

# Studies on Intermediates Involved in the Syntheses of Pentaerythritol and Related Alcohols. V.\* On the Kinetics of the Base-catalyzed Aldol Condensation Reactions of Intermediate Aldehydes with Formaldehyde

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Rate constants for the base-catalyzed aldol condensation reactions of 3-hydroxypropanal, 2-propenal, 2-hydroxymethyl-2-propenal, 2-methyl-2-propenal, and 2-ethyl-2-propenal, respectively, with formaldehyde have been obtained from kinetic experiments.

In alkaline, dilute aqueous solutions the unsaturated aldehydes mentioned undergo hydration to give equilibrium mixtures with their saturated,  $\alpha$ -hydroxymethyl-substituted counterparts. In these mixtures the unsaturated aldehyde dominates except in the pair 2-propenal  $\rightleftharpoons$  3-hydroxypropanal. The hydration  $\rightleftharpoons$  dehydration reactions are rather rapid. By studying UV-spectrophotometrically the rates of disappearance of the latter three of the unsaturated aldehydes enumerated above, it was therefore thought possible indirectly to determine the rates whereby the corresponding three saturated aldehydes 3-hydroxy-2-hydroxymethylpropanal, 3-hydroxy-2-methylpropanal, and 2-ethyl-3-hydroxypropanal are converted into aldol condensation products with formaldehyde. Experimentally, however, the observed rates of condensation at higher formaldehyde concentrations were found to be faster than the known rates of hydration and this in spite of the activation energies for the condensations being higher. The explanation for this latter observation seems to be that the activation energy for dehydration of methylene glycol with formation of free formaldehyde, the reacting species, is included in the activation energies for the aldol condensations. The experimental findings thus indicate that the rate of condensation of each of the unsaturated aldehydes

may differ from the corresponding rate for its saturated, hydrated counterpart and that equilibrated mixtures of these two aldehydes probably only are formed when the condensation reactions are carried out at relatively low concentrations of formaldehyde.

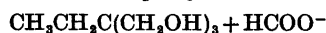
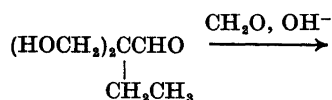
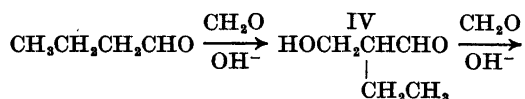
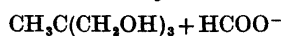
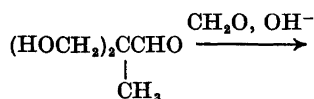
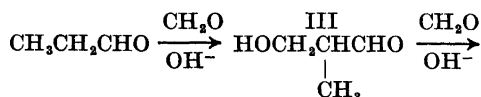
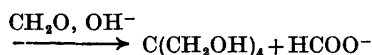
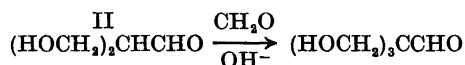
The condensation reactions with formaldehyde of 3-hydroxypropanal and of 2-propenal were followed by means of a gas chromatographic determination method. The sum of the concentrations of 2-propenal and of 3-hydroxypropanal was determined as an apparent concentration of 2-propenal after quantitative dehydration of 3-hydroxypropanal in the injection block. Both aldehydes were found, within experimental errors, to react with formaldehyde at the same rate. Furthermore, at higher formaldehyde concentrations, the reactions of these two aldehydes with formaldehyde, like those of the other aldehydes examined, are faster than their hydration and dehydration reactions.

