

KINETICS OF THE REACTION OF SODIUM FORMALDEHYDESULPHOXYLATE WITH UNSATURATED ALDEHYDES

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Distribution equilibria of propenal, 2-methylpropenal and 2-ethylpropenal between the aqueous phase and toluene have been measured. Kinetic characteristics of the reaction of sodium formaldehydesulphoxylate with the above unsaturated aldehydes in water emulsion have been determined. Activation energies of the reaction in the aqueous phase for the temperature range from 0 to 40°C are identical for all three aldehydes and equal to 13.5 kcal/mol. The frequency factor of the reaction decreases with increasing molecular weight of the aldehyde. The reaction is of the first order with respect to the concentration of formaldehydesulphoxylate and unsaturated aldehydes.

Recently 2,3-unsaturated aldehydes have gained in importance as comonomers in rubber production¹⁻³. The aldehyde groups in the polymer raise its adhesive properties and enable it to undergo further polymeranalogous transformations⁴⁻¹¹. The investigation of the emulsion copolymerization of butadiene with styrene and unsaturated aldehydes with sodium formaldehydesulphoxylate as the reduction component of the initiation system revealed that the limit conversion of the monomers was the lower the more unsaturated aldehyde there was in the mixture and the smaller the aldehyde molecule was. In the case of a spontaneous termination of polymerization it was sometimes possible to attain the original polymerization rate by a further addition of sodium formaldehydesulphoxylate. We then proved that the reaction of sodium formaldehydesulphoxylate with propenal, 2-methylpropenal and 2-ethylpropenal occurred also in the emulsion systems which did not contain styrene and butadiene.

To characterize the reaction of formaldehydesulphoxylate with the above 2,3-unsaturated aldehydes in more detail, we studied the dependence of its rate on the concentration of the initial compounds and on temperature. The data thus obtained were used to determine the order of the reaction with respect to both reaction components and the characteristics of its temperature dependence.

EXPERIMENTAL

Chemicals. Propenal (Fluka), b.p. 51—53°C, d_4^{20} 0.84. Commercial 2-methylpropenal (Spolana, Neratovice) was rectified under reduced pressure, 99.5% by gas chromatography. 2-Ethylpropenal

(Chemical Works, Záluží) contained 99% of the active component, 0.4% water, 0.3% methyl alcohol, 0.2% butanol (determined by gas chromatography). Sodium formaldehydesulphoxylate, $\text{CH}_2(\text{OH})\text{SO}_2\text{Na} \cdot 2 \text{H}_2\text{O}$ was prepared from a technical sample (rongalite) by double recrystallization from water and contained 1.5% $\text{CH}_2(\text{OH})\text{SO}_3\text{Na}$. Neokal (technically pure sodium dibutyl-naphthalenesulphonate) was a product of United Chemical and Metallurgical Works (Production Company) Ústí n. L.; it contained 97% of the active component and 3% of sodium sulphate. The other chemicals were analytical purity grade.

Methods. The reactions of sodium formaldehydesulphoxylate with the aldehydes were performed in emulsion. The composition of the reaction mixture was adjusted to that of the emulsion system used in the investigation of the copolymerization of butadiene and styrene and unsaturated aldehydes. The sodium rosin soap was replaced by neokal which allows to determine sodium formaldehydesulphoxylate in an acid medium without breaking the emulsion. Toluene was used instead of butadiene and styrene; the unsaturated aldehydes were stabilized with hydroquinone. The composition of the reaction mixture was as follows (in g): water 196.4; toluene with aldehyde 100; KCl 0.6; neokal 4.5 and sodium formaldehydesulphoxylate 0.3. Hydroquinone was used in an amount 0.05% by mass with respect to the aldehyde. The individual components were dosed in nitrogen into glass bottles, one litre in volume, provided with a metallic closure and a special seal allowing to draw samples by means of a syringe during the reaction. First, an aqueous solution of the reduction component was introduced, followed by toluene; after thermostating and analysis of sodium formaldehydesulphoxylate the respective aldehyde was added with the syringe. The sealed bottles were fixed in a frame immersed into a water bath; the frame was revolving about a horizontal axis at a speed of 45 r.p.m. The temperature of the bath was maintained with an accuracy of $\pm 0.1^\circ\text{C}$. The sodium formaldehydesulphoxylate content was determined^{1,2} in the samples of the reaction mixture during the reaction (the contents of an Erlenmeyer titration flask were thermostated to $0-1^\circ\text{C}$ with ice from distilled water prior to sampling in order to reduce the rate of reaction of formaldehydesulphoxylate with the aldehyde during titration).

RESULTS

It has been established by preliminary experiments that if the amounts of formaldehydesulphoxylate and 2-methylpropenal in the toluene-water mixture (without emulsifier) are small, the reaction product remains in the aqueous solution, while at higher concentrations of the reaction components it separates out from the solution. The product is insoluble in water and in toluene, but it can be dissolved in acetone, alcohol, dioxan and chloroform. According to the conditions of preparation, its molecular weight ranges from 500–1 000; it contains 30–40% of free aldehyde groups, 1.4–2.5% of sulphur, and can be formed also in the presence of inhibitors of the radical polymerization.

