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A Study of the Low-temperature Oxidation of Cumene in the Presence of Triphenylsulfonium Chloride. Propagation and Termination Steps

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The low-temperature liquid-phase oxidation of cumene using triphenylsulfonium chloride was studied in order to establish the nature of the activity of sulfonium catalysts and the oxidation mechanism. The oxidation occurs in an autocatalytic fashion below 70°C, while it proceeds in an auto-retarding fashion above 85°C. This is a characteristic feature of this oxidation. The cause of the deactivation at higher temperatures is mainly the deoxygenation of the assumed complex (Cat.$\cdots$O$_2$). The decomposition of cumene hydroperoxide and the subsequent formation of α-cumyl alcohol, acetophenone, and dicumyl peroxide were seriously affected by the presence of sulfonium salts. The formation of acetophenone was accelerated thermally, while that of α-cumyl alcohol was not accelerated much, though it was accelerated by the catalyst-oxygen complex. Dicumyl peroxide, once formed in an appreciable amount, was gradually decomposed, both thermally and catalytically. The catalyst was deactivated by the product formed. This phenomenon was attributed to the masking action of oxygen-containing products. The mechanism oxidation was discussed on the basis of these observations.

Our previous reports[1,2] revealed the outstanding nature of sulfonium salts as a catalytic substance for the liquid-phase oxidation of cumene with molecular oxygen in the low-temperature range (55—85°C). This type of oxidation is initiated through hydrogen abstraction from cumene by a complex which is postulated to form as a consequence of the reversible association of molecular oxygen with the sulfonium catalyst.

$$\text{Cat.} + \text{O}_2 \rightleftarrows \text{Cat.}\cdots\text{O}_2$$

$$\text{Cat.}\cdots\text{O}_2 + \text{RH} \longrightarrow \text{R}\cdot + \cdot\text{O}_2\text{H} + \text{Cat.}$$

At the beginning of the reaction, the oxidation of this type proceeds in a simpler fashion; in this period the oxygen absorbed is almost quantitatively used in the formation of hydroperoxide. However, the propagation reaction is composed of several steps, in which not only hydroperoxide, but also acetophenone, dicumyl peroxide, and α-cumyl alcohol are produced in appreciable amounts.

In recent years, the mechanism of cumene oxidation at propagating and terminating steps has received considerable attention.[3-5] Certain aspects of the mechanism, however, still remain obscure. Namely, it has been left unclarified how the behavior of free radicals (RO$\cdot$, RO$_2\cdot$, CH$_3\cdot$, *etc.*) changes at different temperatures with or without catalysts in their competing reactions, including intramolecular ones. Moreover, much work has been done by means of kinetic methods, which usually do not afford much reliable information, in particular about the termination reaction. In addition, a majority of the experiments in these works were carried out at relatively high temperatures (100—200°C) with heterogeneous metal compound catalysts, which inevitably complicated the results. In this regard, the present experimental conditions are quite favorable to make the mechanism clear because of the homogeneity of the reacting system and because of the low temperature employed.

This paper will attempt to clarify the low-temperature oxidation mechanism of cumene with triphenylsulfonium chloride and the nature of its catalytic action by investigating the effects of the temperature and of catalysts upon oxygen absorption and oxidation products.

The present study gives some noticeable results: (1) The propagation reaction proceeds through the decomposition of cumene hydroperoxide, which is caused not so much thermally as by triphenylsulfonium chloride; (2) The formations of acetophenone and dicumyl peroxide are strongly influenced by the temperature, while that of α-cumyl alcohol is not so much affected by the temperature but is, rather, promoted by sulfonium salts; on the contrary, dicumyl peroxide is rather

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[1] K. Fukui, K. Ohkubo and T. Yamabe, This Bulletin, **42**, 312 (1969).

[2] K. Ohkubo, T. Yamabe and K. Fukui, *ibid.*, **42**, 1800 (1969).

[3] P. D. Bartlett and T. G. Traylor, *J. Am. Chem. Soc.*, **85**, 2407 (1963).

