Mechanism of the Silver-on-Silica Catalyzed Oxidation of Cumene in the Liquid Phase

INTRODUCTION

Recently Van Ham, Nieuwenhuys and Sachtler (*1*) reported that silver-on-silica acts as a catalyst for the liquid-phase oxidation of cumene to cumyl hydroperoxide. Following De Boer (*2*), they ascribed the catalytic effect to the unique capacity of silver to chemisorb oxygen in a nondissociative manner (mechanism I):

$$[\mathrm{Ag}] + \mathrm{O_2} \rightarrow [\mathrm{Ag}]\mathrm{O_2}^-, \qquad (1)$$

$$[\mathrm{Ag}]\mathrm{O_2}^- + \mathrm{RH} \rightarrow [\mathrm{Ag}] + \mathrm{ROOH}, \qquad (2)$$

with

$$\mathrm{R} = \mathrm{C_6H_5(CH_3)_2C}.$$

The alternative radical-chain mechanism, in which silver acts by decomposing hydroperoxide into chain-initiating radicals was considered less likely by them.

In this paper we present evidence favoring the view that the silver-catalyzed oxidation of cumene in the liquid phase involves a radical-chain oxidation initiated by the supported silver (mechanism II).

The catalyzed decomposition of ROOH may lead to a variety of radical and nonradical products. Denoting by X· those radicals which are able to initiate a chain reaction, mechanism II comprises:

$$\left.\begin{array}{l} \mathrm{ROOH} \xrightarrow{\mathrm{Ag}} \mathrm{X}\cdot + \text{other products} \\ \mathrm{X}\cdot + \mathrm{RH} \rightarrow \mathrm{R}\cdot + \mathrm{XH} \end{array}\right\} \begin{array}{l}\text{initiation}\\ (d\mathrm{R}\cdot/dt = R_i)\end{array} \qquad \begin{array}{r}(3)\\(4)\end{array}$$

$$\mathrm{R}\cdot + \mathrm{O_2} \xrightarrow{\text{fast}} \mathrm{RO_2}\cdot, \qquad (5)$$

$$\mathrm{RO_2}\cdot + \mathrm{RH} \xrightarrow{k_p} \mathrm{RO_2H} + \mathrm{R}\cdot, \qquad (6)$$

$$2\mathrm{RO_2}\cdot \xrightarrow{2k_t} \text{non-radical products.} \qquad (7)$$

This evidence was obtained by investigating the following aspects: (a) kinetics of the autoxidation; (b) role of the hydroperoxide in the autoxidation; (c) inhibition by 2,6-di-*tert*-butyl-4-methylphenol; (d) kinetics of hydroperoxide decomposition.

The 5% (w/w) $\mathrm{Ag/SiO_2}$ catalyst was prepared by impregnating Davison-grade $\mathrm{SiO_2}$ 952 (av pore diameter 2 μm, specific surface area 350 $\mathrm{m^2\ g^{-1}}$, bulk volume 1.70 $\mathrm{ml\ g^{-1}}$) with an aqueous solution of silver nitrate for 15 min, drying at 120°C and reduction in a flow of hydrogen for 16 hr at 200°C.

The experiments were carried out at atmospheric pressure in a 100-ml Pyrex vessel provided with a magnetic stirrer and a side arm with a stopcock. The vessel was connected to a 100-ml gas buret; both were thermostated. In all experiments a weighed amount of the catalyst was placed in the reaction vessel and, after the air had been replaced by oxygen, 10 ml of freshly distilled cumene was introduced through the side arm from a syringe. Then the vessel was closed, and the uptake of oxygen was measured. The oxygen uptake was corrected for oxygen formed in the termination reaction (7) assuming that in this reaction 1 mole of oxygen is formed. 2,6-Di-*tert*-butyl-4-methylphenol was added as a freshly prepared solution in cumene with a microsyringe through the side arm. Hydroperoxide concentrations were measured by iodine titration of 1-ml samples of the reaction mixture.

