Acetaldehyde Aldol Condensation Kinetics

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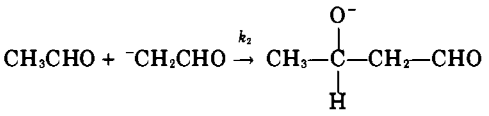
ACETALDEHYDE may react to form aldol whenever acetaldehyde and hydroxide ions are present. While direct applications of this reaction are few, it provides one method of making carbon-to-carbon bonds; and the reaction can and does occur as an undesirable side reaction in many processes. A complete knowledge of the kinetics and mechanisms of this reaction may aid in the study of similar condensation reactions such as the formation of pentaerythrose.

The mechanism of the acetaldehyde aldol reaction has been the object of several studies (*1*, *4*, *8*). However, the results have been indefinite. This work was undertaken to establish the kinetics and mechanism of the reaction.

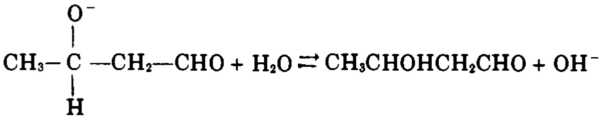
THEORY

A mechanism for the reaction, originally proposed by Hann and Lapworth (*6*) is generally accepted today. It is supported strongly by electronic theories of reaction. This mechanism may be given as follows.

$$CH_3CHO + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} {}^-CH_2CHO + H_2O \qquad (1)$$



$$CH_3CHO + {}^-CH_2CHO \xrightarrow{k_2} CH_3-\underset{H}{\overset{O^-}{C}}-CH_2-CHO \qquad (2)$$



$$CH_3-\underset{H}{\overset{O^-}{C}}-CH_2-CHO + H_2O \rightleftarrows CH_3CHOHCH_2CHO + OH^- \qquad (3)$$

The *k*'s represent the reaction rate constants for the forward and reverse reactions. The reaction is catalyzed by hydroxide ions and does not proceed in acidic solutions. The equilibrium point is too far in the aldol direction to be determined (*10*). On theoretical grounds, Reaction 3 is believed to be fast, and its rate has not been considered.

Among the important early experimental studies that was done by Bell (*1*). Using a dilatometric technique, he studied the acetaldehyde aldol condensation in water solution with sodium hydroxide as the catalyst. Because further condensation also appears and because acetaldehyde exists partly as a hydrate in water solution, definite conclusions could not be made. Later, Bell (*2*) concluded that the data supported a Hann and Lapworth type of mechanism in which the first reaction is slow and rate-controlling. In this case, the rate is proportional to the concentrations of acetaldehyde and hydroxide ions.

Bonhoeffer and Walters (*5*) formed aldol from acetaldehyde in deuterium oxide solutions with potassium carbonate at 0° C. They found that no deuterium became attached to carbon in the aldol product. This evidence supports the mechanism advanced by Bell. The slow step in the reaction is the ionization of acetaldehyde to form a carbonion which reacts immediately with an acetaldehyde molecule in the condensation step. If the condensation reaction were not rapid compared to the ionization reaction, deuterium would become attached to carbon in the reverse of the ionization reaction:

$$^-CH_2-CHO + D_2O \rightarrow CH_2D-CHO + OH^- \qquad (4)$$

Matsuyama (*8*) determined the rate of the acetaldehyde aldol condensation at 35° C. by measuring the heat produced during the course of the reaction. Although the results were not entirely definite, he concluded that the reaction was second order in acetaldehyde and first order in hydroxide.

A general rate equation based on the Hann and Lapworth mechanism may be developed as follows: Assuming the third step is rapid, the reversibility of Reaction 2 can be neglected,and the rate of formation of aldol as given from Reaction 2 is

$$\frac{d[\text{aldol}]}{dt} = k_2[CH_3CHO][^-CH_2CHO] \qquad (5)$$

where t = time in minutes and the brackets indicate concentration in moles per liter. For the carbanion, $^-CH_2CHO$

$$\frac{d[^-CH_2CHO]}{dt} = k_1[CH_3CHO][OH^-] - k_{-1}[^-CH_2CHO][H_2O] - k_2[CH_2CHO][CH_3CHO] \qquad (6)$$

Applying the steady state method by assuming that

$$\frac{d[^-CH_2CHO]}{dt} = 0 \qquad (7)$$

and solving for $[^-CH_2CHO]$,

$$[^-CH_2CHO] = \frac{k_1[CH_3CHO][OH^-]}{k_{-1}[H_2O] + k_2[CH_3CHO]} \qquad (8)$$

Substituting in Equation 5,

$$\frac{d[\text{aldol}]}{dt} = \frac{k_1k_2[CH_3CHO]^2[OH^-]}{k_{-1}[H_2O] + k_2[CH_3CHO]} \qquad (9)$$

For cases in which strong bases other than hydroxide are present, the product $k_1[OH^-]$ would be replaced by $\sum k_1[B_1]$, where k_1 is the individual constant for formation of the carbanion by reaction of acetaldehyde with each base B_1. In this treatment, it is assumed that bases other than hydroxide need not be included.

