same distance for ketene, which has been found by electron diffraction to have a carbon–oxygen distance equal to 1.17 Å.[16]

The large value of the hydrogen–carbon–hydrogen angle, 120°, may be interpreted as indicating that the bonding in formaldehyde is primarily of the sp^2, π type which gives three coplanar bonds at 120°. It has been found that in acetaldehyde[6] a similar situation obtains, the carbon–carbon–oxygen angle being 122 ± 2°. The carbon–oxygen distance in formaldehyde is definitely shorter than that predicted by the covalent radius table for a carbon–oxygen double bond.

Summary

Electron diffraction photographs of monomeric formaldehyde have been obtained using fast electrons. Their interpretation leads directly to a carbon–oxygen distance equal to 1.21 ± 0.01 Å. Using this distance and the accurately known moments of inertia one finds the carbon–hydrogen distance to be 1.09 ± 0.01 Å. and the hydrogen–carbon–hydrogen angle to be 120 ± 1°.

(16) J. Y. Beach and D. P. Stevenson, *J. Chem. Phys.*, **6**, 75 (1938).

The Hydrolysis of Ethylal[1]

BY PAUL M. LEININGER[2] AND MARTIN KILPATRICK

In a study of the inversion of sucrose[3] it was shown that the parameters of the Arrhenius equation

$$\ln k = B - (E_A/RT) \tag{1}$$

depended upon electrolyte concentration and temperature. The present paper extends the study to the hydrolysis of ethylal. This reaction was chosen because the velocity constant can be determined conveniently over similar ranges of hydrochloric acid concentration and temperature.

Skrabal and Schiffrer[4] measured the rate of hydrolysis of ethylal in aqueous hydrochloric acid solutions by indirectly determining the amount of formaldehyde present at suitable intervals. The formaldehyde was oxidized to formic acid and titrated. In 1926 Skrabal and Eger[5] continued the work at 25°, using a modification of the sulfite method of Lemme[6] to determine the quantity of formaldehyde.

Subsequently the hydrolysis of ethylal was studied at 25 and 35° by Salmi[7] and by Palomaa and Aalto[8] using analytical methods. In 1934

Palomaa and Salonen[9] measured the reaction rate dilatometrically. Löbering and Fleischmann[10] investigated the hydrolysis at 10, 20 and 30° in sulfuric acid solutions.

If the claim of an accuracy of ±4% in the measurement of the rate constant, made by one of the authors,[8] can be regarded as typical, it is apparent that for this reaction the data in the literature are insufficiently accurate for a study of the parameters of the Arrhenius equation. In addition, both the temperature and concentration ranges investigated are too limited to enable one to observe possible variations in the parameters, E_A and B.

The present investigation extends over a range of hydrochloric acid concentration from 0.5 to 3.0 molar, at 0, 10, 15, 20, 25, 30, 35 and 40° (concentrations resulting in too rapid reaction being omitted at the higher temperatures).

Experimental

Ethylal.—Ethylal from the Eastman Kodak Company was purified by fractional distillation, the fraction boiling between 87.0 and 88.0° (760 mm.) being used. That the preparation was free of acidic impurities was established by titration of an aqueous solution in an atmosphere of nitrogen using brom thymol blue as indicator. A further check upon the purity of the product was made by determining the refractive index by means of a Zeiss dipping refractometer. At 17.5° different preparations gave values of n_D varying from 1.3736 to 1.3745 as compared with

(1) Abstracted from the dissertation of Paul M. Leininger presented to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfilment of the requirement for the degree of Doctor of Philosophy, April, 1939. Paper presented before the Baltimore Meeting of the American Chemical Society, April, 1939.

(2) E. I. du Pont de Nemours and Company Fellow, 1938–1939.

(3) Leininger and Kilpatrick, THIS JOURNAL, **60**, 2891 (1938).

(4) Skrabal and Schiffrer, *Z. physik. Chem.*, **99**, 290 (1921).

(5) Skrabal and Eger, *ibid.*, **122**, 349 (1926).

(6) Lemme, *Chem. Ztg.*, **27**, 896 (1903).

(7) Salmi, *Annal. Univ. Aboensis*, **A3**, no. 3 (1932).

(8) Palomaa and Aalto, *Ber.*, **66**, 468 (1933).

