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EDIBLE CARBOHYDRATES FROM
FORMALDEHYDE IN A SPACECRAFT

by

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Abstract

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. This is more strongly complexed by base than is formaldehyde and the cocatalyst and sugar products accumulate as catalyst complexes instead of formaldehyde. Because of the presence of α -hydrogen atoms in cocatalysts 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. It is believed that a given catalytic formose complex is not a discrete complexed sugar, but rather, a scrambled dynamic mixture of sugars having weakened structures. The sugar complexes derive 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.

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 auto-catalytic 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 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., the formose reaction rate was found to be very dependent on the ratio of lead oxide catalyst (PbO) to formaldehyde reactant concentration (3). At low concentrations of PbO relative to formaldehyde, the reaction rate decreased gradually until reaction actually stopped - apparently due to 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 "co-catalyst" to the formose reaction mixture results in increased formaldehyde conversion rates (6-9). The effectiveness of a sugar as co-catalyst depends on its structure (6,7). Through the use of "co-catalysts" 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 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 (2). 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 co-authors 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.

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

1. At Worcester Polytechnic Institute

Formaldehyde reactions in the presence of calcium hydroxide catalyst were made in a 300 ml beaker at $50^{\circ} \pm 0.1^{\circ}\text{C}$. 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 1.67M (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 co-catalyst, 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 gms of calcium chloride and if co-catalyst was to be used, 0.5 gms of glucose. The formaldehyde solution was then added to 100 ml of preheated sodium hydroxide solution containing a stoichiometric quantity of sodium hydroxide or to 100 ml of water containing a suspension of 2.0 gms of calcium hydroxide powder at 50°C . The initial concentrations of reactants in both situations were 0.135 M in $\text{Ca}(\text{OH})_2$ and 0.0138 M glucose.

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

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



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.

2. At the Institute of Chemical Physics

Reactions were performed by dissolving glycolaldehyde and CaCl_2 in 1.53 M formaldehyde solution. The reaction was initiated by adding a solution containing the necessary amount of sodium hydroxide such that the initial combined reactant concentrations of 0.187M $\text{Ca}(\text{OH})_2$ and 1.53 M HCHO were obtained. Samples were taken at 2.5 and 10 minute intervals, as required. These were acidified with HCl to stop the reaction, backtitrated with NaOH to determine the extent of Cannizzaro reaction (6), and then adjusted to a constant volume prior to further analysis.

Formaldehyde determinations were made on these neutralized samples both by titration and gas chromatography. Determinations by thermal conductivity gas chromatography were made using a 2m x 3mm stainless steel column packed with 80/100 mesh Porapak N operated isothermally at 115°C with a helium flow of about 40 cc/min.

Methanol formed by Cannizzaro reaction was determined gas chromatographically by FID using a 1m x 3mm glass column packed with 80/100 mesh Porapak Q operated isothermally at 150°C with a helium flow of about 40 cc/min.

3. At the Institute of Physical Chemistry

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 3.0-4.1M, $PbAc_2$ 0.036M, and, where used, glucose cocatalyst 0.017M. UV spectra were obtained with a Specord UV-Vis Spectrophotometer having a quartz cell.

Results and Discussion

A comparison of the results obtained for the conversion of formaldehyde by 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 Figure 1. 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 exhibits the typical "induction-period" during which conversion by Cannizzaro reaction predominates. As the autocatalytic nature of the condensation reaction becomes apparent, conversion of formaldehyde by Cannizzaro reaction begins to approach a maximum value (8,9). Figure 1 also shows that calcium

hydroxide is a more effective catalyst for Cannizzaro reaction than the equivalent amount of sodium hydroxide.

The pH during the reaction changes in a complex manner: 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 $\text{Ca}(\text{OH})_2$ with formaldehyde solution which is a weak acid, forming salt-like products, such as $\text{HOCaOCH}_2\text{OH}$ (14,15).
- 2) the increase in pH corresponds to the region of autocatalytic acceleration and may be due to the rapid complexing of formaldehyde and/or the liberation of complexed calcium hydroxide by product decomplexing.
- 3) the final decrease in pH in the region of high conversion is due to the formic acid product of the Cannizzaro reaction.

The addition of glucose (0.0138μ) to the $\text{HCHO-Ca}(\text{OH})_2$ reaction mixtures as a co-catalyst accelerates the total reaction rate as shown by comparison of Figure 1 and Figure 2 (8,9)

Preparation of a 0.174M calcium hydroxide-glucose complex, a high enough glucose concentration to completely dissolve the $\text{Ca}(\text{OH})_2$, resulted in suppression of Cannizzaro reaction to the level of that obtained with sodium hydroxide only. The net loss in the overall rate of formaldehyde conversion, also seen on Fig. 2, is due to the relatively high concentration of glucose, 0.174M, used in the preparation of the complex. Uspenskaya and co-workers have previously noted that high concentrations of certain monosaccharides, such as glucose, act in this manner (7).

The chromatogram in Figure 3 shows the glucose solution prior to and immediately following the complexing with calcium hydroxide. The complexity of the chromatogram after complexing illustrates the many possible isomers that may be formed by interaction with basic solution and complexing. The "co-catalyst" complex is certainly not a simple glucose₂Ca(OH)₂ moiety.

Glycolaldehyde (HOCH₂CHO), the sugar believed to result as the first condensation step of formaldehyde, is also a co-catalyst for the autocatalytic formose reaction. Figure 4 is a plot of total HCHO conversion using 0 to 0.04M of glycolaldehyde in a solution of 0.2M Ca(OH)₂ and 1.5M HCHO. The induction period for the formose conversion (total conversion less Cannizzaro conversion) disappears with increased quantities of glycolaldehyde co-catalyst. Note that the Cannizzaro reaction conversion was not accelerated by glycolaldehyde. The Cannizzaro envelope plotted on Figure 4 was experimentally determined by titration of every product, and points are omitted for clarity.

The accelerating effect of co-catalyst is not limited to Ca(OH)₂. Figure 5, comparative plots of total conversion vs. reaction time for Pb(OH)₂ catalysis, shows the elimination of the formose induction period by glucose co-catalyst and the same type of Cannizzaro behavior as on Figure 4, i.e., the small quantity of co-catalyst 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 PbAc₂ + NaOH, were essentially the same, indicating no mass transfer limitations in this system, also. However, Figure 5 shows that reaction pH parameters markedly affect the time for HCHO conversion. The pH effect is different from the co-catalyst effect in that, all conditions being equal, higher pH increases rate but does not eliminate the formose induction period.

Of course, 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: 5.0N NaOH solution was added gradually to 200 ml solution and pH values were measured 1 minute after each addition of NaOH, as indicated on Figure 6. The upper curve-1, shows pH variations when NaOH 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 $\text{Ca}(\text{OH})_2$ precipitation (shown by arrow). The pH increased slowly until the amount of NaOH reaches the stoichiometric quantity (vertical line) at 10.8 ml.

Large deviations in pH values occurred when NaOH was added to 1.67M (50% 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 Figure 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 Figure 7. Greater amounts of NaOH and higher pH values were required for $\text{Ca}(\text{OH})_2$ precipitation (arrows), as a result of complex formation between the Ca^{++} and glucose molecules in the presence of hydroxyl ions. The system exhibits the same pH reduction as the CaCl_2 - formaldehyde system in the absence of glucose. Increasing the temperature from room temperature, 25°C 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 $\text{HCHO}/\text{Ca}(\text{OH})_2$

A batch experiment was designed to define the range of pH values and the ratios of $\text{HCHO}/\text{Ca}(\text{OH})_2$ 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^{++} ions in solution is insufficient for the reaction to proceed. After one hour no measurable formaldehyde conversion was observed. Increasing the pH values up to pH9 and pH10 also gave no measurable conversion. The decreasing pH of the reaction mixture at 0.2 pH units per hour can be explained in terms of trace unmeasurable Cannizzaro reaction. Figure 8 shows that formaldehyde conversion using $\text{Ca}(\text{OH})_2$ catalyst was initiated at pH 11 and required two hours for complete conversion. Obviously, it is necessary to have pH values in the interval from pH 10 to pH 11 and this agrees well with the experimental results shown in Figures 1 and 3.

