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Kinetics of pentaerythritol-production reactions

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Abstract—The kinetics of the reactions involved in the formation of pentaerythritol were investigated. The results show that the aldol condensations leading to pentaerythrose are very rapid and the rate-limiting step is the pentaerythrose–formaldehyde Cannizzaro reaction. The rate equations for both the pentaerythrose–formaldehyde and the direct formaldehyde Cannizzaro reactions are shown to be represented satisfactorily as third order. Activation energies and rate-constant expressions are presented for the Cannizzaro reactions with sodium hydroxide as the base.

Résumé—Les auteurs ont étudié la cinétique des réactions mises en jeu dans la formation du pentaerythritol. Les résultats montrent que les condensations d'aldol conduisant au pentaerythrose sont très rapides, la réaction de Cannizaro pentaerythrose – formaldehyde limitant la vitesse. Les équations de vitesse pour les réactions pentaerythrose – formaldehyde et formation directe de formaldehyde par la réaction de Cannizaro sont représentées de façon satisfaisante par une réaction d'orde 3. Les expressions des énergies d'activation et des constantes de vitesse sont données pour les réactions de Cannizaro avec la soude comme base.

Zusammenfassung—Die Kinetik der bei der Bildung von Pentaerythrit auftretenden Reaktionen wurde untersucht. Die Ergebnisse zeigen, dass die Aldol-Kondensationen, die zu Pentaerythrose führen, sehr schnell verlaufen und dass der geschwindig keitsbestimmende Schritt die Pentaerythrose – Formaldehyd-Cannizaro-Reaktion ist. Die Gleichungen für die Geschwindigkeit der Pentaerythrose – Formaldehyd und der direkten Formaldehyd-Cannizaro-Reaktion lassen sich befriedigend durch die dritte Ordnung wiedergeben. Aktivierungsenergien und Ausdrücke für die Geschwindigkeitskonstante werden für die Cannizaro-Reaktionen mit Natriumhydroxyd als Base angegeben.

PENTAERYTHRITOL is an important intermediate in the plastics, paint, dye, and explosives industries. A large amount of information relating to methods of commerical production is available in the form of patents and in the general literature [3, 9, 11]; however, due to the complexity of the reactions that may be involved, very little information has been published on the kinetics or mechanisms of the reactions [2, 12].

In the commercial process, pentaerythritol is produced in an aqueous alkaline medium of formaldehyde and acetaldehyde. Sodium hydroxide or calcium hydroxide are the alkalies most frequently used. The general reaction steps are well understood from the standpoint of organic reactions. The α-hydrogen atoms of an aldehyde are very reactive, and, in a basic medium, they can undergo the aldol condensation reaction with any aldehyde present provided steric hindrance does not rule out the reaction. If there are no α-hydrogen atoms present on the aldehyde molecule, it can undergo the Cannizzaro reaction in which two molecules of aldehyde yield a molecule of an organic acid and an alcohol molecule. The reaction steps of formaldehyde with acetaldehyde are summarized in the following equations :

Aldol condensation reactions,

$$\mathrm{HCHO} + \mathrm{CH_3\,CHO} \xrightarrow{(\mathrm{OH^-})} \mathrm{HOCH_2\,CH_2\,CHO} \qquad \text{(a)}$$

$$\mathrm{HCHO} + \mathrm{HOCH_2\,CH_2\,CHO} \xrightarrow{(\mathrm{HO^-})} (\mathrm{HOCH_2})_2\,\mathrm{CHCHO} \qquad \text{(b)}$$

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$$\mathrm{HCHO} + (\mathrm{HOCH_2})_2\,\mathrm{CHCHO} \xrightarrow{(\mathrm{OH^-})} (\mathrm{HOCH_2})_3\,\mathrm{CCHO} \quad \text{(c)}$$

Pentaerythrose

Cannizzaro reaction,

$$\mathrm{HCHO} + (\mathrm{HOCH_2})_3\,\mathrm{CCHO} + \mathrm{OH^-} \xrightarrow{k_1} (\mathrm{HOCH_2})_4\mathrm{C} + \mathrm{HCOO^-} \quad \text{(d)}$$

Pentaerythritol

The only significant side reaction involving formaldehyde and hydroxyl ion is the formaldehyde Cannizzaro reaction

$$2\mathrm{HCHO} + \mathrm{OH^-} \xrightarrow{k_2} \mathrm{HCOO^-} + \mathrm{CH_3\,OH} \quad \text{(e)}$$

In the production of pentaerythritol, this side reaction and the formaldehyde reaction to form glycollic aldehyde are only of major importance at high formaldehyde concentrations or at temperatures above 50–60°C. Side reactions resulting in the formation of ethers or formals of pentaerythritol may also occur if the unneutralized mixture is allowed to stand for an extended period of time or if the reaction is carried out at an elevated temperature.

The product pentaerythritol is recovered from the reaction mixture by crystallization. Since the presence of formaldehyde increases the solubility of the product in the reaction liquor, various methods, such as the promotion of reaction (e) by increasing the temperature, have been proposed to remove any excess formaldehyde remaining at the end of the primary reactions.

