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NOTES

On The Role of Metallic Copper in The Oxidation of Cumene to Cumene Hydroperoxide

Metallic copper catalyzes the oxidation of cumene to cumene hydroperoxide (*1–12*). However, when the process is carried out at hydroperoxide concentrations which are of interest in industry, one observes a decrease in the catalytic action and in some cases even a negative effect upon the accumulation of hydroperoxide (*9–11*). According to some authors, copper has practically no influence on the oxidation of isopropylbenzene (*13*). The aim of the present study was to obtain information about the role of metallic copper in the liquid-phase oxidation of isopropylbenzene with air under conditions similar to those used in industry (*3*, *6*).

Ordinary laboratory-type equipment was used for the liquid-phase oxidation of cumene with air (*12*). The copper catalyst was introduced into the reaction medium in the form of cylinders (diameter 24 mm, height 165 mm) which were arranged to cover the inner walls of the glass reactor. Cumene and cumene hydroperoxide were purified according the methods described in the literature (*6*). The oxidation was followed by the change in the concentration of cumene hydroperoxide, analyzed iodometrically, and by the overall conversion of the raw material as determined by the refractive index of the mixture n_d^{20} and by gas-chromatographic analysis (*6*). Elementary mathematical processing was also carried out as well as generalization of the results obtained earlier by the authors on the oxidation of cumene hydroperoxide (*9–11*).

The catalytic effect of metallic copper on the oxidation of isopropylbenzene is attributed to initiation by generating radicals on the metal surface (*2*, *6*, *7*, *12*). In the present work the role of the metallic copper on the initiation stage of the oxidation process was studied by surveying the change in the concentration of the hydroperoxide accumulated as a function of the content of the homogeneous initiator in the raw material. The concentration of the cumene hydroperoxide, accumulated upon oxidation of isopropylbenzene with air as a function of the initial content of the cumene hydroperoxide in an interval of 5.00–7.00%, can be presented by the following equations.

(a) in the presence of metallic copper:

$$c = 4.38 + 0.76c_0, \tag{1}$$

(b) in the absence of metal:

$$c = 0.75 + 1.21c_0, \tag{2}$$

where c is the concentration of cumene hydroperoxide accumulated during the oxidation of the raw material, in weight percent, and c_0 is the initial content of cumene hydroperoxide introduced as initiator, in weight percent.

The expressions have been worked out on the basis of experimental results published by us (*11*) and are valid for a flow of the oxidizing air of 1.6×10^{-2} m^3/kg s, temperature 115°, and 60 min duration of the processing of the material. By extrapolation to $c_0 = 0$, we determine the concentration of the product in the absence of cumene

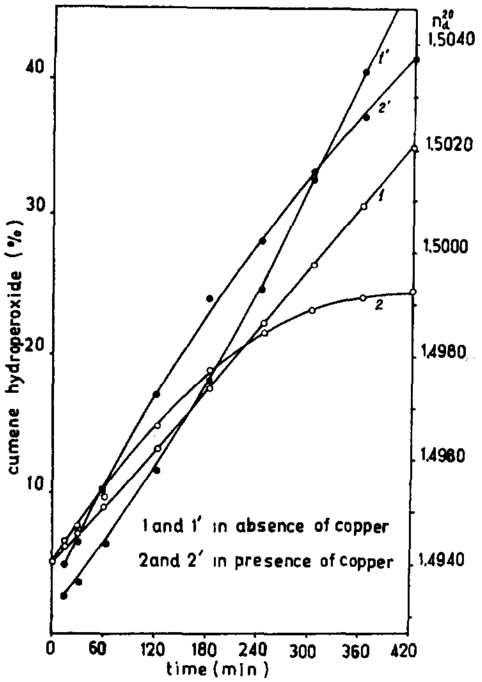

FIG. 1. Variation of cumene hydroperoxide concentration with time (curves 1 and 2) and change of total content of oxygen containing products determined by n_d^{20} (curves 1' and 2') in the process of cumene oxidation. Initial cumene hydroperoxide concentration 5.6%, air supplied at the rate of 1.6×10^{-2} m³/kg s, temperature 115°C.

