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The Oxidation of Cumene and the Decomposition of Cumene Hydroperoxide on Silver, Copper, and Platinum

J. H. R. CASEMIER, B. E. NIEUWENHUYS,
AND W. M. H. SACHTLER

Gorlaeus Laboratoria, Rijksuniversiteit Leiden, Netherlands

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Cumene hydroperoxide dissolved in dodecane is rapidly decomposed by platinum and appreciably by silica gel or by silver in the absence of gaseous oxygen, but virtually no decomposition is observed with unsupported silver in an oxygen atmosphere. The oxidation of cumene to cumene hydroperoxide shows a completely different picture; this oxidation is strongly catalyzed by silver, whereas copper, gold and platinum do not catalyze it. In the reaction mixture of cumene oxidation with silver a free radical (presumably ROO.) is detected by EPR spectroscopy. The results are interpreted by assuming a reaction mechanism in which diatomic oxygen adsorbed on the silver surface is essential.

INTRODUCTION

In a previous paper (*1*) we reported results on the oxidation of cumene to cumene hydroperoxide in the presence of metallic silver, gold, copper and silver–gold alloys. The prominent results were:

1. a drastic reduction by silver of the induction period, characteristic of the free radical chain reaction in a glass vessel;
2. a large increase of the steady-state oxidation rate by silver, the increase being proportional to its surface area;
3. an activation energy of 11 kcal/mole for the reaction on silver compared to 17 kcal/mole for the noncatalyzed reaction;
4. a virtual absence of these effects for copper and gold;
5. an additional increase of the oxidation rate by using an alloy of silver with 5 at% gold instead of pure silver, whereas pure gold does not catalyze the oxidation of cumene.

These results were consistent with a mechanism proposed by De Boer (*2*):

$$[Ag] + O_2 \rightarrow [Ag^+]O_2.^-$$

$$[Ag^+]O_2.^- + RH \rightarrow [Ag] + ROOH \qquad \text{with } R = C_6H_5C(CH_3)_2,$$

in which in addition to the generally accepted chemisorbed oxygen atoms the presence of undissociated diatomic oxygen was postulated on the silver surface, as first suggested by Worbs (*3*) in 1942.

In view of the unique role of silver in oxidation catalysis (*4*), in particular its high selectivity in the oxidation of ethene to ethene oxide, many techniques have been used to prove the existence of diatomic adsorbed oxygen. The results obtained with infrared spectroscopy by Gereĭ, Kholyavenko, and Rubanik (*5*), with secondary ion emission by Honig (*6*) and by Fogel *et al.* (*7*), and with chemical methods by Herzog (*8*), who studied the reaction of ethene with oxygen and nitrous oxide, and by Imre (*9, 10*) who studied the oxidation of ethene and carbon monoxide, make the presence of nondissociated adsorbed oxygen on silver reasonably certain. The decisive experimental evidence has been furnished with infrared spectroscopy by Kilty, Rol, and Sachtler (*11*). They found that the band ascribed to an adsorbed –O–O– species did indeed split into three bands when $^{16}O_2$ was replaced by the isotopic mixture $^{16}O_2 + {}^{16}O^{18}O + {}^{18}O_2$.

As we mentioned, however, in our previous paper (*1*) the mechanism of De Boer is not the only one consistent with our results. The oxidation of cumene might, for instance, also be a radical chain reaction, the radicals being formed by reaction of cumene with the oxygen-covered silver surface, as suggested by Fortuin (*12*) or by a silver-catalyzed decomposition of cumene hydroperoxide present as an impurity in cumene. We have therefore studied the catalytic behavior of silver and other metals in decomposing cumene hydroperoxide dissolved in dodecane, a solvent which is chemically inert with respect to the catalysts. The results presented include also electron paramagnetic resonance data of free radicals detected during the silver-catalyzed oxidation.