This work is a sequel to a study<sup>1</sup> dealing with the base-catalyzed aldol condensations of the lowest molecular weight members of the alkanal series with formaldehyde. The hydroxyaldehydes 3-hydroxypropanal (I, monomethylolacetaldehyde, hydracrolein) and 3-hydroxy-2-hydroxymethylpropanal (II, dimethylolacetaldehyde) constitute the first and the second intermediate in the reaction sequence forming pentaerythritol, ultimately, from acetaldehyde and formaldehyde. Likewise, 3-hydroxy-2-methylpropanal (III, monomethylolpropionaldehyde) and 2-ethyl-3-hydroxypropanal (IV, monomethylolbutyaldehyde) are the first intermediates in

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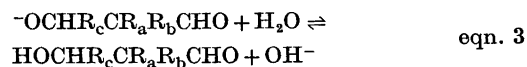
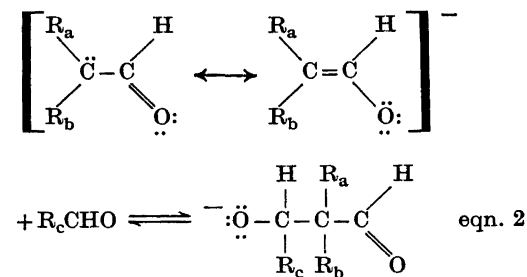
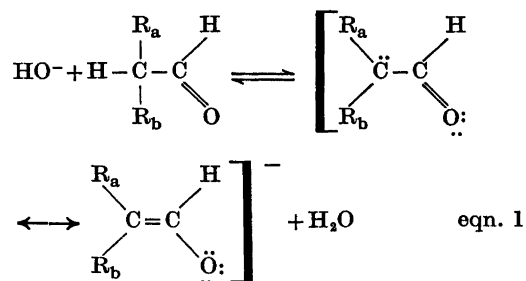
the reaction series leading to trimethylolethane and to trimethylolpropane as products of the corresponding reactions of propionaldehyde and of butyraldehyde with formaldehyde:



One of these reactions, namely the one between I and formaldehyde, has been the subject of a study by Ogata, Kawasaki, and Yokoi,<sup>2</sup> who in the same paper also present data concerning the aldol condensation between acetaldehyde and formaldehyde. Since some aspects of their method seem questionable, independent methods to study these reactions, preferably in a more direct way, have been sought. In the reaction with acetaldehyde its rate of disappearance could be followed by direct gas chromatographic analysis under reaction conditions where its rate of self-condensation was negligible.<sup>1</sup> 3-Hydroxypropanal, on the other hand, is not sufficiently thermally stable to allow direct determination by this method. It has now been found, however, that if a thin glass tube, the walls of which are covered with a mixture of acid sodium and potassium phosphates, is inserted into the heated injection block of the gas chromatograph, 3-hydroxypropanal, present in a neutral-

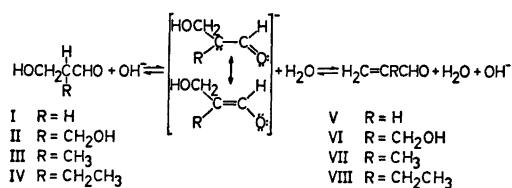
ized reaction mixture, on injection is instantaneously converted into 2-propenal (V, acrolein) and can be quantitatively determined as such. It had to be ascertained, by separate experiments with no formaldehyde present, that the apparent rate of disappearance of V was negligibly small in aqueous solutions of the same nominal alkalinity as used in the experiments with formaldehyde present. Since it is known that in such solutions an equilibrium between I and V, in which I dominates, is rather rapidly established,<sup>3</sup> it follows that the mixture of I with V was quantitatively determined as V. Likewise, in an alkaline solution of the aldehyde I, its concentration, as measured by this method in the form of an apparent concentration of V, was found to be reasonably constant for a few hours in the temperature range investigated (20–40°C). In experimental kinetic runs performed in the presence of formaldehyde by this method, approximately straight pseudo first-order plots of the disappearance of aldehyde I (or V) were always obtained, the plot from a typical run being shown in Fig 1.

The problem to determine the rates of condensation with formaldehyde of the aldehydes II, III, and IV was more complicated, since so far attempts to work out similar gas chromato-



graphic determination methods have been unsuccessful. It could be expected, however, that these reactions follow the commonly accepted scheme for aldol condensations.<sup>4</sup>

Previous work,<sup>3</sup> made possible by the development of methods to obtain the aldehydes I, II, III, and IV,<sup>5</sup> had shown that II, III, and IV, in alkaline aqueous media, are rather rapidly converted into their dehydrated, unsaturated counterparts, 2-hydroxymethyl-2-propenal (VI), 2-methyl-2-propenal (VII, methacrolein), and 2-ethyl-2-propenal (VIII), respectively, until dynamic equilibria are established. In dilute aqueous solutions, at temperatures above 20°, the unsaturated aldehyde constitutes more than 90 mol % of each of these equilibrium mixtures.



eqn. 4

The equilibria presented in eqn. 4 therefore must be taken into consideration when aldol condensations with formaldehyde are investigated kinetically with compounds II, III, and IV.

