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Homogeneous Catalytic Condensation of Methylene Glycol (the Formose Reaction)

Effects of Oxygen and Reducing Sugars

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The calcium hydroxide-catalyzed condensation of methylene glycol to form a racemic mixture of sugars (formose reaction) is characterized by an induction period of variable length. The induction period is shortened when reducing sugars are added and extended when oxygen is present. Oxygen interferes with the formose reaction by forming intermediate products which delay the autocatalytic sugar-forming reaction. Small quantities of added D-glucose shorten the induction period by purging oxygen from the reaction mixture, but there is no increase in the rate of sugar formation once the induction period has passed. Addition of large quantities of reducing carbohydrates to a formose reaction mixture causes a decrease in the conversion rate of methylene glycol to sugars. The progress of the formose reaction can be followed by measuring the pressure above the reaction mixture.

INTRODUCTION

In the presence of a catalytically active base, methylene glycol (hydrated formaldehyde) in aqueous solution condenses to yield a racemic mixture of linear and branched sugars containing 2–8 carbon atoms. The reaction proceeds at room temperature when formaldehyde is added to an aqueous dispersion of calcium hydroxide, with or without added reducing sugars, at a pH of 11.5–12.5 (*1*). Other inorganic (*2*) and organic bases (*3*) will also catalyze the formose reaction, but generally not as effectively. The reaction product, formose (C.A. 8069-42-9), consists of linear and branched sugars, as well as products of Cannizzaro and cross-Cannizzaro reactions of formaldehyde and sugars (*4–6*). In addition, the base can catalyze Lobry de Bruyn-Alberda van Ekenstein rearrangements (*7*) of reaction products and alkaline degradation reactions (*8–10*) which lead to the formation of saccharinic acids.

The formose reaction is characterized by an induction period of variable length during which only Cannizzaro products are generated, a sugar formation period which obeys autocatalytic kinetics, and a final period of sugar degradation brought about by the alkaline environment (*11*). It involves a nonclassical aldol condensation in which an intermediate product is formed from methylene glycol (or formaldehyde), followed by successive regular aldol condensations between the intermediate product and methylene glycol (or formaldehyde). The end of the reaction is indicated by the appearance of a yellow color in the solution (yellowing point). The reaction time depends on the reaction temperature, the presence of additives, and the concentration of reagents.

To date, no reaction mechanism has been established (*6, 12*). Three mechanisms have been proposed. One suggested mechanism involves a nucleophilic carbenoid formed

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from formaldehyde (*13, 14*). However, only a small amount of unhydrated formaldehyde is in equilibrium with methylene glycol, the primary constituent of an aqueous solution of formaldehyde (*15*). A second proposed mechanism involves nucleophilic attack on a methylene glycol molecule by a carbonion formed from methylene glycol (*3*). A third mechanism is based on hydride ion transfer form methylene glycol to formaldehyde (*16*). Other mechanisms, such as a free-radical reaction initiated photochemically (*17, 18*), should also be considered.

Addition of formose product, reducing sugars, and various other α-hydroxycarbonyl compounds to the formose reaction mixture shortens the induction period (*19*). However, no significant differences in formose product, which depend on the kind or quantity of α-hydroxycarbonyl compound added prior to the reaction, have been reported.

Additionally, there is no satisfactory explanation for how α-hydroxycarbonyl compounds facilitate the condensation of methylene glycol or formaldehyde to glycolaldehyde, the first reaction product. The participation of α-hydroxycarbonyl compounds in the formose reaction has been defined as a co-catalytic (*20, 21*) with possible involvement of an enediol. However, ethoxyacetaldehyde, which cannot form an enediol, exhibits about the same activity as does D-glucose in promoting the formose reaction (*22*). Finally, it has been suggested that paraformaldehyde generally contains traces of carbohydrates and that no formose reaction will occur if paraformaldehyde is carefully sublimed prior to preparation of the reaction mixture (*23*).

The present study was designed to evaluate the effects of oxygen and reducing sugars on the formose reaction.