In this study, the kinetics of the primary reactions leading to pentaerythritol were investigated with sodium hydroxide as the alkali. The experimental tests were carried out at concentration and temperature levels such that all side reactions were relatively unimportant; however, in order to obtain the kinetics of the primary reactions, it was necessary to correct for the small consumption of hydroxyl ion and formaldehyde caused by the formaldehyde Cannizzaro reaction.

Analysis of the Kinetics of the Reactions

The results of this investigation show that, below 10°C, the aldol condensation reactions are rapid relative to the pentaerythrose Cannizzaro reaction. Consequently, by carrying out the initial steps of the reaction batchwise at a temperature near 0°C, it is possible to convert the acetaldehyde to pentaerythrose before any appreciable amount of pentaerythritol is formed. After all the pentaerythrose is formed, it is assumed that formaldehyde concentration and temperature are such that only the Cannizzaro reactions (d) and (e) occur. Under these conditions, the following reaction-rate equations can be written :

$$-\frac{dC}{dt} = k_1\,ABC \qquad (1)$$

$$-\frac{dA}{dt} = k_1\,ABC + k_2\,(B)\,(A)^2 \qquad (2)$$

$$-\frac{dB}{dt} = k_1\,ABC + \frac{k_2}{2}\,(B)\,(A)^2 \qquad (3)$$

where A = formaldehyde concentration
B = sodium hydroxide concentration
C = pentaerythrose concentration

The preceding rate equations are expressed in the general empirical form normally assumed for Cannizzaro reactions [1, 5, 6, 8]. They are applicable when changes are considered with respect to concentration [5, 6]. In this work, the initial concentrations used were approximately constant in the range normally encountered in the industrial production of pentaerythritol, and the applicability of equations (1) to (3) is shown by the agreement with the experimental results.

A study of the side reaction reveals that it is is very slow relative to the pentaerythrose-formaldehyde Cannizzaro reaction and can be neglected over the time interval used to study the pentaerythrose–formaldehyde reaction. Under these conditions, $dA = dB = dC$, and equation (1) can be integrated by using the method of partial fractions to give the following result:

$$\frac{1}{(A_0 - B_0)\,(B_0 - C_0)\,(C_0 - A_0)} \times \ln\left(\frac{A}{A_0}\right)^{(B_0 - C_0)} \left(\frac{B}{B_0}\right)^{(C_0 - A_0)} \left(\frac{C}{C_0}\right)^{(A_0 - B_0)} = k_1 t \qquad (4)$$

where A_0, B_0, and C_0 refer to the concentrations of the respective components at the start of the time interval. Letting

$$a = B_0 - C_0 \qquad X = \left(\frac{A}{A_0}\right)^a \left(\frac{B}{B_0}\right)^b \left(\frac{C}{C_0}\right)^c$$

$$b = C_0 - A_0 \qquad N = \frac{1}{abc}$$

$$c = A_0 - B_0$$

equation (4) becomes

$$N \ln X = k_1 t \tag{5}$$

A plot of ln X versus t should yield a straight line with a slope of k_1/N for any given set of initial concentrations of this kinetic analysis corresponds to the actual process.

To determine the influence of the formaldehyde Cannizzaro reaction on the hydroxyl and formaldehyde concentrations, it is necessary to evaluate k_2. This can be accomplished by considering the formaldehyde side reaction alone. After all the pentaerythrose has reacted, the aldehyde concentration of the reaction mixture should follow the kinetics of the formaldehyde Cannizzaro reaction, and equation (2) can be written as

$$-\frac{dA}{dt} = k_2 (B) (A)^2 \tag{6}$$

In a manner similar to that used for obtaining equation (5), equation (6) can be integrated to give

$$P = Kt + S \tag{7}$$

where $P = \dfrac{1}{A} + \dfrac{1}{2B_0 - A_0} \ln \dfrac{A}{B}$

$$K = \frac{k_2}{2} (2B_0 - A_0)$$

$$S = \frac{1}{A_0} - \frac{1}{2B_0 - A_0} \ln \frac{B_0}{A_0}$$

A plot of P versus t should give a straight line with a slope of $\dfrac{k_2}{2}(2B_0 - A_0)$ for any given set of initial concentrations if these kinetics are followed. If $A = 2B$, as is essentially the case for some of the experimental runs reported in this work, the integrated result for equation (6) is

$$\frac{1}{B^2} = 4 k_2 t + \frac{1}{B_0{}^2} \tag{8}$$

and a plot of B^{-2} versus t should be straight line with a slope equal to $4k_2$.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

Experimental data, which followed the course of the reaction, were obtained using an ice bath and a constant-temperature bath. The condensation reactions were carried out in the ice bath and the pentaerythrose–formaldehyde Cannizzaro reaction was performed in the constant-temperature bath.