Of the unsaturated aldehydes, the fastest reaction with formaldehydesulphoxylate in water emulsion at 5°C was observed with propenal and the slowest was observed with 2-ethylpropenal. Sodium formaldehydesulphoxylate does not react with the saturated aldehydes, *i.e.* acetaldehyde and propionic aldehyde: no decrease in the concentration of sodium formaldehydesulphoxylate could be detected after stirring the reaction mixture at 5°C for five hours, nor after stirring at 25°C for 96 hours.

The effect of temperature on the rate of reaction of formaldehydesulphoxylate with propenal, 2-methylpropenal and 2-ethylpropenal was investigated within the temperature range $0-40^\circ\text{C}$ while using 0.3 g of sodium formaldehydesulphoxylate and 3.0 g of an unsaturated aldehyde in the mixture. The reaction with propenal was too fast under these conditions, and its amount was therefore reduced to 0.5 g. The half-times (τ) of the reaction, *i.e.* time in minutes within

which half of the starting amount of sodium formaldehydesulphoxylate has reacted at a given temperature ($^{\circ}\text{C}$), of the individual unsaturated aldehydes are as follows: propenal 15(0), 10(5), 6.3(10); 4.2(15); 2-methylpropenal 132(0), 84(5), 54(10); 24(20); 2-ethylpropenal 420(5), 340(10), 156(20), 111(25), 75(30), 51(35), 36(40). The halftimes decrease with increasing temperature and decreasing number of the carbon in the molecule of the aldehyde. The $1/\tau$ dependences on the reciprocal temperature value were represented by straight lines having the same slope for all aldehydes.

The effect of the concentration of sodium formaldehydesulphoxylate ($[F]$) on the rate of reaction with 2-methylpropenal was verified by experiments with 3 g of 2-methylpropenal and 0.1, 0.4 and 0.6 g of sodium formaldehydesulphoxylate in the reaction mixture. The reactions were carried out at 5°C . In all three experiments the time dependences $\log [F]/[F]_0$ were represented by identical straight lines. The reaction half-times were also identical (τ 84 min). It can be deduced from the experiments that the reaction investigated here is of the first order with respect to the concentration of formaldehydesulphoxylate.

The dependence between the concentration of unsaturated aldehydes and the rate of their reaction with sodium formaldehydesulphoxylate was determined at 5°C . The following half-times were found (at a given amount of aldehyde in the mixture, in g): propenal 87(0.1), 27(0.25), 11(0.5), 4.5(1), 2(2); 2-methylpropenal 366(0.5), 210(1), 84(3), 48(5), 24(10), 14(20); 2-ethylpropenal 420(3), 266(5), 149(10), 91(20). The increase of the half-times with decreasing concentration of aldehydes indicates the participation of the unsaturated aldehydes in the chemical transformation of formaldehydesulphoxylate. Since the solubility of sodium formaldehydesulphoxylate in the organic phase of the emulsion system is negligibly low, the reaction proceeds predominantly in the aqueous phase. To assess an approximate concentration of aldehydes in the aqueous solution, the distribution equilibrium of propenal, 2-methylpropenal and 2-ethylpropenal between the aqueous and organic phases of a model reaction system was determined polaro-

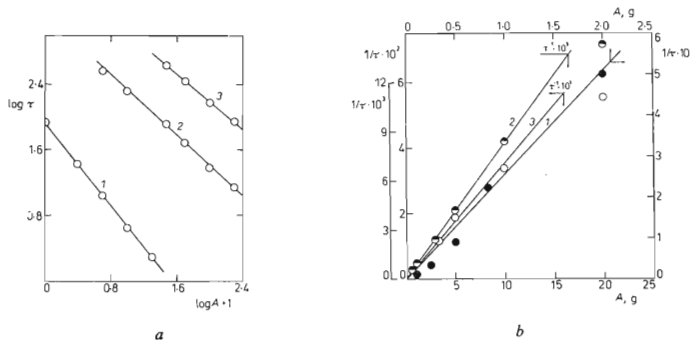


FIG. 1

Determination of the Reaction Order n (a) and of the Reaction Constants k (b) of the Reaction of Formaldehydesulphoxylate with Propenal (1), 2-Methylpropenal (2) and 2-Ethylpropenal (3) according to Eqs (4), (4a)

graphically¹³ (0.1M-H₂SO₄ in a mixture of 90 parts per volume of ethanol and 10 parts per volume of water). The system used did not contain sodium formaldehydesulphoxylate (Table I). It can be seen from the Table that the most favourable conditions for the reaction investigated here are found with propenal, while the most unfavourable conditions are offered by 2-ethylpropenal. The distribution coefficient remained virtually unchanged within the concentration range under investigation.

