

## Formose Reactions. IV. The Formose Reaction in Homogeneous Systems and the Catalytic Functions of Calcium Ion Species

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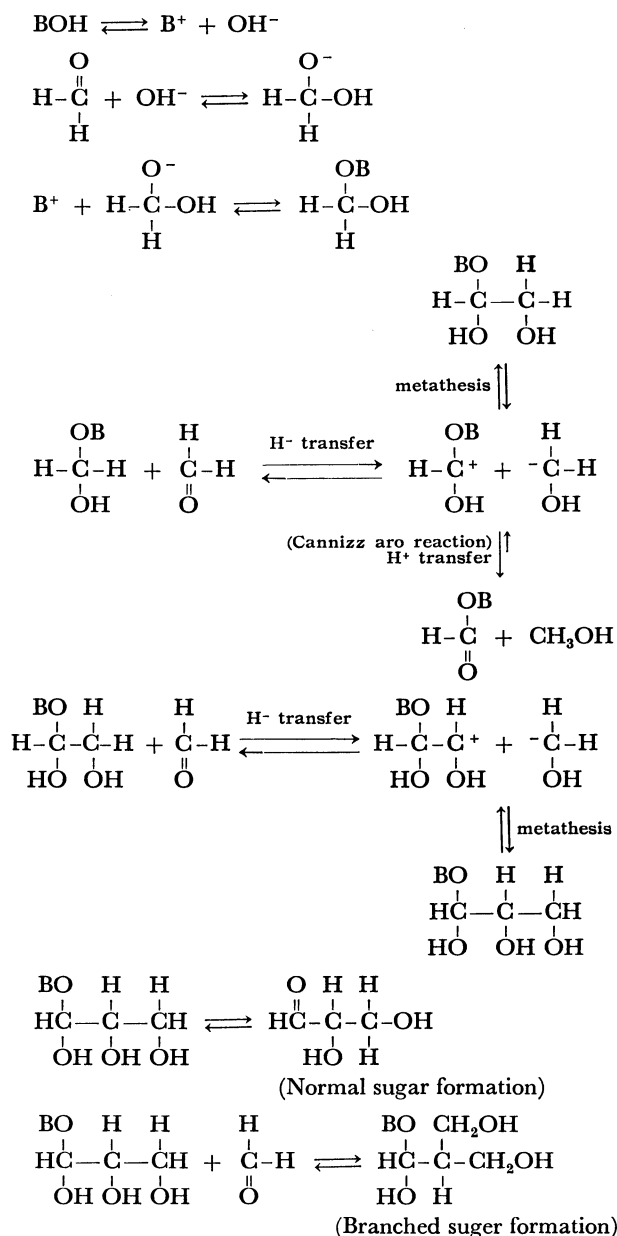
By using the previously developed analytical method of oxidation-reduction potential measurement, the formose reaction homogeneously-catalyzed by calcium formate-potassium hydroxide at pH 10.5–12.0 was found to proceed as effectively as that heterogeneously-catalyzed by calcium hydroxide. Other calcium salts, including chloride, bromide, acetate, and propionate, could be used in place of calcium formate. Kinetic studies with the calcium formate-KOH system showed a linear dependence of the concentration of the dissolved calcium ion species on the induction period ( $T_{\min}$ ) and the formose-forming period ( $T_{\max} - T_{\min}$ ) at a given pH. From the results, the relationships,  $T_{\min} = a[\text{CaOH}^+] + c$  and  $T_{\max} - T_{\min} = a'[\text{CaOH}^+] + b'[\text{Ca}(\text{OH})_2] + c'$ , were obtained, suggesting that  $\text{CaOH}^+$  is the principal catalytic species in the induction step, while both  $\text{CaOH}^+$  and  $\text{Ca}(\text{OH})_2$  (or  $\text{OH}^-$ ) are present in the formose-forming step. The effects of various factors on both steps and the sugar yield were also examined.

