

Studies on Intermediates Involved in the Syntheses of Pentaerythritol and Related Alcohols. IV* The Kinetics of Base-catalyzed Addition of Water to Some 2-Propenals

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The formation of ethers in the syntheses of the industrially important polyalcohols pentaerythritol, trimethylolethane, and trimethylolpropane is believed to involve 2-propenals as intermediates. These aldehydes can be assumed to be formed by reversible dehydration of the corresponding α -hydroxymethyl-substituted aldehydes, present as intermediates in the reaction mixtures. In order to examine the probability of this reaction route, the rates and equilibria of these dehydration-hydration reactions have been studied. The reactions were found to be very efficiently catalyzed by hydroxide ion.

Two alternative mechanisms have been proposed in order to explain the formation of by-products containing ether linkages in the synthesis of pentaerythritol.^{1,2} In a previous study,³ one of these mechanisms² was found to be highly improbable. The other mechanism, originally proposed by Wawzonek and Rees,¹ involves the formation of α,β -unsaturated aldehydes *via* base-catalyzed dehydration of α -hydroxymethyl-substituted aldehydes occurring as reaction intermediates. Base-catalyzed addition of alcohols to these unsaturated aldehydes then results in the formation of α -alkoxymethyl-substituted aldehydes, which contain the ether linkage present in the ultimate products of these side-reactions.

Of the α -hydroxymethyl-substituted aldehydes occurring as intermediates in the synthesis of pentaerythritol from acetaldehyde and formaldehyde, both 3-hydroxypropanal (I, hydracrolein, monomethylolacetaldehyde) and 3-hydroxy-2-hydroxymethylpropanal (III, dimethylolacetaldehyde) can undergo dehydration, leading to propenal (II, acrolein) and 2-hydroxymethylpropenal (IV, α -methylolacrolein), respectively. In the analogous syntheses of trimethylolethane from propionaldehyde and formaldehyde and of trimethylol-

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propane from butyraldehyde and formaldehyde, the corresponding monohydroxymethyl-substituted aldehydes 3-hydroxy-2-methylpropanal (V, monomethylolpropionaldehyde) and 2-ethyl-3-hydroxy-propanal (VII, monomethylolbutyraldehyde) similarly can undergo dehydration to give 2-methylpropenal (VI, methacrolein) and 2-ethylpropenal (VIII), respectively. Since synthetic routes to the aldehydes III, IV, V, and VII have now been worked out,⁴ it has become possible to study all these equilibrium reactions.

It is well known, that II, in the presence of acids but also in neutral aqueous solution, reaches a state of equilibrium with I.⁵⁻⁷ The kinetics of the acid-catalyzed hydration of II has been studied by Pressman and Lucas⁶ and by Hall and Stern,⁷ but so far the base-catalyzed reaction, though more or less recognized,^{1,8} has received considerably less attention. This is probably due to the fact, that the base-catalyzed hydration in more concentrated solutions is accompanied by several side-reactions and therefore lacks preparative interest.

It has now been found, however, that the base-catalyzed hydration of II conveniently can be followed by means of UV-spectrophotometric measurements in 10^{-3} to 10^{-4} M solutions of II. By the same method, it is also possible to follow the dehydration reactions of III, V, and VII, which also lead to equilibria between saturated and unsaturated aldehydes.

The overall reactions follow eqn. (1):



As previously has been shown for the acid-catalyzed hydration of II, the equilibrium in this case lies well to the right at room temperature with about 90 % of the aldehyde mixture present as I.^{6,7} Preliminary experiments with the aldehydes IV, VI, and VIII showed, however, that in these cases the equilibria lie equally well to the left. In order to be able to determine the rate constants with any precision, one therefore has to follow these reactions from the right to the left.

When the hydration of II is followed in aqueous solution, where water is present in large excess and with hydroxide ion acting as catalyst, the reaction follows the rate expression:

$$-\frac{d(a(1-x))}{dt} = k_1' a (1-x) - k_{-1}' a x \quad (2)$$

where the initial concentration of II is denoted a and the concentration at time t is $a(1-x)$. The rate constants k_1' and k_{-1}' are pseudo first-order constants for the forward and reversed reactions, respectively.