A. KINETICS OF THE AUTOXIDATION

In a number of cumene oxidations at 60°C* with Ag-on-$\mathrm{SiO_2}$ the rate of oxygen uptake ($v = d\mathrm{O_2}/dt$) was measured as a function of the amount of catalyst. The reactions started within a few minutes (except for one case, see next section). As the activity of the catalyst dropped slowly

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* The results of oxidations at 30, 60 and 80°C gave an apparent activation energy of 2.3 kJ $\mathrm{mol^{-1}}$, in good agreement with the value of 2.4 kJ $\mathrm{mol^{-1}}$ found by Van Ham, Nieuwenhuys and Sachtler (*1*) for the temperature region of 80–110°C.

during the reaction we used the rates after the consumption of 1 mmol of O_2/10 ml of cumene.

Figure 1 shows that the rate of oxygen uptake is proportional to the square root of the amount of catalyst used. This is in accordance with the rate expression for autoxidation by a radical-chain process (mechanism II) (4):

$$v = dO_2/dt = k_p \cdot [\text{cumene}] \cdot R_i^{1/2} \cdot (2k_t)^{-1/2} \quad (8)$$

if we assume that R_i, the rate of generation of free radicals, is proportional to the amount of catalyst.**

That R_i is indeed proportional to the amount of catalyst was confirmed by direct measurements of R_i in inhibition experiments (see Sect. C). In accordance with this, a plot of v^2 versus R_i gives a straight line (Fig. 2). From the slope of this line the value of $k_p(2k_t)^{-1/2}$ was calculated to be 32×10^{-4} $l^{1/2}$ $mol^{-1/2}$ $s^{-1/2}$. This is in excellent agreement with 35.6×10^{-4} $l^{1/2}$ $mol^{-1/2}$ $s^{-1/2}$ as obtained by Sérée de Roch (*5*) in the azobisisobutyronitrile-initiated autoxidation of cumene at 60°C. This provides very strong evidence that the silver-catalyzed oxidation involves a normal free radical-chain process.

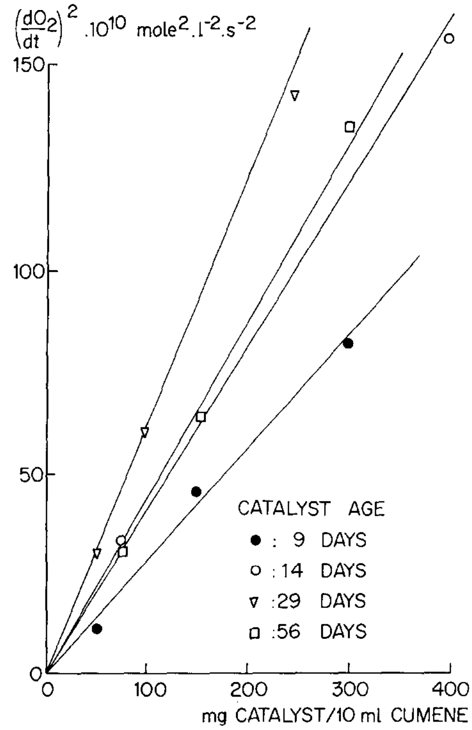

FIG. 1. Rate of oxygen uptake in the oxidation of cumene at 60°C with 5% Ag-on-SiO₂ as catalyst.

It should be noted that the catalyst, on storage at room temperature in contact with "laboratory air," showed an increase in activity (Fig. 1), until after 30 days a maximum was reached. The oxidation mechanism does not alter on aging, as is clearly shown by the fact that, irrespective of their age, the catalysts all give points on the same straight line in the plot of v^2 versus R_i (Fig. 2).