In a preceding paper,<sup>1)</sup> which dealt with an examination of various factors affecting the formose reaction carried out with solid  $\text{Ca}(\text{OH})_2$  in a batch-reactor, it was suggested that the dissolved calcium ion is an essential catalyst for either the induction and the sugar-forming step, and that the hydroxide anion plays a significant role as a catalyst for the latter step. In order to obtain more information on the nature of catalysis in the formose reaction, it appeared necessary to investigate the reaction with a simpler system, such as a homogeneous one, which can excluded the complexity caused by the undissolved  $\text{Ca}(\text{OH})_2$ .

Although Weiss *et al.*, in their studies of the formose reaction using a continuously stirred tank-reactor (CSTR), regarded the reaction as a homogeneously-catalyzed one,<sup>2-4)</sup> both the undissolved and dissolved  $\text{Ca}(\text{OH})_2$  coexist in the reaction mixture. The homogeneously-catalyzed formose reaction has been briefly investigated using alkali-metal hydroxides, organic bases, and other catalysts.<sup>5-12)</sup> These reactions, however, usually need a longer period and a higher temperature than the  $\text{Ca}(\text{OH})_2$ -catalyzed formose reaction, and with alkali hydroxides the Cannizzaro reaction of formaldehyde occurs to a large extent. Among those investigations, only a report by Fujino *et al.*<sup>12)</sup> concerns the calcium salt-catalyzed formose reaction in a homogeneous system, for which a glucose-calcium complex is used as a catalyst.

On the basis of kinetic studies using CSTR and on the basis of the fact that the reaction rate decreases dramatically when the pH is either too low or too high, Weiss and John have reported that  $\text{CaOH}^+$  is the principal catalyst.<sup>4)</sup> They have also proposed a simplified metathesis mechanism involving  $\text{CaOH}^+$ ; it is shown by Scheme 1, where  $\text{B}^+$  denotes  $\text{CaOH}^+$ . However, a question arises whether the  $\text{CaOH}^+$  species is an effective catalyst in both induction and formose-forming steps, because these authors did not perform separate analyses of the two steps.

The purpose of this paper is to explore the standard experimental conditions for the formose reaction catalyzed homogeneously by calcium salts and to obtain evidence for the active catalytic species participating in



Scheme 1.

the induction and the formose-forming steps. The oxidation-reduction potential (ORP) measurement of the reaction system is applied to the analysis of the reaction. The method has been proved to be useful for the separate analysis of each step by observing an ORP minimum at the end of the induction period and a maximum at the end of the formose-forming step.<sup>1,13,14)</sup>

### Experimental

**Procedure.** The apparatus and the experimental procedure are virtually the same as those described previously.<sup>14)</sup> Formaldehyde solutions were prepared from paraformaldehyde by refluxing for 4 h, followed by the filtration of the insoluble substances. The pH of the reaction was maintained by adding concentrated aqueous potassium hydroxide or formic acid. The reactor was flushed with nitrogen which had been bubbled through saturated aqueous barium hydroxide. The temperature was controlled by means of a cooler dipped in a water bath to avoid the significant temperature rise which would otherwise occur in the formose-forming step. The formaldehyde consumption, the sugar yield, the concentration of the dissolved calcium ion species, and the ORP were measured by the method described in the previous paper.<sup>14)</sup> The calcium salts and other reagents were of an analytical grade.

To examine the effect of the pH on the concentration of the calcium ion, an aqueous formaldehyde solution prepared at a desired concentration was maintained at 60 °C in a three-

necked flask and nitrogen was passed through the solution. After the pH of the solution had been adjusted by carbonate-free concentrated KOH, calcium formate was added and stirred until precipitates appeared. A turbid supernatant was filtered through asbestos, and the filtrate was analyzed for the calcium ion by the EDTA method, using NN-reagent as an indicator.<sup>15)</sup> The results are shown in Fig. 1.

### Results and Discussion

The following terms are adopted in this paper:  $[HCHO]$ ,  $[Ca(HCOO)_2]$ , and  $[Ca]$ , the concentrations of formaldehyde, calcium formate, and the dissolved calcium ion species respectively;  $T_{min}$ , the length of the induction step, namely, the time from the start to the ORP minimum;  $T_{max}$ , the time from the start to the ORP maximum, and  $T_{max} - T_{min}$ , the length of the formose-forming step (see the preceding paper<sup>1)</sup>).

