JOURNAL OF CATALYSIS 48, 354–364 (1977)

Homogeneously Catalyzed Condensation of Formaldehyde to Carbohydrates

V. Complexing and pH Behavior with Glucose Cocatalyst

ALVIN H. WEISS[1]

Chemical Engineering Department, Worcester Polytechnic Institute,
Worcester, Massachusetts 01609

VLADISLAV A. SELEZNEV,[2] MICHAEL M. SAKHAROV, AND OLEG V. KRYLOV

Institute of Chemical Physics, USSR Academy of Sciences, Moscow, USSR

YA. B. GOROKHOVATSKY[3] AND N. P. EVMENENKO

L. B. Pisarzhevsky's Institute of Physical Chemistry, Ukranian SSR
Academy of Science, Kiev, USSR

Received August 30, 1976; revised March 15, 1977

It is shown that, although $Ca(OH)_2$ is a catalyst for the Cannizzaro reaction of formaldehyde, the complex of $Ca(OH)_2$ with glucose is not. The complex, which is the catalyst for condensation of formaldehyde to formose sugars, is not a discrete complexed sugar but rather, a scrambled, dynamic mixture of sugars having weakened structures. The *ab initio* complex of HCHO with $Ca(OH)_2$ is a salt-like species that buffers $Ca(OH)_2$ from pH 12.3 to 11.5 at 25°C, while the glucose–$Ca(OH)_2$ complex shows no significant buffering effect. Since formaldehyde has no α-hydrogens, conversion by Cannizzaro proceeds from the *ab initio* complex and formose reaction is disfavored. When sugars containing α-hydrogens become complexed either by addition to a reaction mixture or by generation *in situ*, formose condensation is possible simultaneously with Cannizzaro reaction. A pH of 11.0 is necessary for formose reaction to initiate with $Ca(OH)_2$ catalyst, while a pH of 7.5 is sufficient for $Pb(OH)_2$. Highest selectivity to formose is had by reaction in a continuous stirred tank reactor where complexed sugar products maximize the desired autocatalysis and eliminate the unproductive induction period. Cannizzaro reaction is reduced to only 2% near complete conversion—only one seventh of the amount that takes place in a batch system under optimal conditions.

INTRODUCTION

The formose reaction is the generic name for the base catalyzed condensation of formaldehyde to carbohydrates. Formose suggests the aldose and ketose nature of the complex mixture of branched and straight chain carbohydrates produced by this autocatalytic aldol-type condensation reaction. Cannizzaro reaction proceeds simultaneously and competitively to produce methanol and higher polyols as well as formate. Many alkaline substances are effective catalysts for the formose reaction, all resulting in remarkably similar carbohydrate product distributions. However, the selectivity of Cannizzaro reaction to formose reaction is very dependent on the type of catalyst

---

[1] Correspondence.

[2] Exchange fellow, USA-USSR Cooperative Program in Chemical Catalysis.

[3] Deceased.

ISSN 0021-9517

used. Formose reaction chemistry and product characterizations, as well as feeding studies on purified formose "syrup" are reviewed by Mizuno and Weiss (*1*).

Recently, reaction studies by Weiss and John (*2*) in a continuous stirred tank reactor (CSTR) have shown that rate instabilities are exhibited in the formose reaction. There are temperature instabilities as well as concentration instabilities in calcium hydroxide catalyst, formaldehyde reactant, and hydroxyl ion. The formose reaction was shown to proceed only over a very narrow range of concentrations of formaldehyde and calcium hydroxide and pH values. Overall reaction rate was visualized as a response surface with parameters of calcium hydroxide and formaldehyde concentrations. The formose reaction only occurs in a limited regime of composition space. Too much or too little of either formaldehyde or calcium hydroxide will quench the reaction. In another study by Kornienko *et al.* (*3*), the formose reaction rate was found to be very dependent on the ratio of lead oxide catalyst (PbO) to formaldehyde reactant concentration. At low concentrations of PbO relative to formaldehyde, the reaction rate decreased gradually until reaction actually stopped—apparently due to Cannizzaro reaction.

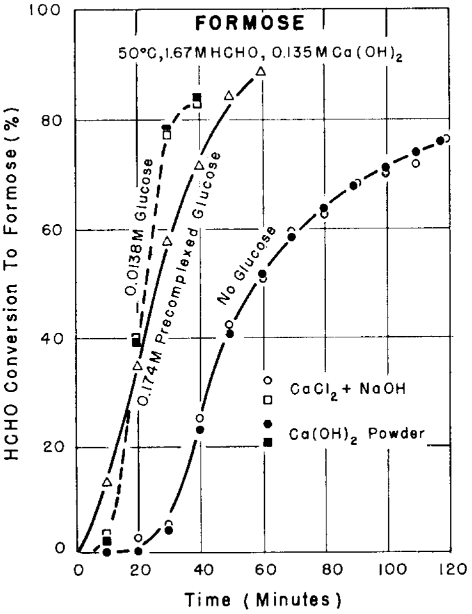


FIG. 1. Use of 0.0138 *M* glucose cocatalyst accelerates the autocatalytic formose reaction. A large excess, 0.174 *M*, causes a noticeable decrease in formose reaction rate.