EXPERIMENTAL METHODS

Reagents, apparatus, and procedures. All chemicals used were reagent grade. Helium used for purging was purified from residual oxygen by passing it twice through Fieser's solution (*24*). The formaldehyde solution contained methanol as a stabilizer. Calcium hydroxide was used as the catalyst; the ratio of formaldehyde to $Ca(OH)_2$ was varied from 1 to 10.

Reaction mixtures were agitated when the catalyst was present as a dispersed solid. However, most reaction mixtures contained a stable, homogeneous solution of the catalyst prepared by generating $Ca(OH)_2$ in the formaldehyde solution; in these cases, the formose reaction could be effected without agitation. A typical experimental procedure was as follows: $CaCl_2$ solution (1 *M*, 125 ml) was added to a 500-ml volumetric flask, followed by addition of a HCHO solution (13.76 *M*, 9.1 ml) and dilution with water to a total volume of 200 ml. To this solution was added slowly, and with continued agitation, NaOH (*1 M, 62.5 ml*). The mixture turned turbid but cleared in a short time. After further dilution, D-glucose was added (to a final concentration of 0.01 *M*) as an accelerator. The flask was then filled to the mark with water, and the contents were carefully mixed. A 25-ml aliquot (the blank) was withdrawn immediately; additional aliquots were taken at specific reaction times. The aliquots were analyzed for residual HCHO, quantity of acids formed, and appearance. The effectiveness of catalyst, reaction accelerators, and reaction inhibitors was ranked according to length of the induction period, rates of formaldehyde consumption and formose formation, and time required to complete the reaction.

For reactions under an inert atmosphere, special equipment was used. A three-neck, 500-ml, round-bottom reaction vessel was modified by replacing the female tapered joints by male tapered joints, and by adding a drain with a stopcock. Stopcocks were also added to three 100-ml, round-bottom vessels with regular female tapered joints. The following procedure was used: the three 100-ml vessels were partially filled with measured quantities of solutions of

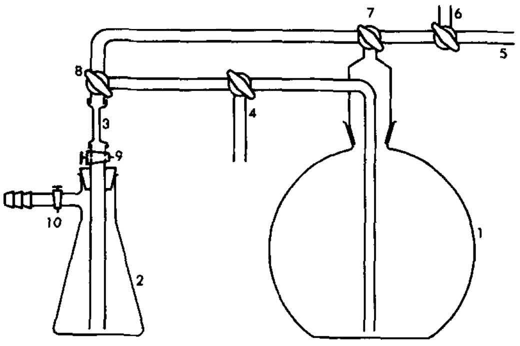

FIG. 1. Apparatus for reagent treatment and product sampling.

formaldehyde, calcium chloride, and sodium hydroxide, and attached to the reactor vessel in the down position. The inlets of the supply vessels were connected to a source of inert gas (helium), and the drain of the reactor vessel was connected to a vacuum source. The reactor was then placed in a controlled-temperature bath, and the liquids in the supply vessels were purged of oxygen by successive applications of heat, vacuum, and helium. After completion of the purges, all stopcocks were closed, and the reactor was lifted from the bath and inverted to mix the reagents and initiate the reaction. The reactor was again placed into the temperature-controlled bath, but this time the supply vessels were in the up position and the reactor drain was in the down position. Aliquots were obtained by forcing the reaction mixture through the main drain with helium introduced through one of the empty supply vessel inlets.

Equipment that allowed the anaerobic transfer of measured quantities of deaerated formaldehyde solutions into measured quantities of deaerated solutions or dispersions of catalysts (Fig. 1) was used in exploratory studies. The apparatus consisted of a storage vessel (1) for deaerated liquid (water, formaldehyde solution, or other reagents) and a series of reaction vessels (2, Erlenmeyer flasks calibrated for volume). The apparatus could be separated at position 3. For reactions, the following procedure was used: ports 4 and 5 were connected to a supply of helium. The contents of vessel 1 were heated, and air was removed by forcing helium through port 4 into the vessel and releasing it through port 6. Prior to the transfer of degassed liquid, the reaction vessel was purged of air by a stream of helium from port 5 through valves 7, 8, and 9, and out through valve 10. This procedure was followed by a purge with helium through port 4. Deaerated liquid was transferred into the reaction vessel under helium pressure from port 5 through valves 4, 8, and 9, followed by another purge from port 4 through valves 8 and 9. Finally, port 10 was closed, the time of the transfer was recorded, and the reaction vessel was separated from the transfer unit.