In the pH 10 regime, partial conversion of formaldehyde takes place when the $\text{HCHO}/\text{Ca}(\text{OH})_2$ ratio is increased beyond 16, because the small amounts of $\text{Ca}(\text{OH})_2$ present are effectively neutralized by Cannizzaro reaction at some point, thus stopping the reaction by eliminating the catalyst. The results obtained for $\text{HCHO}/\text{Ca}(\text{OH})_2$ ratios of 12.3, 16.6, 20.0 and 24.8 are presented in Figure 9. As expected, the higher ratios of 20 and 24.8 limited formaldehyde conversion to 62% and 31% respectively. The lowest pH values in these experiments were in the range of 9.6 to 9.8, representing the lower pH limits for which formose condensation will proceed in the presence of $\text{Ca}(\text{OH})_2$ at 50°C .

The partial conversion influences the selectivity greatly. Selectivity ratios of formaldehyde converted into carbohydrates to formaldehyde converted into Cannizzaro reaction products are listed in Table 1. Increasing the ratio $\text{HCHO}/\text{Ca}(\text{OH})_2$ from 12.3 to 24.8 reduced the formose to Cannizzaro reaction selectivity from 5.7 to 2.3.

Therefore, for higher carbohydrate yields, small $\text{HCHO}/\text{Ca}(\text{OH})_2$ ratios should be used (i.e., high catalyst quantities - but not too high or the reaction is again quenched).

Table 1

Ratio $\frac{\text{HCHO}}{\text{Ca}(\text{OH})_2}$	12.4	16.6	20.0	24.8
Terminal Selectivity	5.7	5.2	3.3	2.3

Reaction Conditions: 50°C , 1.667 m/L HCHO, 0.5 g Glucose

It was shown by Chomenko and Krylov (4) that when glucose is dissolved in NaOH at pH 12.4, two distinctive UV absorption bands result, one at $38,900\text{ cm}^{-1}$, attributable to the carbonyl group, and one at $32,800\text{ cm}^{-1}$ attributable to the dienol structure. Addition of calcium ion to the basic solution shifted the dienol band to $29,600\text{ cm}^{-1}$. At pH 10.15 and lower, the band did not appear. Since, according to the just mentioned results of Figure 8, formose reaction in the $\text{Ca}(\text{OH})_2$ catalyzed system does not initiate below pH 10, a first inclination would be to attribute the efficacy of the cocatalyst to its forming a dienol structure.

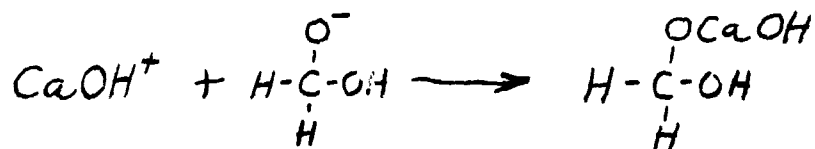
However, $\text{Pb}(\text{OH})_2$ is a catalyst that is effective for both formose condensation and Cannizzaro reaction in the presence of glucose (Fig. 5) even at pH 7.5, where no dienol band is observable.

As an attempt to explain these reactions at low pH, Figure 10 shows UV spectra, all taken at pH 7.0-7.5. No absorption bands are observed in the spectrum of a PbO solution, since PbO is only slightly soluble. Aqueous solution spectra of $\text{Pb}(\text{CH}_3\text{COO})_2$, $\text{Pb}(\text{HCOO})_2$, and $\text{Pb}(\text{NO}_3)_2$ show broad bands at $47,840\text{--}49,240\text{ cm}^{-1}$ attributable to the lead ions. The spectrum of an aqueous solution of formaldehyde plus glucose shows an

absorption band at $50,320 \text{ cm}^{-1}$ and is merely the superposition of the spectra of the individual species. Shaking either formaldehyde or glucose with PbO shifts their absorption bands to $48,000 \text{ cm}^{-1}$, and results in spectra having the same general shape as those of the lead salts. The spectrum of condensate is slightly more complex in exhibiting an additional weakly resolved maximum at about $42,600 \text{ cm}^{-1}$.

Conclusions

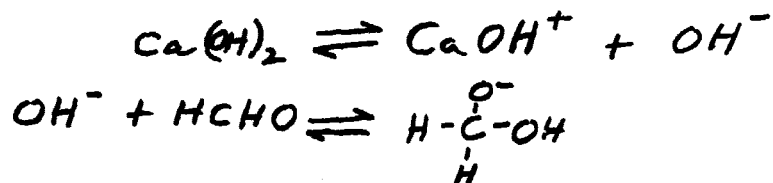
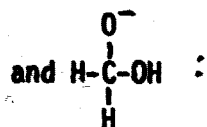
Since both the Pb complexes as well as the Pb salts exhibit identical absorption maxima at $48,000 \text{ cm}^{-1}$, we believe it is an indication that the very nature of the formose complex is a salt-like species. Franzen and Hauck (14) postulated in 1915 that the HCHO complex had the form $\text{HO} \underset{\text{OH}}{\overset{\text{OH}}{\text{C}}} \text{CaOH}$. 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 $\text{Ca}(\text{OH})_2$ reacting with the anionic form of formaldehyde.



Such a complex does not require a bidentate structure resulting from the bivalency of Ca^{++} or Pb^{++} , and is thus consistent with the known catalytic activity of mono-, tri-, and tetravalent cations. It is also consistent with the salt-like nature of the complex suggested by the spectra presented in Figure 10.

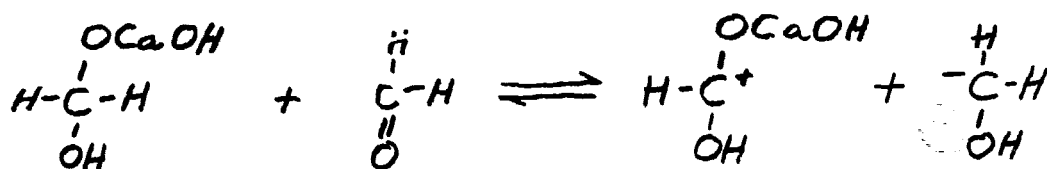
Since the present data, as well as earlier data of Weiss and John, confirm that Cannizzaro and formose reaction always proceed simultaneously, it is not unreasonable to assume then that a common complex is the precursor for both reactions. It is not possible to have formose reaction in the absence of Cannizzaro reactions, although both metal cation and pH affect the selectivity. The pH effect is under-

standable when one considers that an optimal pH is needed to maximize both CaOH^+

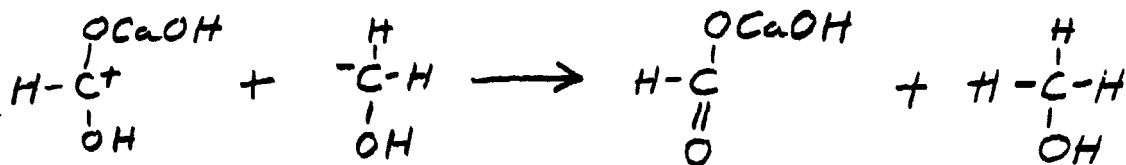


Too low or too high a pH in a given system suppresses one or the other.

