

## 27. Reaction Velocities at Low Temperatures. Part III. The Synthesis of Diethylacetal at Temperatures between $-44^{\circ}$ and $+25^{\circ}$ .

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The kinetics of the formation of acetal in ethyl-alcoholic solution have been studied at six temperatures between  $-44^{\circ}$  and  $+25^{\circ}$  with the hydrogen ion as a catalyst. The course of the reaction obeys the expected laws when the retarding effect of the water produced is taken into account. The values of the catalytic constant at different temperatures can be expressed within the experimental error by the Arrhenius equation, and their order of magnitude agrees with the simple collision theory.

THE formation and hydrolysis of acetals have long been known as examples of acid catalysis, and recent work (Deyrup, *J. Amer. Chem. Soc.*, 1934, **56**, 60) has shown that the formation of acetal from acetaldehyde in ethyl-alcoholic solution takes place at a measurable rate at room temperature at hydrogen-ion concentrations of about  $10^{-4}N$ . In the present work this reaction has been studied at low temperatures with the object of detecting possible deviations from the Arrhenius equation. The catalyst used was hydrogen chloride, which can be assumed to be completely dissociated in ethyl alcohol at the temperatures used.

### EXPERIMENTAL.

*Materials.*—Ethyl alcohol was refluxed for 8 hours over aluminium amalgam and then twice distilled through a 1-m. column; different preparations gave indistinguishable results. Acetaldehyde was freshly distilled in small quantities immediately before use. Hydrogen chloride, prepared from "AnalaR" sodium chloride and concentrated sulphuric acid, was absorbed in alcohol and diluted to the required concentration by weight.

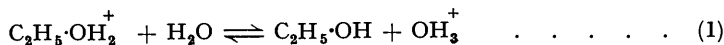
*Measurement of Reaction Velocity.*—The low-temperature thermostat already described (Bell and Thomas, *J.*, 1939, 1573) was used with a few modifications. When ammonia was used as refrigerant the deposition of calcium carbonate in the water pump during the night was avoided by absorbing the greater part of the ammonia gas in a vessel containing 3 l. of water. It was also found convenient to by-pass the mercury column when refilling with refrigerant. In the present work the temperatures were measured with a platinum resistance thermometer, standardised at the f. p. and b. p. of water, the f. p. of chlorobenzene, and the sublimation point of carbon dioxide. Experiments at  $0^{\circ}$  were done in ice, and at  $25^{\circ}$  in an ordinary thermostat.

The reactions were carried out in vessels of the type described by Bell and Levinge (*Proc. Roy. Soc.*, 1935, *A*, **151**, 211) and were started by adding a small quantity of acetaldehyde (which need not be accurately known) from a micro-pipette. The initial acetaldehyde concentration was about  $0.02M$ , and the course of the reaction was followed by extracting from time to time samples of about 0.5 c.c. and determining the acetaldehyde concentration by the method of Friedmann, Cotonio, and Shaffer (*J. Biol. Chem.*, 1927, **73**, 342). A slight modification of the method of estimation is necessary since in an unbuffered solution of bisulphite the acetal formed is hydrolysed back to acetaldehyde at an appreciable rate; on the other hand, if the  $p_H$  of the bisulphite solution is too high, the aldehyde-bisulphite compound is formed too slowly. Satisfactory results were obtained by using a solution containing 0.5 mol. of potassium hydrogen

sulphite and 0.05 mol. of sodium hydroxide per l., each sample being left for 30 mins. before titration. The final titration was done with N/100-iodine solution from a micro-burette.

At the low temperatures used there might be complications due to the formation of paraldehyde or metaldehyde. This was tested by hydrolysing with very dilute acid samples at different stages of the reaction and then estimating the acetaldehyde present. Both at  $-20^\circ$  and  $-40^\circ$  it was found that the quantity of acetaldehyde thus determined did not vary during the reaction. Since neither paraldehyde nor metaldehyde would have been appreciably converted into acetaldehyde under the conditions of hydrolysis employed, this shows that they were not formed at any stage of the reaction.