After substitution of ε for x_∞ and of k' for $(k_1' + k_{-1}')$ the following integrated rate expression is obtained:

$$\ln \frac{\varepsilon}{\varepsilon - x} = k't = \ln \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty} \quad (3)$$

The latter equality is obtained when UV-absorbance units are substituted for the concentration units used previously.

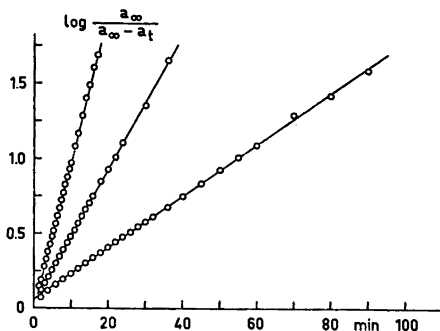


Fig. 1. Dehydration of dimethylolacetaldehyde in water, catalyzed by 0.00100 M OH⁻ at 15.0, 25.0 and 35.0°C, respectively.

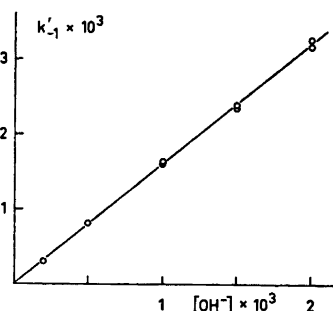


Fig. 2. The pseudo first order rate constant for the dehydration of dimethylolacetaldehyde as a function of the catalyst concentration.

In an analogous manner eqn. (4) is obtained for the case where the dehydration of the saturated aldehyde is followed by measuring the increasing UV-absorption of the product:

$$\ln \frac{\alpha_{\infty}}{\alpha_{\infty} - \alpha_t} = k' t \quad (4)$$

As the example given in Fig. 1 shows, the reactions followed these rate expressions with good precision at least to between four and five half-lives, that is to about 95 % completion. The constants k' for the different reactions were found, as expected, to be linearly dependent on the catalyst concentration (see Fig. 2) and it is therefore possible to define second order rate constants:

$$k' = k[\text{OH}^-] = (k_1 + k_{-1})[\text{OH}^-] \quad (5)$$

Depending on the mechanism of the reactions either k_1 or k_{-1} must be a function of the concentration of water since:

$$K = \frac{[\text{HOCH}_2\text{CHRCHO}]}{[\text{H}_2\text{C}=\text{CRCHO}][\text{H}_2\text{O}]} = \frac{1}{[\text{H}_2\text{O}]} K_{\text{exp}} = \frac{1}{[\text{H}_2\text{O}]} \frac{k_1}{k_{-1}} \quad (6)$$

The equilibrium constants for the reactions could not be obtained directly from the kinetic experiments except for the case of hydration of II, since this is the only case where the relative concentrations of the saturated and the unsaturated aldehyde can be obtained directly from the UV-measurements. In the other cases an accurate knowledge of the absorptivity of the unsaturated aldehydes coupled with an equally accurate knowledge of the initial concentrations of the saturated aldehydes would, in principle, allow calculation of the equilibrium constants from the kinetic experiments. In practice, however, the uncertainties in the experimentally determined absorptivities are of the same order of magnitude as the fraction of saturated aldehyde at equilibrium. In these cases, therefore, the equilibrium constants had to be determined from

separate experiments, where the hydration reactions of the unsaturated aldehydes were followed.

The rate and equilibrium constants, calculated from the experimental data as defined by the equations given, are shown in Table 1.

Table 1. Rate constants and activation energies.

Reactant	Temp °C	k l mol sec	k_1 l mol sec	E_A hydra- tion kcal/mol	k_{-1} l mol sec	E_A dehydra- tion kcal/mol	K_{exp}	% con- version at eq.
II	15.00	0.153	0.143	12.7	0.0101	18.5	14.2	93.4
	25.00	0.335	0.305		0.0301		10.1	91.0
	35.00	0.688	0.607		0.082		7.39	88.1
III	15.00	0.689	0.059	11.2	0.630	15.8	0.094	91.4
	25.00	1.71	0.114		1.60		0.072	93.3
	35.00	3.97	0.212		3.76		0.056	94.7
V	20.00	0.172	0.0089	10.3	0.163	16.2	0.054	94.8
	30.00	0.424	0.016		0.408		0.039	96.3
	40.00	0.986	0.027		0.959		0.029	97.2
VII	20.00	0.171	0.0045	7.2	0.167	14.3	0.027	97.4
	30.00	0.382	0.0068		0.375		0.018	98.2
	40.00	0.808	0.0099		0.798		0.012	98.8