[4] T. G. Traylor, *ibid.*, **85**, 2411 (1963).

[5] T. G. Traylor and C. A. Russell, *ibid.*, **87**, 3698 (1965).

decomposed by the catalyst; (3) The deactivation of the catalyst by certain oxidation products, especially by α-cumyl alcohol, is ascribed to thier masking actions, which retard the reaction.

Experimental

Material and Catalyst. Cumene was washed with concentrated sulfuric acid, dried on magnesium sulfate, and then rectified to collect the center fraction; bp 152.5°C, $n_D^{20}=1.4910$. The fraction was then filtered chromatographically through activated alumina (200—300 mesh) and stored under nitrogen at 0°C. As the oxidation catalyst, triphenylsulfonium chloride was synthesized by the method presented in our earlier report.⁶⁾

Oxidation Procedure. Under a nitrogen atmosphere, triphenylsulfonium chloride and cumene (10 m*l*) were added to an oxidation flask (50 m*l* capacity) attached to a gas burette from which air was then evacuated and which was filled with oxygen several times. The oxidation flask was contained in a thermostated oil-bath, and oxygen absorption was followed in the way previously described.²⁾ The oxidation products were determined by the following analytical procedure.

Analytical Procedure. The main products, cumene hydroperoxide (CHP), dicumyl peroxide (DCP), acetophenone (AP), and α-cumyl alcohol (CA), were determined by the following methods.

Cumene Hydroperoxide (CHP). CHP was determined by an iodometric method which is essentially taken from Fordham and Williams,⁷⁾ but modified in the following points. A 0.5—2.0 m*l* portion of the oxidate was added to 5.0 m*l* of a saturated aqueous potassium iodide solution containing 10 m*l* of glacial acetic acid and 100 m*l* of isopropyl alcohol. The resultant mixture was flushed with nitrogen and then refluxed gently with occasional shaking for 3.0—4.0 min. The liberated iodine was titrated with a 0.1 N sodium thiosulfate solution until the yellow color disappeared. The amount of CHP was then determined from the difference between the titer of the blank and the oxidate-containing mixture.

Dicumyl Peroxide (DCP). A 0.5—1 m*l* portion of the oxidate was added to 50 m*l* of glacial acetic acid containing 3 g of sodium iodide, and then the entire mixture was heated in a nitrogen atmosphere at 110—115°C for 1 hr. After dilution by oxygen-free water (3.0 m*l*), the resulting iodine was titrated in nitrogen with a standard thiosulfate solution. The difference between this determination and that of CHP gave the amount of dicumyl peroxide.

Acetophenone (AP). AP was determined like the 2,4-dinitrophenylhydrazone; mp 248—249°C, mixed mp 249°C.

α-Cumyl Alcohol (CA). CA was determined as the reaction product with thioglycolic acid.⁸⁾

The Solubility of Chlorides to Cumene. Commercially-pure alkali chlorides (LiCl, NaCl, KCl, RbCl, CsCl, and NH_4Cl) were calcined, fused, and then pulverized to about 200 mesh powder. The solubility of these chlorides and triphenylsulfonium chloride to cumene was determined by the following treatment. The chloride (500 mg) was added to cumene (50 m*l*); after the mixture had been vigorously stirred for one hour at two definite temperatures (20 ±0.5°C and 70±0.5°C), the upper layer (10 m*l*) of the mixture was titrated by an alcoholic solution of a N/100 silver nitrate solution, using potassium chromate as the indicator. Table 1 records the solubility of the chlorides to cumene.