At lower formaldehyde concentrations the second reaction step, presented in eqn. 2, can be assumed to be rate determining for the aldol condensations. Under these conditions the initial rate of formation of the aldol condensation product is not necessarily the same for the two possible reactants, the saturated and the unsaturated aldehyde, since the steady state concentrations of enolate ions they give rise to may well differ. After a period of time, however, an equilibrium is expected to be attained between the two aldehydes and from then on the same rate of formation of product must be observed, irrespective of which of the two aldehydes was chosen as starting material. A change in observed rate "constant" during the initial stage of the reaction is therefore not unexpected.

At higher formaldehyde concentrations the reaction given in eqn. 1, *i.e.* the formation of enolate ions, is expected to be rate determining. Again the saturated and the unsaturated aldehyde may show different rates of disappearance

depending on their rates of formation of enolate ions. Besides, since the formaldehyde hydrates, methylene glycol and oligomers, buffer alkaline solutions, the maximum rates of condensation for a certain amount of sodium hydroxide added, would be expected to be lower than the rates of enolate ion formation in mixtures of the same nominal alkalinity, but with no formaldehyde present.

Unfortunately, as mentioned, it has so far not been possible to carry out kinetic investigations on the condensation reactions with formaldehyde of compounds II, III, and IV due to lack of analytical methods to follow the reactions. It then seemed of interest at least to determine the corresponding rates of reaction of the unsaturated aldehydes VI, VII, and VIII. In this way it would be possible to get rate constants for the formation of product from the equilibrium mixtures present at low formaldehyde concentrations. Analytically, it should be possible easily to follow the rates of disappearance of the unsaturated aldehydes by means of UV-spectrophotometry in the same way as the dehydration⇌hydration reactions were followed.<sup>3</sup>

In this earlier investigation it was observed that the addition of a small amount of hydroxide ion to a 10<sup>-4</sup> M solution of any of the aldehydes VI, VII, or VIII caused a rapid decrease by less than 10 % of the UV-absorption, further changes occurring only comparatively slowly. By contrast, in similar experiments now performed with formaldehyde present, a rapid decrease in concentration of the unsaturated aldehyde, starting at once and continuing until this aldehyde had completely disappeared, was observed. In each run the rate "constant" was higher in the beginning of the reaction than later on but reached a fairly stable value after part of the unsaturated aldehyde had disappeared. In Fig. 2 this is illustrated with 2-hydroxymethyl-2-propenal (VI) and formaldehyde.

The assumption that the initial rate deviations could be ascribed to a change in temperature during the first few minutes of reaction can be ruled out, since the rate "constant" was always found to decrease, also at temperatures above ambient. The rate change observed for the disappearance of the unsaturated starting material is probably influenced by the rate change for formation of product expected, when

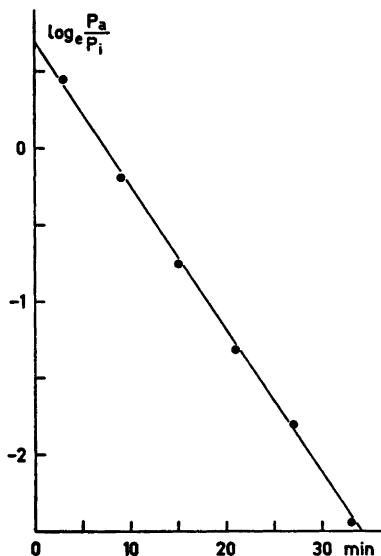


Fig. 1. Pseudo first-order disappearance of acrolein (V) in 0.25 M  $\text{CH}_2\text{O}$ .  $P_a/P_i$ : Peak area of signal from acrolein relative to that of 1-propanol. Nominal concentration of NaOH 0.0030 M. Temperature 20°C.