EXPERIMENTAL METHODS

The decomposition of cumene hydroperoxide and the oxidation of cumene to cumene hydroperoxide were followed by peroxide titration with NaI and $Na_2S_2O_3$ solutions, by glc analysis and by measuring the uptake of oxygen with the aid of a gas buret. The formation of free radicals in the solution was studied by EPR measurements (Varian E-3 EPR spectrometer). Unsupported silver, copper and platinum were prepared by dissolving $AgNO_3$, $Cu(NO_3)_2$ and $PtCl_4$ in water and subsequent reduction by sodium borohydride. The copper catalyst was subsequently reduced with hydrogen at 200–250°C. Cumene hydroperoxide was prepared according to the method described by Hock and Lang (*13*). Most oxidation and decomposition experiments were performed at 90–100°C, with either dodecane or cumene as solvent. Where desired, oxygen was continually passed through the solution.

RESULTS

We describe in this section a number of relevant experiments, stating at the beginning of each paragraph the composition of the reaction mixture. To simplify matters the symbols RH and ROOH are used for cumene and cumene hydroperoxide, respectively, and the results are numbered, continuing the list given in the Introduction. The first result in this section, therefore, is No. 6.

6. ROOH + $C_{12}H_{26}$ + O_2 + SiO_2. Whereas a solution of cumene hydroperoxide in dodecane is very stable, addition of SiO_2 or Al_2O_3 causes a fast decomposition of cumene hydroperoxide at 92°C as is shown in Fig. 1 for SiO_2. The main decomposition products are acetophenone, α,α-dimethylphenylcarbinol and phenol, as determined by GLC. SiO_2 does not catalyze the oxidation of cumene.

7. RH + ROOH + $C_{12}H_{26}$ + O_2 + Ag. Figure 2 shows that the oxidation rate of cumene dissolved in dodecane and containing a small amount of cumene hydroperoxide is strongly catalyzed by unsupported silver, in agreement with our previous results for Ag/SiO_2 catalysts. No decomposition of cumene hydroperoxide is observable under these conditions, as is proven explicitly in the next experiment.

8. ROOH + $C_{12}H_{26}$ + O_2 + Ag. Decomposition of cumene hydroperoxide in dodecane in an oxygen atmosphere is not appreciably catalyzed by unsupported silver. A small decomposition immediately after addition of silver is probably caused by impurities. No additional decomposition of cumene hydroperoxide is detectable by titration after 30 min. Addition of more silver to the solution does not cause a further decrease of the cumene hydroperoxide concentration either (Fig. 3).

9. ROOH + $C_{12}H_{26}$ + N_2 + Ag. Replacing oxygen by nitrogen in the experiments

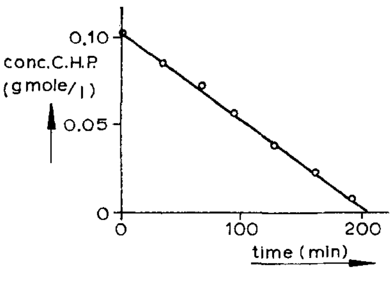

FIG. 1. Decomposition of cumene hydroperoxide dissolved in dodecane at 90°C by 1 g SiO_2 in an oxygen atmosphere.

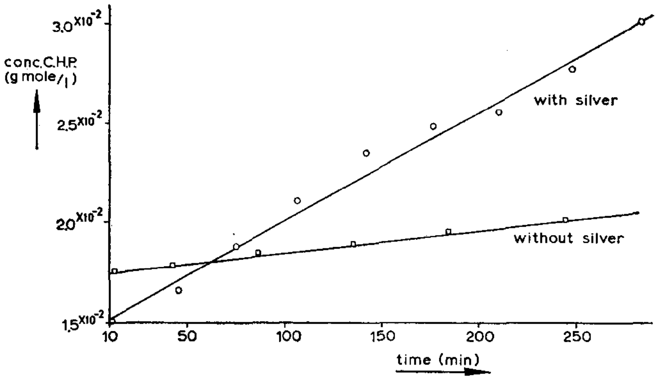

FIG. 2. Oxidation of cumene dissolved in dodecane with and without silver at 90°C.

just mentioned has a remarkable result; in a nitrogen atmosphere a fast decomposition of cumene hydroperoxide takes place as shown in Fig. 4.