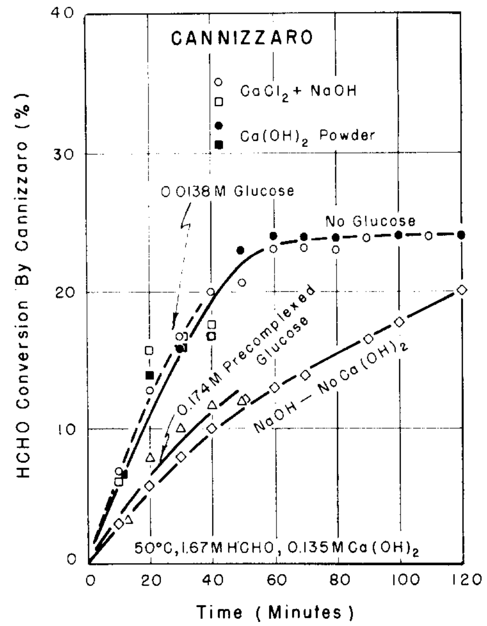


FIG. 2. Ca(OH)$_2$ catalyzes the Cannizzaro reaction when it is present as a formaldehyde solution complex. When it is precomplexed with glucose, it does not catalyze Cannizzaro reaction.

It has also been observed that a lowering of pH below that of saturated calcium hydroxide solution occurs in the formose reaction. Values as low as 10.5 have been measured at 40°C (*4*) and 8.6 at 76°C (*5*). pH minima correspond to reaction rate maxima in a CSTR. The calcium hydroxide in reacting mixtures with formaldehyde is highly complexed.

Addition of small quantities of carbohydrate as "cocatalyst" to the formose reaction mixture results in increased formaldehyde conversion rates (*6–9*). The effectiveness of a sugar as cocatalyst depends on its structure (*6*, *7*). Through the use of cocatalysts the "induction period" of the formose reaction can be effectively eliminated, resulting in suppression of the Cannizzaro reaction and increased formose yields (*8, 9*).

The complexity of the formose reaction has resulted in a number of proposed reaction mechanisms over the years (*1, 2, 8*). Weiss and John (*2*) have recently proposed a unifying mechanism based on observed rate law phenomena to explain why almost any base, regardless of valence, is a catalyst for the formose reaction. The mechanism postulates that reactions proceed from a common intermediate complexed species and that the selectivity for formose and for Cannizzaro reaction depends on the nature of the catalyst forming the carbohydrate complex. Fujino and coauthors have proposed a reaction scheme (*8*) involving observed ene–diol complex structures (*10*) and indicate also that the catalytic activity of the complex is remarkably dependent on the type of catalyst (alkaline earth hydroxide) used. Two similar, yet distinct, complexes are proposed by them: one involving two molecules of formaldehyde complexed with calcium hydroxide (or equivalent) which results in the formation of Cannizzaro reaction products or glycolaldehyde, and a second complex of calcium hydroxide with glycolaldehyde and the higher carbohydrates which on reaction with formaldehyde may result in the formation of the next sequential carbohydrate or glycolaldehyde.

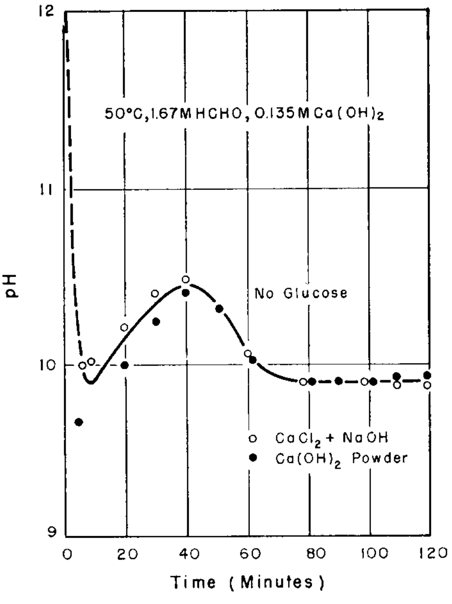


FIG. 3. Typical pH behavior in a batch reactor.

This study was made to provide additional information on the sensitivity of the formose reaction to pH conditions. The role of catalyst is studied, not only as a regulator of the necessary pH, but also in regard to the formation of complexes with reaction products, which are the truly catalytically active species in the formose reaction.

EXPERIMENTAL METHODS

Formaldehyde reactions in the presence of calcium hydroxide catalyst were made in a 300 ml beaker at 50 ± 0.1°C. Solutions of formaldehyde were prepared by dissolving paraformaldehyde (Aldrich Chem. Co. Inc.) under reflux and filtering the remaining solution. Concentrations were determined by using the sodium sulfite titration method (*11*). All other chemicals used were of reagent grade.

