Tetrahedron. Vol. 31, pp. 2841 to 2844. Pergamon Press 1975. Printed in Great Britain

PRO-OXIDANT ACTION OF SULFUR COMPOUNDS

CATALYSIS OF AUTOXIDATION BY ONIUM SALTS

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(*Received in UK* 16 *June* 1975; *Accepted for publication* 23 *June* 1975)

Abstract—It is shown that the initiation of the autoxidation of cumene by triphenylsulfonium salts is due not to oxygen activation, as stated in the literature, but to a sulfonium-catalysed homolytic cleavage of cumene hydroperoxide. The activity of triphenylsulfonium chloride is considerably enhanced by addition of solid calcium carbonate, which effect is attributed to the removal of chloride ions. In keeping with this, triphenylsulfonium hydroxide was found to display an even higher activity.

INTRODUCTION

The activation of molecular oxygen is of great importance in oxidation chemistry.[1] In the literature,[1-12] two general mechanisms can be found:

(I) $O_2 + cat \rightarrow O_2...cat$
$O_2...cat + RH \rightarrow ROOH + cat.$

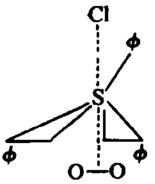
(II) $O_2 + cat \rightarrow O_2...cat$
$O_2...cat + RH \rightarrow R\cdot + \cdot O_2H + cat.$

Initially, mechanism I, which proceeds via insertion of activated oxygen into the R–H bond, was claimed to be operative in the silver-on-silica-catalysed oxidation of cumene,[2] in the $(Ph_3P)_4Pd$-catalysed liquid-phase autoxidation of cumene[3] and in the iridium- and rhodium-catalysed oxidations of cyclohexene.[4] However, later on these claims were found to be incorrect[13-16] and the above oxidations were all shown to proceed via the well-known[16,17] transition-metal-catalysed homolysis of hydroperoxides (mechanism III).

(III) $ROOH \rightarrow RO\cdot + OH\cdot$
$RO\cdot(OH\cdot) + RH \rightarrow ROH(H_2O) + R\cdot$
$R\cdot + O_2 \rightarrow RO_2\cdot$
$RO_2\cdot + RH \rightarrow ROOH + R\cdot$

Mechanism II, according to which the activated oxygen abstracts an H atom from the organic substrate with release of a hydroperoxy radical and regeneration of the catalyst, was proposed by Ohkubo *et al.*[18-30] for the oxidation of cumene catalysed by onium compounds. This mechanism occupies a position between mechanisms I and III, because the oxygen activation takes place only in the initiation step, the propagation being the classical radical chain process.

According to Ohkubo *et al.*,[20] sulfonium compounds are the most active onium-type oxidation catalysts. These workers propose an oxygen-activation mechanism based upon d-orbital participation of the sulfonium S atom, the active species being



Their proposal was substantiated by the results of UV measurements[26,30] of the proposed sulfonium oxygen complex and by ASMO–SCF calculations.[25,27,29,30]

Several inconsistencies in their reported results,[20-23,28] which suggested the occurrence of a normal radical-type initiation (mechanism III), prompted us to re-investigate the mechanism of the initiation effected by these remarkable catalysts.

RESULTS

Autoxidation of cumene, carefully freed from hydroperoxides,† showed, at 80°, an induction period of 102 min. In the presence of a fairly high concentration (2×10^{-2} M) of one of Ohkubo's most active catalysts, triphenylsulfonium chloride, the induction period was practically the same (96 min). If the oxygen activation mechanism had been operative, the oxidation should have started without any induction period.

The inference that Ohkubo's cumene had been insufficiently purified† from cumene hydroperoxide is strengthened by the following observation. Although we found the solubility of triphenylsulfonium chloride to be much lower than the value reported by Ohkubo, it increased rapidly during the oxidation, presumably because of solvation of the catalyst by the hydroperoxide formed.

Autoxidation of cumene at 60°, in the absence of catalysts, gave high selectivities (90–95%) to cumene hydroperoxide, even at a high conversion. In agreement with Ohkubo's findings, we obtained, at a relatively low cumene conversion, a high selectivity to hydroperoxide (up to 95%) in the presence of low concentrations (2×10^{-3} M) of triphenylsulfonium chloride. It is known[14] that homolysis of only a few per cent of the hydroperoxide is sufficient to provide for a high initiation rate. In the

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†The procedure normally used for obtaining hydroperoxide-free samples of cumene (washing with concentrated H_2SO_4 and distilling from sodium under nitrogen) is known[14] to give unsatisfactory results. The cumene thus obtained exhibits induction periods of less than 10 min under autoxidation conditions (1 bar of oxygen). However, we found that subsequent purification by passing the cumene through a column of basic alumina, immediately prior to use, afforded samples having induction periods of about 2 hr. Addition of azoisobutyronitrile (AIBN; 6×10^{-5} M) resulted in an immediate oxygen uptake.

presence of 2×10^{-2} M of triphenylsulfonium chloride, however, the selectivity to hydroperoxides calculated on oxygen uptake decreased to 20%.