Acetaldehyde exists partly as a hydrate in water solutions. The formation of acetaldehyde from its hydrate is fairly rapid compared to the aldol condensation (*3*, *7*). As it is likely that only free acetaldehyde is involved in the aldol condensation, it is necessary to alter the general rate equation when total (as opposed to free) acetaldehyde is used. Assuming that other forms of acetaldehyde may be neglected,

$$[eCH_3CHO] = [CH_3CHO] + [\text{hydrate}] \qquad (10)$$

where eCH₃CHO = total acetaldehyde, including hydrated and ionized forms. For equilibrium with the hydrates,

$$\frac{[\text{hydrate}]}{[CH_3CHO][H_2O]} = K \text{ of hydration} \qquad (11)$$

The value of the constant of hydration has been reported

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to be 0.0485 (moles per liter)$^{-1}$ at 0° C. and 0.0218 (moles per liter)$^{-1}$ at 25° C. (3). Then, at 0° C.

$$[CH_3CHO] = \frac{[eCH_3CHO]}{1 + 0.0485[H_2O]} \qquad (12)$$

For concentrations of acetaldehyde up to $10M$, the concentration of free acetaldehyde may be given by

$$[CH_3CHO] = K'[eCH_3CHO] \qquad (13)$$

where K' varies by only 20% at 0° C. and less at 25° C.
With this substitution, Equation 9 becomes

$$\frac{d[\text{aldol}]}{dt} = \frac{k_1k_2(K')^2[eCH_3CHO]^2[OH^-]}{k_{-1}[H_2O] + k_2K'[eCH_3CHO]} \qquad (14)$$

$$\frac{d[\text{aldol}]}{dt} = \frac{k_5[eCH_3CHO]^2[OH^-]}{k_6[H_2O] + [eCH_3CHO]} \qquad (15)$$

where $k_5 = k_1K'$ and $k_6 = k_{-1}/k_2K'$.

Having made the assumption that the rate of change of concentration of the carbanion is zero.

$$-\frac{d[eCH_3CHO]}{dt} = 2\frac{d[\text{aldol}]}{dt} \qquad (16)$$

Equation 15 may then be written as

$$-\frac{d[eCH_3CHO]}{dt} = \frac{2k_5[eCH_3CHO]^2[OH^-]}{k_6[H_2O] + [eCH_3CHO]} \qquad (17)$$

Integration between $t = 0$ and $t = t$, $[eCH_3CHO] = [eCH_3CHO]^0$ and $[eCH_3CHO] = [eCH_3CHO]$ gives

$$k_6[H_2O]\left\{\frac{1}{[eCH_3CHO]} - \frac{1}{[eCH_3CHO]^0}\right\} + \ln\frac{[eCH_3CHO]^0}{[eCH_3CHO]} = 2k_5\int_0^t [OH^-]\,dt \qquad (18)$$

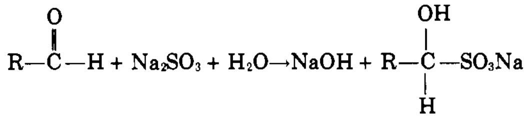
If Reaction 1 is rate-limiting, k_6 becomes negligible and the first terms of Equation 18 may be dropped, giving a rate equation first order in acetaldehyde and first order in hydroxide ion concentrations as reported by Bell. If Reaction 2 is rate-limiting, the second term may be dropped, giving a rate equation that is second order in acetaldehyde and first order in hydroxide ion concentrations. If Reactions 1 and 2 are each partially rate-limiting, all terms in Equation 18 are required.

EQUIPMENT AND PROCEDURE

Experimental data were obtained using an ice bath at 0° C. and a constant temperature bath at 25° C. (Table I). The reactor vessel was a 1-liter, round-bottomed flask, equipped with four necks. A motor-driven stirrer, inserted through the middle neck of the flask, operated continuously throughout each run. A mercury seal was provided to prevent escape of vapors through this neck. Electrodes for a pH meter were inserted into two of the side necks, while a thermometer was inserted into the fourth neck. Samples were taken during the course of each run by introducing pipets into one of the side necks.

