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Oxidation of Cumene to Hydroperoxide in the Presence of Platinum

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The catalytic action of platinum in the oxidation of cumene to cumene hydroperoxide has been studied at a temperature of 110–120°C, a flow rate of the oxidizing air of 1.6×10^{-2} m^3/kg s, a contact time of 60 to 360 min, and an initial content of the initiator (cumene hydroperoxide) from 2 to 5%. It has been established that platinum has a catalytic effect upon the process, which is markedly displayed at high temperature and for a long treatment of the raw material. The homogeneous initiator (cumene hydroperoxide) has a weaker effect upon the cumene oxidation in the presence of platinum than in the absence of a catalyst.

INTRODUCTION

Interest toward heterogeneous catalytic oxidation of hydrocarbons in the liquid phase has lately increased (*1*). Attention has also been drawn to the oxidation of cumene to cumene hydroperoxide, which is one of the basic stages of the cumene method for the production of phenol (*2–5*). Encouraging results have been obtained in the investigation of the catalytic properties of copper, silver, and their alloys upon this process (*2–10*).

The purpose of the present work was to study the catalytic properties of platinum in the oxidation of cumene to cumene hydroperoxide under conditions corresponding to those in industry. Platinum catalysts are most often recommended for oxidation processes (*1*). Literature data on the catalytic effect of platinum on the oxidation of cumene at 90–100°C and in the absence of an initiator (*11*) do not allow any conclusions to be drawn about its catalytic properties in the presence of an initiator and at higher temperature (110–120°C), as actually applied under commercial conditions (*2*).

EXPERIMENTAL

Experiments were carried out using a conventional laboratory apparatus for cumene oxidation (*6, 9*) with a flow rate of the oxidizing air 1.6×10^{-2} m^3/kg s. The platinum was introduced into the reactor in the form of a wire with a diameter of 0.25 mm, coiled as a spiral about the inside wall of the cylindrical glass reactor. The cumene and cumene hydroperoxide used as an initiator were purified beforehand by methods recommended in the literature (*12, 13*). The process was checked by the concentration change of cumene hydroperoxide, analyzed iodometrically (*14*).

RESULTS AND DISCUSSION

Accumulation of cumene hydroperoxide in the reaction medium during cumene oxidation in the presence of platinum was studied as a function of temperature (in the

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range 110 to 120°C), as well as of the initiator concentration (from 2 to 5%), the contact time (from 60 to 360 min), and the amount of catalyst (from 1 to 15 g). The results were compared with those obtained under similar conditions but in the absence of platinum.

The quantitative evaluation of the effect of the above factors upon the concentration of cumene hydroperoxide accumulating during the process was made by the method of experiment design. The experiments were planned according to a central orthogonal design for a complete-factor experiment with four factors in the presence of platinum and three factors in the absence of a catalyst.

The following equations, expressing the concentration of the end product as a function of the factors studied, were obtained after a mathematical treatment of the experimental results:

(a) in the presence of platinum:

$$y = 18.7944 + 3.0656x_1 + 2.0744x_2 + 11.2481x_3 + 2.2394x_1x_3 \quad (1)$$

(b) in the absence of a catalyst:

$$y = 16.9987 + 1.5388x_1 + 2.9488x_2 + 9.7163x_3 + 0.8213x_2x_3 \quad (2)$$

where:

- y is the concentration of the cumene hydroperoxide, accumulated during the oxidation process;
- x_1 is the coded designation of the temperature of the oxidation of the raw material;
- x_2 is the coded designation of the concentration of the initiator (cumene hydroperoxide);
- x_3 is the coded designation of the treatment time of isopropylbenzene.

The adequacy of the expressions obtained was tested with the Fisher number. Its experimental value is 1.311 for Eq. (1) and 6.9088 for Eq. (2) with the tabulated values for the corresponding conditions 8.7 and 9.3, respectively (*15*). It is evident that the condition about the tabulated value exceeding the experimental one was fulfilled, and hence the equations describe adequately the process under investigation (*15–17*).