B. Role of the Hydroperoxide

Whereas with freshly distilled cumene the reactions started within 2 min when moderate amounts of catalyst were used (up to 400 mg/10 ml of cumene), induction periods of 0.5 hr and longer occurred with larger amounts of catalyst. The same effect was obtained when, for example, 1000 mg of pure silica were added to 50 mg of the catalyst (all per 10 ml of cumene). In all these cases the reactions started immediately when as little as 0.05 mmol of hydroperoxide was added.

This observation clearly demonstrates

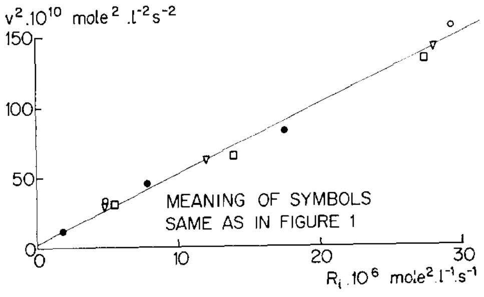

FIG. 2. Rate of oxygen uptake vs rate of free-radical generation in the oxidation of cumene at 60°C with 5% Ag-on-SiO₂ as catalyst.

** At 60°C, the uncatalyzed cumene oxidation is immeasurably slow, R_i being about 10^{-8} mol $l^{-1}s^{-1}$ at a hydroperoxide concentration of 0.1 mol l^{-1} (*3*).

the important role of the hydroperoxide. The occurrence of long induction periods in the presence of large quantities of silica (as catalyst or as pure silica) is believed to be caused by physical adsorption of the hydroperoxide on silica. When the concentration of "free" hydroperoxide (present or added) is above a certain level, the induction period becomes negligibly small.

Mechanism I can in no way account for these phenomena.

C. Inhibition by Hindered Phenols

Addition of 2,6-di-*tert*-butyl-4-methylphenol (inh) to the oxidizing system was found to stop the oxygen uptake for a certain time (inhibition period, t_{inh}). In accordance with the radical-chain autoxidation mechanism II, which requires that $t_{\mathrm{inh}} = 2[\mathrm{inh}]/R_i$, t_{inh} was found to be proportional to the amount of inhibitor added at constant catalyst concentration. R_i, as calculated from this equation, was proportional to the amount of catalyst (Fig. 3).

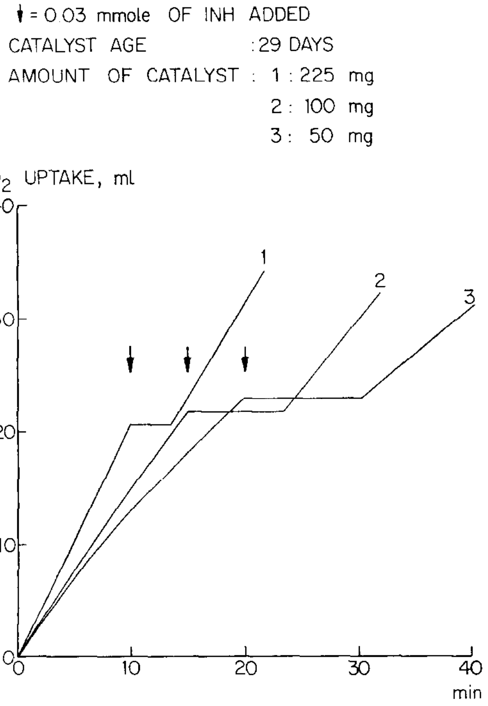

Fig. 3. Effect of 2,6-di-*tert*-butyl-4-methylphenol (inh) on the oxidation of cumene (10 ml) at 60°C with 5% Ag-on-SiO_2 as catalyst.

The results of these inhibition experiments therefore fully support mechanism II. Mechanism I would require a most fortuitous coincidence of rate and inhibitor-adsorption constants to explain quantitatively the observed induction periods.

D. Kinetics of the Hydroperoxide Decomposition

We studied the decomposition of *tert*-butyl hydroperoxide (whose chemical behavior is similar to that of cumyl hydroperoxide) in the presence of the Ag-on-SiO_2 catalyst. The decomposition reactions were carried out in a nitrogen atmosphere with 10 ml of a 1 M solution in chlorobenzene as well as in cumene and 100 mg Ag-on-SiO_2.