For each run, the acetaldehyde (Eastman Organic Chemicals, C.P. grade) and water mixture was placed in the reactor and allowed to reach the proper temperature. Samples were taken to determine the initial amount of acetaldehyde present. Then a known amount of base (potassium hydroxide) was introduced, causing the reaction to begin. At various time intervals, samples were taken for analysis. Readings of pH were taken repeatedly throughout each run.

Samples were collected in 300-ml. Erlenmeyer flasks containing sufficient standard sulfuric acid solution to neutralize the base present and effectively quench the reaction. Analysis for aldehyde content of each sample was made by the sodium sulfite method of Siggia and Maxcy (9). This method is based on the following reaction:


(19)

$$R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}H + Na_2SO_3 + H_2O \rightarrow NaOH + R{-}\overset{\displaystyle OH}{\underset{\displaystyle H}{C}}{-}SO_3Na \qquad (19)$$

A known excess of standard sulfuric acid solution was placed in each sample flask together with an excess of sodium sulfite. The sample was then introduced and allowed to react for several hours at room temperature. Titration for excess acid allowed the amount of sodium hydroxide produced in the above reaction to be calculated, thus giving the amount of aldehyde present. The end point was taken to correspond to the color change with thymolphthalein indicator as established by potentiometric titration. From knowledge of the initial concentration of acetaldehyde and the concentration of aldehyde in each sample, the concentration of acetaldehyde could be calculated. It was assumed that no crotonaldehyde was formed from aldol during the course of the reaction in alkali medium or during the analytical tests when the medium was acidic. This assumption was found to be acceptable by tests with commercial grade aldol.

The pH meter used was a Beckman Model G equipped

Table I. Experimental Data

(Time in minutes. A^* = [eCH$_3$CHO], concentration of free acetaldehyde plus hydrate in moles per liter.)

Run 1, 0° C. pH Constant at 12.84		Run 2, 0° C.			
Time	A^*	Time	A^*	Time	pH
0	0.0830	0	0.2030	1	12.94
2.5	0.0829	3	0.2014	5	13.00
9	0.0833	11	0.1879	7	13.00
20	0.0822	20	0.1822	12	13.00
35	0.0801	36	0.1726	25	12.98
43	0.0789	48	0.1646	39	12.94
61	0.0775	103	0.1490	41	12.94
81	0.0759	108	0.1469	47	12.94
116	0.0707	111	0.1449	106	12.88
161	0.0678	160	0.1345	125	12.88
208	0.0650	219	0.1262	128	12.89
266	0.0608	223	0.1248	162	12.88
268	0.0606	224	0.1242	191	12.88
270	0.0615	312	0.1118	246	12.87
325	0.0598	313	0.1106	322	12.82
378	0.0551	314	0.1112	356	12.82
435	0.0531	407	0.0975	423	12.82
436	0.0530	408	0.0986	425	12.81
437	0.0530	409	0.0967	436	12.82
490	0.0506	518	0.0706	456	12.83
542	0.0479	519	0.0689	489	12.83
595	0.0453	520	0.0705	522	12.81
596	0.0467				
597	0.0456				
Time	A^*	Time	pH	Time	pH
		Run 3, 0° C.			
0	0.637	1	13+	119	12.23
6	0.592	2	13.15	173	12.13
13	0.574	3	13.05	180	12.18
27	0.548	4	13.00	185	12.18
37	0.517	6	12.94	199	12.17
48	0.500	8	12.88	202	12.18
110	0.448	10	12.82	207	12.17
122	0.431	12	12.78	219	12.16
167	0.329	14	12.72	231	12.17
190	0.394	16	12.70	260	12.12
209	0.346	18	12.67	264	12.16
232	0.368	20	12.67	268	12.15
258	0.346	22	12.63	275	12.14
285	0.341	34	12.28	283	12.14
317	0.333	36	12.25	313	12.14
347	0.319	38	12.24	318	12.14
409	0.310	50	12.28	351	12.13
456	0.292	52	12.28	371	12.14
		115	12.24	377	12.14
		117	12.22	407	12.14

Table I. Continued

Run 4, 0° C.

Time	A*	Time	pH	Time	pH
0	0.838	2	11.47		
4	0.831	5	11.48		
12	0.821	11	11.50		
41	0.793	16	11.47		
68	0.783	23	11.47		
69	0.785	37	11.48		
133	0.766	65	11.44		
134	0.763	71	11.42		
218	0.746	135	11.39		
219	0.737	142	11.40		
258	0.729	221	11.34		
259	0.741	238	11.32		
296	0.729	266	11.31		
297	0.727	299	11.30		
344	0.713	336	11.27		
345	0.716	358	11.29		

Run 5, 0° C.