**The Formose Reaction Homogeneously Catalyzed by the Calcium Ion.** The reactant solution was prepared by dissolving a given amount of calcium formate into an aqueous formaldehyde solution and by adjusting the pH by the addition of concentrated aqueous KOH. After the reaction had been started at 60 °C, the pH of the mixture was maintained by adding concentrated aqueous KOH; the subsequent reaction was followed by ORP measurement and analyzed as usual. We have previously shown that the ORP of the reaction mixture increases from the minimum at the beginning of the formose-forming period up to the maximum at its end in the pH-uncontrolled reaction.<sup>13,14)</sup> In the experiments at a constant pH, however, the increase in ORP in this period was found to be very small.

As is shown in Table 1, in a certain range of pH and  $[Ca]$  the formose reaction did occur. At pH 10.5 (Runs 1–3),  $T_{min}$  and  $T_{max} - T_{min}$  were reduced with an increased  $[Ca]$ , indicating that the rates of both the induction and formose-forming processes are dependent on the amount of the dissolved calcium ion species. At higher pHs, the situation became considerably different. At pH 11.0 (Run 4), even though  $[Ca]$  was the same as that of Run 1, in which the reaction was very slow,  $T_{min}$  and  $T_{max} - T_{min}$  were as fast as Run 2, in which  $[Ca]$  was three times higher. At pH 11.5 (Run 5), although part of the calcium ion separated out as solid  $Ca(OH)_2$ , the rate was comparable to that of Run 3,

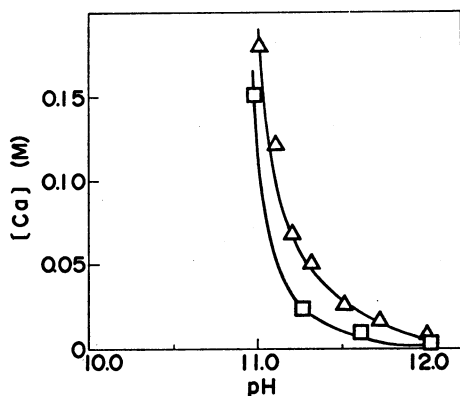


Fig. 1. Relationship between  $[Ca]$  and pH.

Temperature, 60 °C; Under  $N_2$ ;  $[HCHO]$ : □, 0 M; △, 1 M;  $Ca(HCOO)_2$  was used as the source of  $Ca^{2+}$  (See Experimental).

TABLE 1. FORMOSE REACTION AT A CONSTANT pH  
Temp, 60 °C;  $[HCHO] = 1.0$  M.

Run No.	[Ca-(HCOO) <sub>2</sub> ]	pH	HCHO consumption (%) at		[Ca] (mM) at			T <sub>min</sub>	T <sub>min</sub>	T <sub>max</sub> - T <sub>min</sub>	Sugar yield (%) at	
	(M)		T <sub>min</sub>	T <sub>max</sub>	T <sub>s</sub>	T <sub>min</sub>	T <sub>max</sub>	(min)	(min)	(min)	T <sub>max</sub>	T <sub>3</sub> <sup>a)</sup>
1	0.1	10.5	(11.2) <sub>60</sub>		100	(90) <sub>60</sub>		— <sup>b)</sup>	— <sup>b)</sup>	—	(0.3) <sub>60</sub>	
2	0.3	10.5	20.0	97.9	290	290	290	58.0	68.0	10.0	46.8	33.1
3	0.55	10.5	18.7	98.3	530	540	540	8.5	14.5	6.0	53.7	35.4
4	0.1	11.0	31.6	97.8	100	90	100	61.0	69.0	8.0	53.3	34.6
5 <sup>c)</sup>	0.1	11.5	29.2	97.0	70	80	80	12.5	14.5	2.5	52.5	26.3
6 <sup>c)</sup>	0.1	12.0	(29.9) <sub>60</sub>		20	(10) <sub>60</sub>		— <sup>b)</sup>	— <sup>b)</sup>	—	(0.7) <sub>60</sub>	

a)  $T_3 = 3$  min after  $T_{max}$ . b) No minimum ORP or maximum ORP is observed. The subscript number is the reaction time, in min. c) Heterogeneous system.

