditions reported in this paper were chosen, *inter alia*, to avoid this side reaction. Its absence was ascertained in 4 experiments at pH 6.2 to 7.4, using the analytical method described before.<sup>13</sup>

(9) K. C. Grover and R. C. Mehrotra, *Z. physik. Chem.* (Frankfurt), **14**, 345 (1958); **18**, 401 (1958).

(10) I. R. L. Barker, W. G. Overend and C. W. Rees, *Chem. and Ind.* (London), 1297; 1298 (1960); see also J. Honeyman, *Ann. Repts. Progr. Chem. (Chem. Soc.)*, **57**, 333, 1960 (pub. 1961).

(11) G. Stein and J. Weiss, *J. Chem. Soc.*, 3256 (1949).

(12) Preliminary experiments carried out in this Laboratory (L. Binoun and B. Perlmutter-Hayman, unpublished results) had shown that in alkaline solution the reaction products are very complex. In strong alkali the substitution decreased markedly after a day's standing. This latter feature was confirmed in the present work.

(13) R. M. Chapin, *J. Am. Chem. Soc.*, **56**, 2211 (1934); see also P. Engel, A. Oplatka and B. Perlmutter-Hayman, *ibid.*, **76**, 2010 (1954).

The concentration of foreign salts (buffer, and in some cases potassium bromide) was rather high—0.3 to 0.7 M. After preliminary experiments in the presence and absence of sodium nitrate had shown that a change in salt concentration from 0.3 M to 0.6 M at pH 4.4 and 5.6 and from 0.1 M to 0.4 M at pH 1 does not affect the rate of reaction, we took no precaution to keep the ionic strength constant for all experiments. We did not investigate the influence of ionic strength at low salt concentrations.<sup>8</sup>

### Results

**1. Determination of Reaction Products.**—We are interested in the reaction only in so far as it follows the same stoichiometry as in acid solution. However, the first step even in the haloform formation seems to be universally accepted to consist in the oxidation of ethanol to acetaldehyde<sup>14</sup>; it was therefore considered sufficient to determine the conditions under which *acetaldehyde* is oxidized to acetic acid. Up to pH 7.5 no substitution occurred. At pH 9, 9.5 (borax buffer), and 13.0 the bromide formed was about 10% less than the initial normality of bromine. Unfortunately, for the pH range between 7.5 and 9.0 we found no buffer which would not be attacked by bromine. Now this refers to mixtures whose HOBr-content increases considerably with increasing pH. On the other hand, in our kinetic experiments the formation of HOBr was largely suppressed by the addition of potassium bromide (see below). Under these conditions, our analytical method does not allow us to ascertain substitution. It would seem safe to say, however, that the absence of substitution by a *mixture* of bromine and hypobromous acid at a given pH is an indication for the absence of substitution by *bromine* at the same pH.

Furthermore, an experiment was carried out at pH 6 where the ratio  $a/b$  was 1.9 ( $a$  designating the initial concentration of total oxidizing agent, and  $b$  that of acetaldehyde). The amount of bromine used up was exactly equal to  $b$ . This means that no oxidation products higher than acetic acid are formed.

**2. The Rate of Oxidation by Hypobromous Acid.**—The oxidation of acetaldehyde by hypobromous acid was investigated at pH 1.3, 4.6 and 7.6, in 0.02 M aldehyde solution. As an example, Fig. 1 shows a plot of  $\log [(b-x)/(a-x)]$  against time at pH 4.6 (where  $x$  is the amount of total oxidizing agent disappeared at time  $t$ ). The rate is seen to be very low at the beginning, and to increase as the reaction proceeds. Since at the same time bromine is liberated<sup>7,8</sup> this shows that  $k_{Br_2} > k_{HOBr}$ . Accurate values of  $k_{HOBr}$  can therefore only be obtained in the absence of bromine. Whereas this can be achieved by the addition of silver ion, the latter substance had been found to accelerate reactions of this kind.<sup>3,7,8</sup> We therefore contented ourselves with an approximate value obtained by plotting the rate of reaction against  $x$  and extrapolating to  $x = 0$ . At each value of pH, the result obtained for  $k_{HOBr}$  was much lower than the value of  $k_{Br_2}$  at the same pH (reported below). Both values increase with increasing pH, but  $k_{HOBr}$  does so somewhat less than  $k_{Br_2}$ ; at the lower values of pH, the ratio  $k_{HOBr}/k_{Br_2}$  is about 1/50, whereas at pH 7.6 it is about 1/200.

(14) See L. F. Fieser and M. Fieser "Organic Chemistry," 3rd Ed., Reinhold Publishing Corporation, New York, N. Y., 1956, p. 155.