(9) Palomaa and Salonen. *ibid.*, **67**, 424 (1934).

(10) Löbering and Fleischmann, *ibid.*, **70B**, 1713 (1937).

1.3760 in the literature.[11] An examination of the experimental results reveals no difference in the velocity constants for the various preparations.

Hydrochloric Acid.—Baker c. p. analyzed hydrochloric acid was used. Experiments made with solutions prepared from constant-boiling acid checked the others within the experimental error.

Apparatus.—The dilatometers and thermostats were the same as in the study of the inversion of sucrose.[3]

Determination of Temperature.—Temperature regulation was slightly better than in the previous work,[3] the determination of temperature being carried out as previously described.

Determination of Concentrations.—The weight of ethylal used in an experiment was calculated from its density[12] and volume at the temperature of the experiment. The molarity of the ethylal was obtained from the weight of ethylal, the density of the reacted mixture, and the weight of hydrochloric acid solution. This procedure permits the calculation of molalities as well as molarities. The molarity of the hydrochloric acid was determined directly for each solution at the temperature at which the experiment had been performed by titration of the reacted mixture. The validity of the method was established by titrating a blank in the absence of ethylal. The concentration of acid was known to 0.1%.

Determination of the Rate.—A definite volume (150 cc.) of a hydrochloric acid solution of known concentration was introduced into the mixing chamber of the dilatometer and subjected to reduced pressure to prevent subsequent bubble formation. To this solution, at the temperature of the thermostat, 5 cc. of ethylal was added. The mixture was stirred until the solution became homogeneous, sealed off in the dilatometer and the rate of contraction noted. Velocity constants were evaluated by the Guggenheim method.[13]

Results

The hydrolysis of ethylal is represented conventionally as taking place in two steps: first hydrolysis, then the decomposition of the hemiacetal.

$$CH_2(OC_2H_5)_2 + H_2O = CH_2(OC_2H_5)(OH) + C_2H_5OH$$
$$CH_2(OC_2H_5)(OH) = CH_2O + C_2H_5OH$$
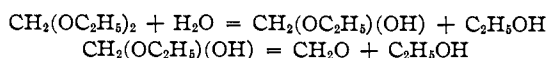
The results of the present work indicate that the reaction is of the first order over the entire range of temperature and concentration investigated. Because of the great difficulty, if not impossibility, of preparing hemi-acetals, Skrabal[4] has concluded that the first of the above steps involves the rate determining process. The actual existence of hemi-acetals seems to be indicated, however, by some work of Adkins and Broderick.[14]

The validity of the dilatometric method is based upon the agreement of the results obtained in the

(11) Ghysels, *Bull. soc. chim. Belg.*, **33**, 57 (1924).
(12) Timmermans and Hennaut-Roland, *J. chim. phys.*, **27**, 401 (1930).
(13) Guggenheim, *Phil. Mag.*, [7] **2**, 538 (1926).
(14) Adkins and Broderick, THIS JOURNAL, **50**, 499 (1928).

present investigation with the values of other workers at 25° using analytical methods (see Fig. 1). As in the case of the other formals,[9] the reaction is accompanied by a contraction.
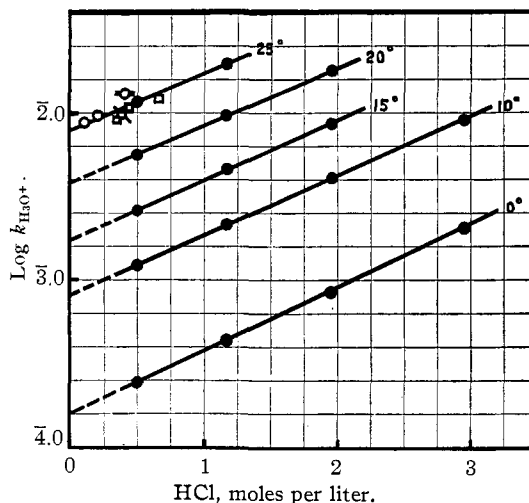

Fig. 1.—Electrolyte effect at various temperatures: ●, this investigation, 0.26 molar ethylal; ○, Skrabal and Schiffrer,[4] 0.2 molar ethylal; -◯-, Skrabal and Eger,[5] 0.022 molar ethylal; □, Palomaa and Salonen,[9] 0.22 molar ethylal; -◇-, Salmi,[7] 0.21 molar ethylal.