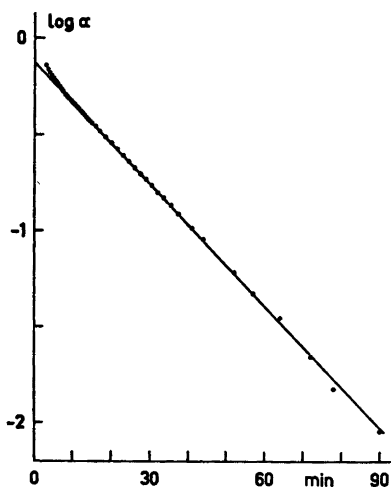
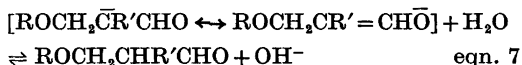
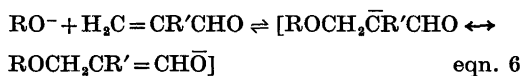
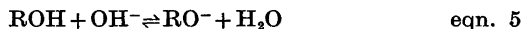


Fig. 2. Condensation of 2-hydroxymethyl-2-propenal (VI) with formaldehyde followed by UV-spectrophotometric measurement of the decreasing absorbance at 213.5 nm. Temperature 20.0° and nominal NaOH-concentration 0.0100 M.

part of this starting material is converted into the saturated aldehyde in their equilibrated mixture, as was discussed earlier. This hydration reaction in itself of course also contributes to the initial faster rate of disappearance of the unsaturated aldehyde but gives no direct contribution to the rate of formation of the aldol condensation product. Moreover, not only water can be reversibly added to the unsaturated aldehyde. Alcohol addition $\rightleftharpoons$ elimination reactions also take place under alkaline conditions.<sup>6</sup> The rates of addition of some alcohols to the unsaturated aldehydes in question have been investigated in a separate study, which will be the subject of a forthcoming paper. These rates have been found to be considerably faster than the rates of addition of water, even in rather dilute aqueous solutions. Under the conditions used in the present work not only methanol, present in a low concentration in the formalin used, but also, and more important, methylene glycol and oligomeric formaldehyde hydrates may add in reversible reactions:



Since the reactions with methanol are known to be fast and the corresponding reactions with methylene glycol presumably are so too, such equilibrium reactions may well be part of the explanation for the initial faster rates observed. The curvatures of the pseudo first-order plots were also found to be more pronounced for experiments carried out at higher formaldehyde concentrations, where the reversible addition of methylene glycol can be expected to be of increasing importance. This state of things made it more difficult to graphically evaluate the rate constants "after stabilization" in these runs. Whereas the values of the rate constants obtained at lower formaldehyde concentrations were within  $\pm 5\%$  of the mean value, reproducibility was only  $\pm 10\%$  at higher formaldehyde concentrations.

If thus the observed rates of disappearance of the unsaturated aldehydes during the initial

period of each run do not represent the rate of any single reaction, once the various equilibria are attained, further changes must be due to the condensation reaction with formaldehyde. It is therefore assumed that the rate constants "after stabilization" represent the true rate of the condensation reaction with formaldehyde of the mixture of unsaturated and saturated aldehyde present at this stage of the reaction. These rate constants, like the ones obtained for the reactions of I and of V, were found to be directly proportional to the amount of NaOH added to the reaction mixtures. Second-order rate constants,  $k'$ , may therefore be calculated referring to the rate expression:

$$-d[A]/dt = k'[A][\text{NaOH}]_{\text{added}}$$

Here [A] denotes the concentration of the aldehyde under study, and  $k'$  times  $[\text{NaOH}]_{\text{added}}$  is equal to  $k_{\text{obs}}$  for the pseudo first-order disappearance of A. The constants,  $k'$ , were found to depend on the formaldehyde concentration in a manner somewhat similar to what was found for acetaldehyde and its homologs in the study referred to previously<sup>1</sup> (Fig. 3 and Table 1).