Analysis showed that the main oxidation product formed in the presence of 2×10^{-2} M triphenylsulfonium chloride, even at a conversion of as low as 0·06%, were cumyl alcohol and acetophenone. These products are known to originate from homolysis of cumene hydroperoxide: they are formed from the cumyloxy radical by abstraction of hydrogen from another hydroperoxide molecule (cumyl alcohol) and by α-cleavage (acetophenone). The ratio of cumyl alcohol to acetophenone depends on the concentration of the hydroperoxide (i.e. the amount of easily abstractable hydrogen present. At high conversions of cumene (20–25%), i.e. at relatively high hydroperoxide concentrations (0·4 M), we observed an alcohol/ketone ratio of 3, and at low conversions (<0·1%) a ratio of about 1. Therefore, it is evident that even in the early stages of the oxidation a substantial part of the hydroperoxide formed is homolytically decomposed by the sulfonium catalyst.

When the catalysed oxidation was carried out in the presence of finely divided $CaCO_3$, the following observations were made:

(1) the induction period was drastically reduced;

(2) the oxidation rate was further increased (Fig. 1);

(3) the yield of hydroperoxide was further decreased (from 20% to less than 10%). In the absence of the catalyst, $CaCO_3$ did not give rise to any decomposition of the cumyl hydroperoxide.

It is known that partially soluble catalysts may reprecipitate on solid particles, with the increased active surface of the catalysts causing an apparent increase in catalytic activity. The effect of added $CaCO_3$ cannot be due to this type of surface effect because no such effect was observed on addition of calcium sulfate to the normal sulfonium-catalysed oxidation mixture. To find out whether the accelerating effect of added $CaCO_3$ could be ascribed to scavenging of chloride ions, we replaced the chloride anion of the catalyst by hydroxide. The resultant triphenylsulfonium hydroxide indeed turned out to be a much more powerful catalyst for cumene oxidation than the chloride (Fig. 1). Even at a concentration of 10^{-3} M it reduced the induction period from 96 min (2×10^{-2} M $Ph_3S^{\oplus}Cl^{\ominus}$) to as little as 7–10 min.

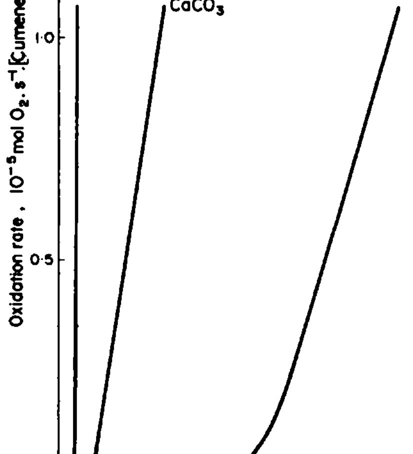

Fig. 1. Catalysis of cumene autoxidation by triphenylsulfonium salts at 80°.

DISCUSSION

(a) *Homolysis of hydroperoxide as the chain-initiating step in the sulfonium-catalysed oxidation of cumene*

Before discussing our results on the sulfonium-catalysed oxidation of cumene we shall briefly comment on some of the main arguments put forward by Okhubo in support of the validity of mechanism II, viz. (a) deactivation of the catalyst during the course of the oxidation, (b) deactivation of the catalyst by acetic acid or molecular iodine, and (c) the detection by UV of a sulfonium-oxygen complex.

(a) Ohkubo found that the oxidation of cumene in the presence of sulfonium salts slowed down during the reaction,[21] which he attributed to deactivation of the catalyst. Since the catalyst could be recovered unchanged after the oxidation, he proposed the "deactivation" to be caused by a coverage[22] of the catalyst by cumene hydroperoxide, preventing the oxygen from diffusing into the catalytic centre. The autoxidation of cumene, however, is known always to slow down at high conversions, even in the absence of a catalyst. This decrease in rate can be attributed to the formation of phenolic compounds via hydroxylation of cumene by hydroxy radicals.

(b) The effect of acetic acid on the rate of oxidation[20] can also be explained by the formation of phenol, which in this case is due to the well-known acid-catalysis heterolytic decomposition of cumene hydroperoxide. Molecular iodine, too, is known[31] to act as an inhibitor in the radical chain autoxidation of cumene.