TABLE 2. EFFECTS OF VARIOUS CALCIUM SALTS ON THE FORMOSE REACTION

Cat.	$T_{\min}$ (min)	$T_{\max}$ (min)	$T_{\max} - T_{\min}$ (min)	HCHO consumption (%) at		Sugar yield (%) at	
				$T_{\min}$	$T_{\max}$	$T_{\max}$	$T_3^b$
$\text{CaCl}_2$	14.0	16.0	2.0	29.4	94.2	55.2	28.0
$\text{CaBr}_2$	17.0	21.0	4.0	26.2	97.3	42.6	32.4
$\text{Ca}(\text{HCOO})_2$	22.0	25.5	3.5	33.7	99.8	45.3	34.6
$\text{Ca}(\text{CH}_3\text{COO})_2$	26.0	30.0	4.0	28.0	98.1	52.3	36.1
$\text{Ca}(\text{C}_2\text{H}_5\text{COO})_2$	30.5	34.0	3.5	38.9	98.1	44.7	36.7

a)  $[\text{HCHO}] = 1.0 \text{ M}$ ;  $[\text{Ca}] = 0.15 \text{ M}$ ; Temp,  $60^\circ\text{C}$ ; pH=11.0. b)  $T_3 = 3 \text{ min}$  after  $T_{\max}$ .

in which  $[\text{Ca}]$  was about seven times higher. The results suggest that the catalytic function of the dissolved calcium ion species increases with an increased pH. As will be discussed later, the active species catalyzing the formose reaction is believed to be  $\text{CaOH}^+$ .

At pH 12.0, most of the dissolved calcium ion species separated out as the solid  $\text{Ca}(\text{OH})_2$  and the reaction rate became very slow. As is shown in Fig. 1, when calcium formate was used as the source of the calcium ion,  $[\text{Ca}]$  decreased sharply above pH 11.0 in both the presence and absence of formaldehyde with an increased pH. The slow-down of the  $\text{Ca}(\text{OH})_2$ -catalyzed formose reaction at a high pH<sup>1,4)</sup> can now be ascribed to the deficiency of the dissolved calcium ion species. It follows that a high concentration of the catalyst cannot be employed for the homogeneously-catalyzed formose reaction carried out at an elevated pH. However, we found that the formose reaction took place smoothly even at pHs above 12, with the appearance of both an ORP minimum and a maximum, when an ion-exchange resin, Amberlite IR 120 ( $\text{Ca}^{2+}$ ), was used as the catalyst in place of  $\text{Ca}(\text{OH})_2$  or a calcium salt-KOH system. The pH dependence of  $T_{\min}$  and  $T_{\max}$  in the formose reaction with the resin had a relation parallel to that of the  $\text{CaOH}^+$  distribution in an aqueous  $\text{Ca}(\text{OH})_2$  solution shown in Fig. 4.

Next, a homogeneous formose reaction using other calcium salts was examined. If the formose reaction is mainly dependent on the dissolved calcium ion concentration and on the pH, it will not be much affected by the nature of the counter anion of calcium salts. The results summarized in Table 2 indicate that this is indeed the case. So far as the sugar formation is concerned, the formose reaction with these calcium salts was virtually the same as that with calcium formate-KOH or with calcium hydroxide. However, the reaction rate estimated by  $T_{\min}$  and  $T_{\max}$  showed a tendency to decrease with a decrease in the dissociation ability of the calcium salts.