10. RH + ROOH + O_2. In the presence of cumene hydroperoxide, cumene is oxidized by oxygen at room temperature, even in the absence of a heterogeneous catalyst. Although this reaction is generally assumed to be of a radical chain type, no radicals are detected by electron paramagnetic resonance between 20 and 150°C. The radical concentration during the homogeneous oxidation appears to be too small to be observable with our experimental techniques (less than 10^{-6}–10^{-7} mole/liter).

11. RH + ROOH + O_2 + Ag. a. When silver is added at room temperature to the mixture of the previous run, a small EPR signal appears immediately near 3310 G. This signal is a wide singlet with a ΔH_{value} of 18 G and a g-factor of 2.016. For a readily observable signal it is necessary to use fivefold the amount of silver normally used in the oxidation experiments. The signal decreases until a steady-state value is reached. Raising the temperature to 100°C causes only a small enhancement of the signal and does not give other peaks. The peak intensity is independent of the original cumene hydroperoxide concentration. Adding more cumene hydroperoxide does not change the steady-state signal. The signal increases with the amount of silver.

b. Above 150°C the 3310 G signal disappears completely; upon lowering the temperature the signal does not return. Titration shows that most of the cumene hydroperoxide has been decomposed. The GLC analysis shows the presence of α,α-dimethylphenylcarbinol, acetophenone, phe-

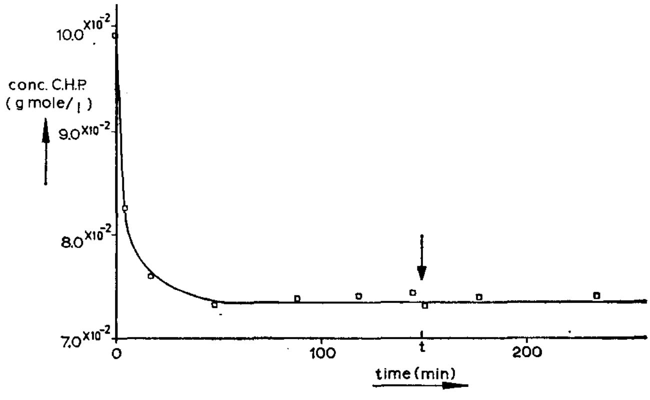

FIG. 3. Decomposition of cumene hydroperoxide dissolved in dodecane at 90°C by 1 g silver. An additional amount of 1 g silver is added at time t.

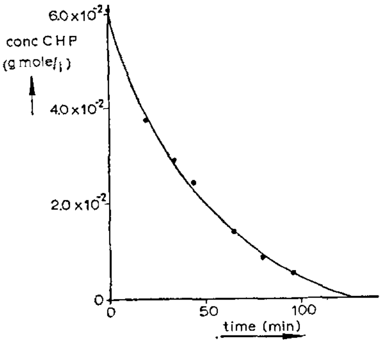

FIG. 4. Decomposition of cumene hydroperoxide dissolved in dodecane at 90°C by silver in a nitrogen atmosphere.

nol and other decomposition products of cumene hydroperoxide.

12. RH + ROOH + N_2 + Ag. If oxygen is replaced by nitrogen the signal described in (11) disappears completely.

13. RH + ROOH + O_2 + Cu. With copper a very weak signal is observed near 3335 G, both in an oxygen and in a nitrogen atmosphere. The oxidation rate of cumene is hardly influenced by the presence of copper. Cumene hydroperoxide is not decomposed on copper.