The reagents were added to an agitated, 1l. Erlenmeyer flask located in the ice bath, and the solution temperature was maintained below 10°C. The mixture was formed by adding sodium hydroxide to a homogeneous solution of acetaldehyde and formaldehyde. After the initial mixing, the temperature of the reaction mixture dropped to almost 0°C in about 30 min. After one hour of reaction time in the ice bath, the reaction mixture was introduced into an agitated, three necked, 1l. flask in the constant-temperature bath. A high rate of agitation was maintained to give a homogeneous mixture and kinetic results that were independent of the agitation rate. About 6 min were required for the cold reaction mixture to reach the bath temperature. Samples were taken periodically by introducing 25 ml pipette into one of the side necks, and the temperature of the reaction mixture was determined by means of a thermometer inserted in one of the side necks.

The samples were placed in 300 ml Erlenmeyer flasks containing an excess of 1N HCl above that required to neutralize the uncombined NaOH, thus stopping all aldol condensations and Cannizzaro reactions. The samples were than titrated with 1N NaOH to the phenolphthalein end-point. From this titration, the NaOH concentration of the reaction mixture was calculated. Following the NaOH titration, the samples were titrated with a $NaHSO_3 - Na_2SO_3$ solution that had previously been standardized against a standard formaldehyde solution. This sodium bisulphite solution was approximately 1·7 N relative to HCHO and contained a small amount of ethanol to inhibit oxidation. The total aldehyde (i.e., $-$CHO) concentration of the reaction mixture was calculated from the results of the sodium bisulphite titration. This procedure gives accurate quantitative results for formaldehyde and acetaldehyde. Careful checks of the analytical procedure for determination of — CHO on pentaerythrose indicates that it gives slightly low results; however, the procedure gives a reasonably accurate method for following over-all changes in — CHO concentration with time.

All the pentaerythritol runs were made using a 5 to 1 molal ratio of formaldehyde to acetaldehyde and an 8 per cent excess of sodium hydroxide. The excess sodium hydroxide was based on the theoretical amount needed for complete conversion of acetaldehyde to pentaerythritol and complete removal of remaining formaldehyde by reaction (e). Considering only the total weight of water and formaldehyde initially present, the amount of formaldehyde used was 13 per cent by weight. These values were used because they were recommended by earlier investigators [3, 4, 7, 10, 11, 13] and are compatible with those used in commercial processes. The concentrations, expressed in terms of initial moles/l. were approximately 1·30 M in NaOH, 0·797 M in acetaldehyde, and 1·14 M in methanol. The methanol was introduced with the formaldehyde because commercial formalin was used. The pentaerythrose–formaldehyde reaction was studied at temperatures of 0°C, 24°C, 31·0°C, and 41°C.

The formaldehyde side reaction alone was studied at temperatures ranging from 0°C to 70°C. In these tests, formalin, water and sodium hydroxide were mixed thoroughly in a volumetric flask and placed in the constant-temperature bath. Samples were taken and treated in the same manner as those in the pentaerythritol runs.

RESULTS AND DISCUSSION

The basic experimental data are presented in Tables 1 and 2. Figs. 1 and 2 show a graphical representation of the data for typical runs. The fast initial decrease in (— CHO) content at low temperature due to the rapid aldol condensation reactions is illustrated in Figs. 1 and 2. The theoretical analysis of the results is based on dividing the concentration versus time plots into three distinct sections. In the first section, corresponding to a reaction temperature less

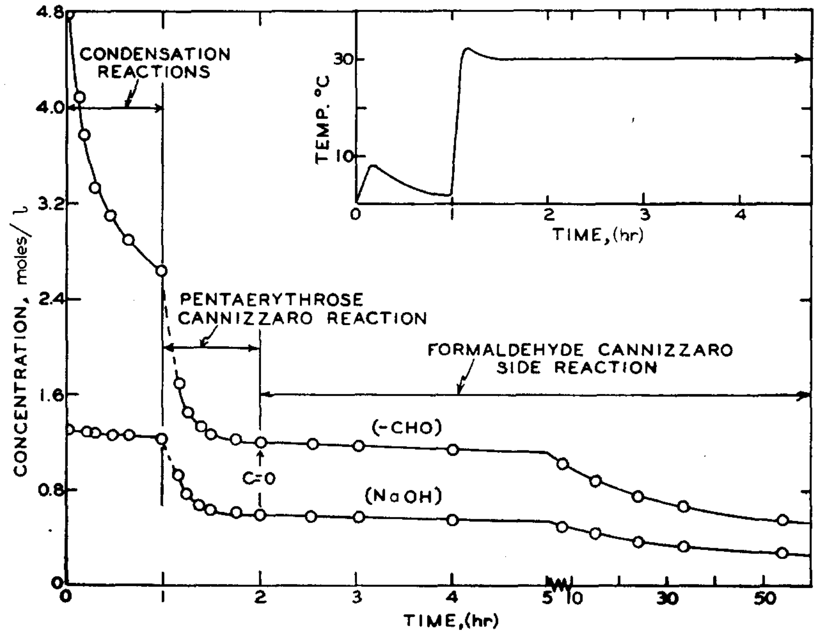

FIG. 1. Variation of concentration and temperature with time for pentaerythritol formation at 30°C (Run No. 3).

