R. V. KUCHER, A. I. YURZHENKO, and M. A. KOVBUZ

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Abstract

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R. V. KUCHER, A. I. YURZHENKO, and M. A. KOVBUZ

OXIDATION OF CUMENE BY MOLECULAR OXYGEN IN EMULSIONS IN THE PRESENCE OF VARIOUS EMULSIFIERS

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The chain theory of hydrocarbon oxidation was developed by N. N. Semenov (^{1}) on the basis of experimental data obtained by a number of investigators. Liquid-phase oxidation of hydrocarbons was studied from the kinetic standpoint in the works of N. M. Emanuel and co-workers (^{2}), the process being carried out in a homogeneous phase in the presence of various catalysts. A work (^{3}) is devoted to the liquid-phase oxidation of cumene and to the influence on it of various initiating and inhibiting additives.

The presence of an aqueous solution of alkali has a substantial effect on the rate of the oxidation process of hydrocarbons (^{4}); from our point of view, the role of the aqueous phase (and of its composition) as a kinetic factor is of great interest, but data on the influence of the aqueous phase on the kinetics of hydrocarbon oxidation are very limited and unsystematic.

The study of emulsion oxidation of hydrocarbons is of interest above all in connection with the mechanism of reactions in emulsions in general and, in particular, in connection with the topochemistry and mechanism of oxidative processes in emulsion systems. The kinetics of the process may be affected by the phase ratio, the electrolyte composition of the aqueous phase, and the presence of colloidal electrolytes (emulsifiers), owing to the specific properties of the latter (micellar structure, coupled solubility of the initial hydrocarbon and of the peroxides formed, stabilization of the emulsion, etc.). In addition, knowledge of the mechanism of hydrocarbon oxidation reactions in emulsions opens up prospects for the industrial use of emulsion oxidation because of the technical conveniences in controlling the process. Finally, the formation and decomposition of hydroperoxides in emulsions is also of great importance for the emulsion polymerization of unsaturated compounds, since in this case peroxide compounds are initiators of the reaction.

The aim of the present work was to study the rate of cumene oxidation in an emulsion in the presence of various emulsifiers, in relation to the phase ratio and also to the nature of the emulsifiers employed.

Oxidation of the purified (^{3}) hydrocarbon was carried out in glass flasks by

Figure 1: Kinetic curves of the yield of cumene hydroperoxide at different phase ratios (cumene : aqueous phase) in the absence of emulsifiers. I –1 : 4; II –1 : 1; III –in the absence of an aqueous phase.

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bubbling pure oxygen through it (the flow rate of the latter was controlled rheometrically) in a thermostat at 80°. At definite time intervals, samples were taken from the reaction mixture for analysis of the hydroperoxide content (the hydrocarbon and aqueous phases separately) (^{5}). In addition, the cumene phase was analyzed for the total yield of carbonyl compounds (^{6}). The rate of passage of O_2 was constant in all cases and was equal to 20 ml/min. The aqueous phase always contained 0.1 g-equiv/l of sodium carbonate, which produced pH 9.9.

Figure 1 presents the kinetic curves for the yield of cumene hydroperoxide at different phase ratios in the absence of an emulsifier. These data show that an increase in the volume of the aqueous phase greatly increases the rate of accumulation of cumene hydroperoxide. Thus, these data, confirmed also on other systems, show that the aqueous phase is a substantial kinetic factor in

oxidation of hydrocarbons in emulsions as a zone of initiation of the process and formation of hydroperoxide. The significance of the aqueous phase in the emulsion oxidation of cumene increases especially, as experiment shows, in the presence of colloidal electrolytes (emulsifiers) containing a surface-active anion. Figure 2 presents kinetic curves for the accumulation of cumene hydroperoxide in the presence of various emulsifiers. As can be seen from these data, other conditions being equal, emulsifiers accelerate the formation of hydroperoxide. In this case the role of the emulsifiers cannot be reduced completely to simple stabilization of emulsions, since differences in the nature of the emulsifiers only slightly change the degree of dispersion of the emulsions, whereas the rate of accumulation of cumene hydroperoxide changes considerably.

Fig. 1. Kinetic curves of the yield of cumene hydroperoxide at different ratios of the phases (cumene : aqueous phase) in the absence of emulsifiers. *I* –1 : 4; *II* –1 : 1; *III* –in the absence of an aqueous phase.