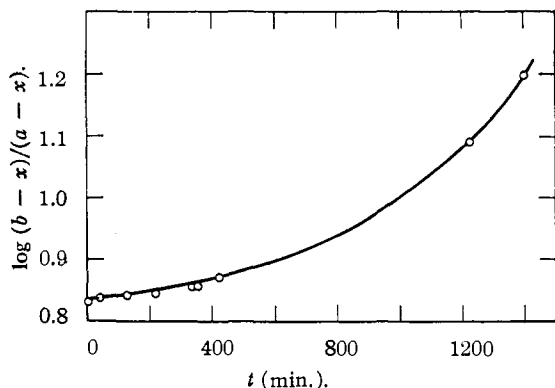


Fig. 1.—The reaction of acetaldehyde with hypobromous acid;  $\log(b-x)/(a-x)$  as a function of time.

Our data for ethanol refer to the preliminary experiments carried out at 25° and an alcohol concentration of 0.167 *M*. The qualitative picture was very similar to Fig. 1. At pH 2 and 3.5,  $k_{\text{HOBr}}$  was  $\sim 30$  times lower than  $k_{\text{Br}_2}$  obtained under the same experimental conditions.

Thus, whereas the results reported in this section are only qualitative, they establish beyond doubt that again  $k_{\text{HOBr}} \ll k_{\text{Br}_2}$ .

This is of some importance also for the design of the experiments carried out on the oxidation by bromine reported in the next sections: the presence of a varying percentage of the total oxidizing power in the form of hypobromous acid will not affect the kinetic results, provided this percentage is small.

It might be added that the reaction with hypobromous acid is much more sensitive to the influence of light than the reaction with bromine.

**3. The Kinetics of the Oxidation of Acetaldehyde by Bromine.** (a) **Influence of pH.**—Up to pH  $\sim 6$  the solutions were prepared from bromine, acetaldehyde and buffer. Under these conditions, the formation of tribromide can be neglected provided only the first 50 to 60% of the reaction is taken into account. (Tribromide constitutes  $\sim 8\%$  of the total oxidizing capacity after 50% reaction).

On the other hand, at pH  $\sim 4$  to 6 part of the oxidizing agent is present in the form of hypobromous acid, owing to the hydrolysis of bromine. The hydrolysis is considerable at the beginning of the reaction but soon decreases because of the bromide formed.<sup>15</sup> In this pH range we therefore did not carry out measurements during the first 20% of reaction.

At pH above 6, the concentration of hypobromous acid is no longer small even during the later stages of reaction. We therefore added bromide at an initial concentration of 0.30 *M* which sufficiently suppresses the hydrolysis of bromine up to the highest pH employed by us. Preliminary experiments in which bromide was added at concentrations between 0.1 and 0.4 *M* had shown that at pH 6.3 the tribromide ion is again<sup>2,3,5-8</sup> kinetically inactive, and the rate constant was calculated from the rate equation<sup>2,3</sup>

(15) Using  $[\text{Br}^-][\text{H}^+][\text{HOBr}]/[\text{Br}_2] = 7.10 \cdot 10^{-10}$  (H. A. Liebhafsky, *J. Am. Chem. Soc.*, **61**, 3513 (1939)), we find that for instance at pH 5.6, hypobromous acid constitutes  $\sim 20\%$  of the total oxidizing capacity at  $x = 0$ ; after  $x$  equals about 0.2 *a*, hypobromous acid is only 11% of the total oxidizing capacity.

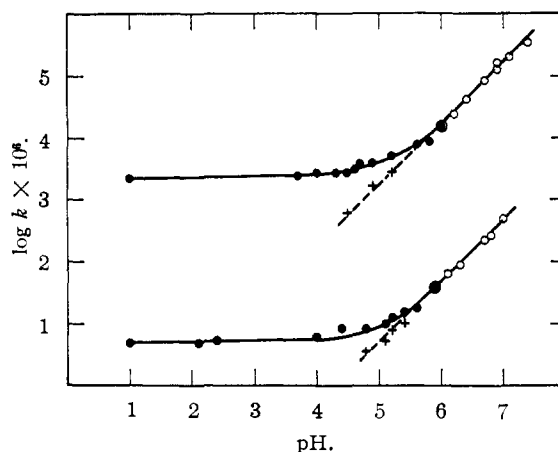


Fig. 2.—The dependence of the logarithm of the rate constant on pH. Upper curve: acetaldehyde; lower curve: ethyl alcohol. The experiments in the absence of bromide are designated by full circles, and those in the presence of 0.3 *M* bromide by open circles. The crosses (dashed line) are obtained by subtracting the rate constant in strongly acid solution from the experimental value of  $k$ .

$$dx/dt = k_{\text{ald}}(a-x)(b-x)/(1 + K_3[\text{Br}^-]) \quad (1)$$

where  $K_3$  is the association constant of tribromide.