In all experiments using calcium hydroxide as the catalyst, the initial concentration of formaldehyde in the reaction mixture was 1.67 *M* (5.0% wt). Calcium hydroxide was introduced into the reactor both as a slurry of the reagent grade powder and by generation *in situ* from calcium chloride and sodium hydroxide in stoichiometric proportions. For many of the experiments, pure glucose was added to the reaction mixture as a cocatalyst, to increase the rate of formose reaction (*7, 8*).

The experiments were conducted as follows: 100 ml of 10% formaldehyde solution was brought to 50°C. For generation of calcium hydroxide *in situ*, this solution also contained 3.0 g of calcium chloride and if cocatalyst was to be used, 0.5 g of glucose. The formaldehyde solution was then added to 100 ml of preheated sodium

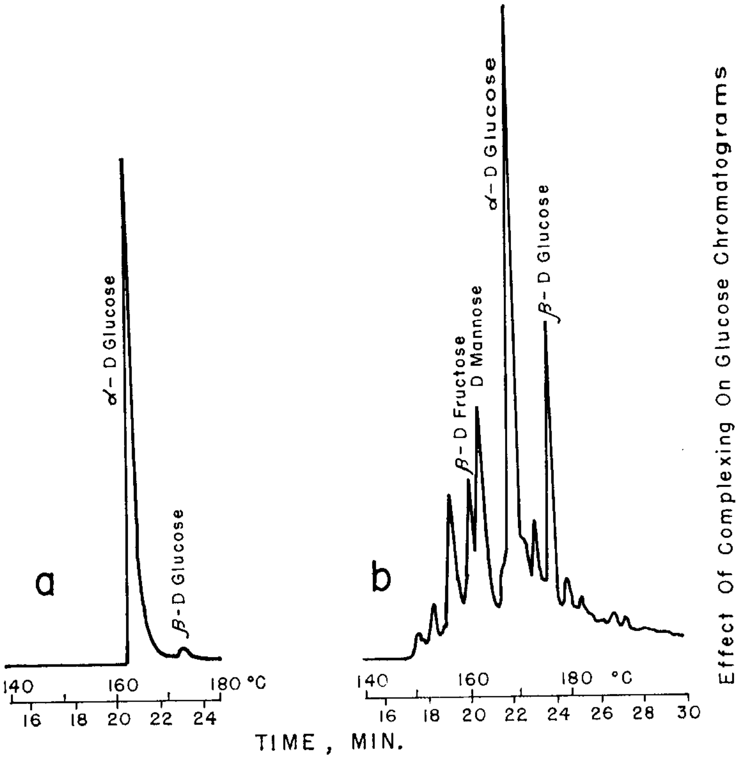


FIG. 4. Comparative chromatograms of trimethylsilyl ethers of α-D-glucose before (a) and after (b) 2 hr complexing with $Ca(OH)_2$. Bonds rearrange easily in the complex. TMS derivitation and analysis procedure described in Ref. (*12*).

hydroxide solution containing a stoichiometric quantity of sodium hydroxide or to 100 ml of water containing a suspension of 2.0 g of calcium hydroxide powder at 50°C. The initial concentrations of reactants in both situations were 0.135 *M* $Ca(OH)_2$ and 0.0138 *M* glucose.

Calcium hydroxide–glucose complex was also prepared prior to reaction by saturating a solution containing 12.5 g of glucose in 200 ml of water with 4.1 g $Ca(OH)_2$ powder by stirring for 2 hr at room temperature. The light yellow solution was filtered and 100 ml were used for reaction with 100 ml of 10% formaldehyde solution. The complex solution contained 1.55 g of $Ca(OH)_2$ in 100 ml of clear solution as determined by titration, resulting in final reactant concentrations of 0.105 *M* $Ca(OH)_2$ and 0.174 *M* glucose.

Samples taken from the reactor were cooled in ice water to stop the reaction. The concentration of $Ca(OH)_2$ in the sample was determined by titration with 0.1 *N* HCl. The conversion of formaldehyde by Cannizzaro reaction was calculated from the analysis of the $Ca(OH)_2$ content in the sample in accordance with the stoichiometry of the reactions:

$$4\,HCHO + Ca(OH)_2 \rightarrow Ca(COOH)_2 + 2CH_3OH.$$

Total formaldehyde conversion was determined by the sodium sulfite titration method and by gas chromatography. The difference between the total formaldehyde conversion and conversion by Cannizzaro represents formaldehyde condensed to formose sugars.

Batch reactions using lead salts as catalysts were studied at 75°C, using a pH meter and NaOH addition to control reaction pH. Initial formaldehyde concentrations ranged from 3.0 to 4.1 *M*; $PbAc_2$, 0.036 *M*, and, where used, glucose cocatalyst, 0.017 *M*.