*Effects of pH in a Homogeneously Catalyzed Formose Reaction.*

As is shown in Table 1 (Runs 1, 4, and 5), the induction period is shortened with an increase in the pH in the range from pH 10.5 to 11.5 in the homogeneous system. The pH dependence of the formose-forming period and the sugar yield was examined, after the homogeneous formose reaction using calcium formate had been started at pH 11.0, by varying the pH at  $T_{\min}$  and by determining  $T_{\max} - T_{\min}$  and the sugar yield. The results are shown in Figs. 2 and 3. The formose-forming step was shortened at

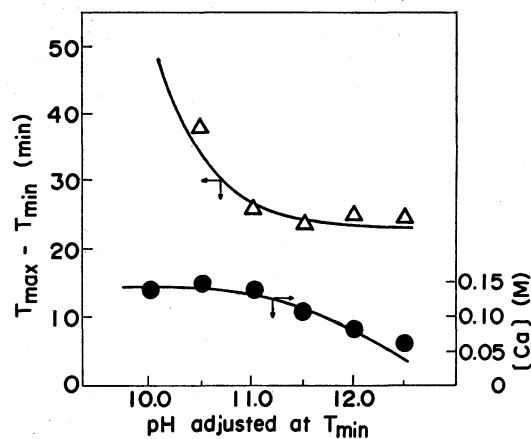


Fig. 2. Effect of pH variation at  $T_{\min}$  on  $T_{\max} - T_{\min}$  and  $[\text{Ca}]$ .

$[\text{HCHO}] = 1.0 \text{ M}$ ;  $[\text{Ca}(\text{HCOO})_2] = 0.15 \text{ M}$ ; Starting pH=11.0 (Under these conditions,  $T_{\min}$  was ca. 22 min).

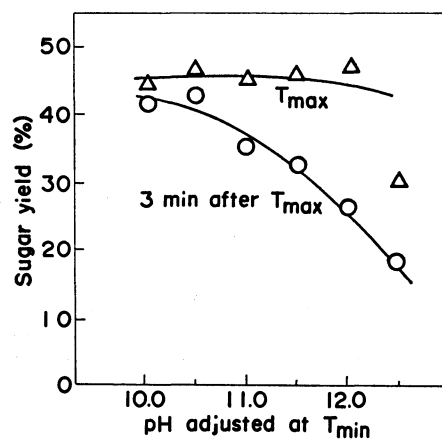


Fig. 3. Effect of pH variation at  $T_{\min}$  on the sugar yield. Reaction conditions; same as those in Fig. 2.

higher pHs, although  $[\text{Ca}]$  came to decrease at pHs above 11.5 as a result of the precipitation of the solid  $\text{Ca}(\text{OH})_2$ . On the other hand, the sugar yield practically remained unchanged upon pH variation except for at pH 12.5, but the decomposition of the sugars occurring after  $T_{\max}$  became more significant with an increased pH. The results indicate that the hydroxide ion may be as an effective catalyst in the formose-forming step as the dissolved calcium ion species.

*Active Catalytic Species in the Formose Reaction Homogeneously Catalyzed by Calcium Ions.* In view of the

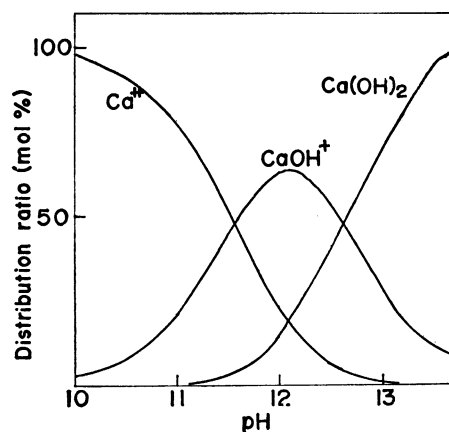
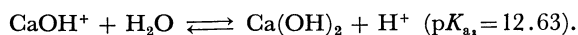
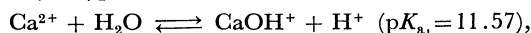


Fig. 4. Calculated distribution of dissolved  $\text{Ca}^{2+}$ ,  $\text{CaOH}^+$ , and  $\text{Ca(OH)}_2$  at different pHs.

importance of the dissolved calcium ion species and the pH in the formose reaction, the distribution of  $\text{Ca(OH)}_2$ ,  $\text{CaOH}^+$ , and  $\text{Ca}^{2+}$  in solution at different pHs was calculated (Fig. 4) on the basis of the acid-base equilibria of  $\text{Ca(OH)}_2$ :<sup>17)</sup>



