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Abstract

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DECOMPOSITION OF CUMENE HYDROPEROXIDE CATALYZED BY THE CATION-EXCHANGE RESIN KU-2

As is known, cation-exchange resins in the acid form can serve as catalysts for acid-catalyzed reactions. On this basis, we assumed that such catalysts would accelerate the decomposition of cumene hydroperoxide by an acid mechanism. This assumption has been fully confirmed, as is evident from the present communication, which contains the results of a study of the decomposition of cumene hydroperoxide in several solvents in the presence of the cation-exchange resin KU-2.

Cumene hydroperoxide and the solvents were carefully purified, especially from traces of water. The cation-exchange resin KU-2, a sulfonated copolymer of styrene with divinylbenzene, was ground and converted to the acid form by treatment with hydrochloric acid. It was then thoroughly washed and dried at room temperature. It was then ground again, and the fraction with a grain diameter from 0.3 to 0.4 mm was selected. After this, the resin was dried once more at 90–95° and reduced pressure (about 1 mm Hg) for 25–30 hr.

The experimental procedure used by us made it possible to carry out experiments in such a way that the catalyst was suspended at all times and was distributed uniformly throughout the entire volume of the solution. Consequently, one may assume that there is a certain concentration m of the heterogeneous catalyst in the reaction mixture.

The procedure for carrying out the experiment in this work differed only in details from that described earlier (^{1}).

We studied the decomposition of cumene hydroperoxide, catalyzed by the ion-exchange resin KU-2, in acetone, dioxane, chlorobenzene, and glacial acetic acid, as well as in several mixed solvents. The main products of this reaction were acetone and phenol, the yield of which reached 95–97% of the theoretical amount. The decomposition of cumene hydroperoxide catalyzed by KU-2 proceeded with self-acceleration in dioxane and in glacial acetic acid, whereas in acetone, chlorobenzene, and in mixtures of acetone with phenol or with dioxane, and also in aqueous dioxane, this reaction proceeded as first order with respect to hydroperoxide up to an 80–90% decrease in its initial concentration. The deviation of this reaction from first order may be explained by the influence of the conversion products on the rate of the chemical process. Our experiments showed that additions of acetone in all cases caused an increase in the reaction rate, whereas additions of phenol, depending on the nature of the solvent, caused in some cases an increase and in others a decrease in the rate of decomposition of cumene hydroperoxide. The results of some such experiments are summarized in Table 1, in which γ denotes the ratio of the value of the maximum reaction rate in the presence of acetone, phenol, or their mixtures to its value in the pure solvent.

The decomposition of cumene hydroperoxide at 30° in dioxane containing 2 mol/l acetone proceeded 20 times faster than in dioxane without additives.

acetone. Additions of phenol, however, accelerated this reaction in dioxane quite insignificantly. It was accelerated substantially by additions of equimolar amounts of acetone and phenol.

If the influence of the final products of the catalytic decomposition of cumene hydroperoxide (CHP), i.e., acetone and phenol, on the rate of this process was insignificant or could be greatly reduced, for example by lowering the initial concentration of the compound undergoing transformation, then the reaction rate W depended linearly on the concentration of hydroperoxide C_{CHP}.

$$W = k_{\text{eff}} \cdot C_{\text{CHP}}. \tag{1}$$

The effective rate constant k_{eff} of this reaction, depending on the nature of the solvent, changed differently with changes in the concentration of catalyst. In the reaction both in aqueous and in anhydrous dioxane, and also in glacial acetic acid, k_{eff} depended linearly on the catalyst concentration m. Such a dependence of k_{eff} on m indicates that the entire surface of the catalyst was equally accessible for adsorption of cumene hydroperoxide from the reaction mixture. If, however, this reaction was carried out in a solution of acetone or chlorobenzene, then its order with respect to the catalyst was higher and amounted to 1.3–1.5. In our opinion, such a dependence of k_{eff} on m is caused by adsorption from the solution of impurities, for example,

Table 1

Catalyst concentration 5 g/l

Solvent	Experiment temp., °C	Initial concentration, mol/l: hydroperoxide	Initial concentration, mol/l: acetone	Initial concentration, mol/l: phenol	γ
Chlorobenzene	50	0.1	0.1	–	2.3

Solvent	Experiment temp., °C	Initial concentration, mol/l: hydroperoxide	Initial concentration, mol/l: acetone	Initial concentration, mol/l: phenol	γ
Chlorobenzene	50	0.1	–	0.1	0.6
Acetone	30	0.1	90*	10*	3.7
Acetone	30	0.1	70*	30*	11.3
Dioxane	40	0.05	0.1	–	3.4
Chlorex	40	0.05	0.1	–	3.0
Chlorex	40	0.05	–	0.1	1.2

* In mole percent.