TABLE 1. THE SOLUBILITY OF VARIOUS CHLORIDES TO CUMENE

Chloride (MCl) (M)	Solubility (mg-atom/100 mg of cumene) Cl at 20±0.5°C	Cl at 70±0.5°C
Li	0.041	0.221
Na	0.017	0.116
K	0.017	0.116
Rb	0.029	0.150
Cs	0.029	0.231
NH_4	0.041	0.234
$(C_6H_5)_3S$	0.206	0.244

Results and Discussion

In the initial range of the reaction, the amount of oxygen absorbed is consumed only to form CHP, and the rate of its formation depends almost linearly upon the amount of the sulfonium catalyst.²⁾ In the propagation and termination steps, however,

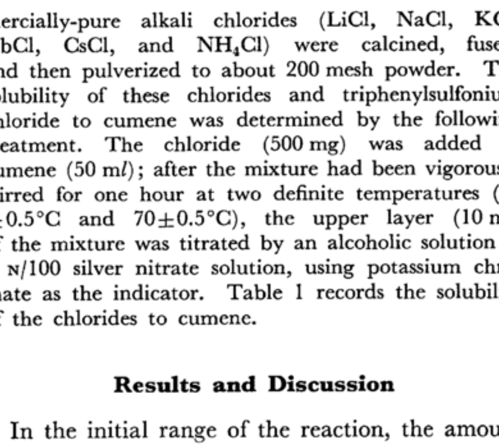

Fig. 1. The influence of the amount of triphenylsulfonium chloride on the oxygen absorption at 70°C.
The amount of $(C_6H_5)_3SCl$ (mmol/m*l*$\times 10^3$): 1, 36.85; 2, 26.80; 3, 16.65; 4, 10.05; 5, 3.35; 6, none

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6) K. Fukui, K. Kanai, Takezono and H. Kitano, *Kogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **67**, 1131 (1964).

7) T. W. L. Fordham and H. L. Williams, *Can. J. Research*, **B27**, 943 (1949).

8) B. Holmberg, *J. prakt. Chem.*, **141**, 93 (1934).

the hydroperoxide decomposes, both thermally and catalytically. The decomposition products (AP, DCP, and CA) complicate the oxidation mechanism. First, the catalytic effect of the sulfonium salt upon oxygen absorption and the composition of the oxidation products in these steps were investigated at 70 and 85°C. The oxygen absorption curves at 70°C in Fig. 1 indicate that the oxygen absorption of an autocatalytic nature increases monotonously with the amount of the catalyst. The dwindling of absorption began after *ca.* 4 hr, and the retardation appeared about 8 hr after the start. Therefore, the oxidation products after 4.0 and 8.0 hr may afford information about the propagation and the termination processes respectively. This point will be discussed below.

The decrease in oxygen absorption may be attributed to the deactivation of the catalyst, itself probably caused by the masking action of the accumulated CHP, as was discussed in our previous report.[2] Actually, the rates of absorption declined upon the addition of CHP, as is shown in Table 6. This may be connected with the fact that sulfonium catalysts are easily dissolved in polar solvents, especially those containing oxygen lone-pairs, which might cause a strong interaction with sulfonium ions. Namely, such molecules as CHP blocking the active sites of sulfonium ions may prevent oxygen molecules from approaching there; hence, they may depress the catalytic activity. This masking action of CHP might be assisted by the association of the hydroperoxides through hydrogen-bonds between them.*1 The circumstances of the masking action are illustrated schematically in Fig. 2.

Table 2 indicates that the accumulation of CHP diminishes in proportion to the amount of the catalyst. In fact, in the absence of any catalyst, CHP is preserved from secondary changes almost completely, even a 17.5 hr reaction. This fact suggests that CHP is decomposed essentially catalytically, whereas it is little converted thermally. Actually, the sulfonium catalyst decomposes CHP exclusively in this temperature range; this will be discussed in detail in a subsequent paper.

Mention should be made here of the decomposition of CHP. There are three possible paths to be considered for the generation of α-cumyloxy radicals, the main source of the formation of products. The first one is the unimolecular thermal decomposition:

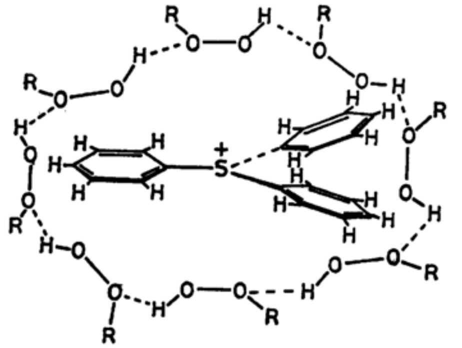
$$ROOH \xrightarrow{\text{unimol. decomp.}} RO\cdot + \cdot OH \qquad (1)$$