In Table I are listed the values of $k_{H_3O^+}(k_{obsd.}/C_{H_3O^+})$ obtained. The molarity of the ethylal is 0.260 ± 0.004 unless otherwise indicated. The

TABLE I

SUMMARY OF $k_{H_3O^+}$ VALUES

Temp., °C.	No. of expts.	HCl, moles/liter	$10^3 k_{H_3O^+}$
−0.01	3	0.4941	0.2430
−0.01	3	1.165	.4370
−0.01	1	1.945	.8473
−0.01	1	2.940	2.028
10.00	2	0.4959	1.214
10.00	2	1.164	2.151
10.00	2	1.959	4.053
10.00	2	2.945	9.387
15.00	2	0.4963	2.625
15.00	2	1.172	4.602
15.00	2	1.953	8.577
20.00	4	0.4950	5.595
20.00	2	1.164	9.613
20.00	4	1.951	17.76
25.00	2	0.4994	11.63
25.00	2	1.165	19.78
30.00	2	0.4956	23.19
35.00	2	.4998	46.47
35.00	4	.5011	46.37[a]
40.00	3	.4940	91.64
40.00	1	.4751	84.68[b]

[a] 0.234 molar ethylal. [b] 0.362 molar in ethylal; 0.246 molar in reacted ethylal.

average of the average deviations for these experiments has been calculated and is 0.7%.

An examination of Table I shows that the bimolecular constant increases with concentration of hydrochloric acid. In Fig. 1 values of $\log k_{H_3O^+}$ have been plotted against the molarity of the hydrochloric acid. The curves reading from top to bottom are for 25, 20, 15, 10 and 0°, respectively. The straight lines obtained indicate that the effect obeys the equation

$$\log k_{H_3O^+} = \log k^0_{H_3O^+} + \beta C \qquad (2)$$

at each temperature for the concentration range considered. The following equations were obtained from the above data.

$$\begin{aligned}
\log k_{H_3O^+} &= \overline{4}.2001 + 0.3760\ C \text{ (at } -0.01°) &\text{(2A)}\\
\log k_{H_3O^+} &= \overline{4}.9066 + 0.3612\ C \text{ (at } 10.00°) &\text{(2B)}\\
\log k_{H_3O^+} &= \overline{3}.2458 + 0.3529\ C \text{ (at } 15.00°) &\text{(2C)}\\
\log k_{H_3O^+} &= \overline{3}.5790 + 0.3444\ C \text{ (at } 20.00°) &\text{(2D)}\\
\log k_{H_3O^+} &= \overline{3}.8914 + 0.3478\ C \text{ (at } 25.00°) &\text{(2E)}
\end{aligned}$$

The effect of ethylal concentration upon $k_{H_3O^+}$ is small, as evidenced by the value in Table I with superscript "a". A further examination of Fig. 1, however, shows that the value of $k_{H_3O^+}$ reported by Skrabal and Eger[5] is considerably higher (ca 20%) than one would expect for that concentration of hydrochloric acid. Since the only difference between this experiment and all the others is the fact that the molarity of ethylal was about 0.02 instead of 0.2, one would conclude that the bimolecular constant increased with decreasing ethylal concentration. This conclusion is further substantiated by the experiment reported in Table I with a superscript "b". In this case another portion of ethylal was added to the reacted mixture from a previous run (which might be considered equivalent to increasing the concentration of ethylal). Here a marked decrease in $k_{H_3O^+}$ was noted.

In Table II are recorded the values of E_A calculated from the data of Table I by the equation

$$E_A = \frac{RT_1T_2}{(T_1 - T_2)} \ln \frac{k_{T_1}}{k_{T_2}} \qquad (3)$$

The maximum error, ΔE_M, in E_A is calculated from the relation

$$\Delta E_M = \Sigma(\delta E_x) \qquad (4)$$

where δE_x represents the change in E_A due to the variation, δ_x, in the quantity x (x representing in turn T_1, T_2, ΔT, $k_{H_3O^+(T_1)}$ and $k_{H_3O^+(T_2)}$). The values assigned to δT_1 and δT_2 are 0.01°, to $\delta(\Delta T)$ 0.01° and to δk_1 and δk_2 ± 0.7%. ΔE_M is approximately ±300 cal. A calculation of the

$$\Delta E_{PM} = \sqrt{\Sigma(\delta E_x)^2} \qquad (5)$$

precision measure, ΔE_{PM}, yields ±200 cal. Two things become apparent: E_A increases with increase in temperature, and decreases with increase in hydrochloric acid concentration. The concentration effect is also indicated by the decrease in the slope of the equations (2A) to (2D) as the temperature increases.