Time	A*	Time	pH	Time	pH
0	0.913	1	12.52	99	12.10
4	0.896	2	12.52	103	12.10
13	0.862	3	12.50	111	12.10
31	0.807	4	12.45	118	12.09
47	0.766	6	12.44	121	12.10
67	0.729	7	12.42	126	12.09
96	0.703	8	12.42	143	12.08
124	0.658	10	12.41	163	12.07
146	0.625	20	12.30	168	12.06
167	0.614	23	12.28	173	12.05
190	0.591	25	12.28	178	12.04
212	0.575	30	12.25	188	12.04
233	0.559	34	12.23	211	12.03
256	0.553	40	12.21	214	12.02
286	0.526	43	12.21	222	12.02
		51	12.19	232	12.01
		54	12.18	248	12.01
		62	12.17	254	12.00
		69	12.15	261	11.99
		71	12.15	271	12.00

Run 6, 0° C.

Time	A*	Time	pH	Time	pH
0	2.975	1	11.82	350	11.28
2	2.959	3	11.77	377	11.29
16	2.857	5	11.74	434	11.28
33	2.725	7	11.72	457	11.28
43	2.651	14	11.66		
55	2.565	17	11.62		
82	2.449	20	11.61		
108	2.385	32	11.58		
121	2.315	40	11.54		
146	2.279	45	11.51		
168	2.215	54	11.50		
188	2.141	59	11.49		
224	2.093	93	11.42		
243	2.085	109	11.40		
260	2.041	122	11.39		
294	2.013	147	11.35		
347	1.935	169	11.33		
356	1.891	184	11.32		
374	1.891	226	11.30		
429	1.841	246	11.30		
453	1.811	252	11.29		
454	1.811	262	11.29		

Run 7, 0° C.

Time	A*	Time	pH	Time	pH
0	3.12	3	12.15	238	11.75
2	3.03	5	12.13	252	11.74
7	2.87	8	12.09	264	11.73
14	2.70	9	12.07	274	11.73
28	2.46	12	12.01	292	11.73
47	2.29	16	12.00	301	11.72
48	2.22	23	11.96	320	11.73
77	2.09	28	11.92	360	11.71
94	2.03	33	11.91	381	11.72
95	1.94	35	11.91	412	11.72
160	1.76	40	11.90		
161	1.82	48	11.88		
236	1.65	56	11.86		
237	1.63	77	11.83		
272	1.61	84	11.81		
273	1.57	89	11.80		
318	1.53	92	11.80		
319	1.55	97	11.80		
379	1.47	167	11.77		
380	1.49	170	11.77		

Run 8, 0° C.

Time	A*	Time	pH	Time	pH
0	10.37	3	11.86		
1.5	9.32	6	11.80		
5	9.57	11	11.73		
10	9.11	13	11.71		
12.5	9.06	18	11.67		
20	8.96	21	11.67		
22.5	8.61	25	11.64		
26.5	8.49	29	11.60		
30.5	8.16	32	11.60		
34	8.13	36	11.60		
37	8.00	40	11.60		
40	7.86	44	11.58		
45	7.79	50	11.57		
48	7.67	54	11.56		
51	7.47	60	11.55		
55	7.29	64	11.55		
59	7.29				
63	7.26				

Run 11, 25° C.

Time	A*	Time	pH	Time	pH
0	0.1048	1	11.33	240	11.59
4	0.1032	5	11.35	275	11.62
10	0.0962	7	11.35	290	11.60
36	0.0755	12	11.38		
54	0.0669	21	11.38		
55	0.0654	38	11.38		
132	0.0380	43	11.40		
133	0.0379	53	11.40		
195	0.0225	58	11.43		
196	0.0214	131	11.50		
289	0.0074	153	11.56		
290	0.0063	177	11.58		

Run 12, 25° C.

Time	A*	Time	pH	Time	pH
0	0.346	1	11.93	34	11.78
2	0.315	3	11.98	38	11.78
5	0.275	6	11.80	42	11.78
11	0.211	10	11.78	47	11.78
16	0.182	12	11.76	49	11.78
24	0.144	14	11.76	53	11.78
31	0.128	16	11.75	61	11.78
37	0.110	19	11.74	69	11.79
48	0.097	22	11.74	76	11.79
54	0.081	25	11.75	86	11.79
63	0.600	26	11.76		
72	0.044	29	11.77		
78	0.030	32	11.78		

Run 13, 25° C.