The Weiss proposal that  $\text{CaOH}^+$  might be the active catalyst in the formose reaction catalyzed by calcium hydroxide now becomes very plausible. The calculated distribution of  $\text{CaOH}^+$  at different pHs could not be applied exactly to our experimental data because of the differences of the conditions employed. However, the distribution was proved to be very useful for interpreting the experimental facts thus far obtained, provided that the pH of the maximum distribution of  $\text{CaOH}^+$  under either heterogeneously- or homogeneously-catalyzed formose reaction conditions is shifted to ca. 11.5 from the calculated pH of 12. An example is given by a comparison of Runs 3 and 5 in Table 1. Although the initial concentration of the dissolved calcium ion species in Run 5 is considerably lower than that in Run 3, the rate of the induction and the formose-forming steps are comparable in both cases. This can be qualitatively explained by assuming that the concentrations of the active catalytic species, namely,  $\text{CaOH}^+$ , are almost equal in both runs.

(1) *CaOH<sup>+</sup> as the Catalyst in the Induction Step*: More quantitative experiments became necessary for proving the role of  $\text{CaOH}^+$  as the catalyst. Figure 5 shows plots of  $T_{\min}$  as a function of  $[\text{Ca}]$  at different pHs (10.5, 11.0, and 11.5) in a homogeneously-catalyzed formose reaction using  $\text{Ca(HCOO)}_2$ -KOH. An approximate linear relation was obtained at each pH. This relation led us to express  $T_{\min}$  by

$$T_{\min} = af_i[\text{Ca}] + c, \quad (1)$$

where  $a$  and  $c$  are constants, and where  $f_i$  is the molar fraction of  $\text{CaOH}^+$  in the dissolved calcium ion species at  $\text{pH}=i$ . The values of  $af_i$  and  $c$  are obtained from the slope and the interception of each line respectively. The same plots were made for the formose reaction catalyzed by  $\text{CaCl}_2$ -KOH, and a linear relation was again obtained at each pH. The  $c$  value was 130 min for

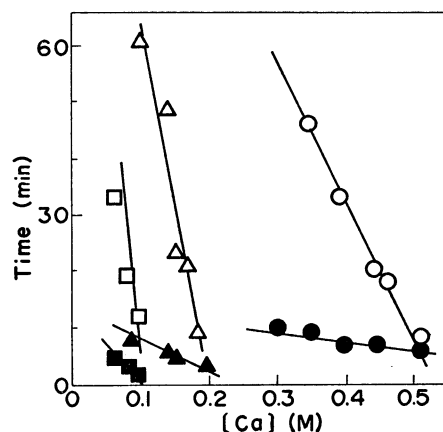


Fig. 5. Relationship between  $T_{\min}$  or  $T_{\max} - T_{\min}$  and  $[\text{Ca}]$  at different pHs.

$[\text{HCHO}]=1.0 \text{ M}$ ; Catalyst,  $\text{Ca(HCOO)}_2$ ; Temp,  $60^\circ\text{C}$ ;  $T_{\min}$ :  $\circ, \triangle$  and  $\square$ , pH 10.5, 11.0 and 11.5, respectively;  $T_{\max} - T_{\min}$ :  $\bullet, \blacktriangle$ , and  $\blacksquare$ , pH 10.5, 11.0, and 11.5, respectively.

the  $\text{Ca(HCOO)}_2$ -KOH system (105 for the  $\text{CaCl}_2$ -KOH system). When  $a = -2000 \text{ min M}^{-1}$  ( $-2056$ ),  $f_i$  is 0.12 (0.10), 0.33 (0.30), and 0.67 (0.69) at pH 10.5, 11.0, and 11.5 respectively. These  $f_i$  values are in fairly good agreement with the calculated values of Fig. 4. The constants,  $a$  and  $c$ , would depend on the reaction conditions, such as  $[\text{HCHO}]$  and the reaction temperature. Thus, Eq. 1 can be simplified to

$$T_{\min} = a[\text{CaOH}^+] + c. \quad (2)$$

Equation 2 means that the induction period is shortened linearly with an increase in the concentration of  $\text{CaOH}^+$  at the same  $[\text{HCHO}]$  and pH in a certain range of  $[\text{Ca}]$ .