hydroperoxide introduced in advance. This quantity is much greater in value in the presence of metallic copper [Eq. (1)]. This confirms the literature data on the initiating effect of metallic copper on the oxidation of isopropylbenzene to hydroperoxide. A comparison between the coefficients preceding c_0 in Eqs. (1) and (2) shows that copper decreases the initiating action of the hydroperoxide. This is in agreement with the established increased stability of the hydroperoxide in the presence of metallic copper (*2*, *12*).

Under certain conditions of oxidation, however, copper brings about a sharp deterioration in the trend of the process toward obtaining cumene hydroperoxide without reducing appreciably the overall oxidation rate of the raw material (*9–11*).

This can also be seen from the results obtained on the oxidation of cumene containing 5.6% cumene hydroperoxide with air supplied at the rate of 1.6×10^{-2} m³/kg s, temperature 115°C and with the duration of the processing the raw material 420 min (Fig. 1). At first glance this result is in contradiction with the established stability of cumene hydroperoxide in the presence of metallic copper. To explain this phenomenon we must take account of the fact that there exists conditions for metal corrosion at the contact of the metallic copper with the reaction medium during the oxidation of cumene. The metal extracted into the reaction medium can change appreciably the nature of the effect of the catalyst. We know that the ions of metals with variable valency cause intense decomposition of the peroxide (*6*, *12*). Favorable to this process are the high concentrations both of the metal dissolved in the medium and the hydroperoxides. Such conditions are created under an advanced oxidative process and elevated temperatures of processing.

This assumption can be tested by examining the influence of the temperature and of the duration of oxidation of isopropylbenzene on the content of the accumulated cumene hydroperoxide.

The concentration of cumene hydroperoxide accumulated upon oxidation of isopropylbenzene with air supplied at the rate of 1.6×10^{-2} m³/kg s and an initial concentration of hydroperoxide of 6.00% as a function of the temperature in the interval of 110–120°C and a processing time of 60–360 min can be presented by the expressions

(a) in the presence of metallic copper:

$$c = -39.62 + 0.50t \qquad (\text{at } \tau = 210 \text{ min}), \quad (3)$$

$$c = 4.94 + 0.076\tau \qquad (\text{at } t = 120°\text{C}), \quad (4)$$

(b) in the absence of metal:

$$c = -61.84 + 0.69t \quad (\text{at } \tau = 210 \text{ min}), \quad (5)$$

$$c = 3.66 + 0.082\tau \quad (\text{at } t = 120°\text{C}), \quad (6)$$

where c is as in Eqs. (1) and (2), t is the temperature of the oxidation in °C, and τ is the duration of the experiment in minutes.

Expressions (3)–(6) have been worked out on the basis of experimental results published by us (*11*). The comparison of Eqs. (3) and (5) and correspondingly of (4) and (6) confirms the assumption made that the unfavorable influence of copper on the process is manifested under conditions which intensify the corrosion of the metal: an advanced oxidative process and elevated temperatures of processing.

Since in the selected interval of varying the duration of cumene oxidation (*11*) the concentrations of cumene hydroperoxide calculated from Eqs. (5) and (6) have similar values, the results of the oxidation of cumene for 480 min processing time are presented in Table 1 as another confirmation for the conclusion drawn. The selectivity S_{CHP} of the process toward obtaining cumene hydroperoxide(s) has been calculated from the ratio between the content of the hydroperoxide and the total content of the oxidized product.

We have demonstrated the presence of copper in the dissolved state in the product obtained on cumene oxidation by qualitative spectrum analysis of samples from the mixture with a diffraction spectrograph PGS-2 (Carl Zeiss, Jena) using dc exitation at 8 A. The extraction of copper into the reaction medium has been established also in the oxidation of cumene using oxidized Raney-copper catalysts (*5*).

