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> ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Effect of Acetophenone on Liquid-Phase Dehydration of Dimethylphenylmethanol

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Abstract—The acid-catalyzed liquid-phase dehydration of dimethylphenylmethanol to α -methylstyrene was considered. The scheme and mathematical model of liquid-phase dehydration of dimethylphenylmethanol were proposed, and the effect of acetophenone on the reaction kinetic parameters was studied.

Combined production of phenol and acetone by the cumene method is a widely used process of chemical technology [1]. It yields, along with the target products, many by-products, including dimethylphenylmethanol (DMPM). DMPM is formed through nonselective consumption of cumene hydroperoxide in the stages of cumene oxidation and acid decomposition of hydroperoxide into phenol and acetone. The presence of DMPM in the reaction mixture leads to formation of products impairing the quality of commercial phenol.

As noted in [2–7], DMPM can be dehydrated to obtain α -methylstyrene (α -MS), which is the initial monomer for production of various polymeric materials.

At present, α -MS is prepared in Russia mainly by high-temperature catalytic dehydrogenation of cumene [8]. This process is very power-consuming. Therefore, development and promotion of a process for α -MS production from DMPM, which finds no commercial application yet, is of practical interest.

Dehydration of DMPM to α -MS can be performed in both gas and liquid phases. We consider here the liquid-phase process as the most cost-efficient.

EXPERIMENTAL

DMPM obtained by base decomposition of cumene hydroperoxide was used as a raw material [1]. The sample contained (wt %) DMPM 91.7, acetophenone (ACP) 7.6, α -MS 0.53, cumene 0.28, and cumene hydroperoxide 0.50. A 0.5 M solution of sulfuric acid in acetic acid was taken as catalyst. Kinetic studies were performed in a temperature-controlled glass cell equipped with a magnetic stirrer. During the reaction, an inert gas (nitrogen) was bubbled through the reaction mixture. The reaction course was monitored chromatographically by the concentrations of the initial substances and reaction products [9].

Initially cumene was taken as a reaction medium, since it was the initial substance in DMPM synthesis, which eliminates the stage of additional purification of alcohol.

It is commonly believed [10, 11] that the acid-catalyzed dehydration of alcohols in the liquid phase proceeds via formation of carbocation by the scheme

$$ROH + H^{+} \rightleftharpoons ROH_{2} \rightleftharpoons R^{+} + H_{2}O$$
$$\rightleftharpoons Olefin + H_{2}O + H^{+}, \qquad (1)$$

where R is a hydrocarbon radical.

It was found experimentally that DMPM dehydration in cumene decelerates in the course of time (Fig. 1), which is probably due to inhibition of the catalyst by water formed, rather than to attainment of a chemical equilibrium. Special experiments showed that α -MS is not hydrated under these conditions. Since water exhibits higher proton affinity than the other reaction components, its accumulation in the system can cause resolvation of protons with water and, as a result, a decrease in the catalyst activity.

In experiments with various initial DMPM concentrations (Fig. 1), we found that the DMPM dehydration is first-order with respect to the substrate and that the reaction selectivity with respect to α -MS is 100%. The use of special procedures [12] and analysis of the



Fig. 1. Kinetic curves of (a) DMPM dehydration and (b) α -MS accumulation in cumene at various initial DMPM concentrations. $c_{\text{H}_2\text{SO}_4} = 5 \times 10^{-3}$ M, 80°C. (c_{DMPM}) DMPM concentration, $(c_{\alpha-\text{MS}}) \alpha$ -MS concentration, and (τ) time.



Fig. 2. Effect of the ACP concentration on the kinetics of DMPM dehydration in cumene. $c_{\text{DMPM}}^0 = 3$, $c_{\text{H}_2\text{SO}_4} = 5 \times 10^{-3}$ M, 110°C; the same for Figs. 3, 4. (c_{DMPM}) DMPM concentration and (τ) time; the same for Fig. 5. ACP concentration (M): (1) 0.28, (2) 0.57, (3) 1.50, (4) 2.10, and (5) 5.0.

kinetic data allowed us to suggest a scheme of DMPM conversion, which takes into consideration the stage of catalyst inhibition:

DMPM + cat_a
$$\stackrel{k_1}{\longleftrightarrow}$$
 [X] $\stackrel{k_2}{\longleftrightarrow}$ α -MC + H₂O + cat_a,
cat_a $\stackrel{k_1}{\longleftrightarrow}$ cat_i, (2)

where cat_a and cat_i are the active and inactive forms of the catalyst; [X] is the intermediate; k_1 and k_{-1} are constants of [X] formation and decomposition, respectively; k_2 is the rate constant of decomposition of [X] with the formation of reaction products; and k_i is the rate constant of catalyst inhibition.

When conversion of [X] into the reaction products is the limiting stage, the concentration of the active form of the catalyst is described by the equation

$$c_{\text{cat}}^{a} = c_{\text{cat}}^{0} \exp\left(-k_{1}\tau\right), \qquad (3)$$

where c_{cat}^{a} is the concentration of the active form of the catalyst, c_{cat}^{0} is the initial concentration of the catalyst, and τ is the reaction time.

Thus, the DMPM concentration c_{DMPM} changes in time by the equation

$$-\frac{dc_{\rm DMPM}}{d\tau} = k_{\rm app} c_{\rm DMPM} \exp(-k_{\rm i}\tau), \qquad (4)$$

where k_{app} is the apparent rate constant defined by

$$k_{\rm app} = k_2 \frac{k_1}{k_{-1}} c_{\rm kat}^0.$$
 (5)

Integration of Eq. (4) gives a kinetic equation for DMPM in the integral form, which adequately describes all the experimental data:

$$c_{\text{DMPM}} = c_{\text{DMPM}}^{0} \exp\left\{\frac{k_{\text{app}}}{k_{\text{i}}} [\exp\left(-k_{\text{i}}\tau\right) - 1]\right\}, \quad (6)$$

where c_{DMPM}^0 is the initial DMPM concentration.