TABLE II

SUMMARY OF ACTIVATION ENERGIES

Temp. range, °C.	HCl, moles/liter	k_{T_1}/k_{T_2}	E_A, cal.
−0.01 to 10.00	0.4950	4.996	24,690
− .01 to 10.00	1.165	4.922	24,460
− .01 to 10.00	1.952	4.783	24,020
− .01 to 10.00	2.943	4.629	23,520
− .01 to 20.00	0.4946	23.02	24,940
− .01 to 20.00	1.165	22.00	24,570
− .01 to 20.00	1.948	20.96	24,190
10.00 to 20.00	0.4955	4.609	25,200
10.00 to 20.00	1.164	4.469	24,690
10.00 to 20.00	1.955	4.382	24,370
15.00 to 25.00	0.4979	4.430	25,410
15.00 to 25.00	1.169	4.298	24,890
20.00 to 30.00	0.4953	4.145	25,110
25.00 to 35.00	.4997	3.996	25,290
30.00 to 40.00	.4948	3.952	25,920

There are only three values of E_A available in the literature for the hydrolysis of ethylal by hydrochloric acid. From the work of Salmi[7] one calculates an activation energy of 25,760 cal., from that of Palomaa and Aalto[8] 24,620 cal., and from that of Palomaa and Salonen[9] 25,910 cal. An average value of 25,430 cal. is thus obtained for solutions approximately 0.4 molar with respect to hydrochloric acid and 0.2 molar with respect to ethylal. In this investigation the value of E_A at 30° for solutions 0.5 molar with hydrochloric acid was found to be 25,290 cal.

The effect of hydrochloric acid concentration is illustrated by a plot of values of E_A (taken from Table II) against molarity of acid.

In similar fashion, one can show the effect of temperature by plotting E_A against the midpoint of the temperature interval. This is done in Fig. 3, using values from Table II for 0.5 molar solutions of hydrochloric acid. The position of the line in Fig. 3 was determined by least squares.

Values of E_A for 0, 1 and 2 molar solutions of acid (read from Fig. 2) and for 0.5 molar acid (read from Fig. 3) are summarized in Table III. Values of E_A for zero molarity were likewise checked by calculation from the intercepts of equations (2A) to (2E).
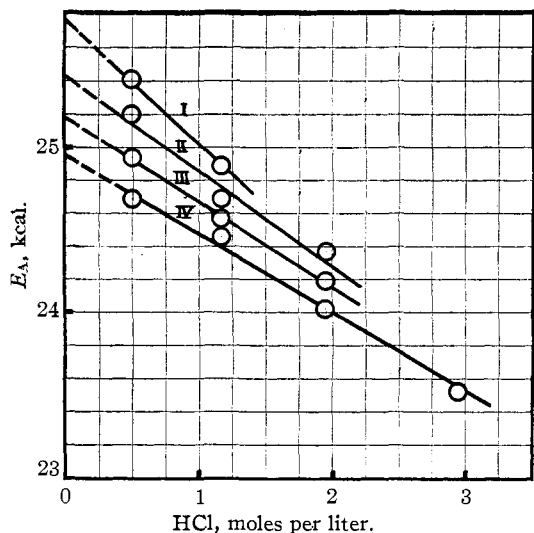
Fig. 2.—Electrolyte effect on energy of activation:
I, 15.00 to 25.00°; II, 10.00 to 20.00°; III, −0.01 to
20.00°; IV, −0.01 to 10.00°.