Table 1. *Experimental data for pentaerythritol runs*

Run No. 1

Time		*Temp.* (°C)	NaOH moles/l.	(– CHO) moles/l.
(hr)	(min)			
0	0·0	0	(1·30)	(4·7808)
0	7·5	10	1·3004	3·7627
0				
0	13·25	8	1·2904	3·1244
0	16·25	7	1·2840	2·9564
0	22·0	5	1·2660	2·7347
0	30·0	3	1·2596	2·6204
0	50·5	1	1·2272	2·4189
1	20·0	1	1·2008	2·2509
2	0·0	0	1·1560	2·1367
2	13·0	0	1·1420	1·9822
3	0·0	0	1·1136	1·9284
14	45·0	0	0·7436	1·2766
20	0·0	0	0·6784	1·1893
26	15·0	0	0·6380	1·1557
40	0·0	0	0·6012	1·1086
50	0·0	0	0·5908	1·0952
63	0·0	0	0·5868	1·0851
73	30·0	0	0·5808	1·0808
382	30·0	1	0·5176	0·9440
575	0·0	1	0·4837	0·9096

Run No. 2

Time		*Temp.* (°C)	NaOH moles/l.	(– CHO) moles/l.
(hr)	(min)			
0	0·0	0	(1·30)	(4·7808)
0	8·0	8	1·2344	4·2499
0	12·0	8	1·2256	3·8224
0	20·0	6	1·2204	3·3730
0	30·0	4	1·2100	3·1802
0	40·1	3	1·2000	2·9894
0	50·0	2	1·1876	2·8758
0	57·5	2	1·1796	2·8464
1	0	(Put in 23·5°C bath – 6 min required to reach 23·5°C).		
1	10·25	25·1	1·0120	1·9696
1	16·0	24·8	0·8884	1·7200
1	26·75	24·3	0·7388	1·5183
1	35·0	24·0	0·6736	1·4362
1	48·25	23·8	0·6144	1·3473
2	3·0	23·6	0·5760	1·2994
2	32·5	23·5	0·5480	1·2584
3	8·75	23·5	0·5400	1·2378
4	2·0	23·5	0·5316	1·2242
6	15·0	23·5	0·5204	1·1968
8	0·0	23·5	0·5097	1·1729
22	0·0	23·5	0·4651	1·0874
79	0·0	23·5	0·3460	0·8481

Run No. 3

Time		*Temp.* (°C)	NaOH moles/l.	(– CHO) moles/l.
(hr)	(min)			
0	0·0	0	(1·30)	(4·7808)
0	8·12	8	1·2976	4·0946
0	11·25	8	1·2932	3·7889
0	17·37	6	1·2872	3·3314
0	27·37	5	1·2732	3·1173
0	39·62	3	1·2568	2·8971
0	58·50	2	1·2364	2·6470
1	0·0	(Put in 30·2°C bath – 6 min required to reach 30°C).		
1	9·25	32·5	0·9320	1·7098
1	14·25	32·0	0·7804	1·4738
1	21·62	30·7	0·6816	1·3371
1	29·62	30·4	0·6452	1·2789
1	45·0	30·2	0·6172	1·2379
2	0·0	30·2	0·6092	1·2174
2	32·0	30·2	0·5956	1·1968
3	1·0	30·2	0·5940	1·1763
4	0·0	30·2	0·5674	1·1558
8	0·0	30·2	0·5134	1·0293
15	0·0	30·2	0·4450	0·8920
24	0·0	30·2	0·3906	0·7728
33	30·0	30·2	0·3442	0·6873
54	0·0	30·11	0·2846	0·5676
124	30·0	30·2	0·1935	0·3830
151	0·0	30·2	0·1749	—
193	0·0	30·2	0·1544	—

Run No. 4

Time		*Temp.* (°C)	NaOH moles/l.	(– CHO) moles/l.
(hr)	(min)			
0	0·0	0	(1·30)	(4·7808)
0	23·0	6	1·2844	3·0776
1	24·5	1	1·2174	2·3527
1	48·0	(Put in 40°C bath).		
1	55·1	41·5	0·8346	1·3199
1	58·5	41·0	0·6861	1·1627
2	1·5	40·0	0·6582	—
2	4·5	40·3	0·6281	—
2	8·5	40·0	0·6251	1·0806
2	14·5	40·0	0·6154	—
2	20·0	40·0	0·6098	1·0532
2	29·5	40·0	0·6009	—
2	47·0	40·0	0·5756	1·0088
3	7·0	40·0	0·5577	—
4	45·0	40·0	0·4670	0·8446
7	38·0	40·0	0·3963	—
11	16·0	40·0	0·3431	—
21	16·0	40·0	0·2623	—
32	53·0	40·0	0·2177	—
46	8·0	40·0	0·1823	—

than 8°C and the first hour in Fig. 1, it is assumed that the aldol condensation reactions go to completion to form pentaerythrose and a small amount of pentaerythritol. In the second section, corresponding to the second hour and an average reaction temperature of 31°C in Fig. 1, the pentaerythrose-formaldehyde Cannizzaro reaction occurs, and the pentaerythrose concentration is