Since ACP always accompanies DMPM in phenol and acetone production, it was interesting to study the effect of ACP on DMPM dehydration. ACP, as a more polar solvent than cumene, must undoubtedly affect the process.

To reveal this effect, we performed experiments at 110°C, varied initial ACP concentration, and equal other conditions. It was found that ACP is not consumed; its concentration determined chromatographically remained unchanged. The kinetics of the DMPM dehydration in cumene with various ACP additives is shown in Fig. 2, and the constants calculated by

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Eq. (6) and the initial reaction rates v_0 are listed in the table. The initial reaction rates were determined by differentiation of the kinetic curves. The selectivity of DMPM dehydration under these conditions was also 100%.

As seen, the initial reaction rate and the degree of DMPM conversion grow with increasing ACP concentration in the system, which is probably due to a change in the solvent properties, namely, in its dielectric constant.

The dielectric constant of a mixture of substances can be determined from the equation [13]

$$\log \varepsilon = n_1 \log \varepsilon_1 + n_2 \log \varepsilon_2 + \dots + n_i \log \varepsilon_i, \quad (7)$$

where ε_i is the dielectric constant of *i*th component and n_i is the mole fraction of *i*th component of the mixture.

Using Eq. (7), we calculated ε of a mixture of cumene and ACP and correlated the results with the reaction rate. Figure 3 shows the dependence of the apparent dehydration rate constant on ACP concentration, and Fig. 4, the dependence of log k_{app} on the Kirkwood parameter (KP), which characterizes the solvent polarity [13] and is defined by

$$KP = (\varepsilon - 1)/(2\varepsilon + 1).$$
(8)

As seen (Fig. 3), the reaction rate grows with increasing solvent polarity.

In accordance with the classic Arrhenius theory of reaction kinetics, a certain energy barrier must be overcome before conversion of the initial substances into the reaction products. The solvent can change the activation Gibbs energy due to different degrees of solvation of the initial reactants and the activated complex [13]. The degree of solvation is determined by the electric charge of the reacting species: it grows with increasing charge. Reactions in which the activated complex has higher charge density (is more polar) than the initial molecule are accelerated in more polar solvents.

A similar trend is observed in dehydration of DMPM at its various initial concentrations in ACP (Fig. 5): the reaction is accelerated with increasing solvent polarity (Fig. 6). However, the dependence of the apparent rate constant on KP is nonlinear, which suggests the effects of the specific and nonspecific solvation. The rate constants of DMPM dehydration in ACP calculated by Eq. (6) and the initial reaction rates are listed in the table.

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Kinetic parameters of DMPM dehydration $c_{\rm H_2SO_4} = 5 \times 10^{-3}$ M, 110°C

		$v_0 \times 10^3$,	սիհ	<i>n</i> ₁ ~ 10	DMPM
М		mol l ⁻¹ s ⁻¹	s^{-1}		sion, %
Dehydration in cumene					
3	0.28	5.656	3.525	3.225	87
3	0.57	5.698	3.525	2.933	90
3	1.50	6.241	4.176	2.979	98
3	2.10	6.659	4.650	2.901	95
3	5.00	8.446	6.067	2.231	99
Dehydration in acetophenone					
0.71	a^*	15.000	34.00	7.537	100
1.47	a	13.000	13.000	2.917	100
2.96	a	9.453	5.755	1.933	99
4.32	a	11.000	4.311	1.674	98
5.14	а	4.194	4.153	3.581	80
6.38	а	4.119	3.384	4.334	65

Acetophenone as solvent.

Thus, we can assume that, under conditions of DMPM dehydration, the activated complex is more polar than the initial DMPM molecule. This is confirmed by quantum-chemical calculations of the DMPM molecule and transition complex (protonated DMPM), which were performed using the MORAC program. Calculations showed that dipole moments of



Fig. 3. Apparent rate constant of DMPM dehydration k_{app} in cumene vs. ACP concentration.



Fig. 4. Effective rate constant of DMPM dehydration k_{app} in cumene with various ACP content vs. Kirkwood parameter KP.



Fig. 5. Kinetic curves of DMPM dehydration in ACP. $c_{\text{H}_2\text{SO}_4} = 5 \times 10^{-3}$ M, 110°C; the same for Fig 6. Initial concentration of DMPM (M): (*1*) 6.38, (*2*) 5.14, (*3*) 4.32, (*4*) 2.96, (*5*) 1.47, and (*6*) 0.71.



Fig. 6. Apparent rate constant of DMPM dehydration k_{app} in ACP vs. Kirkwood parameter KP.

DMPM and protonated DMPM are 1.549 and 1.915 D, respectively. This fact, combined with the above results, accounts for the acceleration of DMPM dehydration in the presence of acetophenone as a more polar compound.

CONCLUSIONS

(1) The kinetics of dimethylphenylmethanol dehydration in cumene and in acetophenone was studied; it was shown that acetophenone accelerates dehydration. (2) The rate of dimethylphenylmethanol dehydration in acetophenone is higher than that in cumene under the same conditions.

(3) Dehydration of dimethylphenylmethanol in both cumene and acetophenone is characterized by 100% selectivity; its conversion reaches 87% in cumene and 99% in acetophenone at substrate concentration of 3 M and 110° C.

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