Some authors recommend activation of the metallic copper before use as catalyst by treatment with nitric acid, with the aim of destroying the oxide crust at the metal surface (*2*). Others report that the catalytic action of oxidized Raney-copper catalysts is increased with increase of their degree of oxidation (*5*).

TABLE 1

Oxidation of Cumene Containing 5.6% Cumene Hydroperoxide (CHP) with Air Supplied at a Rate of 1.6 × 10^{-2} m^3/kg s, Temperature 115°C, and Duration of Experiment 480 Min.

Additional condition	Characteristics of the oxidized product		
	CHP (%)	Total content of oxygen-containing products	S_{CHP}
1. In the presence of copper	28.8	49.9	0.58
2. In the absence of copper	42.6	57.2	0.75

Keeping in mind the tendency of copper to react with oxygen and the analogy with the general catalytic properties of copper and its oxides (*14*), one could assume that in the oxidation of cumene in the presence of metallic copper, the actual catalyst of the process would be the system Cu–Cu_2O–CuO produced in the oxidation medium. Presumably, the effect of the catalyst does not directly depend on its degree of oxidation.

If the effect of the copper catalyst upon the oxidation of cumene depended on its corrosion resistance, a previous treatment with nitric acid could not ensure a permanent activation of the catalyst. The metal surface, prepared in this manner, is subjected to intensive corrosion throughout the oxidation of the initial product. A permanent favorable effect of the action of the copper catalyst can be achieved by improving its resistance to corrosion. This could be attained by oxidation (*15*). Figure 2 illustrates the results on the oxidation of the initial products in the presence of oxidized copper and in the presence of copper treated previously with nitric acid juxtaposed with the data obtained in the

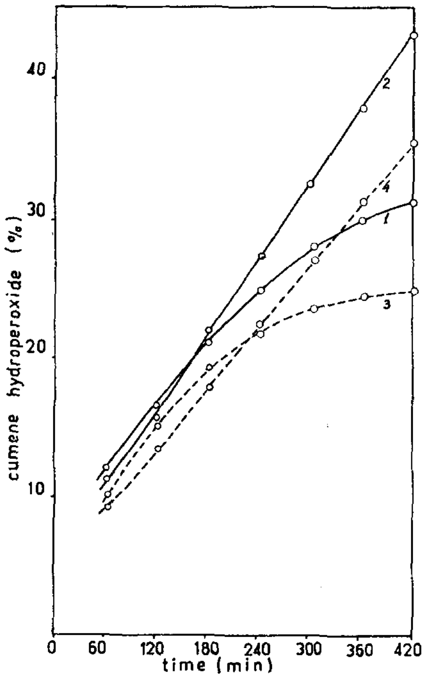

FIG. 2. Variation of cumene hydroperoxide concentration with time in the process of cumene oxidation; the conditions are the same as in Fig. 1. (1) In the presence of copper, treated previously with fuming nitric acid; (2) in the presence of oxidized copper; (3) in the presence of copper, which was not pretreated; (4) in the absence of metal.

presence of copper which had had no pretreatment and those obtained in the absence of the metal. These results confirm the above statement about the possibilities of improving the catalytic effect of metallic copper. The pretreatment with nitric acid results in a temporary increase of the accumulation rate of cumene hydroperoxide, whereas the oxidized copper exercises its catalytic action throughout the reaction.

We conclude that at moderate temperatures of oxidation of isopropylbenzene and at the beginning of the process in the presence of metallic copper, the latter initiates the oxidation and protects the cumene hydroperoxide against decomposition. Copper corrosion takes place upon continuous processing of the raw material, particularly at high temperatures. The interaction between the metal extracted into the reaction medium and the cumene hydroperoxide leads to intense decomposition of the hydroperoxide. The favorable effect of the copper catalyst can be increased by improving its resistance to corrosion.

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