RESULTS AND DISCUSSION

A comparison of the results obtained for the reaction of formaldehyde with calcium hydroxide catalyst prepared as a suspension of the reagent grade powder and by generation *in situ* by the equivalent stoichiometric amounts of calcium chloride and sodium hydroxide is shown in Figs. 1, 2, and 3. Both catalyst preparations give similar results suggesting that there are no particle size or dissolution limitations with respect to catalyst and that the reaction is truly homogeneous. The time required to obtain a completely clear solution, free of $Ca(OH)_2$ turbidity, is (not unexpectedly) longer for the larger particle-size $Ca(OH)_2$ powder than for $Ca(OH)_2$ generated *in situ*. The conversion of formaldehyde to formose sugars exhibits the typical "induction-period" during which conversion by Cannizzaro reaction predominates (Fig. 1). As the autocatalytic nature of the condensation reaction becomes apparent, Fig. 2 shows that conversion of formaldehyde by Cannizzaro reaction begins to approach a maximum value (*8*, *9*). Figure 2 also shows that calcium hydroxide is a more effective

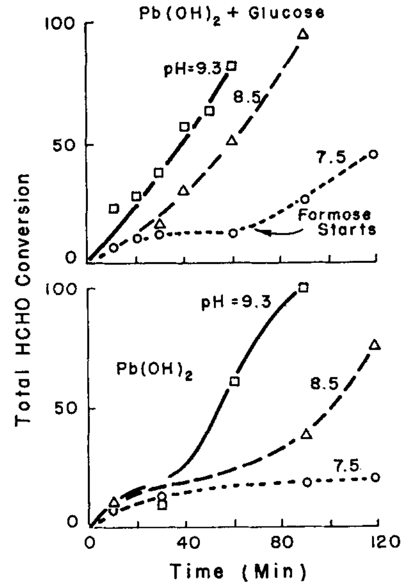


FIG. 5. Use of 0.017 *M* glucose cocatalyst allowed formose reaction to proceed even at pH 7.5 with $Pb(OH)_2$ catalyst. Cannizzaro reaction occurred in the absence of cocatalyst at pH 7.5. 75°C; 3.0–4.1 *M* HCHO; 0.036 *M* $Pb(CH_3COO)_2$,

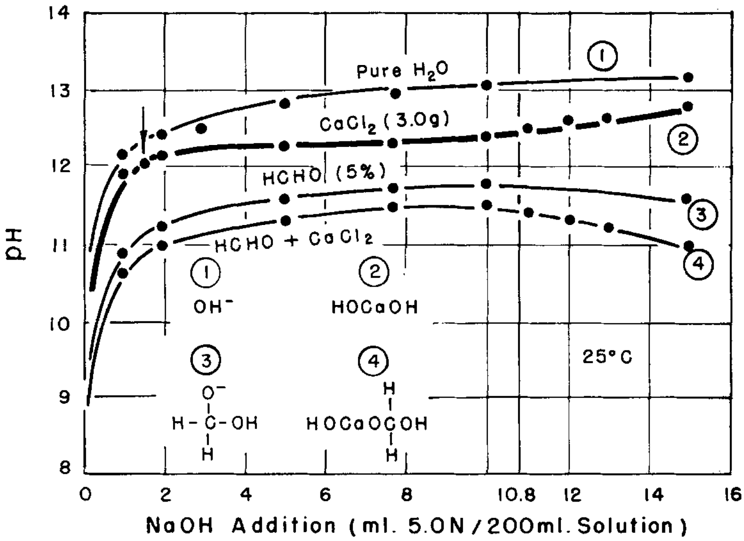


FIG. 6. Buffering effects in formose reaction solutions are due to the indicated species. The initiation of $Ca(OH)_2$ precipitation is shown by the arrow.

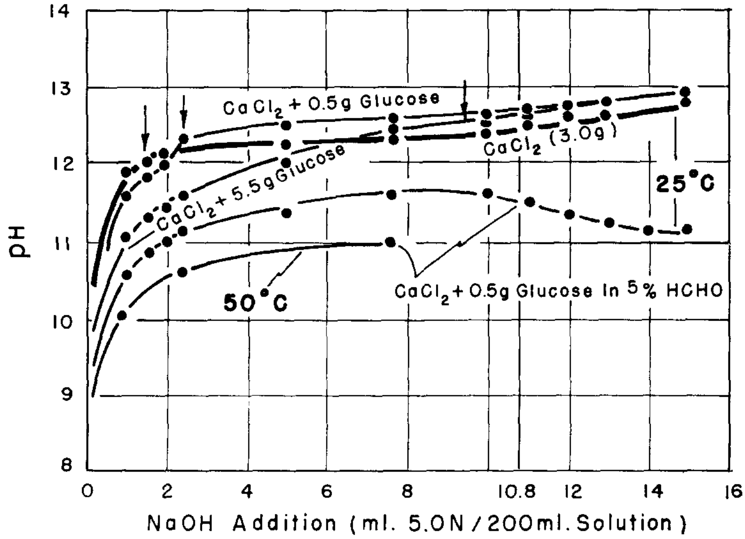


FIG. 7. Glucose complexes with $Ca(OH)_2$, consequently, $Ca(OH)_2$ does not precipitate until well beyond its solubility. Temperature intensifies pH reduction in the presence of HCHO.

catalyst for Cannizzaro reaction than the equivalent amount of sodium hydroxide added to a formaldehyde solution that does not contain $CaCl_2$.