With the normal aldol condensation reaction mechanism operating one expects reaction step 1 (eqn. 1), that is the rate of formation of enolate ions, to become rate determining at higher formaldehyde concentrations. This simple picture is, however, partly obscured due to the

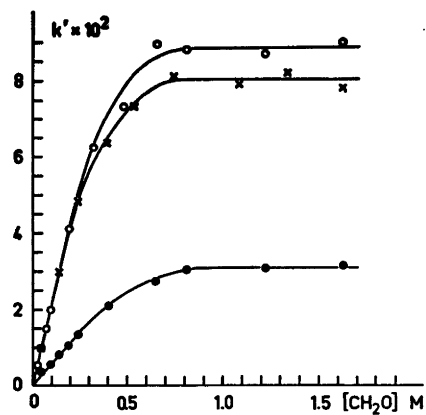


Fig. 3. Pseudo first-order rate constants for the condensation reactions of 2-hydroxymethyl-2-propenal (VI, ×), 2-methyl-2-propenal (VII, O), and 2-ethyl-2-propenal (VIII, ●), respectively, with formaldehyde.

Table 1. Pseudo second-order rate constants,  $k'$   $\text{M}^{-1} \text{sec}^{-1}$ , for the disappearance of 3-hydroxypropenal (I) at different temperatures and concentrations of formaldehyde.

$T^\circ\text{C}$	$[\text{CH}_2\text{O}]_{\text{tot}}, \text{M}$	$k'$
20	0.10	0.43
	0.25	0.52
	0.50	0.46
	0.75	0.39
	1.00	0.33
	1.50	0.27
	2.00	0.23
	3.00	0.17
30	4.00	0.14
	0.50	1.27
40	0.50	2.90

behaviour of formaldehyde in alkaline, aqueous solutions. Firstly, the concentration of the reacting species, free, monomeric formaldehyde, is not linearly increasing with the total concentration of formaldehyde due to extensive formation of mono- and oligomeric hydrates. Secondly, because these hydrates are weakly acidic they buffer alkaline solutions increasingly with increasing concentration of formaldehyde. Of course it is still possible with the help of a pH-meter to adjust the hydroxide ion activity to the same value at the different formaldehyde concentrations. This would still leave open the question, however, to what extent the different amounts of anions of methylene glycol and oligomers present catalyze the condensation reaction. Furthermore, from an industrial viewpoint the interesting question is which rate is to be expected with a certain amount of alkali added, an amount determinable by titration. Anyhow, both the factors mentioned contribute to cause a less than proportional increase in rate constant for a certain increase in formaldehyde concentration. The levelling off of the values of the rate constants at concentrations of formaldehyde higher than about 1 M observed for the aldehydes VI, VII, and VIII does therefore not necessarily imply that the rates of enolate ion formation are becoming rate determining at this particular concentration.

In order to examine this, experiments have also been performed using the corresponding saturated aldehydes as starting materials for the condensations with formaldehyde. In these runs

too the concentration of the unsaturated aldehyde in the equilibrium couple was followed by means of UV-spectrophotometry. The UV-absorptions of the unsaturated aldehydes were found at first to increase to a maximum and then to decrease to zero. This was the case both at lower and, more remarkably, also at higher formaldehyde concentrations in the region where the rates of the condensation reactions of the unsaturated aldehydes had been found to be unaffected by further increase of the formaldehyde concentration. The maximum concentration reached by the unsaturated aldehyde was highest with II as the starting material at equal formaldehyde concentrations. It was also higher when this concentration was low. This seems reasonable since the difference in rate between the dehydration of the saturated aldehyde and the condensation reaction of the unsaturated is greatest for the couple II and VI and also must be greater at lower formaldehyde concentrations. The very fact that unsaturated aldehyde is formed also at the higher of the formaldehyde concentrations used shows, anyhow, that not all enolate ions formed condense with formaldehyde even at these concentration levels. For this reason the rates of enolate ion formation cannot be completely rate determining even under these conditions.