This is, however, hardly conceivable, because CHP is sufficiently stable in hydrocarbons up to 130—140°C.[10]

The second is the following bimolecular decomposition through dimer formation by the hydrogen bond when the concentrations of CHP are high:

$$2ROOH \rightarrow \left[RO\cdots\overset{\overset{H}{|}}{O}\cdots H\cdots O_2R\right] \xrightarrow{\text{bimol. decomp.}} RO\cdot + RO_2\cdot + H_2O \qquad (2)$$

This implies that the hydrogen-bond formation



$R = C_6H_5C(CH_3)_2$-

Fig. 2. A proposed model for the makings effect of CHP on triphenylsulfonium ion catalyst.

Table 2. Effect of catalyst amount upon CHP formation at 70°C

Catalyst amount (mmol/m*l* ×10^3)	Reaction time (hr)	O_2 absorbed (mmol)	CHP (mmol)	CHP (%)*
3.35	1.0	0.98	0.95	97.2
	4.0	7.10	5.71	80.5
	8.0	11.80	8.9	75.4
10.05	1.0	1.25	1.17	93.5
	4.0	8.90	6.20	68.6
	8.0	16.7	9.2	55.1
16.65	1.0	1.60	1.47	92.1
	4.0	12.1	7.25	59.9
	8.0	18.1	9.4	51.9
26.80	1.0	2.07	—	—
	4.0	14.2	7.10	50.0
	8.0	19.5	9.5	48.7
36.85	1.0	2.38	2.16	91.0
	4.0	15.0	—	—
	8.0	25.5	9.0	35.5
None	17.5	5.73	5.63	98.20

* Calculated as mol CHP per 100 mol oxygen absorbed.

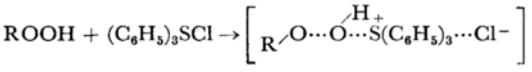
[*1] In fact, Bateman and Hughes,[9] in their study of the infrared spectrum of cyclohexenyl hydroperoxide, showed that, in a diluted hydroperoxide solution in benzene, OH groups appear at 3500 cm^{-1}, while in an undiluted solution they appear at 3350 cm^{-1}; this apparently indicates the formation of intermolecular hydrogen bonds between them.

9) L. Bateman and H. Hughes, *J. Chem. Soc.*, **1952**, 4594.

10) M. S. Kharasch, A. Fono and W. Nundenberg, *J. Org. Chem.*, **16**, 113 (1951).

promotes the fission of the oxygen-oxygen bond of CHP.*[2] At any rate, the thermal decomposition of CHP in cumene is actually very small in the temperature range of 60—80°C.*[3]

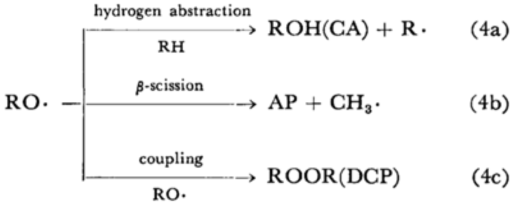
Hence, the only reasonable path is the third one (reaction (3)). This may, then, be proposed as the main reaction giving α-cumyloxy radicals. A more detailed discussion of this will be presented in a subsequent paper.



$$ROOH + (C_6H_5)_3SCl \rightarrow \left[{}_{R}\!\diagup O\cdots \overset{\diagup H_+}{O}\cdots S(C_6H_5)_3\cdots Cl^- \right]$$

$$\rightarrow RO\cdot + \cdot OH + (C_6H_5)_3SCl \qquad (3)$$

Products of Oxidation. The α-cumyloxy radicals thus formed are readily converted to the major products through chain-transfer reactions (4a and 4b) or a chain-terminating reaction (4c).