The reaction vessels were calibrated for volume. The apparatus was used for transferring measured quantities of deaerated formaldehyde solution in the absence of air into measured quantities of deaerated solutions or dispersions of catalysts.

Evaluation of the effects of oxygen. The apparatus used to evaluate the effect of oxygen consisted of a reaction vessel and a manometer. A measured portion of the reaction mixture was transferred into the reaction vessel, and after pressure equilibration, a valve connecting the reaction vessel to the atmosphere was closed and another connecting the reaction vessel to the manometer was opened. Pressure readings were taken at regular intervals during the reaction; corrections were made for changes in ambient temperature and pressure. For comparison, part of the reaction mixture was stored in a flask placed in the vicinity of the reaction vessel; at regular intervals, samples were withdrawn from it to determine the progress of the reaction and for correlation with the concurrent pressure changes.

For studies of the formose reaction in the absence of oxygen, the reaction mixture was prepared in the reaction vessel with the aid of a transfer unit (Fig. 1).

Analytical methods. The progress of the

TABLE 1

Formose Reaction as a Function of Gas Blanket and D-Glucose Addition to the Reaction Mixture[a]

Trial	Trial conditions		Reaction conditions		Product composition		
	Co-catalyst	Blanket	Temp (°C)	Time (min)	% Cannizzaro products	% Sugar	% Residual HCHO
1	1 g Glc	air	65	15	10.5	86.7	2.9
2	—	He	65	15	12.4	84.3	3.3
3	—	O_2	65	15	13.3	44.3	42.4
4	—	He	60	20	16.7	79.0	4.3
5	—	O_2	60	20	18.1	47.1	38.8

[a] Reaction conditions: 10 ml M $CaCl_2$, 10 ml M NaOH, 5 ml 13.76 M HCHO, demineralized water to 100 ml; 6-min gas purge.

formose reaction was followed with the sodium sulfite method of Lemme as described by Walker (*25*). This method permits, in a single analysis, determination of both acid generated during the reaction and unreacted formaldehyde. The procedure had been appraised in previous studies (*2, 16*) by comparison with other methods for HCHO analysis, including GLC analyses of HCHO and low-molecular-weight reaction products. The procedure is subject to some interference by glycolaldehyde, but the amount of glycoaldehyde in the formose reaction product is small and does not significantly affect the analytical results.

RESULTS AND DISCUSSION

At an early stage in this study, it was noticed that the pressure above a sealed formose reaction mixture decreased during the reaction. This observation led to an investigation of the effects of air (oxygen) on the formose reaction.

Data from studies of formaldehyde conversion under various gas blankets and with added D-glucose co-catalyst are summarized in Table 1. In Figs. 2–6, experimental results are correlated with pressure changes in the atmosphere above the formose reaction mixture. Five specific periods can be identified (Figs. 2, 3, and 5): an initial period of pressure decrease possibly owing to the endothermic heat of depolymerization of polyoxymethylene glycol (*27*) and the absorption of carbon dioxide (when present) into the alkaline reaction mixture; a period of gradual pressure increase during the induction period which includes the Cannizzaro reaction; a period of rapid pressure increase coinciding with the sugar formation period; a pressure maximum followed by a rapid decrease during the advanced stage of sugar formation; and a pressure decrease which resulted in a pressure below the initial pressure owing to absorption of oxygen by the reaction mixture.