14. RH + ROOH + O_2 + Pt. In the presence of unsupported platinum, cumene hydroperoxide dissolved in cumene is rapidly decomposed. EPR measurements show an intense, broad EPR peak immediately after addition of platinum to the cumene hydroperoxide solution in an oxygen atmosphere (Fig. 5). The EPR signal decreases with time and splits into two peaks, one near 3310 G which is completely comparable to the signal found with silver, while the second peak near 3335 G is equal to that which was found with copper. When after some time all the cumene hydroperoxide has been decomposed, the peak near 3310 G disappears but the peak near 3335 G persists. The GLC analysis shows the presence of α,α-dimethylphenylcarbinol, acetophenone and phenol. No increase in the oxidation rate of cumene over the noncatalyzed reaction could be detected in the presence of platinum.

15. RH + ROOH + N_2 + Pt. In a nitro-

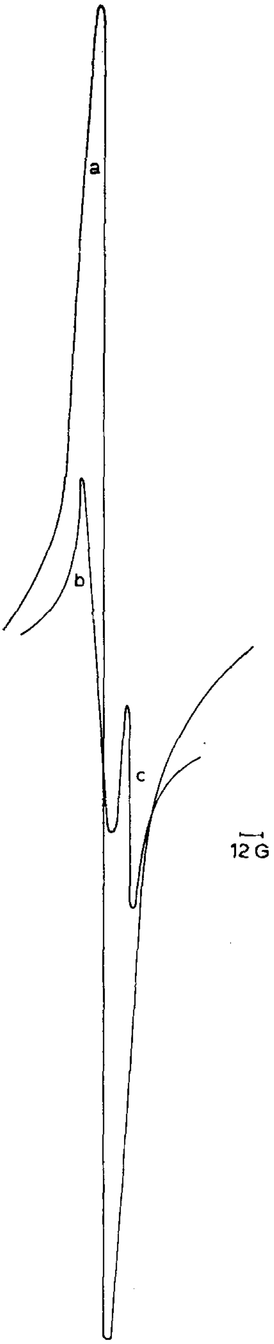

FIG. 5. EPR signal of the system RH + ROOH + O_2 + Pt. The initial EPR signal (a) decreases with time and splits into two peaks, (b) at 3310 G and (c) at 3335 G. After 10 min peak (b) disappears completely.

gen atmosphere only the 3335 G signal is observable, irrespective of the presence of cumene hydroperoxide.

DISCUSSION

The present results show as a new fact that a radical species with an EPR signal at 3310 G and characterized by a g-factor of 2.016 and a ΔH of 18 G is present in the reaction mixture of the silver-catalyzed cumene oxidation. This signal is absent if oxygen is replaced by nitrogen. The species responsible for this signal, therefore, appears to be a radical containing oxygen. The signal is virtually identical with that found by Lebedev (g-factor $= 2.015 \pm 0.001$, $\Delta H = 18 \pm 2$ G) and identified as due to the ROO. radical. Also an inspection of other possible candidates confirms that the ROO. radical is most likely to be responsible for this signal. The EPR signal shows that the silver-catalyzed oxidation must be at least partly a radical reaction in the solution. The original version of the mechanism of De Boer (*2*) mentioned in the Introduction appears to be not valid.

The signal at 3335 G which was never observed in reaction mixtures with silver catalysts is less clearly assigned. It might be due to a by-product or an impurity of the platinum catalyzed decomposition reaction. In our further discussion we shall therefore not make use of this information.

We may consider two different types of reaction mechanism, both involving the radical species ROO. in the solution.

I. Mechanisms in which silver initiates the oxidation by catalyzing the decomposition of cumene hydroperoxide, present as an impurity in cumene, into free radicals, e.g.,

$$\left.\begin{array}{ll} \text{a.} & \mathrm{ROOH} \xrightarrow{\mathrm{Ag}} \mathrm{RO.} + \mathrm{OH.} \\ \text{b.} & \mathrm{OH.} + \mathrm{RH} \rightarrow \mathrm{H_2O} + \mathrm{R.} \\ & \mathrm{RO.} + \mathrm{RH} \rightarrow \mathrm{ROH} + \mathrm{R.} \end{array}\right\} \text{initiation,}$$

$$\left.\begin{array}{ll} \text{c.} & \mathrm{R.\,O_2} + \mathrm{RH} \xrightarrow{\text{fast}} {}^{\cdot}\mathrm{ROO} \\ \text{d.} & \mathrm{ROO.} + \mathrm{RH} \rightarrow \mathrm{ROOH} + \mathrm{R.} \end{array}\right\} \text{propagation,}$$

$$\text{e. } 2\mathrm{ROO.} \rightarrow \text{nonradical product} \quad \text{termination.}$$