Time	A*	Time	pH	Time	pH
0	0.796	1.5	10.88	210	10.41
3.5	0.729	4	10.82	238	10.38
11	0.699	9	10.76		
18	0.674	14	10.69		
27	0.632	19	10.68		
35	0.597	21	10.67		
43	0.568	28	10.65		
53	0.554	33	10.62		
61	0.530	40	10.59		
105	0.465	44	10.58		
106	0.454	51	10.53		
117	0.448	54	10.53		
127	0.432	62	10.53		
128	0.432	107	10.48		
200	0.352	110	10.48		
201	0.352	118	10.47		
240	0.332	129	10.47		
241	0.331	202	10.42		

Run 14, 25° C.

Time	A*	Time	pH	Time	pH
0	1.028	1	10.92	46	10.56
4	0.988	2	10.90	49	10.58
10.5	0.933	4.5	10.86	51	10.57
16.25	0.885	8.5	10.77	54	10.56
22	0.836	12	10.72	59	10.55
26	0.803	14	10.70	64	10.56
30.5	0.793	17	10.68	68	10.54
35	0.787	20	10.66		
38.5	0.777	23	10.64		
43.5	0.776	27	10.62		
50	0.756	32	10.62		
57.5	0.739	36	10.62		
66	0.706	39	10.61		
69	0.692	42	10.60		

with a Type E glass electrode and a calomel reference electrode. Standardization of the electrodes was checked periodically during each run. Because potassium hydroxide was used as the basic catalyst, no sodium ion corrections were necessary. The total base content of the reaction mixture was determined by titration of samples in the standard manner.

DISCUSSION OF RESULTS

Table II contains summarizing data for runs at 0° and 25° C., indicating the ranges of total acetaldehyde concentrations and pH values. Figure 1 shows typical curves of acetaldehyde concentration and pH changes with time during a run. In one run at 25° C. the pH increased; in all others, the pH decreased in value with time. The total base content of the reaction mixture (as determined by titration) remained essentially constant throughout each run, although a very slight decrease was observed. The observed values of pH were less than those obtained from calculations considering the total base content of the system to exist as hydroxide ions. This indicates that some of the base added as catalyst reacted to form anions of acetaldehyde and aldol. The calculated amounts of these anions were small in relation to the total acetaldehyde present.

Table II. Summarized Data for all Runs Showing Ranges of Acetaldehyde Concentration, pH, and Rate Constants

Run No.	Temp., °C.	Time Range, Min.	[eCH$_3$CHO] Range, Moles/L.	pH Range	Rate Constants, (L./Mole)^2 (Min.)$^{-1}$	
					$2k_5/k_6(H_2O)$	$2k_5$
						$k_6 = 0.184$
1	0	0–597	0.0830–0.0456	12.84	2.21	22.1
2	0	0–520	0.2030–0.0705	12.94–12.81	1.77	17.7
3	0	0–456	0.637 –0.292	13.15–12.14	2.06	20.6
4	0	0–345	0.838 –0.716	11.47–11.29	1.72	18.2
5	0	0–286	0.913 –0.526	12.52–12.00	1.89	19.1
6	0	0–454	2.975 –1.811	11.82–11.28	...	22.1
7	0	0–380	3.120 –1.490	12.15–11.72	...	20.0
8	0	0– 63	10.37 –7.26	11.86–11.55	...	21.0
						$k_6 = 0.0063$
11	25	0–290	0.1048–0.0063	11.33–11.60	...	16.7
12	25	0– 78	0.346 –0.031	11.93–11.79	...	14.6
13	25	0–241	0.796 –0.331	10.88–10.38	...	15.8
14	25	0– 69	–.028 –0.692	10.92–10.54	...	18.5

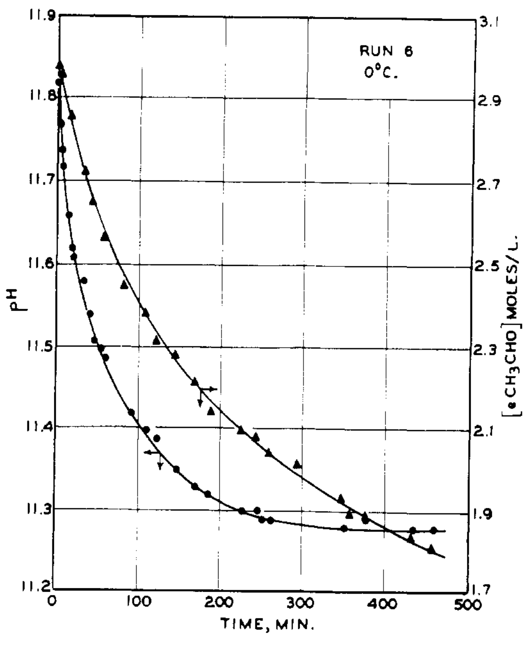


Figure 1. For a typical run at 0° C., both acetaldehyde concentration and pH of the liquid solution decrease with time

Further condensation of acetaldehyde and aldol can occur. Although the rate of condensation of aldol is slow, greater emphasis was placed on the data from the early stages of each run.