At the high conversions experimentally observed, it has to be noted, that even small errors in the absorbance measurements and thereby the concentration determinations lead to relatively large errors in the determinations of K_{exp} and consequently also in the values given for k_{-1} in the case of the equilibrium between I and II and for k_1 in the other cases. The same is true for the values given for the corresponding activation energies. The rate constants given for the reverse reactions, on the other hand, are only to a minor degree affected by these experimental errors, and the values of the corresponding activation energies are therefore much more reliable.

Values for the changes in free energy, enthalpy, and entropy associated with the hydration reactions at 25.0°C have been calculated from the data presented in Table 1 and are given in Table 2. As seen, the negative enthalpy changes associated with the formation of saturated systems are balanced by the loss of entropy connected with the formation of a larger molecule from two smaller.

In the case of the equilibrium between I and II the values of K_{exp} are in excellent agreement with the values given by Pressman and Lucas.⁶ The value of ΔH°_{298} , calculated from a plot of $\log K_{\text{exp}}$ against $1/T$, therefore is the same, -5.8 kcal/mol, as that given by them. The rate constants for the base-catalyzed reactions, however, differ by several orders of magnitude from the rate

Table 2. Changes in free energy, enthalpy and entropy for the hydration reactions at 25.0°C.

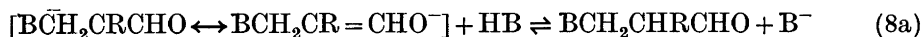
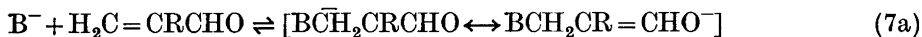
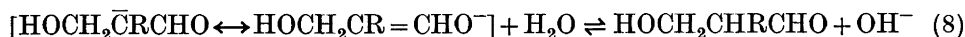
Reactant	ΔF_{298}° kcal/mol	ΔH_{298}° kcal/mol	ΔS_{298}° cal/°C, mol
II	+1.0	-5.8	-23
IV	+3.9	-4.6	-29
VI	+4.2	-5.9	-34
VIII	+4.6	-7.1	-39

constants for the acid-catalyzed reactions. Thus, at 25.0°, hydroxide ion is about 5000 times as effective a catalyst as hydronium ion.

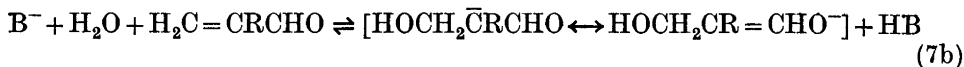
When comparing the rate constants for the different aldehydes, it is seen, that at 25.0° II is hydrated about twice as fast as IV, whereas III is dehydrated fifty times as fast as I. The two aldehydes V and VII are dehydrated about eight times as fast as I, while of the corresponding unsaturated aldehydes II is hydrated more than twenty times as fast as VI and almost fifty times as fast as VIII. The effectiveness of the α -substituents, as compared with hydrogen, in promoting the dehydration reaction thus is in the order $\text{CH}_2\text{OH} > \text{CH}_3 \approx \text{CH}_2\text{CH}_3$, whereas they retard the hydration reactions of the 2-propenals in the order $\text{CH}_2\text{CH}_3 > \text{CH}_3 > \text{CH}_2\text{OH}$.

The Arrhenius activation energies for the forward and reverse reactions of the different aldehydes are roughly comparable and so are the values for the changes in the other thermodynamic functions. The small differences in these values, however, cause relatively large differences in the equilibria between I and II on one hand and between the other aldehydes on the other hand (Tables 1 and 2).