On the other hand, the results of many earlier studies as well as the present data show that it is possible to have Cannizzaro reaction in the absence of formose reaction and that sugars accelerate the formose reaction. These can now be explained using the present data and the mechanism postulated by Weiss and John. They suggested that the common Formose-Cannizzaro complex could react with additional formaldehyde by a hydride transfer reaction



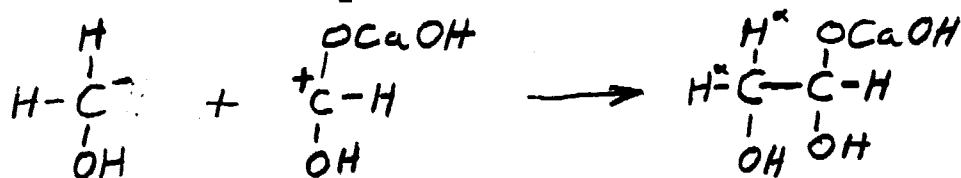
to produce a cation and an anion. The cation and the anion react by proton transfer to form calcium formate and methanol.



using up the $\text{Ca}(\text{OH})_2$, generating Cannizzaro products, and stopping reaction.

Having the catalyst incorporated in the mechanism accounts for catalyst effect on Cannizzaro rate. Mechanisms for Cannizzaro reaction are customarily written in ionic form, ignoring the cation.

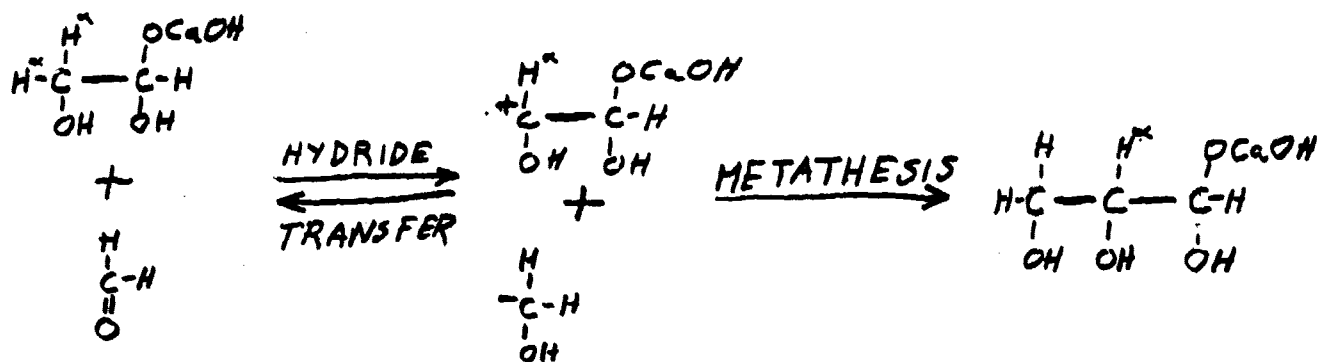
The first step of the formose reaction itself was postulated as a metathesis (experimentally observed to be slow and unfavored) between the cation and anion to yield complexed glyceraldehyde, which then can continue to condense with more HCHO by aldol condensation, since it contains α -hydrogens; or it can dissociate to the free sugar, regenerating $\text{Ca}(\text{OH})_2$.



The fact that glycolaldehyde has α hydrogens (noted on the above formula) is the essence of the effect of the cocatalyst and the reason for the autocatalytic nature of the formose reaction. It is well known that compounds with α -hydrogen do not undergo Cannizzaro or cross-Cannizzaro reaction. Thus, if either the first step of the formose reaction has proceeded or a sugar cocatalyst is added, the reaction proceeds from the complex in the formose direction only, and more α -hydrogen containing complexes accumulate. Figure 9 shows that, at similar concentration, the intensity of the absorption maximum for PbO-glucose is ten times that of PbO-formaldehyde, indicating much greater sugar complex stability over HCHO complex stability. Thus, the cocatalyst displaces formaldehyde from complexes and, if it has α -hydrogens, permits formose condensation to proceed. If a large, rather than catalytic quantity of cocatalyst is used, e.g., the glucose experiment on Figure 2, then it competes so strongly for complex that Cannizzaro reaction is reduced.

The gas chromatograms on Figure 3 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 following approach of a formaldehyde molecule to a labile

glycolaldehyde 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 α -hydrogen to form sugars.

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List of Figures

1. Ca(OH)_2 particle size varied by using powder or generating Ca(OH)_2 in situ does not affect reaction rate. Ca(OH)_2 catalyzed both Cannizzaro and Formose reactions. 50°C , 1.67M HCHO, 0.135M Ca(OH)_2 . Arrows indicate time at which solutions clarified.
2. Use of 0.0138M glucose cocatalyst accelerates formose reaction. A large excess, 0.174M, causes a noticeable decrease in Cannizzaro reaction. 50°C , 1.67M HCHO, 0.135M Ca(OH)_2 .
3. Comparative chromatograms of trimethylsilyl ethers of α -D-Glucose before (a) and after (b) 2 hours complexing with Ca(OH)_2 . Bonds rearrange easily in the complex. TMS derivatation and analysis procedure described in (12).
4. Glycolaldehyde cocatalyst in small amounts accelerates formose reaction and eliminates the induction period. Cannizzaro reaction is not measurably affected. 40°C , 1.53M HCHO, 0.187M Ca(OH)_2 .
5. Use of 0.017M 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 , 3.0-4.1M HCHO, 0.036M $\text{Pb(CH}_3\text{COO)}_2$.
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.
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.
8. Reaction does not proceed measurably when aliquots of NaOH are added to 200 ml HCHO- CaCl_2 -Glucose solution until pH above 10 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.
9. UV absorption maxima at $48,000\text{ cm}^{-1}$ for both lead salts and lead complexes suggest that the complex is salt-like.

TABLE 1

RATIO $\frac{\text{HCHO}}{\text{Ca(OH)}_2}$	12.4	16.6	20.0	24.8
TERMINAL SELECTIVITY	5.7	5.2	3.3	2.3
<u>REACTION CONDITIONS:</u> 50°C, 1.667 M/L HCHO, 0.5 g GLUCOSE				

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Ca(OH)₂ PARTICLE SIZE DOES NOT AFFECT REACTIONS