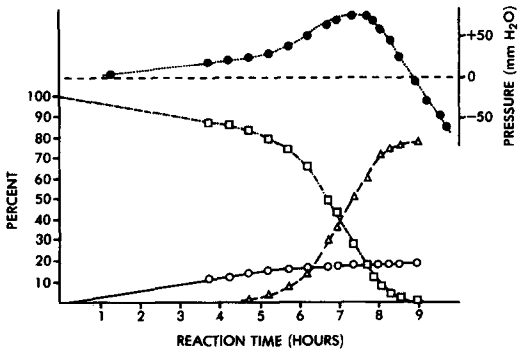

FIG. 2. Pressure variations above a formose reaction mixture. Reaction conditions: 75 ml 1.0 M $CaCl_2$, 25 ml 12.7 M HCHO, 90 ml M NaOH, and 385 ml water; room temperature, no agitation. (The reaction mixture contained some undissolved calcium hydroxide.) (●) Unadjusted manometer readings, mm H_2O; (□) remaining HCHO, %; (○) Cannizzaro reaction products, %; (△) reducing sugars generated, %.

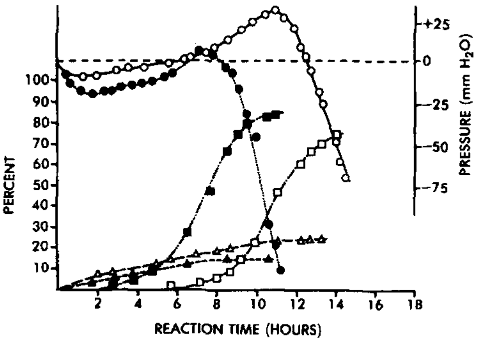

FIG. 3. Effect of added D-glucose (filled symbols) on the pressure above a formose reaction mixture. Reaction conditions: 75 ml 1.0 *M* $CaCl_2$, 25 ml 13.78 *M* HCHO, 90 ml 1.0 *M* NaOH, 2 g D-glucose, and 310 ml water; room temperature, no agitation, clear solution. Open symbols are for the same reaction without added D-glucose (0.4%). (○, ●) Unadjusted manometer readings, mm H_2O; (□, ■) reducing sugars generated, %; (△, ▲) Cannizzaro reaction products, %.

Significant oxygen absorption sometimes occurred well before completion of the sugar formation reaction, depending upon the amount of sugar co-catalyst present in the reaction mixture. After the reaction, there was a steady and constant uptake of oxygen by the formose product. This uptake continued until almost all oxygen in the atmosphere above the reaction mixture was consumed. The addition of D-glucose to a formose reaction mixture under air caused a shortening of the induction period and a lowering of the concentration of acids and Cannizzaro products, but it had no significant effect on the rate of sugar formation (Fig. 3).

Formose reactions conducted under helium were characterized by a shortened induction period, comparable to that of a reaction conducted in the presence of D-glucose, and an increased rate of sugar formation following the induction period (Figs. 4 and 5). In contrast, reactions under air or oxygen involved an extended induction period, the generation of increased quantities of acids and Cannizzaro products, and a reduced rate of sugar formation. These observations are in agreement with those of Shigemasa *et al.* (*11*) who observed a weak inhibition of the formose reaction by oxygen during potentiometric analysis of the course of the reaction. When the formose product was exposed to air, the quantity of acids produced was greater than the stoichiometric equivalent of the absorbed oxygen (Fig. 6). This could be the result of base-catalyzed conversion of sugars to saccharinic acids (*8–10*) and/or competing free-radical reactions.

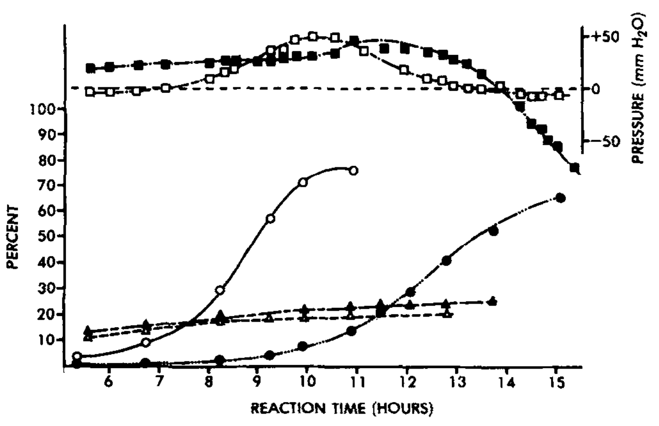

FIG. 4. Comparison of gas absorption by formose reactions under blankets of helium (open symbols) and oxygen (filled symbols). For reaction conditions, see legend to Fig. 3. (□, ■) Unadjusted manometer readings, mm H_2O; (○, ●) reducing sugars generated, %; (△, ▲) Cannizzaro reaction products, %.