In this scheme the silver-catalyzed reaction is essentially a free radical chain reaction in solution; the role of the silver surface is restricted to the initiation of free radicals. The propagation steps (c and d) and the termination step (e) are the same in the cumene oxidation reaction without silver.

The essential element in this mechanism is that initiation proceeds from a formation of *free radicals*. Variations of (a) and (b) are possible. The decomposition of cumene hydroperoxide might, for example, occur in a manner similar to the decomposition mechanism in the presence of some metal ions (*15*).

II. Mechanisms in which the catalytic effect of silver is related with the rather special capacity of silver to chemisorb oxygen in a nondissociative manner (*11*). Reaction of cumene oxidation may be visualized, for instance, in the following way:

$$\begin{array}{ll} \text{a.} & [\mathrm{Ag}] + \mathrm{O_2} \rightarrow [\mathrm{Ag^+}]\mathrm{OO.}^{-}_{\mathrm{ads}} \end{array} \qquad \text{initiation,}$$

$$\left.\begin{array}{ll} \text{b.} & [\mathrm{Ag^+}]\mathrm{OO.}^{-}_{\mathrm{ads}} + \mathrm{RH} \rightarrow [\mathrm{Ag^+}]\mathrm{OOH^-} + \mathrm{R.} \\ \text{c.} & \mathrm{R.} + \mathrm{O_2} \xrightarrow{\text{fast}} \mathrm{ROO.} \\ \text{d.} & [\mathrm{Ag^+}]\mathrm{OOH^-} + \mathrm{ROO.} \rightarrow [\mathrm{Ag^+}]\mathrm{OO.}^{-}_{\mathrm{ads}} + \mathrm{ROOH} \end{array}\right\} \text{propagation,}$$

$$\text{e. } 2\mathrm{ROO.} \rightarrow \text{nonradical products} \qquad \text{termination.}$$

In this mechanism no impurities need to be postulated, since the diatomic oxygen adsorbed on the silver surface acts as an initiator. For convenience this adsorbed species has been written as a superoxide ion although its actual charge may differ from -1. In the sequence a–e the reaction is assumed to be mainly a heterogeneous process on the silver surface, but the radical ROO. will also diffuse to the liquid phase. Variations of this reaction scheme are possible. For instance, silver covered with diatomic oxygen might play a less essential role in the propagation step, in which case its main function would be the formation in the initiation step of free radicals, which react then further in solution. This may be written as:

$$\left.\begin{array}{l}\text{a. } [\mathrm{Ag}] + \mathrm{O_2} \rightarrow [\mathrm{Ag^+}]\mathrm{OO.}_{\mathrm{ads}}^{-} \\ \text{b. } [\mathrm{Ag^+}]\mathrm{OO.}_{\mathrm{ads}}^{-} + \mathrm{RH} \rightarrow [\mathrm{Ag^+}]\mathrm{OOH^-} + \mathrm{R.}\end{array}\right\}\text{ initiation,}$$

$$\left.\begin{array}{l}\text{c. } \mathrm{R.} + \mathrm{O_2}^- \xrightarrow{\text{fast}} \mathrm{ROO.} \\ \text{d. } \mathrm{ROO.} + \mathrm{RH} \rightarrow \mathrm{ROOH} + \mathrm{R.}\end{array}\right\}\text{ propagation,}$$

$$\left.\begin{array}{l}\text{e. } \mathrm{AgOOH} + \mathrm{ROO.} \rightarrow \mathrm{AgOO.} + \mathrm{ROOH} \\ \text{or} \\ \text{e}' \ \mathrm{AgOOH} + \mathrm{R.} \rightarrow \mathrm{AgOO.} + \mathrm{RH}\end{array}\right\}\text{ reactivation of the silver surface,}$$

$$\text{f. } 2\mathrm{ROO.} \rightarrow \text{nonradical product} \qquad \text{termination.}$$

We have also no reasons to exclude other variations of these mechanisms, e.g., a mechanism where the oxygen molecule required in step (c) is first adsorbed on a silver site adjacent to that used in (a) and (b).