Ca(OH)₂ CATALYZES CANNIZZARO REACTION

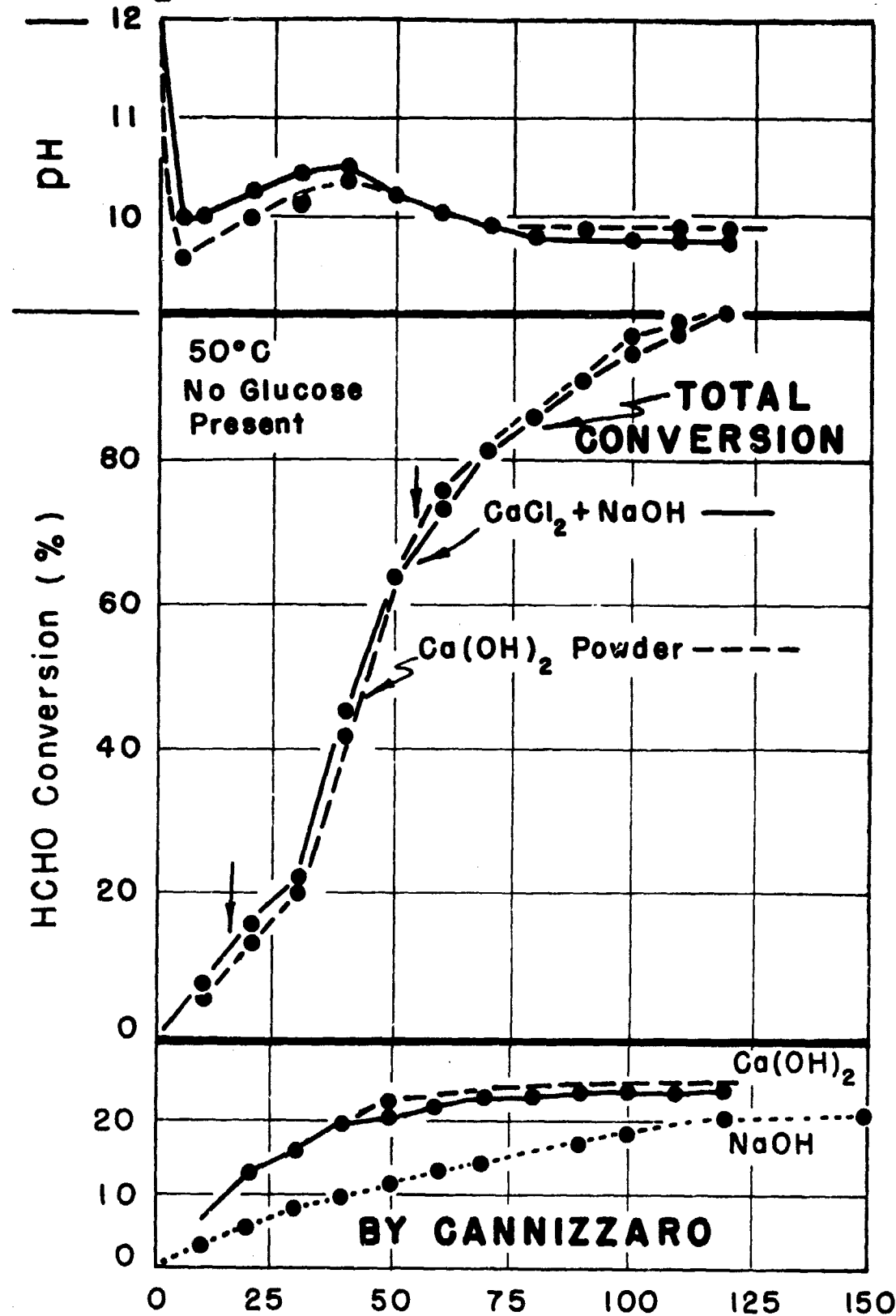


Figure 1

COMPLEXED $\text{Ca}(\text{OH})_2$ DOES NOT CATALYZE CANNIZZARO REACTION

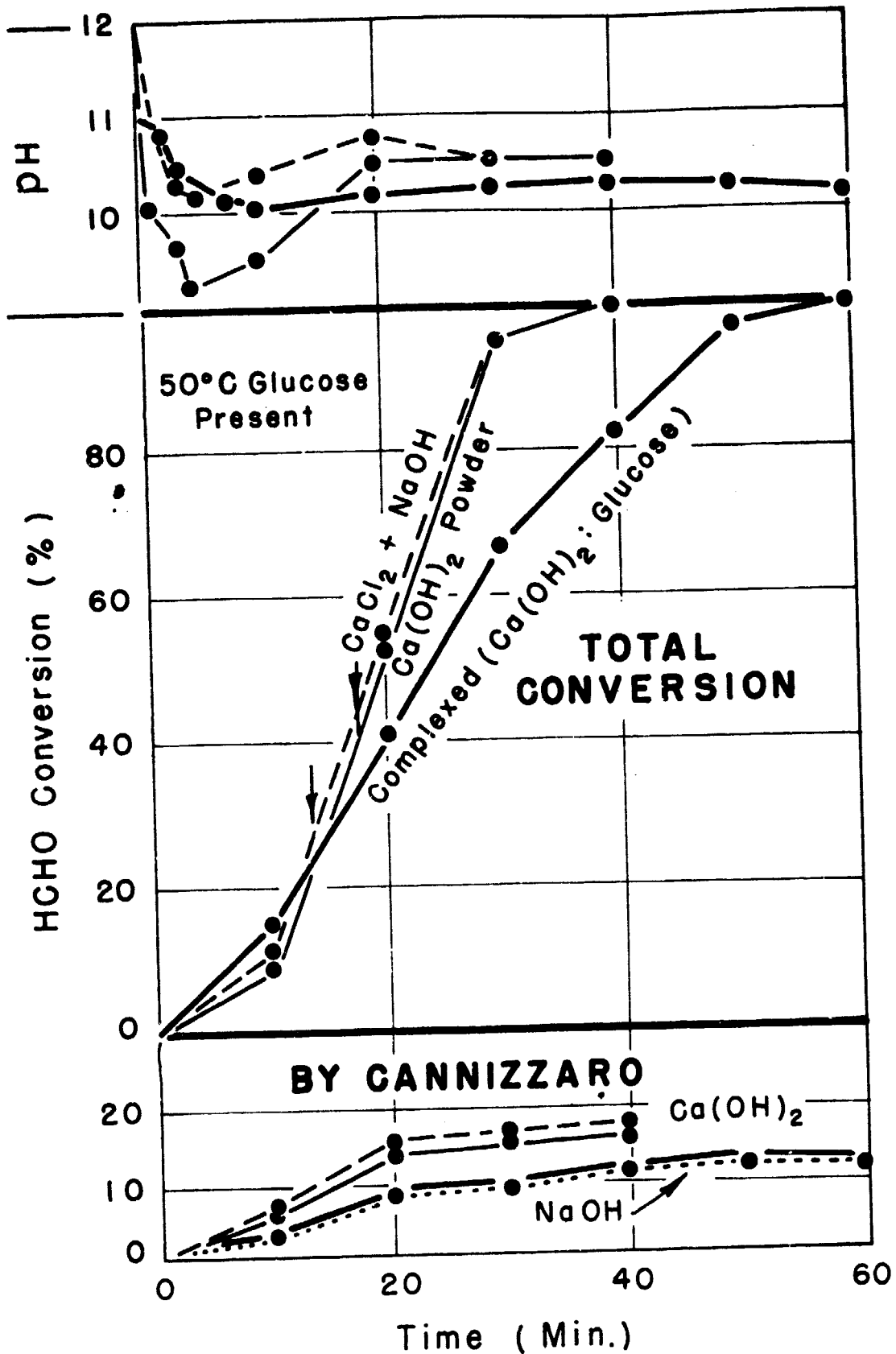
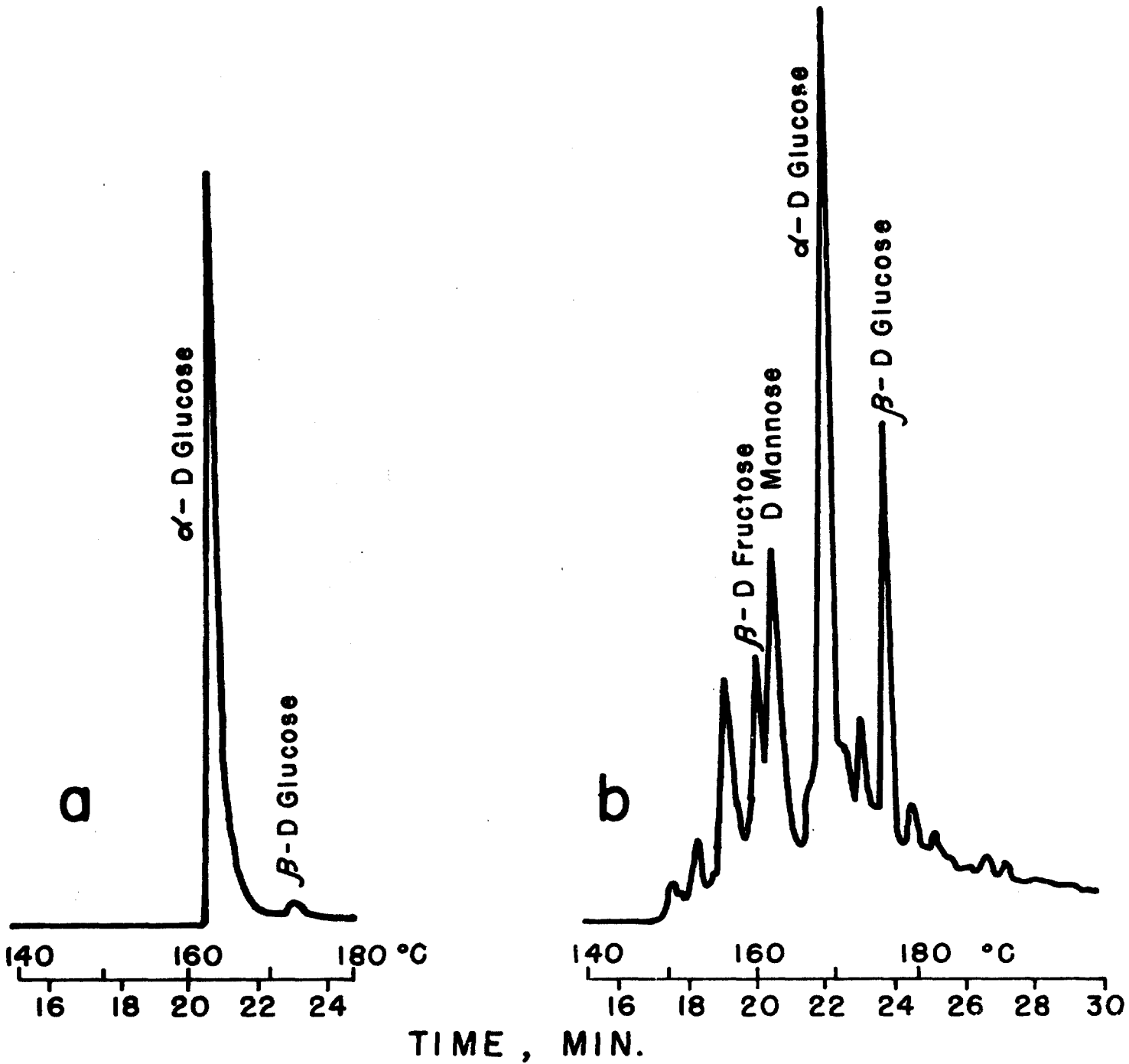