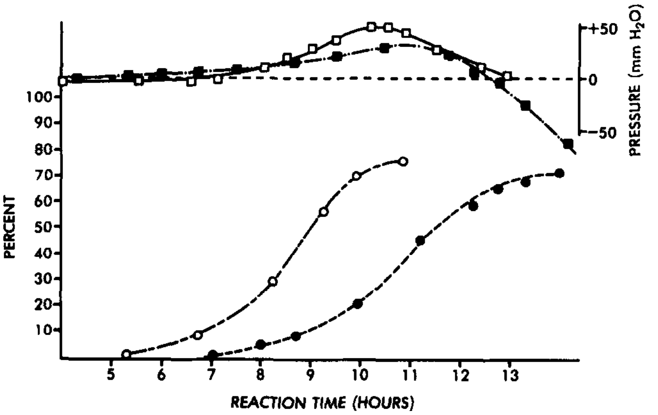

FIG. 5. Gas absorption during the formose reaction under blankets of helium (open symbols) and air (closed symbols). For reaction conditions, see legend to Fig. 3. (□, ■) Unadjusted manometer readings, mm H_2O; (○, ●) reducing sugars generated, %.

In the presence of a large quantity of D-glucose, there was a significant decrease in the overall rate of conversion of formaldehyde to sugars (Table 2). A maximum conversion rate appears at a mole ratio of D-glucose : $Ca(OH)_2$ of 1.0. At higher ratios, there is an apparent transition region, followed by a significant reduction in the rate of formaldehyde conversion and, apparently, a different pathway of conversion.

The central portion of the plots of sugar formation versus time is almost linear, and this portion has been assumed to have pseudo-zero-order kinetics (*12*, *26*). Using this assumption, the retarding effects of air, oxygen, and high D-glucose concentration on the rate of formaldehyde conversion to sugars were calculated (Table 3). Similarly, using the rate constants of formose reactions in the temperature range 20–65°C, an active energy of 19.9 kcal/mol (data not given) was calculated. This value is in close agreement with those previously reported (*12*).

TABLE 2

Effect of High Levels of D-Glucose on the Rate of the Formose Reaction[a]

D-Glucose (mol)	Mole ratio of D-glucose to $Ca(OH)_2$	% Residual HCHO after	
		190 min	280 min
10^{-5}, 10^{-4}	0.00032	88	83
10^{-3}	0.032	84	72
10^{-2}	0.32	74	28
2×10^{-2}	0.64	63	17
3×10^{-2}	0.96	58	12
4×10^{-2}	1.28	69	32
5.56×10^{-2}	1.78	72	41

[a] Reaction conditions: 0.125 *M* $CaCl_2$, 0.625 *M* NaOH, 0.125 *M* HCHO, total volume 500 ml; room temperature.

The S-shaped course of the plot for sugar formation with time suggests and autocatalytic reaction, as previously postulated (*2*, *27*). This hypothesis was tested by comparing experimental results with predictions, using the equations

$$\frac{dx}{dt} = k \cdot a \cdot x = k(a_0 - x) \cdot (x + x_0)$$

$$kt = \frac{1}{a_0 - x_0} \cdot \ln \frac{a_0(x_0 + x)}{x_0(a_0 - x)}$$

where dx/dt = rate of sugar formation, a = concentration of formaldehyde, x = concentration of sugars, a_0 = initial concentration of formaldehyde at the onset of the reaction, x_0 = initial (autocatalytically active) concentration of sugar.