In all experiments, straight lines were obtained when  $\log(b-x)/(a-x)$  was plotted against time. The results of 19 experiments in the pH range between 1.0 and 7.4 are shown in Fig. 2 (upper curve), where the logarithm of the rate constant is plotted against pH. At low pH the influence of pH is only slight, but it increases gradually with increasing pH; from pH 5.7 upwards a straight line of slope unity is obtained. The experiments in the absence and presence of bromide are seen to fall on a smooth curve. At pH 6 the results of the two series coincide within the limit of error. The value of  $k_{\text{ald}}$  at pH 1.0 is equal to  $2.1 \times 10^{-3}$  mole<sup>-1</sup> l. sec.<sup>-1</sup>, in reasonable agreement with Bugarszky's value<sup>1</sup> of 1.95 in unbuffered solution.

(b) **Reaction Order with Respect to Acetaldehyde.**—The first order in acid solution may be considered as established.<sup>1</sup> It was confirmed at pH 6.7 by carrying out three experiments where  $b$  was 0.005, 0.01 and 0.02 *M*. The values of  $k_{\text{ald}}$  obtained agreed within  $\pm 2\%$ .

**4. The Kinetics of the Oxidation of Ethanol by Bromine.** (a) **The Steady State Concentration of Aldehyde.**—In all the experiments, the alcohol concentration was considered constant during each run. The kinetic equation is

$$dx/dt = (k_{\text{alc}}[\text{CH}_3\text{CH}_2\text{OH}] + k_{\text{ald}}[\text{CH}_3\text{CHO}])(a-x) = k_{\text{exp}}(a-x) \quad (2)$$

where  $k_{\text{exp}}$  is equal to  $(-d \ln(a-x)/dt)$ . As the acetaldehyde concentration increases from its initial value of zero to its stationary state value of

$$[\text{CH}_3\text{CHO}]_s = k_{\text{alc}}[\text{CH}_3\text{CH}_2\text{OH}]/k_{\text{ald}} \quad (3)$$

the value of  $k_{\text{exp}}$  increases to twice its initial value of  $k_{\text{alc}}[\text{CH}_3\text{CH}_2\text{OH}]$ . We therefore found it convenient<sup>2</sup> to add acetaldehyde to the reaction mixture of alcohol and bromine at an initial concentration equal to  $[\text{CH}_3\text{CHO}]_s$ .

The value of  $[\text{CH}_3\text{CHO}]_s$  was determined in the reaction product when alcohol at the appropriate concentration had been allowed to react with bromine (0.04 to 0.06  $M$ ).<sup>16</sup> A sample was taken after about two days (the unreacted bromine being again reduced with bisulfite) and the aldehyde concentration measured. After another 10–24 hours' standing the analysis was repeated. Only when two consecutive samples gave identical results was the stationary concentration considered to be reached. At  $[\text{CH}_3\text{CH}_2\text{OH}] = 2 M$ , and pH between 1 and 6.4 we found  $[\text{CH}_3\text{CHO}]_s$  between 5 and  $6 \times 10^{-3} M$ , with no significant trend with pH.<sup>17</sup> It should be emphasized that even if we start our kinetic experiment with an aldehyde concentration which is not *exactly* equal to the stationary concentration, the correct value will be practically reached after a small percentage of reaction.

In the range of alcohol concentrations between 1 and 2  $M$  the value of  $[\text{CH}_3\text{CH}_2\text{O}]_s$  was found to be proportional to the alcohol concentration, at pH 1 and 5.2.

(b) **The Dependence of the Rate of Oxidation on pH.**—The dependence of the rate of oxidation of ethanol on pH can again be seen from Fig. 2 (lower curve), where  $\log k_{\text{alc}}$  is plotted *vs.* pH for 16 experiments in the pH range between 1 and 7. At the higher values of pH, the hydrolysis of bromine was again suppressed by the addition of potassium bromide. The curve is seen to be very similar to that obtained for aldehyde.

In preliminary experiments (at 25°, and an alcohol concentration of 0.167  $M$ ) where no bromide was initially added the influence of pH was much less pronounced than in Fig. 2. Furthermore, at the higher values of pH the rate constant increased as the reaction proceeded, the more so, the higher the initial concentration. These effects are easily explained: the relative concentration of the kinetically almost inactive hypobromous acid increases with increasing pH. This increase is partly counteracted by the bromide formed during the reaction.