The [OH$^-$] was determined from pH readings using values for the ion product of water of $10^{-14.95}$ and $10^{-13.97}$ at 0° and 25° C., respectively. Plots of [OH$^-$] *vs.* time were drawn for each run and the integral, $\int_0^t [OH^-]dt$ was evaluated graphically at various values of time, *t*.

For runs at 0° C. with acetaldehyde concentrations below 2*M*, the logarithmic term in Equation 18 could be neglected; and plots of

$$\left\{ \frac{1}{[eCH_3CHO]} - \frac{1}{[eCH_3CHO]^0} \right\} vs. \int_0^t [OH^-]dt$$

gave straight lines. The slopes of these lines, equal to $2k_5/k_6[H_2O]$, are shown in Table II. The average deviation is 8.5%. Thus, under conditions of low acetaldehyde concentration and at 0° C., the reaction appears to be second order in acetaldehyde and first order in hydroxide ion concentrations—i.e., [eCH$_3$CHO] is negligible with respect to k_6[H$_2$O] in Equation 15.

With higher acetaldehyde concentrations at 0° C., [eCH$_3$CHO] becomes important with respect to k_6[H$_2$O] and the logarithmic term in Equation 18 must be included.

An over-all plot of

$$k_6[H_2O] \left\{ \frac{1}{[eCH_3CHO]} - \frac{1}{[eCH_3CHO]^0} \right\} + \ln \frac{[eCH_3CHO]^0}{[eCH_3CHO]} vs. \int_0^t [OH^-]dt$$

for 0° C. is shown in Figure 2. The slope of the straight line is equal to $2k_5$. The correct valve of k_6 was determined by trial and error with the aid of the ratio $2k_5/k_6[H_2O]$ determined previously. The average values of the constants determined are:

k_5 = 10 (liters)/(mole)(minute)
k_6 = 0.184 (no units)

The average deviation of k_5, with k_6 equal to 0.184, is 6.7%. Thus, at 0° C., the theoretically derived Equation 15 agrees with the experimental data; the Hann and Lapworth mechanism with the first and second steps partially rate-controlling at high acetaldehyde concentration and the second step rate-controlling at low acetaldehyde concentration appears to be valid.

At 25° C., in the acetaldehyde concentration range

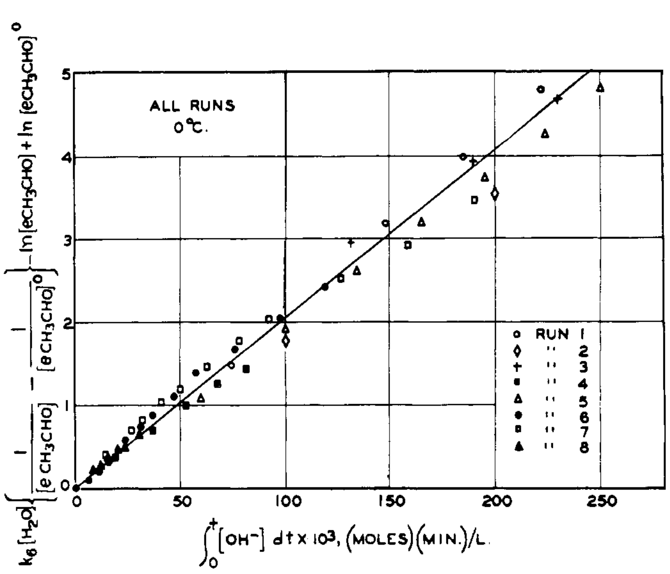


Figure 2. On the basis of the Hann and Lapworth type of mechanism with Reactions 1 and 2 rate-controlling, this plot should give a straight line through the origin with a positive slope at 0° C. The mechanism applies over a wide range of acetaldehyde concentrations

studied, the experimental data agreed with Equation 15. Figure 3 is a plot of

$$k_6[H_2O]\left\{\frac{1}{[eCH_3CHO]}-\frac{1}{[eCH_3CHO]^0}\right\}+\ln\frac{[eCH_3CHO]^0}{[eCH_3CHO]}\ vs.\ \int_0^t[OH^-]dt$$

The integral was determined by graphical integration, and the correct value of k_6 was determined by trial and error. The required straight line was obtained. The average values of the constants determined are

k_5 = 8.2 (liters)/(mole)(minute)

k_6 = 0.0063 (no units)

The average deviation of k_5, with k_6 equal to 0.0063, is 7.3%. This agreement between the experimental data and the theoretical equations indicates that the Hann and Lapworth mechanism with the first and second steps each partially rate-controlling is valid at 25° C.