It should be noted that the initial form of Eq. (1) deduced directly from the experimental data is:

$$\begin{aligned} y = {} & 18.7944 + 3.0656x_1 + 2.0744x_2 \\ & + 11.2481x_3 + 0.4594x_4 \\ & + 0.3631x_1x_2 + 2.2394x_1x_3 \\ & + 0.1356x_1x_4 + 0.0281x_2x_3 \\ & + 0.0969x_2x_4 + 0.2156x_3x_4 \qquad (3) \end{aligned}$$

where y, x_1, x_2, and x_3 are the same as in Eqs. (1) and (2), and x_4 is the coded designation of the amount of platinum catalyst. After checking the significance of the coefficients (*17*), Eq. (3) acquires the form shown by Eq. (1). It proved that the coefficients before the independent variable x_4 are insignificant. Hence the change of this factor within the investigated limits does not affect the process. This result is of commercial interest, due to the high price of the catalyst studied.

Since the aim of our experiments was only to establish the activity of Pt-catalyst, our results give no explanation of the fact that the amount of Pt had no effect on the process. However, examples of possible explanations may be given as follows:

(a) An intermediate complex is formed on the heterogeneous surface and diffuses in the solution. Its saturation concentration controls the process independently of the platinum amount.

(b) The Pt surface enhances the initiation rate as well as the termination rate. These effects balance each other in the range of Pt amounts investigated, but the influence on the initiation rate dominates at smaller Pt amounts.

The mathematical designs allow certain conclusions about the influence of the factors studied upon the course of the process of oxidation. The duration of treatment has the most significant effect upon the accumulation of cumene hydroperoxide under the conditions of investigation, in the presence and in the absence of platinum. The coefficient in front of the independent variable x_3 has the greatest value both in Eqs. (1) and (2).

We can judge the effect of platinum upon the oxidation of cumene to cumene hydroperoxide by comparing the coefficients in front of identical independent variables in Eqs. (1) and (2). On comparing the coefficients in front of x_1 in these two equations, the conclusion is drawn that the rise of temperature within the inverval chosen has a more favorable effect upon the accumulation of cumene hydroperoxide during oxidation in the presence of platinum [the value of the coefficient in front of x_1 in Eq. (1) is higher]. The analysis of the coefficients in front of the independent variable x_2 shows that the initiating action of the homogeneous catalyst is more markedly displayed in the absence of platinum.

The graphical expression of the results on the oxidation of raw material offers a better possibility for their discussion. The process of accumulation of cumene hydroperoxide as a function of the alteration of one of the independent variables with the values of the other two kept constant is of interest. For this purpose, one calculates the amount of cumene hydroperoxide obtained on oxidizing the raw material at definite values of the independent variables using Eqs. (1) and (2).

Figure 1 shows the concentration of cumene hydroperoxide accumulated in the oxidation process as a function of the treatment time at constant values of the initial content of hydroperoxide and temperature. The results obtained in the presence of platinum (the solid lines on the figures) are juxtaposed with the ones obtained in the absence of a catalyst (the dotted lines). The data presented show that the concentration of cumene hydroperoxide is a linear function of the contact time within the time interval chosen.

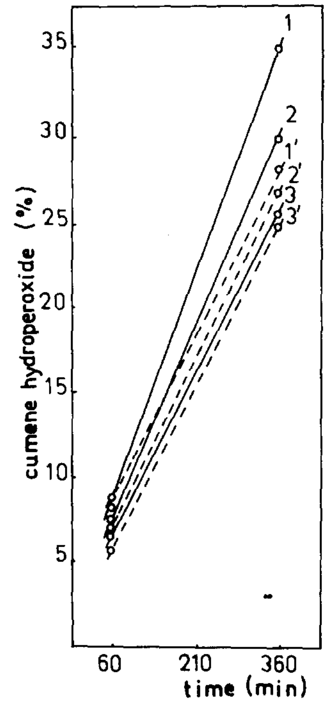

FIG. 1. Accumulation of cumene hydroperoxide in the oxidation of isopropylbenzene with air at a flow rate of 1.6×10^{-2} m^3/kg s as a function of the contact time; initial concentration of hydroperoxide 3.5% and temperature: 1–120, 2–115, 3–110°C. The solid lines, numbered without primes, refer to experiments made in the presence of platinum; the dotted lines, numbered with primes, refer to experiments made in the absence of a catalyst.