(c) Close inspection of Ohkubo's results[26,30] reveals that the "red-shift" of the absorption maximum observed upon addition of oxygen to a solution of triphenylsulfonium chloride in alcohols is due to an artifact, viz. an earlier solvent cut-off. This is demonstrated by the following facts: (1) the effect did not occur in water, (2) only the high-frequency part of the absorption showed the "red-shift", the low-frequency side was virtually unaffected, (3) the phenomenon was not accompanied by an increase in extinction (actually, the cut-off caused a decrease of integrated intensity), and (4) the observed† cut-offs agreed with reported data on charge transfer between oxygen and alcohols.[32]

Our results are inconsistent with Ohkubo's conclusion of oxygen activation since:

(a) in the early stages of the oxidation only products derived from homolytic decomposition of hydroperoxides are formed (at the expense of the hydroperoxide yield);

(b) rather long induction periods are observed even in the presence of the most powerful catalysts such as triphenylsulfonium hydroxide;

(c) the rate of initiation during these induction periods must be lower than‡ 6×10^{-12} $M.s^{-1}$; therefore, if owing to these catalysts any oxygen activation should occur, its magnitude will never exceed this value.

From the above data it is evident that any observable catalytic effect of sulfonium compounds on the autoxida-

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†In fact, Ohkubo and Yamabe[26] measured zero transmittance over zero transmittance, which was systematically recorded as zero absorbance by their spectrometer.

‡See Experimental.

tion of cumene must be due to a homolytic decomposition of hydroperoxides.

(b) *Mechanism of sulfonium-catalysed homolysis of hydroperoxides; effect of bases*

The catalytic effect of sulfonium salts is promoted by the addition of bases or far better, by the use of the hydroxyl ion as the counter ion. The influence of the basicity of the anion is also reflected in Ohkubo's[20,23] measurements of the effect of the anionic part of the catalyst on its activity (Table 1).

Table 1. Effect of anion basicity on activity of triphenylsulfonium catalysts

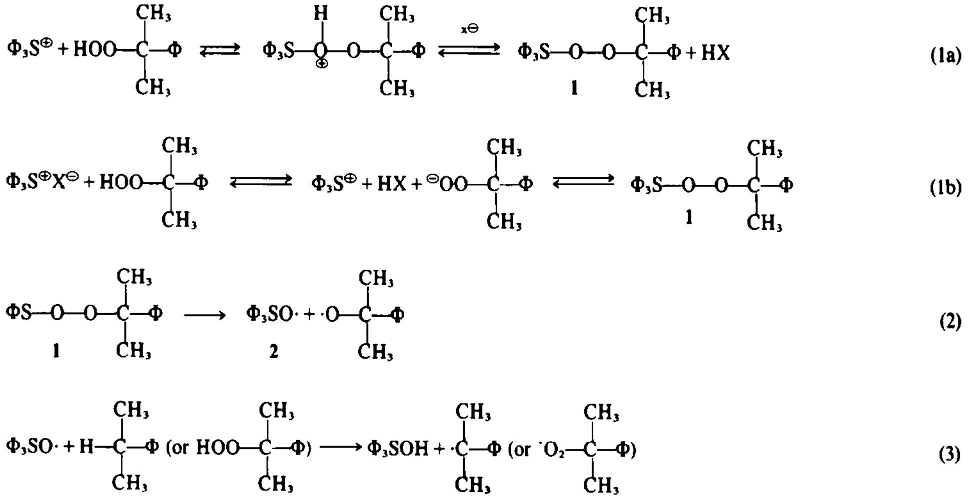
Anion[a]	Conversion[b]	pK_b[c]
PO_4^{3-}	19·5	1·6
CO_3^{2-}	9·6	3·8
CrO_4^{2-}	8·1	7·5
SO_4^{2-}	6·6	12
$Cl^{\ominus}$	4·9	21

[a] Strongly oxidizing anions have been omitted.

[b] Catalytic activity measured as the amount of oxygen (mmoles) taken up by 10 ml of cumene, containing 0·02 mmol of catalyst, after 4 h at 85°C; data obtained by Ohkubo.[20]

[c] Basicity in water.