Calculations using the data from Fig. 3

TABLE 3

Pseudo-Zero-Order Rate Constants[a] for the Formose Reaction

Reaction condition	Mole ratio of glucose : HCHO	Source	Rate of HCHO conversion to sugars r_F (mol/l · min)	Rate constant k_F (min^{-1})
Air blanket	—	Fig. 5	0.00206	0.023
Air blanket	0.032	Fig. 5	0.00230	0.026
He blanket	—	Fig. 6	0.00316	0.035
O_2 blanket	—	Fig. 6	0.00178	0.020
Air blanket	—	Fig. 9	0.00224	0.025
Air blanket	0.16	Fig. 9	0.00171	0.019

[a] Rate equation: $r_F = k_F\,[Ca(OH)_2]$; $[Ca(OH)_2] = 0.09$; room temperature; activation energy 19.9 kcal/mol.

were based on the autocatalytic action of the initial 0.0017 mol of sugar formed in the reaction ($t = 0$). The autocatalytically rate constant under the conditions of the experiment was 0.0418 min^{-1} (Table 4). A similar result was obtained when the formose reaction mixture contained 0.011 mol of D-glucose added as co-catalyst.

Analysis of reaction kinetics of formose reactions (after the induction period) in the presence of a large quantity of added D-glucose (Fig. 7) indicated again autocatalytic kinetics, since k is almost constant (k = 0.0404 min^{-1}) and no drift is apparent (Table 5). Only initially formed formose sugar acted as an autocatalyst; the large quantity of D-glucose present did not increase the maximum rate of the reaction.

TABLE 4

Derivation of the Autocatalytic Rate Constant for the Formose Reaction

Reaction time (min)	a (mol)		x (mol)		k (min^{-1})
0	0.332	$= a_0$	0.00167	$= x_0$	
30	0.327		0.0047		0.1365
101	0.314		0.0043		0.0385
158	0.300		0.0153		0.0453
218	0.276		0.032		0.0431
272	0.243		0.060		0.0424
320	0.202		0.095		0.0416
384	0.127		0.165		0.0417
440	0.063		0.227		0.0418
476	0.030		0.259		0.0413
500	0.016		0.273		0.0413
526	0.008		0.281		0.0403
563	0.005		0.284		0.0380

In a previous kinetic analysis of the formose reaction, Khomenko *et al.* (*12*) had observed that addition of glycoaldehyde resulted in a progressive decrease in the length of the induction period; and at a certain concentration, the formose reaction proceeded at a practically constant rate up to 90% conversion, eliminating the autocatalytic character of the reaction while maintaining zero-order kinetics at 50% conversion. At intermediate conversion levels, there were slight increases in the formose reaction rates with increasing glycoalde-

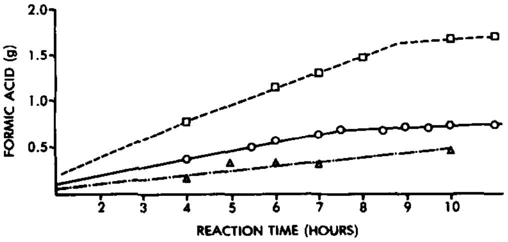

FIG. 6. Formation of acids (reported as g of formic acid) per 500 ml during the formose reaction. For reaction conditions, see legend to Fig. 3. (□) Reaction without added D-glucose; (○) reaction in the presence of 0.4% D-glucose; (△) reaction without HCHO, but with D-glucose.

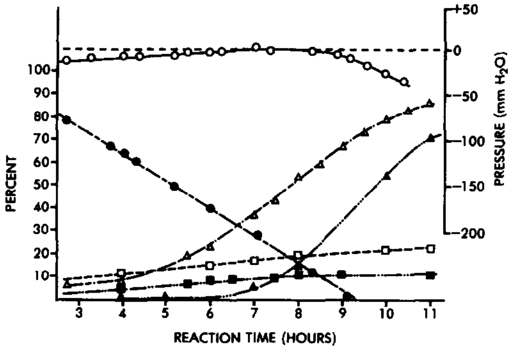

FIG. 7. Oxygen absorption during the formose reaction (closed symbols, control, without added D-glucose; open symbols, in the presence of 2% D-glucose). Reaction conditions: 75 ml *M* $CaCl_2$, 25 ml 13.78 *M* HCHO, 90 ml *M* NaOH, 10 g D-glucose (when present), and 310 ml water; room temperature, no agitation, clear solution (see Table 2). (○, ●) Unadjusted manometer readings, mm H_2O; (△, ▲) reducing sugars generated, %; (□, ■) Cannizzaro reaction products, %.