(2) *Effective Catalytic Species in the Formose-forming Step*: We have suggested in the preceding paper and this paper that the  $\text{OH}^-$  as well as  $\text{CaOH}^+$  participates in the catalysis in the formose-forming step in either a heterogeneous or homogeneous formose reaction.<sup>1)</sup> Weiss and John have concluded, from their experiments using CSTR, that the rate of the formose reaction at the intermediate conversion level of formaldehyde, which is regarded as the actual formose-forming step, is first-order for calcium hydroxide ( $r_F = k_F[\text{Ca(OH)}_2]$ ).<sup>4)</sup> However, since their reaction system was heterogeneous, both dissolved and undissolved calcium hydroxide must contribute to the reaction rate. In order to clarify the role of the dissolved calcium ion species in the formose-forming step,  $T_{\max} - T_{\min}$  was plotted as a function of  $[\text{Ca}]$  at different pHs (10.5, 11.0, and 11.5) in the homogeneously catalyzed formose reaction.

The results, shown in Fig. 5, indicate that  $T_{\max} - T_{\min}$  and  $[\text{Ca}]$  have a linear relation at different pHs. Similar relations were obtained with the  $\text{CaCl}_2$ -KOH system. These relations, however, are not simple as in Eq. 1, but can be expressed by

$$T_{\max} - T_{\min} = af_i^a[\text{Ca}] + bf_i^b[\text{Ca}] + c, \quad (3)$$

where  $af_i^a$ ,  $bf_i^b$ , and  $c$  are constants and where  $f_i^a$  and  $f_i^b$  are the molar fractions of  $\text{CaOH}^+$  and  $\text{Ca(OH)}_2$  respectively in the dissolved calcium ion species at  $\text{pH}=i$ . The experimental data eventually gave the following values:

$a$ ,  $-133 \text{ min M}^{-1}$  for the  $\text{Ca}(\text{HCOO})_2$ -KOH system ( $-67$  for the  $\text{CaCl}_2$ -KOH system);  $b$ ,  $-537 \text{ min M}^{-1}$  ( $-33$ );  $c$ ,  $14.1 \text{ min}$  ( $3.7$ );  $f_{10.5}^a$ ,  $0.12$  ( $0.10$ );  $f_{11.0}^a$ ,  $0.33$  ( $0.30$ );  $f_{11.5}^a$ ,  $0.67$  ( $0.69$ );  $f_{10.5}^b$ ,  $0$  ( $0$ );  $f_{11.0}^b$ ,  $0.03$  ( $0.03$ );  $f_{11.5}^b$ ,  $0.07$  ( $0.09$ ). The  $f_i^a$  and  $f_i^b$  values are in fairly good agreement with the values calculated from Fig. 3. Thus, Eq. 3 can be simplified to

$$T_{\max} - T_{\min} = a[\text{CaOH}^+] + b[\text{Ca}(\text{OH})_2] + c, \quad (4)$$

which means that, under these conditions, both dissolved  $\text{CaOH}^+$  and  $\text{Ca}(\text{OH})_2$  act as effective catalytic species in the formose-forming step.

Equation 4 implies that the formose-forming step may occur when either  $\text{CaOH}^+$  or  $\text{Ca}(\text{OH})_2$  is present in solution. For example, the reaction occurs at pH 10.5, where, practically,  $[\text{Ca}(\text{OH})_2]=0$ . Furthermore,  $\text{Ca}(\text{OH})_2$  can be replaced merely by the  $\text{OH}^-$  ion. In fact, as was shown in Fig. 2, the formose-forming step still occurs even at pH values above 12, where  $[\text{Ca}]$  becomes very small due to the precipitation of the solid  $\text{Ca}(\text{OH})_2$ . However, for such a case and for the formose reaction heterogeneously-catalyzed by  $\text{Ca}(\text{OH})_2$ , one cannot neglect the possibility that the solid  $\text{Ca}(\text{OH})_2$  also participates in the catalysis in the formose-forming step, as has been proposed by Weiss *et al.*<sup>2-4)</sup>