Table 2

Values of the effective rate constant of the catalyzed decomposition reaction of cumene hydroperoxide
($k_{\text{eff}} \cdot 10^{-4}$ s^{-1}) as a function of temperature and the nature of the solvent
(catalyst concentration 5 g/l)

Solvent	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°
Acetone	0.1	0.37	1.18	3.25	7.85	–	–	–	–	–
90 mol.% acetone + 10 mol.% phenol	0.48	1.70	4.87	12.08	25.7	–	–	–	–	–
70 mol.% acetone + 30 mol.% phenol	2.06	6.51	16.22	37.06	–	–	–	–	–	–
Dioxane	–	–	0.4	1.0	2.0	4.1	–	–	–	–

Solvent	0°	10°	20°	30°	40°	50°	60°	70°	80°	90°
Dioxane + 0.1 mol/l acetone + 0.1 mol/l phenol	–	–	0.4	–	2.35	4.85	–	–	–	–
Dioxane + 0.5 mol/l acetone + 0.5 mol/l phenol	–	–	0.8	1.7	4.6	7.9	–	–	–	–
Dioxane + 1.8 mol/l acetone + 1.8 mol/l phenol	–	–	1.5	3.3	7.3	17.6	–	–	–	–
95 mol.% dioxane + 5 mol.% water	–	–	–	–	–	–	–	0.2	–	–
Chlorobenzene*	–	–	–	–	0.09	0.16	0.27	0.42	0.79	1.25

* Concentration of air-dry catalyst 25 g/l.

traces of water, which strongly inhibited the acid decomposition of cumene hydroperoxide, so that in the case of water additions, as observed both in the present study and in an earlier work ([2], [3]) on the homogeneous decomposition of hydroperoxide.

The rate of decomposition of cumene hydroperoxide catalyzed by the cation-exchange resin KU-2 depended strongly on the nature of the solvent and of certain additives. The results of studying this quantitative dependence are summarized in Table 2.

It is evident from Table 2 that the decomposition of CHP in acetone proceeded 3–4 times faster than in dioxane. This reaction proceeded especially slowly in chlorobenzene. It was also established that the rate of the heterogeneous catalytic decomposition of cumene hydroperoxide in benzene was still lower than in chlorobenzene. Additions of phenol to acetone greatly accelerated this reaction, and to a greater extent the higher the phenol concentration was. Additions of acetone, as well as of an equimolar mixture of acetone and phenol, to dioxane had an analogous effect. It is characteristic that at high concentrations (greater than 0.5 mole/liter) of acetone additions to dioxane, the acceleration of the reaction was the same as in experiments with additions of an equimolar mixture of acetone and phenol. If, however, the concentration of the added equimolar mixture of acetone and phenol in dioxane was of the order of 0.1–0.2 mole/liter or still lower, then the effect was considerably smaller than in the case of additions of an equal amount of pure acetone.

The value of k_{ef} for the reaction in dioxane increased linearly with increasing concentration of the added equimolar mixture of acetone and phenol. This made it possible, by graphical extrapolation, to determine at different temperatures the values of k_{ef} for the reaction in dioxane, given in Table 2. It is possible that these values differ somewhat from the values determined directly from the kinetic curves by ordinary calculations. However, it is difficult to calculate the values of k_{ef} reliably in these cases, since the reaction proceeded with self-acceleration, the degree of which depended in a complex way on the concentration of the reaction products formed.

Additions of water to dioxane, even at comparatively low concentration, very strongly decreased the rate of decomposition of cumene hydroperoxide catalyzed by the cation-exchange resin KU-2. A completely analogous effect of water additions had previously been found in the sulfuric-acid-catalyzed decomposition of CHP in dioxane ([2], [3]) and in glacial acetic acid ([2]).

Additions of benzene, toluene, meta- and para-xylenes, and *n*-nonane in an amount of 10 mole % to dioxane slowed the decomposition of cumene hydroperoxide catalyzed by KU-2 resin to a comparatively small extent (by a factor of 1.2–1.5). It is characteristic that these additions did not eliminate self-acceleration. The degree of retardation of the reaction caused by hydrocarbon additions increased with increasing molecular weight and was completely independent of their basicity. Thus, for example, additions of meta- and para-xylenes decreased the rate of catalytic decomposition of CHP to exactly the same extent, whereas according to data (4) the basicity of meta-xylene is 20–26 times greater than the basicity of para-xylene.

From the temperature dependence of k_{ef}, values of the apparent activation energy E were calculated; these varied with the nature of the solvent. These values proved to be equal (in kcal/mole): in acetone, 18.6; in a mixture of 90 mole % acetone with 10 mole % phenol, 17.0; in a mixture of 70 mole % acetone with 30 mole % phenol, 15.5; in dioxane, as well as in dioxane with additions of equimolar amounts of acetone and phenol, 14.5; in chlorobenzene, on absolutely dry KU-2 resin, 8.2, and on air-dry KU-2 resin, 12.2. The value of the apparent activation energy calculated from the temperature dependence of the initial reaction rate in glacial acetic acid is 14.8 kcal/mole.

Comparison of the values of k_{ef} and E for the reaction carried out in different solvents shows that the rate of the heterogeneous catalytic decomposition of cumene hydroperoxide is not determined solely by the magnitude of E,

and apparently also depends on a number of other factors, including those determining the adsorption of dissolved substances on the catalyst.

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Note: Figure translations are in progress. See original paper for figures.