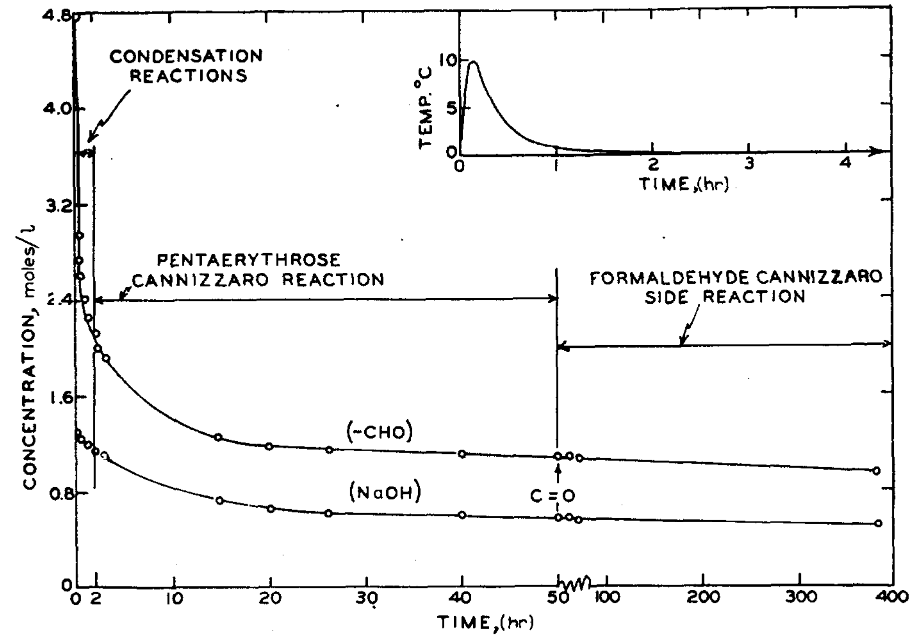

Fig. 2. Variation of concentration and temperature with time for pentaerythritol formation at 0°C (Run No. 1).

assumed to be zero at the end of this section. The last section corresponds to the occurrence of only the formaldehyde Cannizzaro reaction to give a slow, but steady, decrease in (— CHO) and hydroxyl content.

Formaldehyde side reaction

The kinetics of the formaldehyde Cannizzaro reaction was investigated extensively at various concentrations and a temperature of 30°C. In agreement with the work of other investigators, it was found that the rate constant was a constant with respect to time but was dependent upon initial concentrations. Consequently, in order to obtain rate constants that would be applicable in the balance of this work, the kinetics of the formaldehyde Cannizzaro reaction was established on the basis of the experimental data obtained in the third section of the concentration-time plots.

Equation (7) or (8) can be used to establish the kinetics of the formaldehyde side reaction. Examination of the experimental data for the pentaerythritol run presented in Fig. 1 shows that the concentration of formaldehyde was essentially twice the concentration of the sodium hydroxide when the pentaerythrose reaction was completed; therefore, equation (8) applies in this case and a plot of $(B)^{-2}$ versus t should be a straight line. The reaction rate constant k_2 can be determined from the slope of the line. Figure 3 is such a plot for the pentaerythritol mixture at 30·2°C. Similar plots, based on equation (7) or (8), were made for the other temperatures at which the reaction was studied, and straight lines equally as good as that in Fig. 3 were obtained. Reaction-rate constants were evaluated from the slopes of the straight lines, and the results are presented in Table 3. Figure 4 (line 1) presents an Arrhenius-type plot for the reaction rate constants determined from the data obtained with the pentaerythritol mixture. The activation energy for the side reaction is 23,645 cal/g mole as evaluated from Fig. 4. The resulting equation for k_2 is

$$k_2 = 4{\cdot}85 \times 10^{15} \exp\left[-\frac{23{,}645}{RT}\right] \mathrm{l}^2\,\mathrm{moles}^{-2}\,\mathrm{hr}^{-1} \quad (9)$$

Rate constants for the formaldehyde Cannizzaro reaction were also obtained at various initial concentrations and temperatures with no pentaerythritol present. In every case, using both

Table 2. Experimental data for formaldehyde Cannizzaro single-reaction runs

Na^+ = 1·2901 M
H_2O = 43·9 M

CH_3OH (initial) = 1·14 M
HCHO (initial) = 3·98 M

Time		*Temp.* (°C)	NaOH moles/l.	HCHO moles/l.	k_2 l^2 moles^{-2} hr^{-1}
(hr)	(min)				
0	0	0·7	1·1725	(3·7448)	0·000324
15	16	0·8	1·1333	(3·6664)	
41	40	0·7	1·0795	(3·5588)	
94	20	0·7	0·9782	(3·3562)	
0	0	30	1·1663	(3·7018)	0·0220
1	33·5	30	0·9389	(3·2470)	
3	19·5	30	0·7383	(2·8458)	
6	20·5	30	0·6080	2·5852	
10	14·5	30	0·4777	(2·3246)	
23	2·0	30	0·2750	1·8876	
0	0	40	1·0154	(3·3277)	0·0837
0	26	40	0·8334	(2·9637)	
1	47·5	40	0·5484	2·3937	
3	46·5	40	0·3722	(2·0413)	
0	0	50	0·7135	(2·7652)	0·249
0	52	50	0·3619	2·0620	
1	59·5	50	0·2151	(1·7684)	
3	40·5	50	0·1199	1·5523	

equations (7) and (8) for the analysis, the activation energy was the same, but the frequency factor depended upon the initial concentration. The results of experimental tests at identical initial concentrations, with the exception that no pentaerythritol or initial acetaldehyde was present, are shown in Fig. 4 (line 2) for comparison to the case when pentaerythritol was present. The fact that the expected kinetics for the formaldehyde side reaction is obeyed and the