In chlorobenzene the following phenomena were observed: (a) addition of an extra amount of hydroperoxide did not alter the rate of decomposition; (b) addition of another 100 mg of the catalyst doubled the rate of decomposition; (c) oxygen was evolved in an amount of about 0.9 mmol/2 mmol of hydroperoxide decomposed.

This means that the decomposition of hydroperoxide qualitatively parallels the oxidation phenomena. The third fact is in quantitative agreement with an induced radical-chain decomposition mechanism with a chain length of about 10 (*6*).

In cumene as the solvent the rate of decomposition was much lower than in chlorobenzene (1.4×10^{-5} versus 1.0×10^{-4} mol l^{-1} s^{-1}), because part of the peroxy radicals reacted with cumene molecules.

In both solvents the addition of 2,6-di-*tert*-butyl-4-methylphenol stopped the oxygen evolution for a certain period, from which R_i was calculated to be 8.0×10^{-6} mol l^{-1} s^{-1} in chlorobenzene and 6.7×10^{-6} mol l^{-1} s^{-1} in cumene. These values, compared with the value of R_i measured in the autoxidation of cumene with the same amount of catalyst (9.0×10^{-6} mol l^{-1} s^{-1}), clearly show the quantitative agreement between the catalytic activity of silver in the cumene oxidation and the hydroperoxide decomposition.

From the present results we conclude that the catalytic activity of silver-on-silica is mainly if not entirely due to its capability of decomposing hydroperoxides into chain-initiating radicals.

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Koechlinite. An Active, Selective and Sensitive Acrylonitrile Catalyst

In a previous paper (*1*) we reported on the preparation of bismuth molybdates and in particular on the preparation of Bi_2MoO_6, koechlinite, which was a highly active and selective catalyst for 1-butene oxidation. The latter was obtained from a slurry reaction between basic bismuth nitrate (bismuthyl nitrate) and molybdic acid in boiling water. The inorganic synthesis was proved to proceed according the following equation:

$$2(BiO)NO_3 + H_2MoO_4 \rightarrow (BiO)_2MoO_4 + 2HNO_3 \quad (1)$$

During 20 hr stirring and boiling of the slurry, the pH was found to decrease from 7 to 2. After filtration, drying and calcination at 500°C a sample with an X-ray pattern was obtained similar to that of the mineral koechlinite. This catalyst (selective for 1-butene oxidation), which was discussed during a recent A.C.S. Meeting (Boston, April 9–14, 1972), was not very selective for ammoxidation of propene. The yield of acrylonitrile was found to be about 45% and in particular ammonia combustion was high on this catalyst. To explain this behavior we have to consider that recently Bi_2O_3 was reported as a catalyst for ammonia combustion (*2*). One possibility therefore is that our prepared koechlinite was not completely pure. It might have contained small amounts of Bi_2O_3, difficult to detect by X-ray measurements. We decided therefore to restudy our method of preparation with a view to improving it, and to examine two important aspects: (1) by eliminating the possibility that some Bi_2O_3 could be present to see whether this leads to a good acrylonitril catalyst, (2) the aspect of olefin adsorptions. The koechlinite phase prepared as described earlier (*1*) showed olefin adsorptions of the order of 0.12 $cm^3\ g^{-1}$ catalyst (*3*). This amount is lower than on a commercial Bi/Mo catalyst (US P 2.904.580) where silica as a carrier was used. Considering the 50% silica content, this number becomes 0.50 $cm^3\ g^{-1}$ Bi/Mo compounds. Since the carrier interferes in the characterization of the physical properties of the active component and creates uncertainty, we were interested in preparing a pure koechlinite phase with a comparable or even higher olefin adsorption. Such a material could then be valuable in solving the difficult problems in ESR and infrared adsorption measurements.