At the upper limit of the temperature interval, the slope of the straight lines expressing the increase of cumene hydroperoxide as a function of time is steeper for the experiments carried out in the presence of platinum. Consequently, the increase of treatment time has a favorable effect upon the accumulation of cumene hydroperoxide in the process of cumene oxidation in the presence of a catalyst.

The change of concentration of cumene hydroperoxide obtained during oxidation of isopropylbenzene with air as a function of the initial content of homogeneous initiator is shown in Fig. 2. This figure gives a better illustration of the catalytic action of platinum upon the process studied. The straight lines expressing the relationship in the presence of a catalyst have a smaller inclination

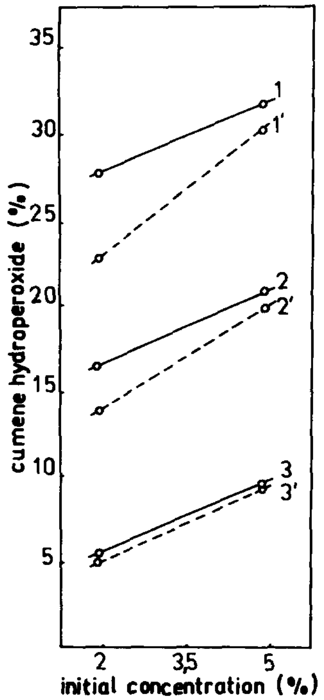

FIG. 2. Content of cumene hydroperoxide in the reaction medium as a function of the concentration of the hydroperoxide introduced beforehand in the isopropylbenzene; flow rate of the oxidizing air 1.6 × 10^{-2} m^3/kg s, temperature 115°C, and contact time: 1–360, 2–210, 3–60 min. The solid lines are results in the presence of platinum, the dotted lines in the absence of a catalyst.

than the ones concerning the experiments made in the absence of a metal. This shows that platinum has some hampering effect upon the action of the homogeneous initiator.

The influence of temperature upon the accumulation of cumene hydroperoxide in cumene oxidation is shown graphically in Fig. 3. It confirms the catalytic effect of platinum upon the process. It is evident that the rise of temperature favors more markedly the formation of cumene hydroperoxide in the presence of the catalyst studied. Platinum has no catalytic effect at the lower limit of the temperature interval chosen. This is in agreement with the literature data on the lack of a catalytic effect of platinum upon cumene oxidation at 90–100°C (*11*). The catalytic activity of platinum in our experiments is in agreement with the formation of $ROO^{\cdot}$ radicals by the decomposition of cumene hydroperoxide in the presence of Pt, cumene, and oxygen, observed by Casemier *et al.* (*11*). Under the conditions used in our experiments with relatively long chain length the reaction rate is approximately proportional to hydroperoxy radical concentration $[ROO^{\cdot}]$ (*9*):

$$\frac{d[ROOH]}{dt} \approx K[RH] \cdot [ROO^{\cdot}].$$

One can notice from Fig. 3 that the apparent activation energy seems to be bigger with Pt than without it. Although the aim of this work was not to investigate reaction mechanism, we give one example of an explanation to demonstrate that this is not a contradiction. It Pt is assumed to enhance initiation of radicals in parallel