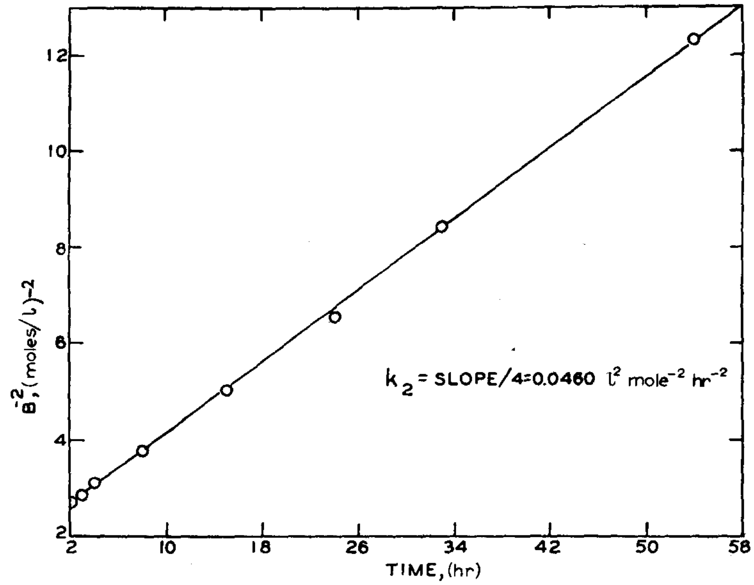

FIG. 3. Kinetic analysis of data from pentaerythritol run at 30·2°C showing applicability of equations (6) and (8) for formaldehyde Cannizzaro reaction.

activation energy is independent of concentration supports the assumption that only the formaldehyde Cannizzaro reaction takes place in the last section of the concentration-time plots.

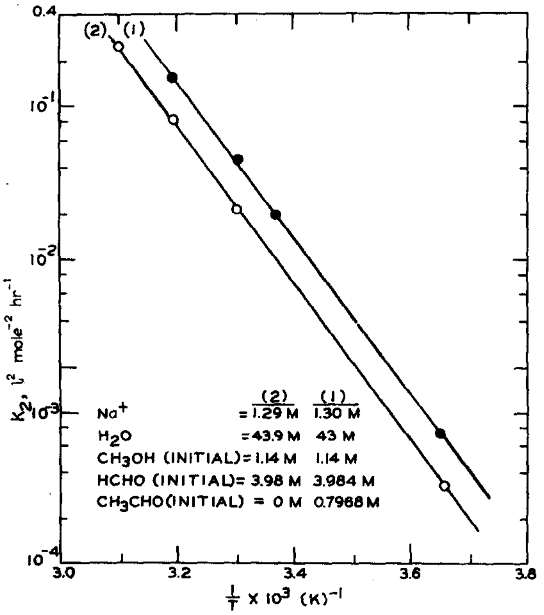

FIG. 4. Arrhenius plot for formaldehyde Cannizzaro reaction.

Table 3. Experimental values of reaction rate constants for pentaerythrose-formaldehyde Cannizzaro reaction (k_1) *and formaldehyde Cannizzaro reaction* (k_2).

Na^+ = 1·30 M
H_2O = 43 M
CH_3OH (initial) = 1·14 M
HCHO (initial) = 3·9840 M
CH_3CHO (initial) = 0·7968 M

Temp. (°C)	k_1 (l^2 moles^{-2} hr^{-1})	*Temp.* (°C)	k_2 (l^2 moles^{-2} hr^{-1})
0	0·0978	1	0·000703
24·0	2·802	23·5	0·01958
31·0	7·446	30·2	0·0460
41·0	23·544	40·0	0·1506

Pentaerythritol-formation reaction

The pentaerythrose-formaldehyde Cannizzaro reaction was found to be the rate-controlling step in the formation of pentaerythritol. Consequently, no attempt was made to evaluate rate constants for the rapid aldol condensation.