The pH during the reaction changes in a complex manner: Figure 3 shows typical results: initially there is a sharp decrease in pH (to 9.6–10.2); pH then increases in the formaldehyde conversion interval from 5 to 50%; and finally pH decreases in the region of high conversion.

This complex picture of pH variations may be explained in the following manner:

1. The first sharp decrease is a result of interaction of $Ca(OH)_2$ with formaldehyde solution which is a weak acid, forming salt-like products, such as $HOCaOCH_2OH$ (*14*, *15*).

2. The increase in pH corresponds to the region of autocatalytic acceleration and there is some possibility that it may be due to the rapid complexing of formaldehyde and/or the liberation of complexed calcium hydroxide by product decomplexing. However, the major probability is that initially HCHO concentration is high and $Ca(OH)_2$ dissolved in solution is complexed faster than $Ca(OH)_2$ solid dissolves. The resulting unsaturated $Ca(OH)_2$ solution is evidenced by the drop in pH. However, when free HCHO concentration diminishes, $Ca(OH)_2$ dissolved in solution can then be used because of lower complexing rates, and so it follows that pH rises.

3. The final decrease in pH in the region of high conversion is due to $Ca(OH)_2$ neutralization by the formic acid product of the Cannizzaro reaction.

The addition of glucose (0.0318 *M*) to the $HCHO–Ca(OH)_2$ reaction mixtures as a cocatalyst accelerates the formose reaction rate as shown by comparison of results on Fig. 1 (*8*, *9*).

Preparation of a 0.174 *M* calcium hydroxide–glucose complex, a high enough glucose concentration to completely dissolve the $Ca(OH)_2$, resulted in suppression of Cannizzaro reaction to the level of that obtained with sodium hydroxide only (Fig. 2). The net loss in the overall rate of formaldehyde conversion to sugars (Fig. 1) is due to the relatively high concentration of glucose, 0.174 *M*, used in the preparation of the complex. Glucose must first be displaced from the complex before HCHO can enter and react. Uspenskaya and coworkers (7) have previously noted that high concentrations of certain monosaccharides, such as glucose, act in this manner.

The chromatogram in Fig. 4 shows the glucose solution prior to and immediately following the complexing with calcium hydroxide. Lobry de Bruyn–Alberda Van Eckenstein transformations are rapid at these conditions. The complexity of the chromatogram after complexing illustrates the many possible isomers that may be formed by interaction with basic solution and complexing. The "cocatalyst" complex is certainly not a simple glucose–$Ca(OH)_2$ moiety.

The accelerating effect of cocatalyst is not limited to $Ca(OH)_2$. Figure 5 comparative plots of total conversion vs reaction time for $Pb(OH)_2$ catalysts, shows the elimination of the formose induction period by glucose cocatalyst and the same type of Cannizzaro behavior as on Fig. 2, i.e., the small quantity of cocatalyst does not catalyze the Cannizzaro reaction, and a conversion envelope for Cannizzaro conversion results. Results obtained using powdered PbO, rather than $Pb(OH)_2$ generated *in situ* by the reaction of $PbAc_2$ + NaOH were essentially the same, indicating no mass transfer limitations in this system, also. However, Fig. 5 shows that reaction pH parameters markedly affect the time for HCHO conversion. The pH effect is different from the cocatalyst effect in that, all conditions being equal, higher pH increases rate but does not eliminate the formose induction period.

pH values are complex functions of all interactions taking place in the reaction system at any given moment. To interpret these interactions, a series of experiments was carried out on pH variations when NaOH was added to solutions containing only one or two components of the reaction mixture.

The experiments were made as follows: 5.0 *N* NaOH solution was added gradually to 200 ml solution and pH values were measured 1 min after each addition of NaOH, as indicated on Fig. 6. The upper curve 1 shows pH variations when NaOH