It should also be noted that the oxygen absorbed in the initial stage of the reaction goes practically completely to the formation of hydroperoxide. When up to 15-20% cumene hydroperoxide has accumulated, the amount of oxygen converted into hydroperoxide decreases somewhat (to 90%). The final yield of hydroperoxide in the presence of emulsifiers (OT aerosol, potassium palmitate) is about 95% of the oxidized cumene, which is considerably higher than the yield of cumene hydroperoxide in homogeneous oxidation in the condensed phase (50%). In addition, as the oxidation reaction proceeds in emulsions in the presence of emulsifiers, a change in the stability of the emulsion is observed:

Figure 2: Curves of the yield of cumene hydroperoxide in the presence of emulsifiers (phase ratio 1 : 4). I –2% potassium palmitate; II –2% OT aerosol; III –2% sodium caprylate; IV –2% leukanol; V –in the absence of emulsifier.

Figure 2: Figure 2: Curves of the yield of cumene hydroperoxide in the presence of emulsifiers (phase ratio 1 : 4). I –2% potassium palmitate; II –2% OT aerosol; III –2% sodium caprylate; IV –2% leukanol; V –in the absence of emulsifier.

during the first 16-20 h the cumene emulsion is stable, so that prolonged centrifugation is required for phase separation; later the emulsion becomes much less stable and rapidly separates.

Fig. 2. Curves of the yield of cumene hydroperoxide in the presence of emulsifiers (phase ratio 1 : 4). *I* –2% potassium palmitate; *II* –2% OT aerosol; *III* –2% sodium caprylate; *IV* –2% leukanol; *V* –in the absence of emulsifier.

The data obtained make it possible to conclude that, in the emulsion oxidation of hydrocarbons, initiation of the reaction and formation of hydroperoxide occur mainly in the aqueous phase. The initial formation of hydroperoxide in the aqueous phase is due primarily to an increase in oxygen absorption in the presence of an emulsifier—a colloidal electrolyte. As we established in additional experiments, the solubility of oxygen in this case increases.

several times. In the aqueous phase there is also conjugately dissolved cumene. This part of the hydrocarbon, owing to the increased absorption of O_2, is under exceptionally favorable conditions for oxidation. The development of the reaction chain may be represented by the scheme

$$\dot{R} + O_2 \rightarrow RO\dot{O}; \qquad RO\dot{O} + RH \rightarrow ROOH + \dot{R}.$$

The initial initiation of these processes consists in the formation of free hydrocarbon radicals $\dot{R}$. The latter may be generated as a result of partial thermal decomposition of the hydroperoxide formed, according to the scheme

$$ROOH \rightarrow R\dot{O} + \dot{O}H; \qquad R\dot{O} + RH \rightarrow ROH + \dot{R}.$$

Such decomposition of hydroperoxide proceeds in an aqueous alkaline medium at a noticeably higher rate than in a hydrocarbon medium. The thermal decomposition of peroxide is affected, in addition to hydroxyl ions, also by the presence of emulsifiers (Table 1), which either accelerates or retards it.

Table 1

Solubility and rate constants of the decomposition of cumene hydroperoxide in aqueous solutions of emulsifiers

Medium	Solubility of CHP, in %, at 20°	$k \cdot 10^6$ at 98.5°
Water	1.46	0.183
0.1 N solution of Na_2CO_3	1.38	1.57
2% aerosol OT	3.39	1.27
2% sodium caprylate	1.61	2.08
2% potassium palmitate	4.87	1.96
2% leukanol	1.98	1.83
Cumene	∞	0.242

In addition to the specific influence of the emulsifier on the decomposition of cumene hydroperoxide, the conjugate solubility of hydroperoxide in the aqueous phase must also be taken into account. An increase in the concentration of cumene hydroperoxide in the aqueous phase promotes the generation of free radicals. However, accumulation of hydroperoxide in the aqueous phase can occur only up to a certain limit: it is limited by the solubility of cumene hydroperoxide. With a further increase in the hydroperoxide content in the reaction mixture, it passes into the hydrocarbon phase, where its decomposition proceeds to a much smaller extent. Thus, the hydrocarbon phase is a kind of "depot" for the hydroperoxide. In this connection, the decrease in the stability of the emulsion in the course of the process becomes understandable. With considerable accumulation of hydroperoxide in the hydrocarbon phase, it is adsorbed at the phase boundary owing to its surface activity; at the same time, the mechanical strength of the adsorption layer of the emulsifier is lowered and, consequently, so is its stabilizing action. Such "deposition" of cumene hydroperoxide in the hydrocarbon phase may also explain the increase in the yield of hydroperoxide during the oxidation of cumene.

Thus, the reaction of emulsion oxidation of cumene by free oxygen is accelerated because the principal stages of it (initiation and development of the reaction of hydroperoxide formation) proceed in the aqueous phase, with an essential and specific role belonging to the emulsifying agent. The latter makes it possible to increase the yields of hydroperoxide, and also facilitates control of the process.

Lviv State University
named after Ivan Franko

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