The kinetic analysis for the pentaerythritol-formation reaction is based on the application of equation (5). To use this equation, it is necessary to evaluate *A*, *B* and *C* at various times during the second section of the concentration-time plot. The value of B is given directly from the experimental data at time t. The rate constant k_1 is much larger than k_2, and the effect of the formaldehyde Cannizzaro reaction can reasonably be neglected during most of the pentaerythrose reaction ; however, the formaldehyde side reaction must be considered in evaluating C, because C approaches a limit of zero. Accordingly, the following procedure can be used to determine the instantaneous values of C and A :

Combining equations (1), (2) and (3), and expressing the result in difference form gives

$$\Delta C = \Delta B + \frac{k_2}{2}(BA^2)_{\text{avg}}\,\Delta t \qquad (10)$$

$$\Delta A = \Delta B - \frac{k_2}{2}(BA^2)_{\text{avg}}\,\Delta t \qquad (11)$$

Because ΔA is small relative to A at any time, equation (11) can be simplified to $\Delta A = \Delta B$. Under these conditions, the values of A, B and C at any given time can be calculated by the stepwise procedure illustrated in Table 4, and a plot of ln X versus t, in accordance with equation (5), can be prepared. A plot of this type for a reaction temperature of 31·0°C is presented in Fig. 5. It can be seen that the expected straight-line relationship is obtained.

Plots similar to Fig. 5 were prepared for the pentaerythritol reaction at other temperatures, and values of the reaction rate constant k_2 were determined from these plots. The results are tabulated in Table 3. The Arrhenius-type plot of the resultant values of the rate constants is presented in Fig. 6. From Fig. 6, the activation energy for the pentaerythrose-formaldehyde

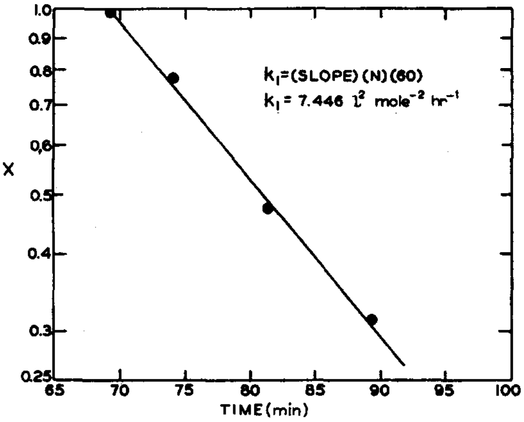

FIG. 5. Kinetic analysis of data for pentaerythrose–formaldehyde Cannizzaro reaction at 31°C showing applicability of equations (1) and (5).

Table 4. *Method for evaluation of concentrations and terms in equation* (5) *based on run* 3. *Temperature* = 31°C $k_2 = 7·5 \times 10^{-4}$ l² moles⁻² min⁻¹.

t (min)	B moles/l.	$-\Delta B$ moles/l.	Δt (min)	A moles/l.	$\frac{k_2}{2}(BA^2)_{\text{avg}}\,\Delta t$	$-\Delta C$ moles/l.	C mules/l.	X
69·25	0·9320			1·5402			0·3018	1·0000
		0·1516	5·00		0·0035	0·1481		
74·25	0·7804			1·3886			0·1537	0·7740
		0·0988	7·37		0·0036	0·0952		
81·62	0·6816			1·2898			0·0585	0·4750
		0·0364	8·00		0·0032	0·0332		
89·62	0·6452			1·2534			0·0253	0·3128
		0·0280	15·38		0·0056	0·0224		
105·00	0·6172			1·2254			0·0029	0·0856*
		0·0080	15·00		0·0051	0·0029		
120·00	0·6092			1·2174			0	

$A_0 = 1·5402$ $B_0 = 0·9320$ $C_0 = 0·3018$ $N = -2·1067$

*This point is not included on Fig. 5 because C is close to zero and equation (5) does not apply for this condition.

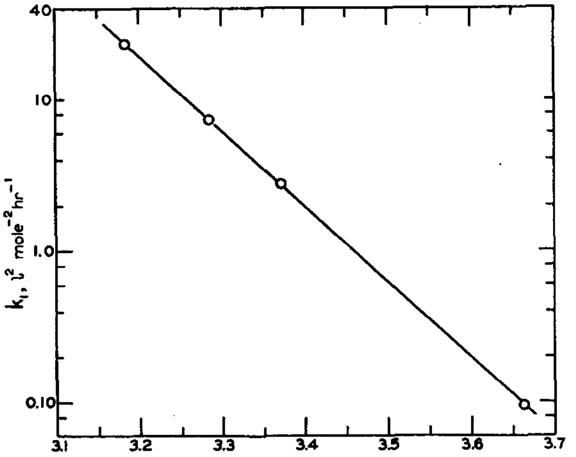

FIG. 6. Arrhenius plot for pentaerythrose–formaldehyde Cannizzaro reaction.

Cannizzaro reaction is 22,800 cal/mole and the equation for the rate constant is

$$k_1 = 1{\cdot}82 \times 10^{17} \exp\left[-\frac{22{,}800}{RT}\right] \mathrm{l}^2\,\mathrm{moles}^{-2}\,\mathrm{hr}^{-1} \quad (12)$$

Yields

By observing the change in hydroxide concentration and making a correction for the formaldehye side reaction, the yield of pentaerythritol in solution can be calculated. On the basis of the experimental data for Run 3, the corrected change in NaOH concentration is 1·300–0·6092–0·0210 = 0·670 from time zero to the time indicated by $C = 0$ in Fig. 1. The per cent conversion of initial acetaldehyde to pentaerythritol therefore is (0·670/0·7968) 100 = 84·1 per cent. Approximately the same yields (± 0·5 per cent) were obtained for all runs in which the reaction mixture was held at 0°C until the pentaerythrose was formed.