TABLE 5

Formose Reaction Order in the Presence of a Large Quantity of D-Glucose

Reaction time (min)	Moles of product	Rate constants		
		Autocatalysis (min^{-1})	First order (min^{-1})	Second order ($l \cdot mol^{-1} \cdot min^{-1}$)
90	0.0653	0.042	0.0028	0.0108
120	0.0773	0.039	0.0025	0.0101
150	0.1022	0.040	0.0029	0.0121
180	0.1232	0.039	0.0030	0.0136
210	0.1469	0.039	0.0033	0.0162
240	0.1825	0.041	0.0040	0.0232
270	0.2001	0.040	0.0042	0.0268
300	0.2258	0.040	0.0049	0.0375
330	0.2504	0.041	0.0058	0.0592
360	0.2671	0.041	0.0066	0.0935
390	0.2827	0.042	0.0084	0.2178
420	0.2917	0.041	0.0115	1.0138

hyde concentrations, but there was no change in the zero-order rate constant of the formose reaction with increasing concentrations of D-glucose.

The rate of HCHO conversion to Cannizzaro products during the induction period of the formose reaction was also tested for kinetic order (Table 6). The induction period obeyed first-order kinetics in formaldehyde at a constant quantity of base. This finding is in agreement with some previous

TABLE 6

Reaction Order of Formaldehyde Conversion during the Induction Period of the Formose Reaction[a]

Reaction time (min)	With D-glucose		Without D-glucose	
	Moles of product	*k* (min^{-1})	Moles of product	*k* (min^{-1})
240	0.0177	0.00023	0.0350	0.00045
330	0.0240	0.00022		
360	0.0280	0.00024	0.0520	0.00046
390	0.0286	0.00023		
420	0.0300	0.00022	0.0589	0.00045
450	0.0326	0.00023		
480	0.0350	0.00023	0.0669	0.00046
510	0.0333	0.00020		
540	0.0356	0.00021		
600			0.0756	0.00042
660			0.0779	0.00040
Range	0.00020–0.00024		0.00040–0.00046	
Mean	0.00023		0.000455	

[a] Rate equation: $k = \frac{1}{t} \ln \frac{a_0}{a_0 - x}$; room temperature.

studies (*28, 29*), but does not correspond to the frequently postulated higher orders for the Cannizzaro reaction (*30*).

The rate of formation of acidic matter in formose reaction mixtures under air was about the same as that observed for an alkaline sugar solution, viz., 8.2×10^{-4} mol formic acid/h. Data for rate of product formation, expressed as equivalents of formic acid (Fig. 6), indicate that the Cannizzaro reaction reached an endpoint at the onset of sugar formation and that subsequent formation of acidic matter was the result of the oxidation of formose sugar and of sugar cocatalyst in the alkaline reaction mixture. The rate of the reaction appeared to be almost independent of sugar concentration and primarily controlled by the size of the liquid–air interface and the rate of transfer of oxygen into the liquid.

CONCLUSIONS

From these results, four conclusions can be drawn. Oxygen interferes with the formose reaction. Oxygen dissolved in the reaction mixture from air above the reaction mixture extends the induction period of the formose reaction, increases the quantity of acids and Cannizzaro products in the formose product, and reduces the rate of sugar formation. Therefore, reliable investigations of the mechanism, kinetics, and products of the formose reaction require either complete exclusion of oxygen or careful control of the quantity present.

The addition of reducing sugars to the formose reaction mixture is not essential for initiating the formose reaction or significantly accelerating its rate. The co-catalytic effect of α-hydroxycarbonyl compounds in the formose reaction appears to be, at least in part, due to removal of oxygen from the system.

At low quantities of sugar, the extent of the competing Cannizzaro reaction is limited; and at high quantities, the rate of sugar formation is reduced, but there is no significant change in reaction order from autocatalysis when a large quantity of D-glucose is added to a formose reaction mixture. Both sugars added to a formose reaction mixture and sugars formed during the formose reaction may participate in aldol condensations (particularly when formaldehyde is present), retro-aldol reactions, cross-Cannizzaro reactions, and rearrangements, all of which make the formose product a complex mixture of reducing sugars, polyols, and acids.