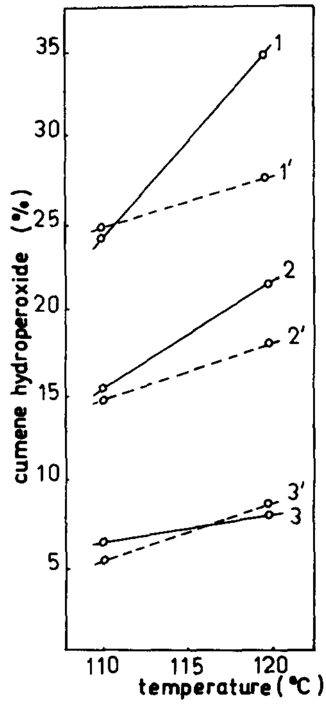

FIG. 3. The dependence of cumene hydroperoxide content on the temperature of isopropylbenzene oxidation at a flow rate of the oxidizing air of 1.6 × 10^{-2} m^3/kg s, initial concentration of hydroperoxide 3.5% and contact time: 1–360, 2–210, 3–60 min. The solid lines are results in the presence of platinum, the dotted lines in the absence of metal.

with noncatalyzed initiation, we have:

$$r_i = r_{i1} + r_{i2}$$

where r_{i1} is the noncatalyzed initiation rate and r_{i2} is the initiation rate caused by Pt. If the activation energy for the initiation caused by Pt, r_{i2}, is higher than for r_{i1}, the observed effect appears. In parallel reactions like these, the reaction with the lower activation energy predominates at low temperatures, while the reaction with higher activation energy predominates at higher temperatures. This is in line with our result that no effect of Pt was indicated at a temperature lower than 110°C.

From this work one can draw the conclusion that in the oxidation of cumene with air in the presence of cumene hydroperoxide as an initiator, platinum has a catalytic effect upon the process at a temperature higher than 110°C. This effect improved with increase of temperature and increase of treatment time. The role of cumene hydroperoxide as an initiator of cumene oxidation becomes less significant in the presence of platinum.

REFERENCES

1. Margolis, L. Ya., "Heterogeneous Catalytic Oxidation of Hydrocarbons." Khimiya, Leningrad, 1967.
2. Kruzhalov, B. D., and Golovanenko, B. I., "Copreparation of Phenol and Acetone." Goskhimizdat, Moscow, 1963.
3. Fortuin, J. P., and Watterman, W., *Chem. Eng. Sci.* **2**, 182, (1953).
4. Fortuin, J. P., Thesis, Technische Hogeschool Delft, 1952.
5. Lesczynski, Z., *Przem. Chem.* **43**, 255, 32 (1964).
6. Panayotova, E. N., Dissertation, VKhTI, Sofia, 1972.
7. Dimitrov, D. I., Panayotova, E. N., and Petkov, A. A., *Khim. Industriya* **43**, 4, 157 (1971) (Bulg.).
8. Panayotova, E. N., Dimitrov, D. I., Papazov, S. D., and Petkov, A. A., *Khim. Industriya* **44**, 3, 110 (1972) (Bulg.).
9. Emanuel, N. M., Denisov, E. T., and Mayzus, Z. K., "Chain Reactions of Hydrocarbon Oxidation in the Liquid Phase." Nauka, Moscow, 1965.
10. Van Ham, N. H. A., Nieuwenhuys, B. E., and Sachtler, W. M. H., *J. Catal.* **20**, 408 (1971).
11. Casemier, J. H. R., Nieuwenhuys, B. E., and Sachtler, W. M. H., *J. Catal.* **29**, 367 (1973).
12. Solomko, N. I., Tsepalov, V. F., and Yurzhenko, A. I., *Kinet. Catal.* **IX**, 4, 767 (1968).
13. Kulitskii, Z. I., Terman, L. I., Tsepalov, V. F., and Shlyapintoh, V. Ya., *Izv. AN USSR* 254 (1963).
14. Lea, C. H., *Proc. Roy. Soc. B* **108**, 175 (1931).
15. Ruzinov, L. P., "Statistical Methods of Optimization of Chemical Processes." Khimiya, Moscow, 1972.
16. Bozhanov, E. S., and Vuchkov, I. N., "Statistical Methods of Design and Optimization of Multifactor Subjects." Tekhnika, Sofia, 1973.
17. Adler, Yu. P., "Introduction to Experiment Design." Metalurgiya, Moscow, 1969.