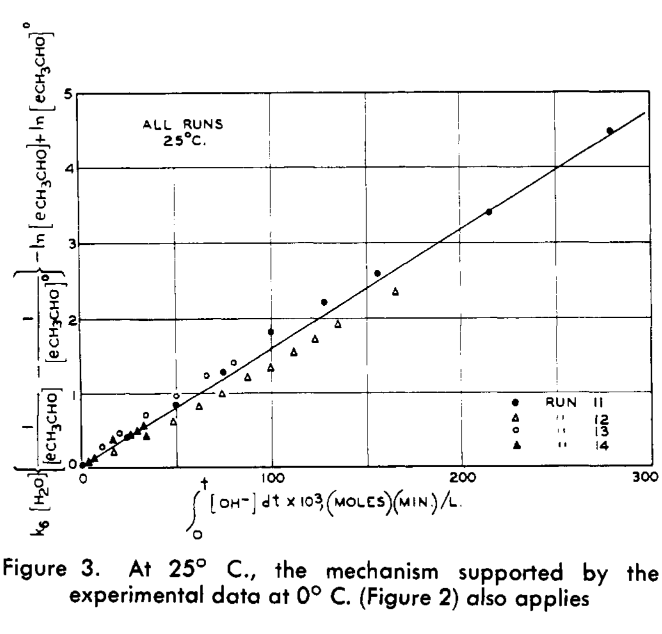


Figure 3. At 25° C., the mechanism supported by the experimental data at 0° C. (Figure 2) also applies

The kinetics of reaction reported here differ from those reported by Bell. He concluded that the reaction was first order in acetaldehyde and first order in hydroxide ion concentrations. Because further condensation of the aldol product occurs, it has been impossible to perform experiments in which the concentration of acetaldehyde varied widely during an individual run. For this reason, a wide range of initial acetaldehyde concentrations was used in this work. For an individual run, the data might be interpreted as indicating kinetics first order in acetaldehyde. This may be seen in Figure 4 where $\ln \frac{[eCH_3CHO]^0}{[eCH_3CHO]}$ is plotted against $\int_0^t [OH^-]dt$ for runs at 0° C. A similar plot may be made for runs at 25° C. If the kinetics were first order in acetaldehyde, each line in Figure 4 would have the same slope.

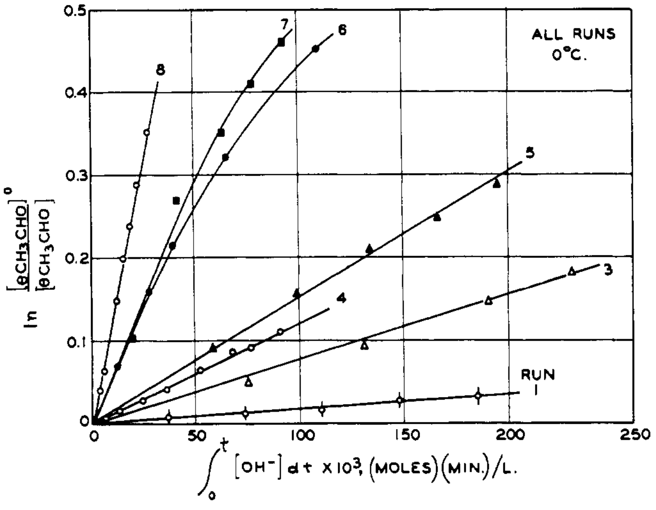


Figure 4. Although the kinetic equation first order in acetaldehyde concentrations appears to apply when the kinetics are considered with respect to time, the first-order equation does not hold when large ranges of concentrations are considered. If the first-order equation were correct, all points on this plot would have fallen approximately on one straight line

The wide variation in slopes shows that such an interpretation is impossible. It is believed that if Bell had used a wide range of initial acetaldehyde concentrations, he could not have reported kinetics first order in acetaldehyde. Also, because of the variation in hydroxide ion concentration during individual runs (which Bell failed to recognize), the results reported here should supersede his work.

Figure 5 is a plot of the rate expression for second order in acetaldehyde, $\frac{1}{[eCH_3CHO]}-\frac{1}{[eCH_3CHO]^0}$ vs. $\int_0^t [OH^-]dt$. For kinetics second order in acetaldehyde, the plot would show a single line of constant slope. The variation in slopes is such that the slopes decrease with increasing acetaldehyde concentration.