*Calculation of Velocity Constants.*—The kinetics of the reaction are complicated by the water produced, which reacts partly with the ion  $C_2H_5\cdot OH_2^+$  according to the equation



where  $OH_3^+$  is much less active as a catalyst than  $C_2H_5\cdot OH_2^+$ . The equilibrium constant for the reaction,  $r = [C_2H_5\cdot OH_2^+][H_2O]/[OH_3^+]$ , has been determined at  $25^\circ$  by Goldschmidt (*Z. physikal. Chem.*, 1907, 60, 728) and Millar (*ibid.*, 1913, 85, 129). In order to obtain values for lower temperatures we have made approximate calorimetric measurements of the heat change in reaction (1). Three measurements at  $25^\circ$  gave heat evolutions of 4940, 5290, and 4910 cal./mol., and one measurement at  $0^\circ$  gave 4800 cal./mol. Taking 5000 cal./mol. as a mean value, we obtain the following values for  $r$ : 0.15 at  $+25^\circ$ , 0.097 at  $+10^\circ$ , 0.070 at  $0^\circ$ , 0.034 at  $-20^\circ$ , 0.018 at  $-35^\circ$ , 0.013 at  $-44^\circ$ . It may be noted that values for the corresponding equilibrium constant in methyl alcohol (Smith, *J. Amer. Chem. Soc.*, 1939, 61, 256) lead to a heat of reaction of 4800 cal./mol.

If the concentration of acid catalyst is small compared with that of acetaldehyde (as was the case at temperatures of  $-20^\circ$  and higher) the course of the reaction is given by the equation

$$kt = [(a + r)/r] \log_{10} a/(a - x) - 0.434x/r \quad (2)$$

where  $a$  is the initial concentration of acetaldehyde and  $x$  the concentration of acetal after time  $t$ . For higher acid concentrations, however, a more complicated expression is necessary. If  $A$  is the total acid concentration and  $y$  the concentration of  $OH_3^+$  formed after time  $t$ , the relevant equations are

$$(A - y)(a - x)/y = r$$

$$dx/dt = 2.303 k_c(a - x)(A - y)$$

where  $k_c$  is the catalytic constant of the  $C_2H_5\cdot OH_2^+$  ion, and it is assumed that catalysis by the  $OH_3^+$  ion can be neglected. The solution of these equations is

$$k_c t + C = \frac{-0.434}{A - y} + \frac{A - a - r}{2Ar} \log_{10} \frac{y^2 - (A + a + r)y + Aa}{(A - y)^2}$$

$$+ \frac{(A - a - r)^2 + 4Ar}{4Ar\{\frac{1}{2}(A + a + r)^2 - Aa\}^{\frac{1}{2}}} \log_{10} \frac{y - \frac{1}{2}(A + a + r) + \{\frac{1}{4}(A + a + r)^2 - Aa\}^{\frac{1}{2}}}{y - \frac{1}{2}(A + a + r) - \{\frac{1}{4}(A + a + r)^2 - Aa\}^{\frac{1}{2}}} \quad (3)$$

where  $2y = A + x + r - \{(A + x + r)^2 - 4Ax\}^{\frac{1}{2}}$  and  $C$  is a constant for each reaction. The velocity constants were determined from the experimental data by plotting the right-hand side of equation (2) or (3) against the time, straight lines being obtained within the experimental error.

*Results.*—The following table gives the velocity constants and catalytic constants obtained at six temperatures. Concentrations are expressed in mols./1000 c.c., and the time in mins. The results at  $-44^\circ$  are less accurate than those at higher temperatures, partly because of unsatisfactory temperature control.