Figure 2



Effect Of Complexing On Glucose Chromatograms

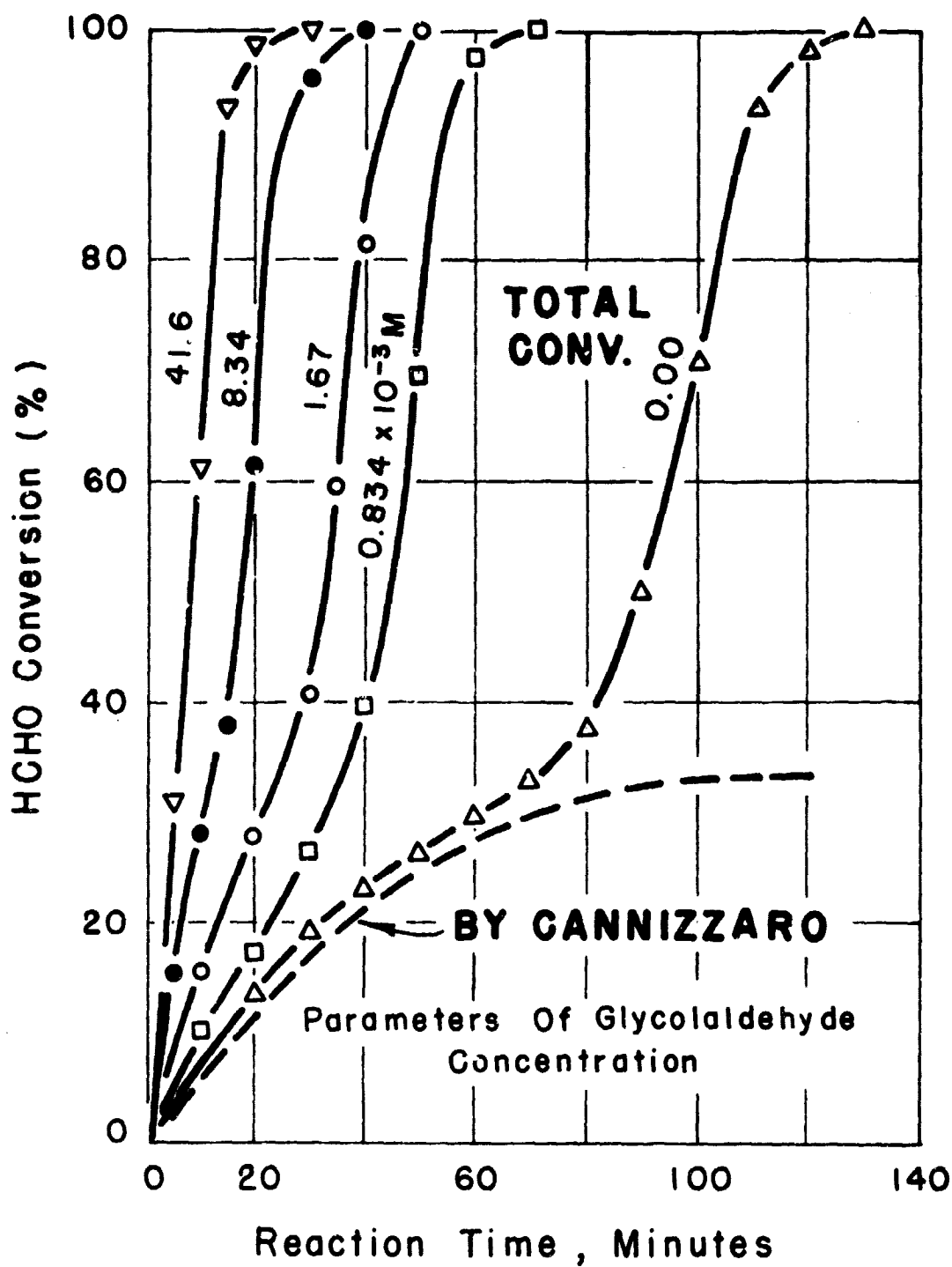


Figure 4

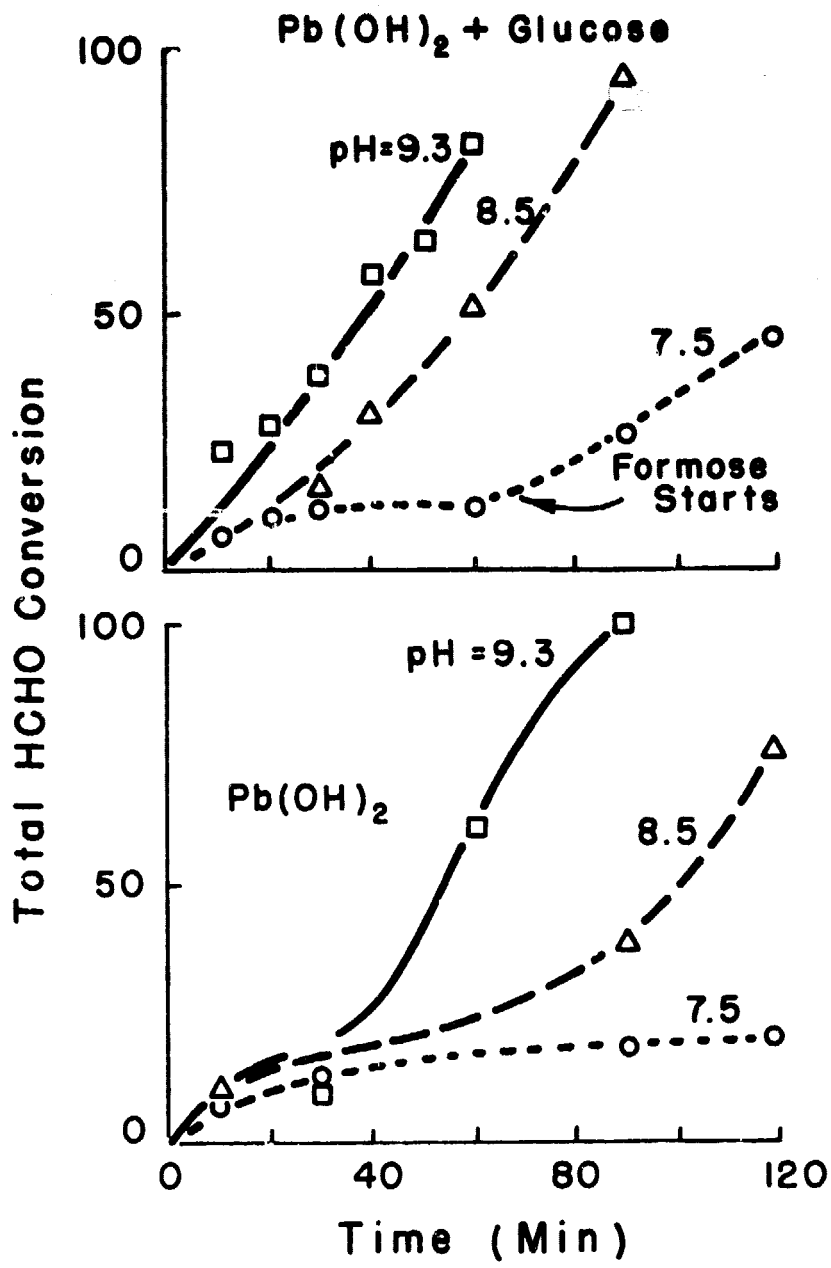


Figure 5

BUFFERING EFFECTS IN FORMOSE