The hydration of II was studied also at increased ionic strength of the medium. By means of added sodium chloride experimental runs were made at the ionic strengths 0.050 N, 0.100 N, and 0.250 N, respectively, but neither the rates nor the equilibria were significantly altered within the temperature range 15.0° to 35.0°. The use of phosphate buffer solutions influenced the observed rates, but since the mechanism of the hydration reaction involves nucleophilic attack by hydroxide ion on the β -carbon atom (eqns. 7 and 8), "direct" catalysis by other bases actually should give different products (eqns. 7a and 8a):



General base catalysis is therefore only possible in a concerted "indirect" reaction involving base equilibration. The question whether such general base catalysis (eqns. 7b and 8b) occurs cannot be answered at present.



EXPERIMENTAL

The acrolein and methacrolein were commercial pract. grade chemicals and were freshly distilled each day before use. 2-Ethylpropenal was prepared by the method of Marvel *et al.*⁹ and was also redistilled before use. The other aldehydes used, 2-hydroxy-methylpropenal, 3-hydroxy-2-hydroxymethylpropanal, 3-hydroxy-2-methylpropanal, and 2-ethyl-3-hydroxypropanal, were synthesized in the form of their diethyl acetals.⁴ The free aldehydes were prepared when needed (see General procedure) and the stock solutions prepared were never used for more than five days although they were found to be reasonably stable for longer periods. At room temperature a slow approach to the hydration-dehydration equilibrium was found to occur in such solutions, but the rates were several orders of magnitude lower than for the base-catalyzed reactions. Sodium hydroxide stock solutions were freshly prepared each week from Merck Titrisol ampoules. These and all other aqueous solutions were made up with boiled carbon dioxide-free distilled water. The UV-measurements were made using a Beckman DU instrument with the cell compartment thermostatted by circulating water from a thermostatted bath of type Lauda. The temperatures in the cuvettes were checked in separate experiments to be within $\pm 0.05^\circ$ from the temperature wanted.

General procedure. The following aqueous stock solutions were prepared: Of 2-propenal (II) 10^{-2} and 10^{-3} M solutions, of the aldehydes III to VIII 10^{-3} M, and of sodium hydroxide 0.100 and 0.010 M solutions.

The stock solutions of the aldehydes III, IV, V, and VII were prepared in the following way. About 0.25 mmol of their respective diethyl acetal was weighed on an analytical balance and then dissolved in about 15 ml of water. This solution was then passed through an H^+ -saturated, carefully washed ion exchange column, 80×1 cm, filled with analytical grade Amberlite IR 120 resin. With water as eluent 250 ml of eluate was collected in a volumetric flask. The whole operation was made under exclusion of carbon dioxide from the air.

In the kinetic runs with the aldehydes II, III, V, and VII, respectively, 10 ml of the stock solution was added to 70 to 80 ml of distilled water in a 100 ml volumetric flask, which was then immersed in a thermostatted bath for adjustment to the proper temperature. After about half an hour the reactions were started by means of addition of the proper amount of catalyst and the solutions were diluted to the mark and thoroughly shaken. Then a quartz cell with 1.000 cm optical path length and equipped with a teflon plug was filled with the reaction solution and inserted in the cell compartment. A cell filled with an equally concentrated catalyst solution was used as reference. With the more concentrated solution of II a 0.100 cm cell was used instead. The first absorbance reading could normally be taken about 90 sec after the start of the reaction as measured after addition of about half of the amount of sodium hydroxide. When the kinetic runs were performed more than 5° from ambient temperature the rates during the first 5 min deviated slightly from the rates during the remainder of the runs due to temperature deviations in the solutions caused by the mixing and filling procedures.

The determinations of the equilibrium constants with the help of the aldehydes IV, VI, and VIII, respectively, were performed in an analogous way, except that only 4 to 5 ml of the stock solutions were used in order to keep the absorbance between 0.3 to 0.5 where the accuracy is best. In these cases the starting value for the absorbance was obtained by means of graphical extrapolation of the expression $\log(\alpha_t - \alpha_\infty)$ as plotted against time.

The absorbance measurements were made at 210 nm for II, at 213.5 nm for IV, at 218.5 nm for VI, and at 220 nm for VIII. Even if the absorbance of II was found to have its maximum nearer 208 nm the measurements thus were made at 210 nm, since the background absorbance of the alkaline solutions rises rapidly below 210 nm and therefore

necessitates excessively wide slits at lower wavelengths. This could partly be overcome in the experiments with the more concentrated solution of II where the shorter path length was used. The observed rates, however, were the same within experimental error.

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