(c) **The Reaction Order with Respect to Ethanol.**—The first order in acid solution was again considered as established.<sup>1</sup> It was confirmed at pH 4 by three experiments in 1.0, 1.5 and 2.0  $M$  alcohol, where the rate was found to be proportional to the alcohol concentration.

### Discussion

The most striking feature about our results is the form of the  $\log k$  *vs.* pH curves, and their close parallelism (see Fig. 2). This parallelism implies that the ratio  $k_{\text{alc}}/k_{\text{ald}}$  is independent of pH—in good agreement with the constancy of  $[\text{CH}_3\text{CHO}]_s$ .

The increase of the rate constants with increasing pH definitely cannot be due to the influence of hypobromous acid; (a) the reaction with hypobromous acid is much slower than with bromine, and (b) the rate of oxidation increases with increas-

ing pH under conditions where the formation of hypobromous acid is largely suppressed.

In view of the similarity between Fig. 2 and the corresponding plot for glucose,<sup>8</sup> we propose that the anions of ethanol and of acetaldehyde are oxidized much more rapidly than the undissociated molecules; the quantitative agreement between this assumption and the observed pH dependence has been discussed before.<sup>8</sup>

The existence of the anion  $\text{CH}_3\text{CH}_2\text{O}^-$  in alcoholic solution is well established. However, the data for the acidic properties of alcohol in dilute aqueous solutions are somewhat contradictory. In 1936 McEwen<sup>18</sup> measured  $pK = 18$ ; more recently,<sup>19</sup>  $pK = 15.8$  is reported. Using the more recent value we calculate<sup>20</sup>  $k_{\text{anion}} \approx 3 \times 10^6 \text{ mole}^{-1} \text{ l. sec.}^{-1}$ . This would mean that the anion reacts about  $6 \times 10^{10}$  times faster than the undissociated molecule. The result may be compared with glucose<sup>8</sup> where the ratio is about  $4 \times 10^{10}$ . In view of the uncertainty in the value of  $pK$ , this close similarity is probably fortuitous. In any case, however, glucose is a considerably stronger acid than ethanol. It is therefore not surprising that the reaction involving the anion should make itself felt with glucose at a lower pH than with ethanol.

Aldehyde, of course, can ionize only in the form of its hydrate. Since in aqueous solution about 70% of the total aldehyde are present in the form of the hydrate at 0°,<sup>21</sup> it seems very reasonable to assume this substance as a kinetic entity.<sup>4</sup> The corresponding anion has been suggested by Bell and co-workers<sup>22</sup> as an intermediate in the hydrate formation. However, nothing quantitative seems to be reported about the acidic properties of the hydrate, and we therefore cannot calculate the rate constant corresponding to the anion. Furthermore, we cannot say whether the close parallelism in the pH dependence of ethanol and of acetaldehyde (see Fig. 2) is due to a similarity in both  $pK$  and  $k_{\text{anion}}/k_{\text{molecule}}$ , or whether it is a coincidence.

Our results with hypobromous acid indicate that although the ion is again oxidized at a much higher specific rate than the molecule, the difference is slightly less pronounced in the case of hypobromous acid than in the case of bromine. A similar effect had been observed with glucose.<sup>8</sup>

From the smallness of the solvent isotope effect in acid solution,<sup>5</sup> it was concluded that the proton transfer between the hydroxyl group and a water molecule is not involved in the rate determining step but constitutes a following reaction.<sup>5</sup> According to our explanation of the pH effect, this same proton transfer in less acid solution is again not involved in the rate determining step but precedes the actual reaction. The negative charge thus left on the organic molecule can easily be imagined<sup>8</sup> to facilitate hydride transfer.

(18) W. K. McEwen, *J. Am. Chem. Soc.*, **58**, 1129 (1936).

(19) J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p. 68. No source is quoted by the author.

(20) The higher  $pK$  yields a rate constant which is of course correspondingly higher, but not prohibitively high.

(21) R. P. Bell and J. C. Clunie, *Trans. Faraday Soc.*, **48**, 439 (1952).

(22) R. P. Bell and B. de B. Darwent, *ibid.*, **46**, 34 (1950); R. P. Bell, M. H. Rand and K. M. A. Wynne-Jones, *ibid.*, **52**, 1093 (1956).

(16) The stationary concentration will be practically reached<sup>8</sup> when  $x \geq 8[\text{CH}_3\text{CHO}]_s$ . From preliminary experiments we can estimate that for this purpose the initial bromine concentration must be at least  $0.02[\text{CH}_3\text{CH}_2\text{OH}]$ .

(17) The reproducibility of the analysis of the reaction product was much less satisfactory than that of pure acetaldehyde—for reasons which we have not been able to determine.