DISCUSSION

The data obtained in the present work allow to express the rate of the loss of formaldehydesulphoxylate during its reaction with the aldehydes by equation

$$-d[F]/dt = k(fA)^n \{(fV_w + V_{T_o}) M_A\}^{-n} [F], \quad (1)$$

where $[F]$ is the molar concentration of formaldehydesulphoxylate in the aqueous phase at time t (s), k is the rate constant of the reaction in the aqueous phase, A is the amount of aldehyde in grams in the reaction mixture, V_w and V_{T_o} are the volumes of the aqueous (200 cm³) and toluene (115 cm³) phases, M_A is the molecular weight of the unsaturated aldehyde, f is the distribution coefficient of aldehyde between the aqueous phase and toluene and n is the reaction order with respect to aldehyde. If the aldehyde is present in excess, and assuming that the distribution equilibrium between the aqueous and organic phases is quickly established in the emulsion system, Eq. (1) can be expressed in the integral form

$$\log ([F]/[F]_0) = -k't, \quad (2)$$

where $[F]_0$ is the initial concentration of formaldehydesulphoxylate in the aqueous phase and the pseudoconstant of the first order $k' = 0.434k(fA)^n[(fV_w + V_{T_o}) M_A]^{-n}$. The time τ needed for the decomposition of one half of the formaldehydesulphoxylate

TABLE I

Average Value of Coefficient (f) for the Distribution Equilibrium of Unsaturated Aldehydes Between the Aqueous Phase and Toluene (5°C) and Characteristics of the Reaction of Formaldehydesulphoxylate with Unsaturated Aldehydes in an Aqueous Solution within the Range 0–40°C

k Rate constants at 5°C (mol⁻¹ l s⁻¹), E activation energy (kcal/mol), P frequency factor (mol⁻¹ l s⁻¹).

Aldehyde	f	$k \cdot 10^2$	E	$P \cdot 10^{-8}$
Propenal	1.118 ± 0.161	4.99	13.5 ± 0.3	20.80
2-Methylpropenal	0.160 ± 0.008	0.91	13.5 ± 0.3	3.79
2-Ethylpropenal	0.057 ± 0.006	0.28	13.5 ± 0.3	1.16

present depends on k' according to

$$k'_1\tau_1 = k'_2\tau_2 = \dots = k'_i\tau_i = \log 2. \quad (3)$$

Relationship (3) was used to calculate the activation energy of the reaction of aldehydes with formaldehydesulphoxylate by substitution of the values of $1/\tau$ determined for the reactions of formaldehydesulphoxylate with the aldehydes within the temperature range from 0 to 40°C for the rate constant in Arrhenius' equation. The same value (13.5 kcal/mol) was found for all aldehydes. This value can be somewhat distorted by a temperature change of the distribution coefficient f ; as a consequence, the terms $(fA)^n [(fV_w + V_{T_0}) M_A]^{-n}$ in Eq. $k'_1/k'_2 = \tau_2/\tau_1$ do not cancel each other at constant initial concentrations of aldehydes. Since f does not change with the concentration of the aldehyde in the reaction mixture, the dependence of τ on the amount of the aldehyde present in the mixture can be expressed on the basis of Eq. (3) by

$$\tau = 0.692k^{-1}(fA)^{-n} [(fV_w + V_{T_0}) M_A]^n. \quad (4)$$

The reaction order (n) calculated graphically (Fig. 1a) by means of (4) from the half-times determined at various concentrations of the aldehydes is 1.25, 0.93 and 0.86 for propenal, 2-methylpropenal and 2-ethylpropenal. It can be derived from the values of n that the reaction of the aldehydes with formaldehydesulphoxylate is of the first order with respect to the aldehyde concentration. A value of n smaller than unity found for 2-methylpropenal and 2-ethylpropenal can be explained by a decrease in the concentration of the aldehyde in the aqueous phase below a value corresponding to the distribution equilibrium; the difference between the effective and equilibrium concentrations increases with the amount of the aldehyde present in the mixture. An n higher than unity for propenal can be explained by increasing difference between the equilibrium and effective concentrations of aldehyde in the aqueous phase if the concentration of propenal in the mixture is reduced; the corresponding increments of τ would raise the slope of the dependence of $\log \tau$ on $\log A$. The secondary reactions of the primary transformation products of propenal with formaldehydesulphoxylate would of course also be reflected in an apparent increase in the effective concentration of aldehyde above the equilibrium concentration, $n > 1$.

For $n = 1$, the rate constants k , of the reaction of formaldehydesulphoxylate with the aldehydes in the aqueous phase of the emulsion system were determined (Fig. 1b) from the dependence of $1/\tau$ vs A by using Eq. (4). It can be deduced from the departure of the experimental points from a linear course that the decrease in the propenal concentration in the aqueous phase below the equilibrium concentration is highest at the lowest concentrations of propenal in the mixture. In the case of substituted aldehydes the decrease in the effective concentration appears at their highest concentrations which probably lie at the limit of the validity of Nernst's distribution

law for a given system. The rate constants recalculated to the dimension $\text{mol}^{-1} \text{l s}^{-1}$ and the frequency factors (P) calculated therefrom are summarized in Table I. The frequency factors for 2-substituted propenals are lower by an order of magnitude than those for an unsubstituted propenal.

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