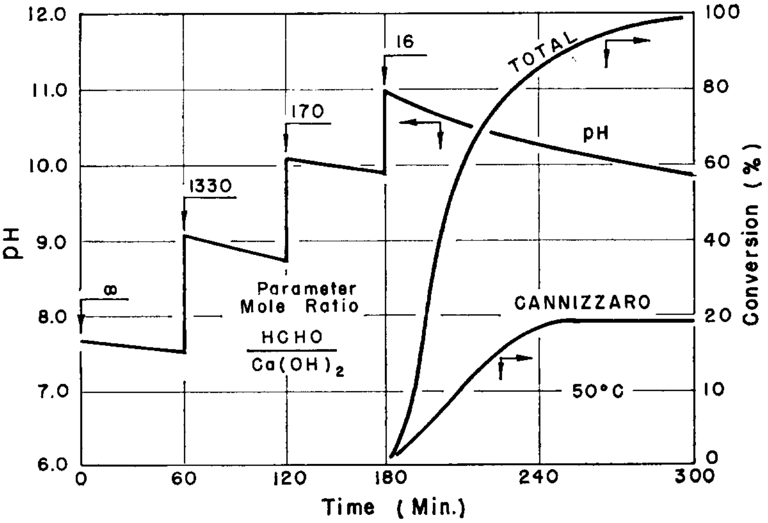


FIG. 8. Reaction does not proceed measurably when aliquots of NaOH are added to 200 ml HCHO–$CaCl_2$–glucose solution until pH 11.0 and HCHO/$Ca(OH)_2$ ratio of 16 are reached. 50°C; 5.0 wt% HCHO; 3.0 g $CaCl_2$; 0.5 g glucose.

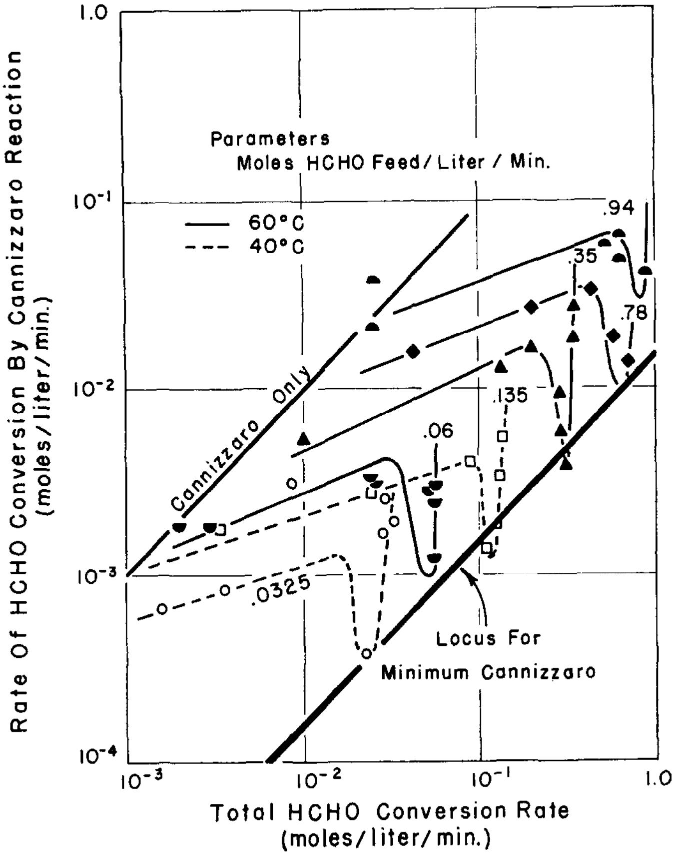


Fig. 9. Only Cannizzaro reaction proceeds at low conversion levels in a CSTR. Near complete conversion a locus of minimum Cannizzaro conversion can be drawn that is only 2% of the total HCHO conversion.

was added to 200 ml of distilled water. When NaOH was added to $CaCl_2$ solution, curve 2, the pH values were lower than those from pure water and remained nearly constant during $Ca(OH)_2$ precipitation (arrow). The pH increased slowly until the amount of NaOH reached the stoichiometric quantity (vertical line) at 10.8 ml.

Large deviations in pH values occurred when NaOH was added to 1.67 *M* (5.0% wt) formaldehyde solution, curve 3. In fact, a buffer (strong base and weak acid) formed and the pH of this mixture changes little with the subsequent addition of NaOH. pH reduction in the $CaCl_2$–formaldehyde system is even more marked, curve 4. Also shown on Fig. 6 are the possible species responsible for the pH values in each case.

The addition of glucose to the $CaCl_2$ solution changed the character of the pH effect as shown in Fig. 7. Greater amounts of NaOH and higher pH values were required for $Ca(OH)_2$ precipitation (arrows), as a result of complex formation between the Ca^{2+} and glucose molecules in the presence of hydroxyl ions. The complex with glucose may not be salt-like, as there was no pH reduction below that for $CaCl_2$ alone. When formaldehyde was added the system exhibited the same pH reduction as the $CaCl_2$–formaldehyde system in the absence of glucose. Increasing the temperature from 25 to 50°C intensified the pH changes and the pH values are shifted down by 0.5 pH units.