At $25^\circ$ : $k_c = 84.3 \pm 2.3$ .							
$10^5 A$	2.2	4.3	6.3	10.3	19.9	48.8	
$1000k$	1.86	3.76	5.15	9.68	15.8	38.5	
$k_c$	84.9	87.0	82.0	93.8	79.3	78.9	
At $10.13^\circ$ : $k_c = 21.6 \pm 1.0$ .							
$10^4 A$	0.24	0.36	1.33	2.67	5.33	7.99	10.64
$1000k$	0.42	0.71	2.65	5.84	12.4	19.3	26.2
$k_c$	17.5	19.5	19.9	21.9	23.3	24.2	24.6

At 0°: $k_c = 7.8 \pm 0.4$ .								
$10^3 A$ .....	0.50	0.75	1.00	1.04	1.04	3.91	6.01	7.37
$1000k$ .....	3.0	5.9	7.6	7.9	7.0	35.4	53.5	66.0
$k_c$ .....	6.0	7.8	7.6	7.5	6.7	9.1	8.9	9.0
At -20.1°: $k_c = 0.84 \pm 0.05$ .								
$10^3 A$ .....	2.0	3.4	4.0	13.1	16.2	26.2		
$1000k$ .....	1.45	2.71	2.87	12.9	25.8	24.8		
$k_c$ .....	0.71	0.79	0.71	0.98	0.98	0.95		
At -35.1°: $k_c = 0.12 \pm 0.006$ .								
$10^3 A$ .....	0.96	1.28	2.02	2.78	4.37	6.92	10.1	
$10^3 k$ .....	0.94	1.73	2.22	3.89	5.33	7.20	23.5	
$10^3 k_c$ .....	0.98	1.35	1.09	1.40	1.22	1.04	1.34	
At -44.0°: $k_c = 0.036 \pm 0.005$ .								
$10^3 A$ .....	1.30	2.07	2.47	6.9	8.7	1.07	12.3	15.7
$10^4 k$ .....	2.9	4.2	7.2	35.1	35.6	21.4	87.5	48.6
$100k_c$ .....	2.2	2.0	2.9	5.1	4.1	2.0	7.1	3.1

## DISCUSSION.

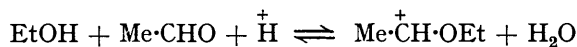
The mean values for  $k_c$  at the six temperatures are expressed excellently by the simple Arrhenius equation. Since the data at  $-44^\circ$  are of lower accuracy, the method of least squares was applied to the values for the other five temperatures, giving the equation

$$k_c = 2.34 \times 10^{13} e^{-15,500/RT} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

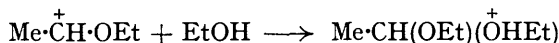
The observed and the calculated value of  $k_c$  are given below :

Temp. ....	25.0°	10.1°	0.0°	-20.1°	-35.1°	-44.0°
$k_c$ { obs. ....	84.3	21.6	7.8	0.84	0.12	0.036
{ calc. ....	84.3	21.7	7.85	0.83	0.12	0.034

It will be seen that the agreement is well within the experimental error. The value of the first constant in equation (4) is of the order of magnitude predicted by the collision theory. There is thus no indication of the "tunnel effect," which might be expected to appear at low temperatures in reactions catalysed by acids or bases (Bell, *Trans. Faraday Soc.*, 1938, **34**, 229). Hammett ("Physical Organic Chemistry," pp. 300, 304, New York, 1940) has suggested that in the acetalisation reaction the equilibrium



is set up instantaneously, followed by the slow reaction



If this mechanism is accepted, no "tunnel effect" would be expected, since the rate-determining step does not involve a proton transfer.

The value we have obtained for the catalytic constant at  $25^\circ$  is about 35% higher than that given by Deyrup (*loc. cit.*), though his value at  $35^\circ$  agrees fairly well with equation (4). It may be noted that the discrepancy at  $25^\circ$  would be accounted for if the alcohol used by Deyrup at this temperature had contained about 0.1% of water. Deyrup also found that added salts had a considerable accelerating effect, and if the hydrogen and chloride ions have a similar effect we might expect  $k_c$  to increase with acid concentration at the lower temperatures, where higher concentrations were used. Our experimental results do not provide any evidence for any variation of  $k_c$ , which might, however, be masked by the decreased experimental accuracy at lower temperatures. In any case it may be easily seen that the presence of a salt effect of the same order of magnitude as that found by Deyrup would not affect the agreement with the Arrhenius equation, though it would slightly affect the values of the constants.

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