TABLE III

VARIATION OF THE ENERGY OF ACTIVATION WITH TEM-
PERATURE AND ACID CONCENTRATION

Temp. range, °C.	0 molar HCl	0.5 molar HCl	1 molar HCl	2 molar HCl
−0.01 to 10.00	24,960	24,760	24,480	24,010
−0.01 to 20.00	25,180	24,920	24,670	24,160
10.00 to 20.00	25,440	25,070	24,860	24,280
15.00 to 25.00	25,760	25,220	25,020	....
20.00 to 30.00	....	25,370	....	....
25.00 to 35.00	....	25,530	....	....
30.00 to 40.00	....	25,680	....	....

Values of B calculated by equation (1), $k_{H_3O^+}$
being expressed in reciprocal seconds, are sum-
marized in Table IV.

TABLE IV

VARIATION OF B WITH TEMPERATURE AND ACID CON-
CENTRATION

Temp. range, °C.	0 molar HCl	0.5 molar HCl	1 molar HCl	2 molar HCl
−0.01 to 20.00	33.54	33.50	33.47	33.39
10.00 to 20.00	34.00	33.76	33.80	33.60
15.00 to 25.00	34.56	34.04	34.08	...
20.00 to 30.00	...	34.28	...	...
25.00 to 35.00	...	34.53	...	...
30.00 to 40.00	...	34.79	...	...

From Table IV it appears that B increases with
increasing temperature. The variation of B
with concentration is within the experimental
error, which is calculated to be ±0.3 of a B unit.

Discussion

From the results it is evident that the energy of
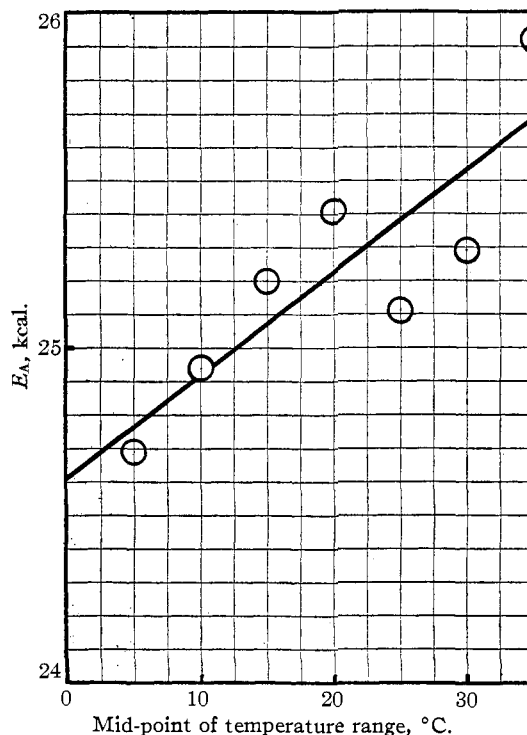activation decreases with increasing hydrochloric

Fig. 3.—Effect of temperature on energy of activation
(0.5 molar HCl).

acid concentration, as in the case of the inversion
of sucrose, but that the effect of temperature on
E_A is in the opposite direction to that for the in-
version of sucrose, dE_A/dT being positive and
equal to 31 cal. per degree. The effect appears to
be linear with temperature.

In a recent paper Moelwyn-Hughes[15] reviews
the examples of the change of E_A with tempera-
ture and reports experiments on the hydrolysis
of methyl halides. He finds that the temperature
coefficient of the apparent activation energy is
always negative in the region explored. This is
not the case for the hydrolysis of ethylal.

Even though the variation of E_A and B with
temperature has been established definitely, it is
still possible to write an expression of the form of
equation (1) which holds for the data in 0.5
molar hydrochloric acid solution. In fact it is
possible to calculate values of $k_{H_3O^+}$ from the
following equation, over the range of temperature
studied, which on the average agree with the ob-
served values to ±1.2%, the maximum devia-
tion being 3.8%. The equation

$$\ln k_{H_3O^+} = 34.175 − (25,304/RT) \qquad (6)$$

(15) Moelwyn-Hughes, Proc. Roy. Soc. (London). A164, 295 (1938).

was determined by considering ln $k_{H_3O^+}$ as a linear function of $1/T$ and determining the intercept and slope of the line by least squares. The constancy of E_A and B cannot be judged from the conventional plot of log k vs. $1/T$.