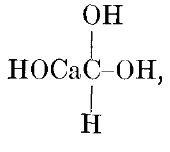
Results from CSTR experiments (*2*, *17*) showed that the formose reaction will proceed only over a definite range of pH values, as determined by the ratio of $HCHO/Ca(OH)_2$. A batch experiment was designed to define the range of pH values and the ratios of $HCHO/Ca(OH)_2$ necessary for formose reaction to proceed. Figure 8 shows formaldehyde conversion as a function of pH values obtained by stepwise NaOH additions (arrows) to the formaldehyde solution containing $CaCl_2$ and glucose. The presence of Ca^{2+} ions in solution is insufficient for the reaction to proceed. After 1 hr no measurable formaldehyde conversion was observed. Increasing the pH values up to pH 9 and 10 also gave no measurable conversion. The decreasing pH of the reaction mixture at 0.2 pH units/hr can be explained in terms of trace unmeasurable Cannizzaro reaction. Figure 8 shows that formaldehyde conversion using $Ca(OH)_2$ catalyst was initiated at pH 11 and required 2 hr for complete conversion. Obviously, it is necessary to have pH values in the interval from pH 10 to 11 and this agrees well with the experimental results shown in Fig. 3.

In the first paper of this series (*12*) it was shown in CSTR studies using $Ca(OH)_2$ as a catalyst that a plot of Cannizzaro rate as measured by $Ca(OH)_2$ conversion vs total HCHO conversion rate passes through a maximum as sugar forms. The curve then ascribes towards a minimum as formaldehyde concentration decreases, and finally, near complete conversion, $Ca(OH)_2$ conversion rises again as reaction severity is forced at fixed $HCHO/Ca(OH)_2$ ratio. Thus, a minimum in the selectivity of the system to the undesired Cannizzaro reaction results at about 90% conversion. It turns out that these minima form a locus for minimum Cannizzaro selectivity over a wide range of concentration. This locus is drawn on Fig. 9, superimposed on the earlier CSTR data. As with a batch reactor, a CSTR at mild conditions can be operated near 100% Cannizzaro reaction selectivity. However, operation at the CSTR locus of minima almost eliminates the side reaction, reducing Cannizzaro selectivity to about 2%. The selectivity behavior of the reaction and its optimization have also been discussed in Ref. (*19*). There it is shown that operation of a batch reactor at optimal reaction conditions at best will only reduce Cannizzaro selectivity to 15% of the total HCHO converted.

CONCLUSIONS

It was shown by Khomenko and Krylov (*10*) that when glucose is dissolved in NaOH at pH 12.4 two distinctive uv absorption bands result, one at 38,900 cm^{-1}, attributable to the carbonyl group, and one at 32,800 cm^{-1} attributable to the dienol structure. Addition of calcium ion to the basic solution shifted the dienol band to 29,600 cm^{-1}. At pH 10.15 and lower, the band did not appear. Since according to the just mentioned results of Fig. 8, formose reaction in the $Ca(OH)_2$ catalyzed system does not initiate below pH 10, one can attribute the efficiency of the cocatalyst to its forming a dienol structure. This is suitable for glycolaldehyde $HOCH_2CHO$ and higher molecular weight sugar complexes, but not the initial complexes of $Ca(OH)_2$ with a single molecule of formaldehyde. A dienol structure is not possible.

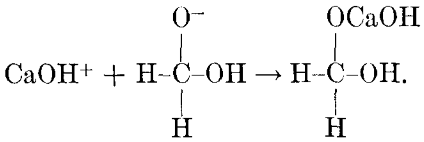
Franzen and Hauck (*14*) postulated in 1915 that the HCHO complex had the form



$$HOCa\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}{-}OH,$$

a salt-like species. Glotova and Irzhak (*15*) isolated such a salt and characterized it using X-ray techniques in 1973. Weiss and John (*2*) explained the kinetic behavior of the calcium hydroxide catalyzed formose reaction by postulating that the complex was the result of singly ionized $Ca(OH)_2$

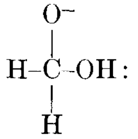
reacting with the anionic form of formaldehyde that is present in basic solution.



$$\mathrm{CaOH^+ + H{-}\overset{\displaystyle O^-}{\underset{\displaystyle H}{C}}{-}OH \rightarrow H{-}\overset{\displaystyle OCaOH}{\underset{\displaystyle H}{C}}{-}OH.}$$

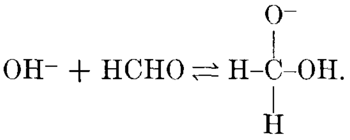
Such a complex does not require a bidentate structure resulting from the bivalency of Ca^{2+} or Pb^{2+}, and is thus consistent with the known catalytic activity of mono-, tri-, and tetravalent cations.

Since the present data, as well as earlier data of Weiss and John (*2*), confirm that Cannizzaro and formose reaction always proceed simultaneously, it is not unreasonable to assume then that a common complex is the precursor for both reactions. It is not possible to have formose reaction in the absence of Cannizzaro reactions, although both metal cation and pH affect the selectivity. The pH effect is understandable when one considers that an optimal pH is needed to maximize both $CaOH^+$ and



$$\mathrm{H{-}\overset{\displaystyle O^-}{\underset{\displaystyle H}{C}}{-}OH:}$$

$$\mathrm{Ca(OH)_2 \rightleftharpoons CaOH^+ + OH^-,}$$



$$\mathrm{OH^- + HCHO \rightleftharpoons H{-}\overset{\displaystyle O^-}{\underset{\displaystyle H}{C}}{-}OH.}$$

Weiss and John have suggested salt-like complexes and hydride transfer to explain subsequent formose and Cannizzaro reactions. Khomenko *et al.* (*18*) proposed enediol complexes. At present all mechanisms are speculative.