The similar yields obtained for different pentaerythrose reaction temperatures indicates that side reactions involving acetaldehyde, with a resultant decrease in ultimate yield, occur during the aldol condensation steps. One possibility is the acetaldehyde aldol condensation with itself. This possibility was checked by making several runs in which the acetaldehyde was added slowly to a mixture of formaldehyde and sodium hydroxide at 0°C. After the pentaerythrose-formation reaction was complete, the final Cannizzaro reaction to produce pentaerythritol was carried out at 30°C. The calculated yield in solutions under these conditions of continuous low acetaldehyde concentration was 90·6 per cent. The observed increase in yield supports the proposal that some of the yield losses in the production of pentaerythritol can be due to side reactions in the rapid aldol condensation reactions.

SUMMARY

Investigation of the kinetics of pentaerythritol-formation reactions shows that the rate of the aldol condensations leading to pentaerythrose is very rapid and the rate-limiting step is the pentaerythrose–formaldehyde Cannizzaro reaction. Under concentration conditions equivalent to those used in industrial operations, the rate of the pentaerythrose–formaldehyde reaction to produce pentaerythritol can be represented as

$$\frac{d\,[(\mathrm{HOCH_2})_4]\,\mathrm{C}}{dt} = k_1\,(\mathrm{HCHO})\,(\mathrm{NaOH})\,[(\mathrm{HOCH_2})_3\,\mathrm{CCHO}]$$

and the rate of the formaldehyde Cannizzaro reaction can be expressed as

$$-\frac{d\,(\mathrm{HCHO})}{dt} = k_2\,(\mathrm{HCHO})^2\,(\mathrm{NaOH})$$

Experimental data verify the preceding equations. The observed values of the rate constants show that the reaction producing pentaerythritol is much faster than the formaldehyde Cannizzaro reaction even at low concentrations of pentaerythrose. Analysis of the " in solution " yields of pentaerythritol based on the amount of acetaldehyde charged indicates that side reactions during the rapid aldol condensation reactions can be one of the causes for yield losses in the production of pentaerythritol.

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NOTATION

A = formaldehyde concentration (subscript 0 refers to start of time interval), moles/l.

B = sodium hydroxide concentration (subscript 0 refers to start of time interval), moles/l.

C = pentaerythrose concentration (subscript 0 refers to start of time interval) moles/l.

$a = B_0 - C_0$ moles/l.

$b = C_0 = A_0$ moles/l.

$c = A_0 - B_0$ moles/l.

k_1 = reaction rate constant for pentaerythrose-formaldehyde Cannizzaro reaction l^2/moles^2 hr

k_2 = reaction rate constant for formaldehyde Cannizzaro reaction l^2/moles^2 hr

$K = \frac{k_2}{2}(2B_0 - A_0)$

$N = 1/abc$

$P = \frac{1}{A} + \frac{1}{2B_0 - A_0} \ln \frac{A}{B}$

R = perfect gas law constant, cal/mole°K

$S = \frac{1}{A_0} - \frac{1}{2B_0 - A_0} \ln \frac{B_0}{A_0}$

t = time

T = temperature

$X = \left(\frac{A}{A_0}\right)^a \left(\frac{B}{B_0}\right)^b \left(\frac{C}{C_0}\right)^C$

REFERENCES

[1] ALEXANDER E. R. *Ionic Organic Reactions.* John Wiley, New York 1950.

[2] BARTH R. H., SNOW J. E. and WOOD E. H. Paper presented at Amer. Chem. Soc. North Jersey Section Meeting-in-Miniature 8th January, 1951.

[3] BERLOW E., BARTH R. H. and SNOW J. E. *Amer. Chem. Soc.* Monograph Series No. 136 Reinhold, New York 1958.

[4] BURGHARDT R. F. and BARTH R. H. (Assrs. to Heyden Chemical Corp.) U.S. patent 2401749 June 11 1946.

[5] CUPIT C. R. *Ph.D. Thesis* University of Illinois, 1958.

[6] MARTIN R. J. L. *Austral. J. Chem.* 1954 **7** 335.

[7] PETERS M. S. and QUINN J. A. *Industr. Engng. Chem.* 1955 **47** 1710.

[8] PFEIL E. *Chemie.* 1951 **84** 229.

[9] SALKIND M., AHERN H. F. and ALBERT A. A. *Industr. Engng. Chem.* 1958 **50** 1106

[10] SHERWOOD P. W. *Petrol. Refin.* 1956 **35** No. 11 171.

[11] WALKER J. F. *Formaldehyde* (2nd ed.) Reinhold, New York 1953.

[12] WAWZONEK S. and REES D. A. *J. Amer. Chem. Soc.* 1948 **70** 2433.

[13] WYLER J. A. (Assr. to Trojan Powder Co.) U.S. patent 2170624 August 22 1939.