As expected, the catalytic activity is directly related to the basicity of the anion rather than to the pK_a of the acid,[20] which refers to the first ionization step. The effect of anion basicity is similar to that encountered in the nitrile-catalysed[33] (*cf* Ref. 34) decomposition of hydroperoxides. It points to the occurrence of a perester-type intermediate (1), as depicted in the following scheme:



$$\Phi_3S^{\oplus} + HOO-\underset{CH_3}{\overset{CH_3}{C}}-\Phi \rightleftharpoons \Phi_3S-\underset{\oplus}{\overset{H}{O}}-O-\underset{CH_3}{\overset{CH_3}{C}}-\Phi \overset{X^{\ominus}}{\rightleftharpoons} \underset{1}{\Phi_3S-O-O}-\underset{CH_3}{\overset{CH_3}{C}}-\Phi + HX \qquad (1a)$$

$$\Phi_3S^{\oplus}X^{\ominus} + HOO-\underset{CH_3}{\overset{CH_3}{C}}-\Phi \rightleftharpoons \Phi_3S^{\oplus} + HX + {}^{\ominus}OO-\underset{CH_3}{\overset{CH_3}{C}}-\Phi \rightleftharpoons \underset{1}{\Phi_3S-O-O}-\underset{CH_3}{\overset{CH_3}{C}}-\Phi \qquad (1b)$$

$$\underset{1}{\Phi S-O-O}-\underset{CH_3}{\overset{CH_3}{C}}-\Phi \longrightarrow \underset{2}{\Phi_3SO\cdot + \cdot O}-\underset{CH_3}{\overset{CH_3}{C}}-\Phi \qquad (2)$$

$$\Phi_3SO\cdot + H-\underset{CH_3}{\overset{CH_3}{C}}-\Phi \text{ (or } HOO-\underset{CH_3}{\overset{CH_3}{C}}-\Phi) \longrightarrow \Phi_3SOH + \cdot\underset{CH_3}{\overset{CH_3}{C}}-\Phi \text{ (or } \cdot O_2-\underset{CH_3}{\overset{CH_3}{C}}-\Phi) \qquad (3)$$

According to this mechanism, the sulfonium salt reacts with cumene hydroperoxide via reactions (1a) or (1b) to form the perester 1. As both reactions involve a deprotonation step, they will be catalysed by bases. The perester will rapidly undergo homolysis (reaction 2) to generate a cumyloxy radical and a sulphoxide radical (2). These radicals further initiate the oxidation by abstraction of hydrogen from the substrate with regeneration of the catalyst (reaction 3).

EXPERIMENTAL

Materials. Cumene was washed with H_2SO_4 until no colouration occurred (6–8 times), and subsequently with water, NaOHaq and water. After drying over $MgSO_4$ it was distilled under N_2 from Na. The purified cumene was stored under N_2 at −20° and percolated over basic alumina immediately before use.

Triphenylsulfonium chloride was prepared according to methods reported in the literature.[21] Triphenylsulfonium hydroxide was obtained from the chloride by treatment with moist silver oxide in MeOH, evaporation of the solvent, extraction of the residue with ether, and evaporation of the solvent after drying over $MgSO_4$. It was recrystalized from ether, m.p. 66–67°; IR(KBr) >2500 cm^{-1} very broad, 3020, 1580, 1470, 1440, 1080, 1030, 1020, 990, 760, 740, 690, 680, 540 and 480 cm^{-1}; NMR(CD_3SOCD_3) δ 3·6 ppm s(1H); δ 7·4–7·9 ppm, m(15H).

Measurements. The oxidations were carried out with 10 ml of cumene in a thermostatted 50 ml flatbottomed Pyrex flask, provided with a side arm. The filled flask (N_2 atmosphere) was allowed to equilibrate for 10 min in the thermostatted bath. Subsequently, the N_2 was replaced by O_2. Saturation by O_2 (atom press) was ensured by fast magnetic stirring. The rate of O_2 uptake was measured with the aid of a thermostatted (30°) bubble counter with a printing device. Calibrations repeated at regular intervals revealed that the volume of one bubble of O_2 was 0·005 ± 0·0002 ml. The detection limit for O_2 uptake was one bubble per 6 min.

Rates of initiation during induction periods. In the presence of 10^{-3} M triphenylsulfonium hydroxide we observed an induction period of 10 min. During this period the amount of O_2 taken up by 10 ml of cumene was less than 0·005 ml/6 min (accuracy of our measurements). Using the oxidation-rate relationship[35]

$$dO_2/dt = k_p[RH]\left(\frac{R_i}{k_t}\right)^{1/2},$$

in which at 60° for cumene[13,36] $k_p/k_t^{1/2} = 3{\cdot}3 \times 10^{-3}\ M^{-1/2}.s^{-1/2}$ and RH = 7·3 M, we found the average rate of initiation (R_i) during this induction period to be less than $6 \times 10^{-12}\ M.s^{-1}$. The long induction periods cannot be due to the presence of traces of inhibitors, since addition of 6×10^{-5} M AIBN ($k_d^{60°} = 1{\cdot}07 \times 10^{-5}\ s^{-1}$, $\beta = 0{\cdot}60$[37] gives $R_i = 7{\cdot}7 \times 10^{-10}\ M\ s^{-1}$) to the cumene caused the oxidation to start immediately.

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