The gas chromatograms in Fig. 4 show that bonds are so easily disrupted in the complex that one should really not try to envision more than a distribution of enantiomers, anomers, isomers, and homologs constantly changing configuration. One might envision the approach of a formaldehyde molecule to a labile sugar complex, but the bonds in the reactant and formose product complexes may be so transient as to not really have molecular strength until dissociation of the complex to free sugar plus base solution. The formose complex may actually be a scrambled dynamic mixture of bonds constantly breaking and forming which reacts with free formaldehyde and sugars. It is derived from a formaldehyde complex which has a very low formose condensation driving force due to the lack of a α-hydrogen to form sugars.

The autocatalytic nature of the base catalyzed condensation of formaldehyde to formose sugars is eliminated by using as a cocatalyst an aldose or ketose having an α-hydrogen, such as glycolaldehyde or glucose. This is more strongly complexed by base than is formaldehyde and the cocatalyst and sugar products accumulate as catalyst complexes instead of formaldehyde complexing with the catalyst. Because of the presence of α-hydrogen atoms in cocatalyst and formose sugars, their removal by cross Cannizzaro reaction of complexed sugars does not occur, and so the formose reaction behaves autocatalytically due to this accumulation. The sugar complexes derive *ab initio* from a common salt-like formaldehyde complex, which, because of the absence of α-hydrogen, has a greater tendency to undergo Cannizzaro reaction, rather than formose condensation. Because of this, the Cannizzaro reaction can proceed without measurable formose condensation. The reverse is not possible. On the other hand, near complete conversion in a CSTR, little formaldehyde and large amounts of sugar are present, so the Cannizzaro reaction is disfavored.

ACKNOWLEDGMENT

This research was part of the joint US–USSR Program in Chemical Catalysis, Topic 4; Application of Catalysis to Life Support Systems for Possible Use in Future Space Exploration, administered by the American Chemical Society. Dr. Seleznev worked at Worcester Polytechnic Institute as an exchange scientist from the USSR Academy of Sciences. The WPI research was supported both by the National Science Foundation and by the National Aeronautics and Space Administration. The authors express their appreciation to Mrs. Maria Snow, Mrs. Dorothy French, and Mr. Osman Gebizlioglu for their invaluable help.

REFERENCES

1. Mizuno, T., and Weiss, A., *in* "Advances in Carbohydrate Chemistry and Biochemistry" (R. S. Tipson and D. Horton, Eds.), Vol. 29, p. 173. Academic Press, New York, 1974.

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

3. Kornienko, T. P., Surzhenko, A. N., Gorokhovatskii, Y. B., Sinyak, Y. E., and Uspenskaya, A., *Kinet. Katal.* **13**, 977 (1972).

4. Weiss, A. H., and Tambawala, H., *J. Catal.* **26**, 388 (1972).

5. Weiss, A. H., and Shapira, J., *Hydr. Proc.* **49**, 119 (1970).

6. Langenbeck, W., Sander, W., Jutin, F., Hunig, S., and Katzschmann, E., *Angew. Chem.* **61**, 186 (1949).

7. Uspenskaya, V. A., Krylov, O. V., and Sinyak, Y. E., *Kosm. Biol. Med.* **4**, 9 (1971).

8. Fujino, K., Kobayashi, J., and Higuchi, I., *Nippon Hagbu Haishu* **12**, 2292 (1972).

9. Kusin, A., *Chem. Ber.* **68**, 619, 1495, 2169 (1935).

10. Khomenko, T. I., and Krylov, O. V., *Kinet. Katal.* **15**, 625 (1974).

11. Walker, J. E., "Formaldehyde" American Chemical Society Monograph Series, **159**, 486, 3rd ed. Reinhold, New York, 1964.

12. Weiss, A. H., LaPierre, R., and Shapira, J., *J. Catal.* **16**, 332 (1970).

13. Partridge, R. D., and Weiss, A. H., *J. Chromatogr. Sci.* **8**, 553 (1970).

14. Franzen, H., and Hauck, L., *J. Pract. Chem.* **91**, 261 (1915).

15. Glotova, Yu. K., and Irzhak, V. I., *Izv. Acad. Nauk SSSR, Ser. Chim.* **N5**, 1134 (1973).

16. March, J., "Advanced Organic Chemistry," pp. 692–697. McGraw-Hill, New York, 1968.

17. Tambawala, H., and Weiss, A. H., *J. Catal.* **26**, 388 (1972).

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

19. Weiss, A. H., Seleznev, V. A., and Partridge, R., presented: Organic Reactions Catal. Soc., 6th Conf. Catal. Organic Systems, Boston, Mass., May 11, 1976. Proceedings, in press.