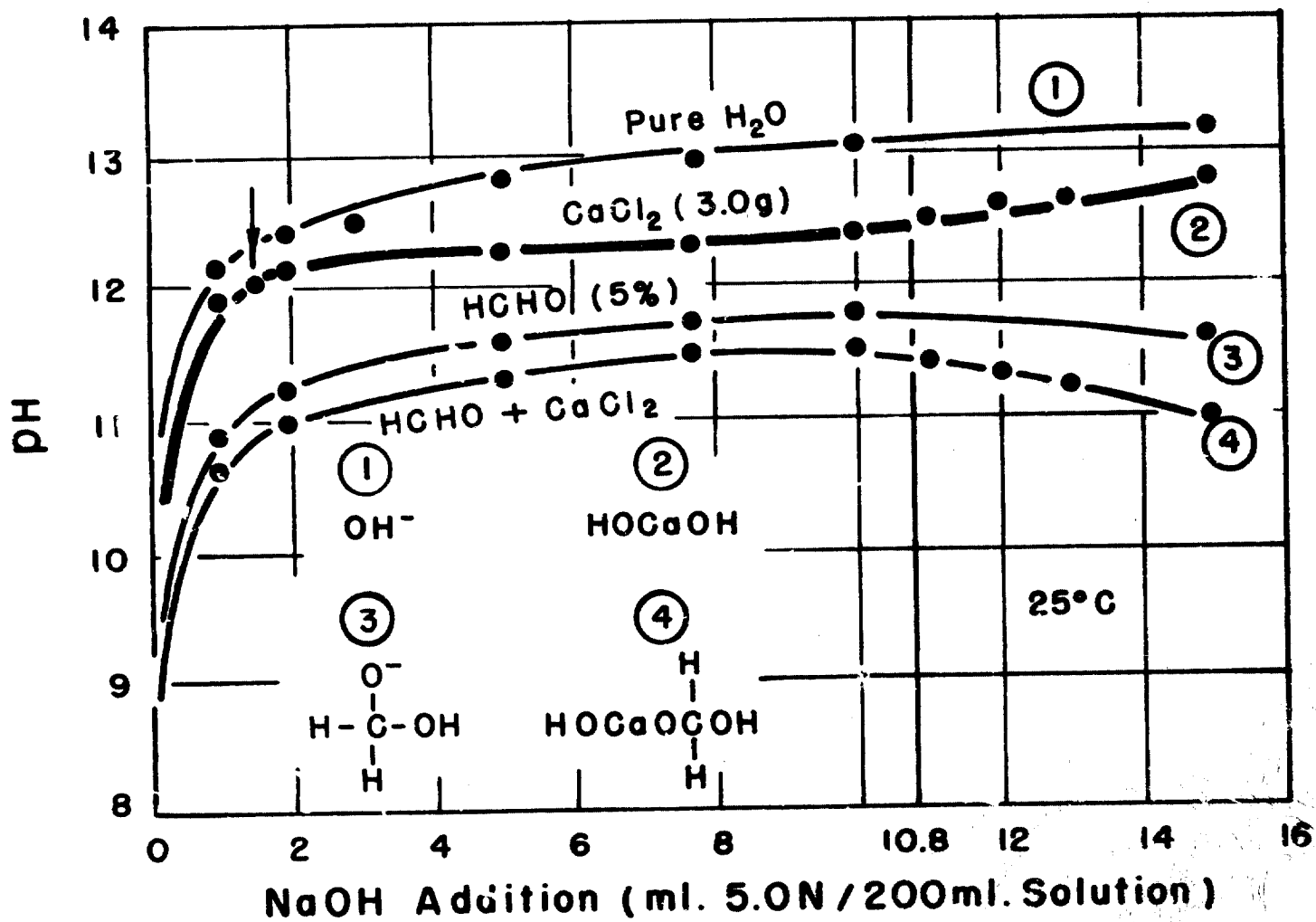


Figure 6

PH SENSITIVITY TO TEMP. AND GLUCOSE

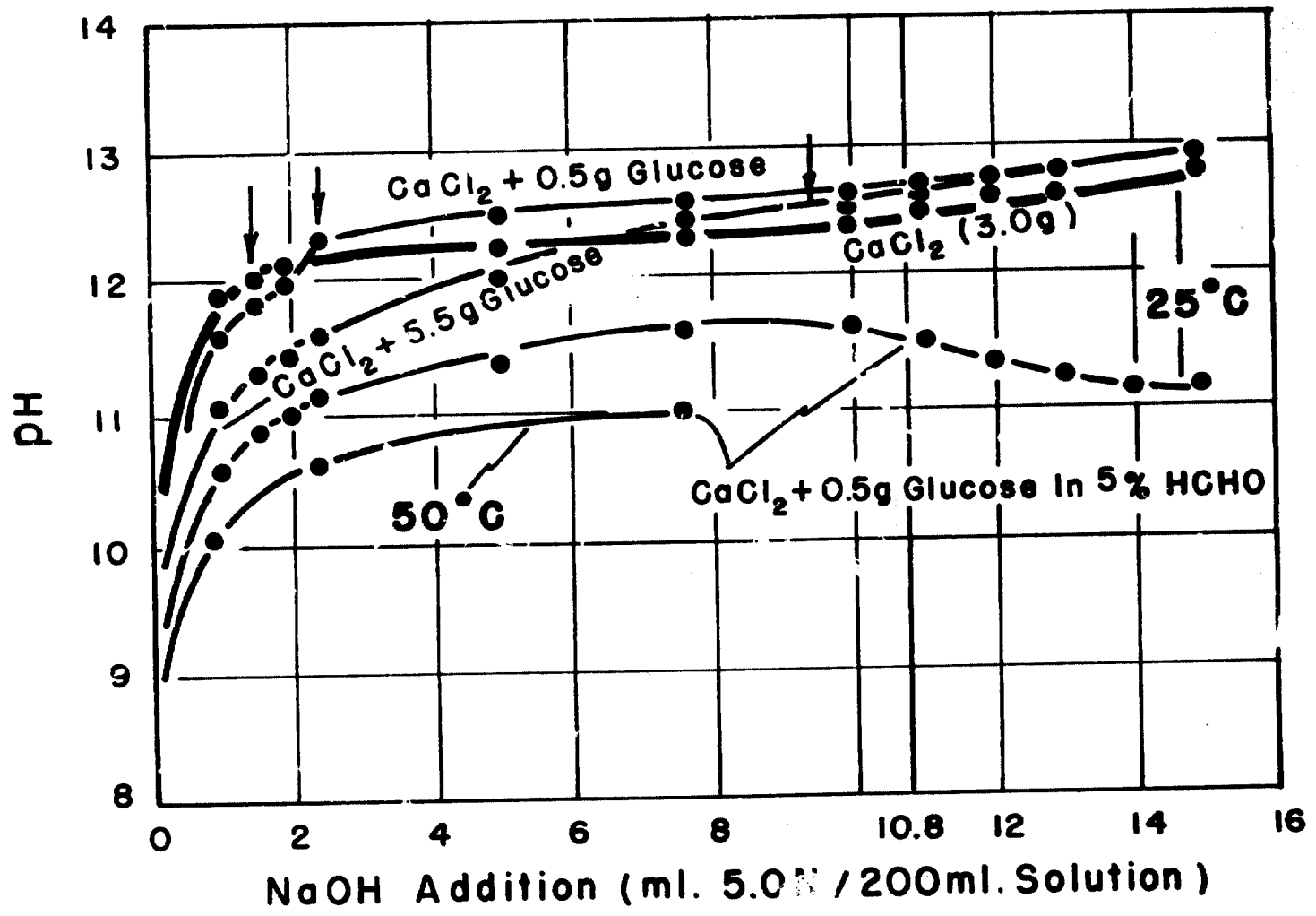
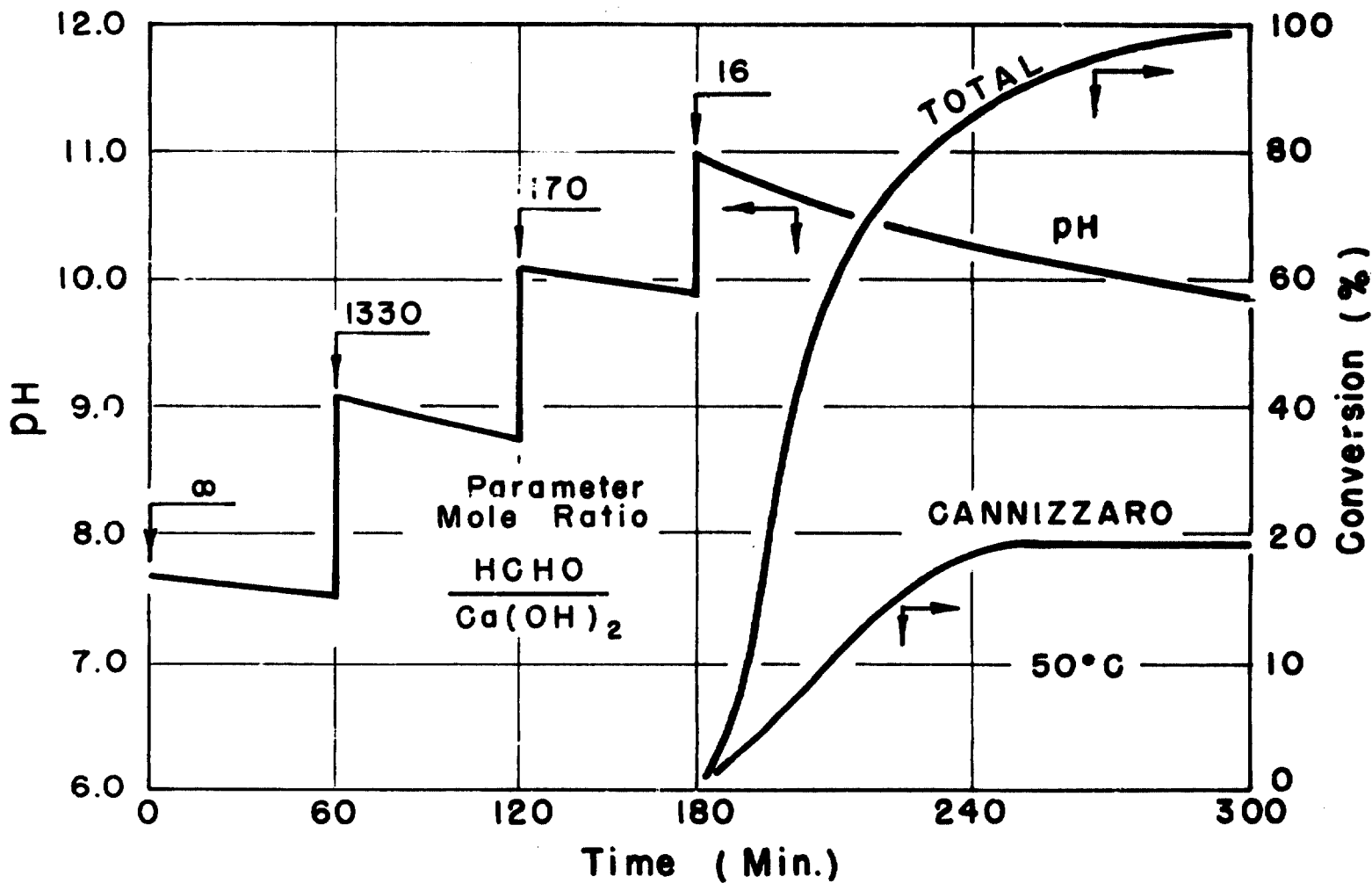