The aldehydes I and V have a very pronounced rate maximum in about 0.25 M formaldehyde solutions, the rate constant having a four times smaller value for the reaction in 4.0 M solutions. The dehydration $\rightleftharpoons$ hydration reactions cannot, as discussed earlier, give contributions to the experimentally observed rates of disappearance in these cases, since the analytical method used did not distinguish between I and V. The same is probably true for the alcohol addition  $\rightleftharpoons$  elimination reactions as well,  $\beta$ -alkoxyaldehydes being split when introduced into the injection block. Experimentally I and V were found to react with the same rate under the different concentration and temperature conditions used and this also helps to explain why changes in rate constant during a single run were not observed with these aldehydes. Their equality of rates is probably incidental since there seems to be no reason why this should be so for the unsaturated and saturated aldehyde in any given equilibrium couple, except under conditions where equilibrium

already is attained.

The Arrhenius activation energies calculated from the experimental data are 17.3, 13.1, 13.1, and 12.6 kcal mol<sup>-1</sup> for I (and V), VI, VII, and VIII, respectively. The experimental errors are estimated to be in the order of  $\pm 0.4$  kcal mol<sup>-1</sup> for I (and V) and  $\pm 0.8$  kcal mol<sup>-1</sup> for the others.

Since both the aldol condensation reactions and the hydration  $\rightleftharpoons$  dehydration reactions are believed to proceed *via* enolate ions it is of obvious interest to compare both rate constants and activation energies obtained.<sup>8</sup> It is then seen, that the condensation reactions have both the highest rates and, remarkably, the highest activation energies. At first sight this seems hard to reconcile with the assumption that all these reactions involve enolate ions. One must bear in mind, however, that only a very small part of the formaldehyde is present in reactive form, monomeric and unhydrated. The activation energies calculated for the condensation reactions thus reflect not only the activation energy for formation of the transition state from a formaldehyde molecule and the enolate ion. At least at lower formaldehyde concentrations, where the second reaction step (eqn. 2) is rate determining, they also contain the enthalpy and entropy changes for dehydration of methylene glycol, 5.7 kcal mol<sup>-1</sup> and 5.4 e.u. according to Gruen and McTigue.<sup>7</sup> Thus, for all the aldehydes V to VIII the activation energies for the actual condensation reaction with formaldehyde are lower or about equal to the activation energies for the corresponding hydration reactions. For aldehyde II it is lower even without considering the influence due to dehydration of methylene glycol.

Ogata *et al.* in their paper report an activation energy of 22.9 kcal mol<sup>-1</sup> for the aldol condensation of I with formaldehyde and the value of 22.1 kcal mol<sup>-1</sup> for the corresponding reaction of acetaldehyde. As is evident from the spread in their presented primary rate data there is a considerable uncertainty inherent in their method. Besides, the temperature range they have investigated is rather narrow. Their values thus seem somewhat doubtful and they also seem high for normal aldol condensations. The rate constants one can calculate from their reported data for runs at 20° are very scattered. For acetaldehyde they are higher by factors between 1.5 to 3.5 but for I they are seven to ten times

smaller than the values reported in this series. It is believed, however, that the methods used in this work allow more accurate determinations with less sources of errors.

When comparing the rate constants and activation energies obtained for the aldehydes examined in this and the preceding study,<sup>1</sup> some notable differences can be observed. 3-Hydroxypropanal and 2-propenal are by far the most reactive ones of all the aldehydes investigated and react at 20° more than ten times faster than acetaldehyde, their precursor in the reaction series leading to pentaerythritol. 2-Methyl-2-propenal reacts in 1 M formaldehyde solutions at 20° with about the same rate as its precursor, propionaldehyde, but at formaldehyde concentrations lower than about 0.5 M this latter aldehyde reacts appreciably faster. 2-Hydroxymethyl-2-propenal and 2-ethyl-2-propenal, finally, react noticeably slower than their respective precursors, 3-hydroxypropanal and butyraldehyde, at all formaldehyde concentrations. The lowest molecular weight compounds among the alkanals and 3-hydroxypropanals, that is acetaldehyde and 3-hydroxypropanal, have distinctly higher activation energies than the other aldehydes. There does not seem to be any single factor causing this order of reactivities. The explanation must rather be sought in a combination of sterical and inductive effects of the various substituents. It could be that a 3-hydroxy group also has a neighbouring group effect in hydrogen bonding the formaldehyde molecule undergoing condensation.