In similar fashion the data for the inversion of sucrose[3] at zero hydrochloric acid concentration can be represented by the equation

$$\ln k_{H_3O^+} = 35.33 - (26,250/RT) \ (0\text{--}40°) \quad (7)$$

The average deviation of the values of $k_{H_3O^+}$ from this equation is 3%, the maximum deviation 6%. Moelwyn-Hughes[16] reports equations of this type for 0.2 molar hydrochloric acid for three temperature ranges.

$$\ln k_{H_3O^+} = 34.19 - (25,430/RT) \ (15.45\text{--}27.26°) \quad (8A)$$
$$\ln k_{H_3O^+} = 32.55 - (24,470/RT) \ (27.26\text{--}41.00°) \quad (8B)$$
$$\ln k_{H_3O^+} = 30.12 - (22,950/RT) \ (41.00\text{--}57.10°) \quad (8C)$$

As already pointed out, the values for E_A and B are lower than the values of Leininger and Kilpatrick.[3] Jackson and Gillis,[17] in a study of the Clerget method, measured the velocity of inversion of sucrose at temperatures from 20 to 90° and conclude that the results are in agreement with the exponential law first proposed by Arrhenius. The exponential equation for 0.01 normal hydrochloric acid may be put in the form

$$\ln k_{H_3O^+} = 34.61 - (25,705/RT) \ (30\text{--}90°) \quad (9)$$

where B is calculated at 49.85°, E_A calculated by equation (3) for each interval shows no trend with increasing temperature, the average deviation being 330 cal. These results, however, are not in disagreement with those of Leininger and Kilpatrick,[3] who found dE_A/dT to approach zero in the range 30–40°. Moelwyn-Hughes, on the other hand, observed no decrease in dE_A/dT at higher temperatures.

In considering a possible theoretical explanation of the variation of E_A with electrolyte concentration, it becomes necessary to decide whether the rate determining step is bimolecular or unimolecular. Unfortunately the kinetic measurements of this investigation permit no decision. In the following discussion the rate determining mechanism is to be considered unimolecular. This latter view seems the more probable in the light of recent investigations of reaction rates in heavy water.[18]

Hornel and Butler[19] noted that the hydrolysis

of acetal proceeded more rapidly in heavy water than in ordinary water. One would logically expect that the substitution of deuterium for hydrogen would slow down the process if the rate determining mechanism involved a proton transfer. The only possible explanation of the effect observed, therefore, seems to be in the consideration of a preëquilibrium.

In a previous discussion[3] the change in E_A with electrolyte concentration was related to a corresponding change in the difference in heat content between the collision complex and the reactants. A comparison of the observed variation of E_A with electrolyte concentration, and the corresponding value of ΔH_2, is given in Table V. ΔH_2 is the heat of dilution of the hydrogen ion between the two solutions. For comparison, the results for the inversion of sucrose are included.

TABLE V

COMPARISON OF ΔH_2 AND ΔE_A

C_2 (moles per liter)	C_1	ΔH_2	ΔE_A, 20° Sucrose	ΔE_A, 15° Ethylal
4	3	300	610	...
3	2	300	620	...
2	1	300	630	580
1	0.5	200	...	210
0.5	0	300	...	370
1	0	500	630	580

(Calories per mole)

From these calculations it appears that the change in energy of activation is understandable on the basis of a preëquilibrium.

Summary

1. The velocity constant, $k_{H_3O^+}$, for the hydrolysis of ethylal has been measured from 0 to 40° over a range of hydrochloric acid concentration.

2. Equations for the effect of the electrolyte, hydrochloric acid, on $k_{H_3O^+}$ are given at −0.01, 10.00, 15.00, 20.00, and 25.00°. The effect of electrolyte decreases with increasing temperature.

3. The energy of activation calculated from the Arrhenius equation shows that E_A and B increase with increasing temperature.

4. A decrease in the energy of activation with increasing concentration of the electrolyte, hydrochloric acid, has been noted.

5. A plausible explanation of the effect of electrolyte concentration upon E_A has been given on the basis of a preëquilibrium.

(16) Moelwyn-Hughes, Z. physik. Chem., B26, 281 (1934).
(17) Jackson and Gillis, Bur. Standards J. Research, 16, 125 (1920).
(18) Bonhoeffer, Trans. Faraday Soc., 34, 252 (1938).
(19) Hornel and Butler, J. Chem. Soc., 1361 (1936).