The observation of Bonhoeffer and Walters (*5*), that no deuterium becomes attached to carbon in the aldol product, does not necessarily disagree with the conclusions set forth here. Their experiment was carried out with a high concentration of acetaldehyde. As the concentration of acetaldehyde is increased, the rate of the mechanism's condensation step increases with respect to the rate of the reverse of the ionization reaction. Thus, it is feasible that under conditions of high acetaldehyde concentration very few deuterium-carbon bonds would be formed when the reaction is carried out in the deuterium oxide solution.

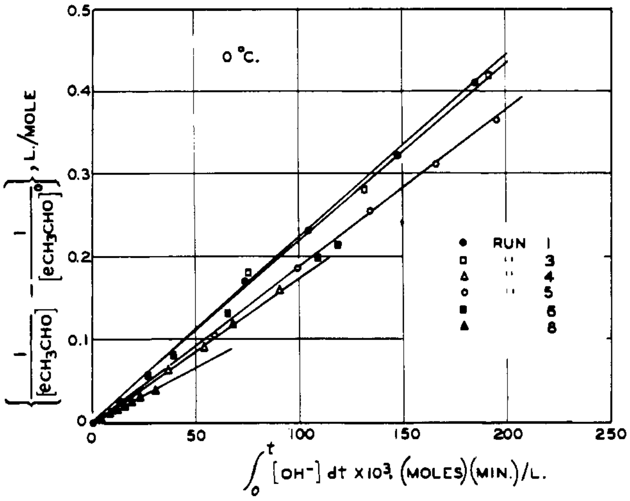


Figure 5. When the rate equation is considered as second order in acetaldehyde concentration, the slopes of the lines on this plot decrease with increasing acetaldehyde concentration instead of remaining constant as a true second-order case would require

ACKNOWLEDGMENT

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CORRECTION

In "Phase Equilibria in Hydrocarbon Systems. Volumetric and Phase Behavior of Ethane-*n*-Pentane System" [H.H. Reamer, B.H. Sage, and W.N. Lacey, J. CHEM. ENG. DATA 5, 44 (1960)] these figures should have appeared instead of the ones on page 49.

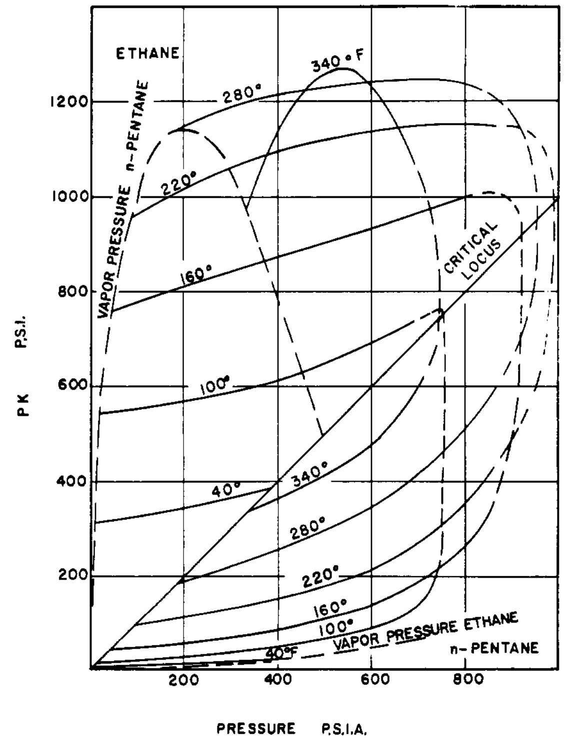

Figure 3. Equilibrium ratios for ethane and *n*-pentane

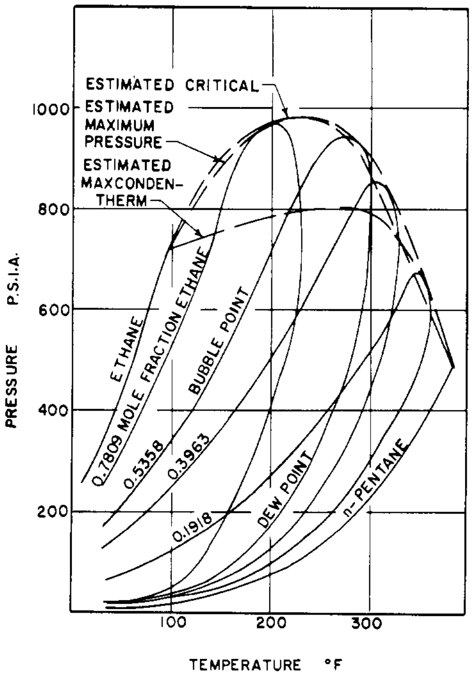

Figure 4. Pressure-temperature diagram for the ethane–*n*-pentane system