## EXPERIMENTAL

**Materials.** The formaldehyde used was of the LM-42 grade of Perstorp AB. This grade is an aqueous solution containing  $42.0 \pm 0.5\%$  of formaldehyde, 0.3 to 0.5 % of methanol, and 0.015 to 0.020 % of acid (calculated as formic acid; all percentages by weight). Acrolein and methacrolein were commercial practical grade chemicals. 2-Ethyl-2-propenal was prepared by the method of Marvel *et al.*<sup>8</sup> These three aldehydes were redistilled each day before use. 2-Hydroxymethyl-2-propenal and 3-hydroxypropanal were prepared in the form of their acetals, and  $10^{-3}$  M stock solutions of the free aldehydes were prepared by the method described in an earlier paper<sup>3</sup> and used with the same precautions. 1-Propanol, used as internal standard in the gas chromatographic determinations, was

of Fischer reagent grade. Sodium hydroxide stock solutions were freshly prepared each week from Merck Titrisol ampoules. These and all other aqueous solutions were made up with boiled, CO<sub>2</sub>-free, distilled water.

The following stock solutions were prepared: of formaldehyde 1.00 and 10.0 M for use in the runs with I and V, 0.5 and 8.2 M for use in the runs with VII and VIII, and 0.5 and 10.9 M for use in the runs with VI; of I and V about  $10^{-2}$  M and of VI, VII, and VIII about  $10^{-3}$  M stock solutions were used; of NaOH 0.100 M and of 1-propanol about 0.08 % by weight solutions. The formaldehyde stock solutions were neutralized to pH 7.0.

**Apparatus.** The reaction mixtures were prepared in volumetric flasks and kept in a thermostatted bath controllable to within  $\pm 0.05^\circ\text{C}$ . Vapour phase chromatography was performed using a Varian 1740 gas chromatograph equipped with FI-detector and connected with an electronic integrator of type Varian 480. The UV-measurements were made using a Beckman DU instrument with cell compartment thermostatted by circulating water from the water bath.

**General procedure.** In the gas chromatographic runs this was identical with the one reported in the study on acetaldehyde and its homologs<sup>1</sup> and in the UV-spectrophotometric runs with the one used in the study on the hydration  $\rightleftharpoons$  dehydration reactions of some 2-propenals and their saturated counterparts,<sup>3</sup> with the exception that formaldehyde was added to the mixtures used in the present study.

**Gas chromatographic runs.** At the start of the experimental runs, the reaction mixtures were about 0.001 M in I (or V) and about 0.004 % in 1-propanol, which was used as internal standard. The NaOH-concentration ranged from 0.001 to 0.005 M and the formaldehyde concentration from 0.10 to 4.0 M. The injection block was glass lined by insertion of a thin glass tube of commercial type to be used for this purpose. The inner wall of this tube was covered with a thin layer of a mixture of acid sodium-potassium phosphates. A syrupy aqueous solution of phosphoric acid and mono- and disodium and potassium phosphates had been prepared and was repeatedly deposited on the inner wall, the tube being dried in an oven after each treatment, until the wall was completely covered. The column was of stainless steel, 2 m  $\times$  0.22 cm. Stationary phase Chromosorb 101 80/100 mesh. Injection temperature 180°, column temperature 140°, detector temperature 150°. Carrier gas 30 ml per minute of N<sub>2</sub>, attenuation  $2 \times 10^{-11}$  on the chromatograph and 1 on the integrator. Injected volume 1.0  $\mu\text{l}$ .

**UV-spectrophotometric runs.** At the start of the experimental runs the reaction mixtures were about  $10^{-4}$  M in VI, VII, or VIII, respectively. The concentration of formaldehyde was varied from 0.05 to 1.64 M. The NaOH-con-

centration was varied from 0.005 to 0.040 M in the runs with VI, from 0.005 to 0.030 M in the runs with VII, and from 0.010 to 0.080 M in the runs with VIII. A 1.000 cm quartz cell was used.

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