Figure 7

STEPWISE ADDITION OF NaOH TO CaCl_2 - HCHO - GLUCOSE SOLUTION

Figure 8



CATALYST UTILIZATION BY CANNIZZARO TERMINATES REACTION

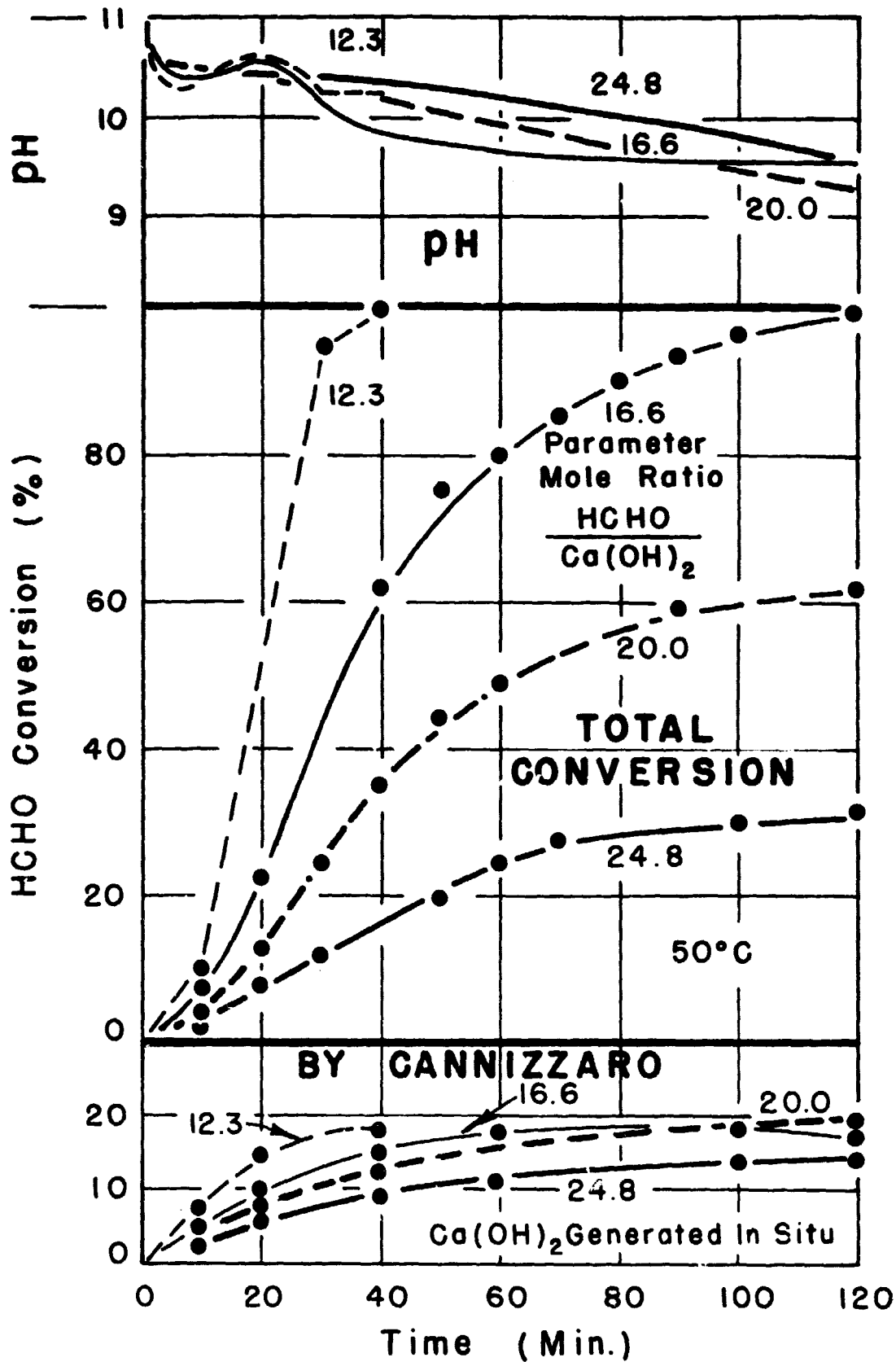


Figure 9

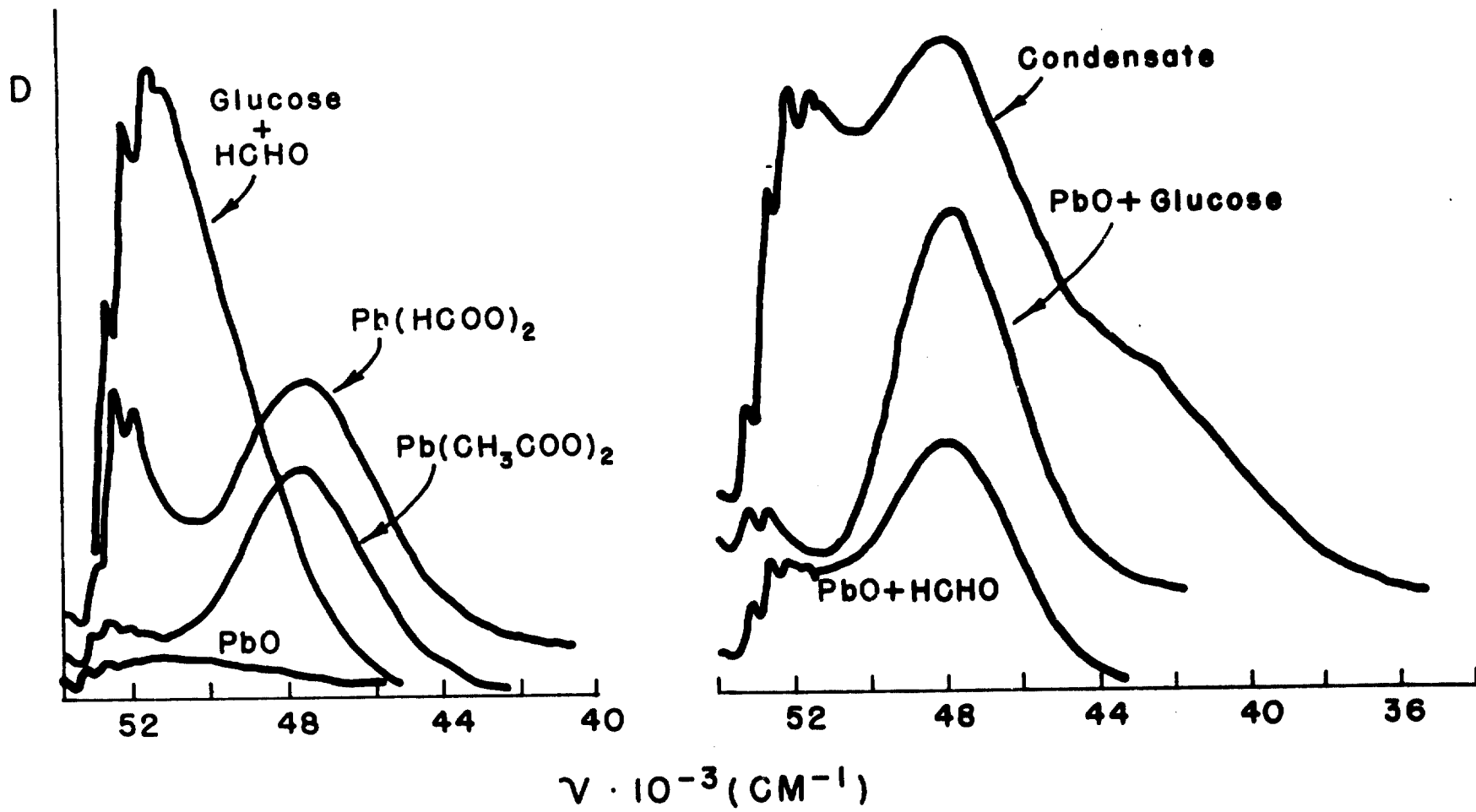


Figure 10