Equations 1—4, on the other hand, can be extrapolated to limiting values of  $c$  when  $[\text{Ca}]$  or  $[\text{CaOH}^+]=0$ . Since the reaction does not, of course, occur without a dissolution of the calcium ion species, it can be said that the  $c$  values have no significant physical meaning, but merely imply the feasibility of the induction and the formose-forming steps under the conditions employed.

*Sugar Yield in the Homogeneously-Catalyzed Formose Reaction.*

The effects of  $[\text{Ca}]$  on the sugar yield at  $T_{\max}$  and at 3 min after  $T_{\max}$  at different pHs are illustrated in Fig. 6. The sugar yield at  $T_{\max}$ , where sugars formed are most accumulated,<sup>1)</sup> has a tendency to increase with an increase in  $[\text{Ca}]$ , but the decomposition of the sugars is more accelerated with an increase in  $[\text{Ca}]$  at the same pH. The latter finding

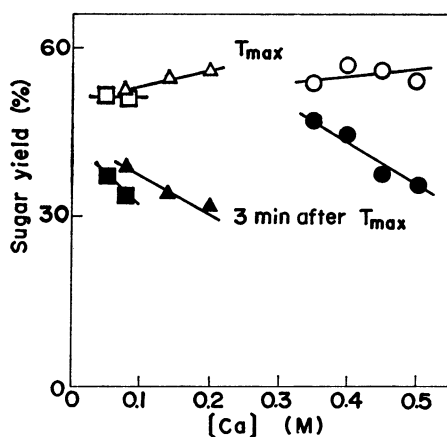


Fig. 6. Effect of  $[\text{Ca}]$  on the sugar yield.  $[\text{HCHO}]=1.0 \text{ M}$ ; Catalyst,  $\text{Ca}(\text{HCOO})_2$ ; Temp,  $60^\circ\text{C}$ ; pH:  $\circ, \bullet$ , 10.5;  $\triangle, \blacktriangle$ , 11.0;  $\square, \blacksquare$ , 11.5.

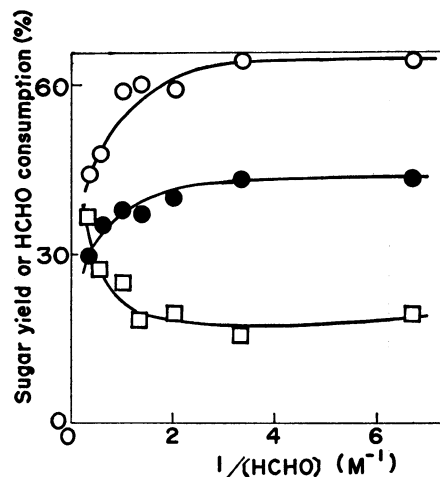


Fig. 7. Effect of the formaldehyde concentration on the sugar yield.

$[\text{Ca}(\text{HCOO})_2]=0.15 \text{ M}$ ; pH=11.0; Temp,  $60^\circ\text{C}$ ;  $\circ$ , sugar yield at  $T_{\max}$ ;  $\bullet$ , sugar yield at 3 min after  $T_{\max}$ ;  $\square$ , HCHO consumption at  $T_{\min}$ .

suggests that the dissolved calcium ion species participate in the sugar decomposition like the hydroxide anion, which may take less part.

The sugar yield was found to be strongly affected by the initial  $[\text{HCHO}]$  in the present homogeneous system. This is shown in Fig. 7. At a constant  $[\text{Ca}]$ , the sugar yield decreases with an increase in  $[\text{HCHO}]$  at relatively high  $[\text{HCHO}]$  values. As may be seen from Fig. 7, the decrease in the sugar yield is due to the increased consumption of formaldehyde by the Cannizzaro reaction in the induction step.

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