$$RO\cdot \xrightarrow[RH]{\text{hydrogen abstraction}} ROH(CA) + R\cdot \qquad (4a)$$

$$RO\cdot \xrightarrow{\beta\text{-scission}} AP + CH_3\cdot \qquad (4b)$$

$$RO\cdot \xrightarrow[RO\cdot]{\text{coupling}} ROOR(DCP) \qquad (4c)$$

$(R=C_6H_5C(CH_3)_2\text{-})$

CA Formation. Among these products, CA was apparently formed in an amount comparable with those of AP and DCP, as is shown in Table 3. This fact is worthy of emphasis since CA formation through hydrogen abstraction by RO· from cumene is difficult in low-temperature thermal oxidation without a catalyst, even if cumene is a good hydrogen donor. This is supported by the study of Blanchard[11)] on cumene oxidation at 60°C by the use of α,α'-azodiisobutyronitrile, in which CA is formed only in an extremely small amount compared with AP and DCP. Table 3 also shows, however, that the accumulation of CA gradually lessened, whereas that of AP increased remarkably, as the reaction proceeded.

Such a remarkable CA formation as is described above may be attributed to the co-existence of oxygen and the catalyst. This is because the amount of CA is very small in the thermal and catalytic decomposition of CHP in cumene at 65°C without oxygen.*[4] Therefore, it may be taken into account that molecular oxygen would participate in the CA formation as a natural consequence of its free radical character in the following "concerted" single-step process:

$$RO\cdot + RH + O_2 \xrightarrow[\text{liquid phase}]{} ROH + RO_2\cdot \qquad (5)$$

A possible alternate pathway may be a consequent process which comprises:

$$RH + O_2 \rightarrow R\cdot + HO_2 \qquad (5a)$$

$$RO\cdot + HO_2\cdot \rightarrow ROH + O \qquad (5b)$$

If we simply assume that the activation energy of the reverse process of (5a) is small, then, accordingly, the activation energy for (5a) is equal to the heat of this step—it is estimated to be about 38 kcal/mol.*[5] This value is nearly equal to the energy of the oxygen-oxygen bond cleavage of CHP. Considering the fact that the thermal decomposition of CHP does not take place below 100°C, the reaction (5a) is also unlikely to occur appreciably at similarly low temperatures. The circumstances are almost same for the former mechanism (5), since, from the energetic point of view, (5) might be not so very different from the combination of the reactions (5a) and (5b).

As a matter of fact, the hydrogen abstraction from RH by O_2 is difficult without activation, as in the form of $(Cat.\cdots O_2)$, as was reported in the previous paper.[2)] However, this "activated form" of oxygen may also promote the formation of CA as might be readily expected from the ability of hydrogen abstraction of activated O_2. This point has already been discussed.[1,2)]

$$RO\cdot + RH + Cat.\cdots O_2 \rightarrow ROH + RO_2\cdot + Cat. \qquad (6)$$

On the other hand, we may consider the process to be divided into three elementary steps:

$$RH + Cat.\cdots O_2 \rightarrow R\cdot + Cat. + HO_2\cdot \qquad (6a)$$

$$RO\cdot + HO_2\cdot \rightarrow ROH + O_2 \qquad (6b)$$

$$R\cdot + O_2 \rightarrow RO_2\cdot \qquad (6c)$$

Reaction (6) would be very easy because of its small activation energy (below 5.25—6.15 kcal/mol).[2)] Therefore, reaction (6) is considered to be more plausible than (5) for the mechanism of CA formation. The saturation phenomena in the CA

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*[2] Reaction (2) is supported by the study of Bateman and Hughes[9)] on olefin oxidation, in which the bimolecular mechanism appears at a temperature lower than about 80°C.

*[3] Following our preliminary experiments, the thermal decomposition of CHP (22.5 mmol) in cumene (20 m*l*) occurred in the amounts of 0.50 mmol for 10.3 hr and 1.20 mmol for 9.0 hr at 65 and 80°C respectively.

11) H. S. Blanchard, *J. Am. Chem. Soc.*, **81**, 4548 (1959).