Determination of gas pressure changes is a valuable tool for noninterfering and nondestructive observations of the progress of the formose reaction.

REFERENCES

1. Mizuno, T., and Weiss, A. H., *Adv. Carbohydr. Chem. Biochem.* **29**, 173 (1974).

2. Krylov, O. V., and Sinyak, Yu. E., *Dokl. Akad. Nauk SSSR, Ser. Phys. Chem.* **199**, 643 (1971).

3. Runge, K., and Mayer, R., *Ann.* **707**, 161 (1967).

4. Partridge, R. D., Weiss, A. H., and Todd, D., *Carbohydr. Res.* **24**, 29 (1972).

5. Mizuno, T., *Shizuoka Daigaku Nogakubu Kenkyu Hokoku* **24**, 49 (1974).

6. Hersch, G., Voelter, W., and Bauer, H., *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **32**, 826 (1977).

7. Speck, J. C., Jr., *Adv. Carb. Chem.* **13**, 63 (1958).

8. Sowden, J. C., *Adv. Carb. Chem.* **12**, 36 (1957).

9. Whistler, R. L., and Bemiller, J. N. *Adv. Carb. Chem.* **13**, 289 (1958).

10. Crum, J. D., *Adv. Carb. Chem.* **13**, 169 (1958).

11. Shigemasa, Y., Shiamo, M., Sakazawa, Ch., and Matsuura, T., *Kagaku to Kogyo (Tokyo)* **48**, 2099 (1975).

12. Khomenko, T. I., Golovina, O. A., Sakharov, M. M., Krylov, O. V., Partridge, R. D., and Weiss, A. H., *J. Catal.* **45**, 356 (1976).

13. Wanzlick, H. W., *Angew. Chem.* **74**, 129 (1962).

14. Guillot, G., Sadet, J., and Rumpf, P., *Bull. Soc. Chim. Fr.*, 2393 (1972).

15. Skell, P., and Suhr, H., *Ber.* **94**, 3317 (1961).

16. Weiss, A. H., and John, T., *J. Catal.* **32**, 216 (1974).

17. Baly, E. C. C., Heilbron, I. M., and Barker, W. F., *J. Chem. Soc.* **119**, 1025 (1921).

18. Shigemasa, Y., Matsuda, Y., Sakazawa, Ch., and Matsuura, T., *Kagaku to Kogyo (Tokyo)* **50**, 222 (1977).

19. Uspenskaya, V. A., Krylov, O. V., and Sinyak, Yu. E., *Kosm. Biol. Med.* **5**, 9 (1971).

20. Kuzin, A., *Ber.* **68B**, 1494 (1935).

21. Langenbeck, W., Krueger, K. H., Schwarzer, K., and Walker, J., *J. Prakt. Chem.* **275**, 196 (1956).

22. Kuzin, A., *Ber.* **68B,** 2169 (1935).

23. Weiss, A. H., Socha, R. F., Likholobov, V. A., and Sakharov, M. M., *CHEMTECH* **10,** 643 (1980).

24. Bemiller, J. N., *Methods Carbohydr. Chem.* **2,** 477 (1963).

25. Walker, J. F., "Formaldehyde," 3rd ed., Amer. Chem. Soc. Monogr. 159. Reinhold, New York, 1964.

26. Weiss, A. H., La Pierre, R. B., and Shapira, J., *J. Catal.* **16,** 332 (1970).

27. Weiss, A. H., Tabawala, H., Partridge, R. D., and Shapira, J., *DECHEMA Monogr.* **68,** 239 (1971).

28. Paul, I. I., *Zh. Obshch. Khim.* **11,** 1121 (1941).

29. Paul, I. I., and Bochkareva, I. V., *Tr. Semipalat. Zoovet. Inst.* **3,** 477 (1963).

30. Gould, E. S., "Mechanism and Structure in Organic Chemistry." Holt, Rinehart & Winston, New York, 1959.