All reaction mechanisms of group II have one essential common element: the role of silver in cumene oxidation is connected with diatomic adsorbed oxygen on the silver surface which is active in the initiation and perhaps also in the propagation steps of a radical reaction. The chain may be terminated by a reaction of two radicals or by a deactivation of the oxygen-covered silver with contaminants originating from side reactions.

All mechanisms discussed so far are in line with the three remarkable observations of our previous and our present article: (a) silver strongly reduces the induction period of cumene oxidation; (b) silver increases the steady-state rate of cumene oxidation, and (c) in the presence of cumene and oxygen, silver increases the steady-state concentration of a stable radical characterized by an EPR signal at 3310 G, ascribed to the ROO. radical.

A decision between the two groups of mechanisms requires a comparison of the activity of various catalysts to decompose cumene hydroperoxide with their activity to oxidize cumene. This comparison is somewhat complicated by the existence of more than one decomposition mechanism. Besides decomposition into free radicals a heterolytic mechanism must be visualized.

In our experiments with SiO_2 and Al_2O_3 (Expt 6) and with silver at high temperature (Expt 11b), the presence of phenol, as detected by GLC analysis, shows that decomposition can at least partly occur via a nonfree radical mechanism. Phenol acts as an oxidation inhibitor by interfering with the radicals in the propagation steps, resulting in rather unreactive radicals. The disappearance of the 3310 G signal in Expt 11b is possibly caused by this phenol inhibition.

It is relevant, however, that in the decomposition of cumene hydroperoxide on platinum a free radical is detected by its EPR signal of 3310 G. This evidence strongly suggests that decomposition on platinum proceeds to a significant extent via a free radical mechanism. This reaction is, however, accompanied by a heterolytic decomposition as evidenced by the presence of some phenol.

Confronting the experimental evidence now available with the two basic mechanisms under discussion, it appears that some of the present results cannot easily be understood with mechanism I. If this mechanism were correct a close relation between the activities of a catalyst to decompose cumene hydroperoxide into free radicals and to oxidize cumene would have to be expected. The results clearly do not support such a relation. Although platinum efficiently catalyzes the decomposition of cumene hydroperoxide into free radicals detected by EPR, we have been unable to detect a catalyzing effect of platinum on the oxidation of cumene. Copper and gold neither catalyze the decomposition of cumene hydroperoxide nor its formation from cumene and oxygen. Silver, on the other hand, is the most efficient metal catalyst for the oxidation of cumene to cumene hydroperoxide in the presence of molecular oxygen. However, the unique behavior of metallic silver and silver–gold alloys can easily be understood in terms of mechanism II based on *the adsorption of oxygen on silver in a form which is con-*

ventionally described as superoxide ion (11) (although its actual charge may be different from −1). Although we cannot exclude, of course, that mechanism I provides a side path to the main reaction, we feel that all attempts to disregard the established existence of diatomic oxygen on silver fail to explain the unique catalytic activity of silver and silver–gold alloys in the oxidation of cumene to cumene hydroperoxide.

CONCLUSION

A reaction mechanism is proposed for the oxidation of cumene to cumene hydroperoxide in the presence of silver or silver–gold alloys. It is found in agreement with the experimental data both of the previous and present article and it implies chemisorbed superoxide ions as well as free radicals in the solution. It relates the unique ability of silver and silver–gold alloys to catalyze the oxidation of cumene to cumene hydroperoxide with the proven ability of silver and silver–gold alloys to chemisorb oxygen nondissociatively, whereas oxygen adsorption on all other metal catalysts is predominantly dissociative.

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