*[4] 0.50 mmol of CHP was subjected to thermal decomposition to produce 5.2 mol% of CA and 63.8 mol% of AP after 10.3 hr, while 12.5 mmol of CHP was decomposed by the use of the sulfonium catalyst to produce 9.6 mol% of CA and 41.2% of AP.

*[5] The bond dissociation energies of H-O_2. and R-H are 47.1±2 kcal[12)] and 85 kcal respectively. Therefore, the activation energy of the reaction (5a) is estimated to be *ca.* 38 kcal. On the other hand, by the use of the $D(H\text{-}O_2\cdot)=36$ kcal/mol estimated by Uri,[13)] it is estimated to be *ca.* 49 kcal/mol.

12) S. N. Fonor and R. L. Hudson, *J. Chem. Phys.*, **36**, 2681 (1962).

13) N. Uri, *Chem. Revs.*, **50**, 375 (1952).

TABLE 3. EFFECT OF CATALYST AMOUNT UPON PRODUCT COMPOSITION AT PROPAGATION AND TERMINATION STEPS* (reaction temperature: 70°C)

Catalyst amount (mmol/ml × 10^3)	Reaction time (hr)	O_2 absorbed (mmol)	CHP (%)**	DCP (%)**	AP (%)**	CA (%)**
3.35	4.0	7.10	80.5	5.4	3.7	9.7
	8.0	11.80	75.4	5.2	5.4	12.4
10.05	4.0	8.90	68.5	5.1	15.5	10.0
	8.0	16.7	55.1	4.4	22.8	14.6
16.65	4.0	12.1	59.9	—	15.57	—
	8.0	18.1	51.9	7.0	25.6	14.1
26.80	4.0	14.2	50.0	6.1	21.60	13.2
	8.0	19.5	48.7	4.2	32.4	14.9
36.85	4.0	15.0	—	—	—	—
	8.0	25.5	35.5	—	48.8	—

* For choice of reaction time of 4 and 8 hr as representing the propagation and termination steps respectively, see the text.

** Percents of CHP, AP and CA are defined by (mol of compound found)/(mol of O_2 absorbed), while DCP% is defined by 2×(mol of DCP found)/(mol of O_2 absorbed).

TABLE 4. OXIDATION PRODUCTS AT TERMINATION STEPS (reaction temperature: 85°C, reaction time: 4.0 hr)

Catalyst amount (mmol/ml × 10^3)	O_2 absorbed (mmol)	Weight increase (mg)	CHP (%)*	DCP (%)*	AP (%)*	CA (%)*
3.35	4.88	114.0	41.0	11.4	32.7	11.5
16.65	7.43	143.8	31.6	9.55	37.4	11.1
20.10	7.81	209.8	29.1	10.0	39.6	17.8
33.5	6.85	168.3	20.5	—	40.2	—
67.0	8.99	233.9	23.4	3.68	41.2	20.5

* Percents of CHP, AP and CA are defined by (mol of compound found)/(mol of O_2 absorbed), while DCP (%) is defined by 2×(mol of DCP found)/(mol of O_2 absorbed).

formation as the reaction proceeds, as may be observed in Table 3, may thus be explained by the deactivation of the catalyst as a result of the masking action of the products.

Traylor and Russell⁵⁾ emphasized that CHP was a better hydrogen atom source than cumene, proposing the reaction:

$$RO\cdot + ROOH \rightarrow ROH + RO_2\cdot \qquad (7)$$

on the basis of the fact that CH_3OD was isolated from the decomposition of deuterated hydroperoxide (CH_3OOD).14) However, the bond-dissociation energy of ROO-H (~89.5 kcal15)) is rather larger than that of hydrocarbon (RH) (~85 kcal). This implies that reaction (7) is not easier than (4a), particularly at low temperatures. Moreover, reaction (7) is not probable at low concentrations of the hydroperoxide.

Further possible paths to CA, for example, $CH_3O_2\cdot + RO_2\cdot \rightarrow CH_2O + ROH + O_2$, seem not to be dominant for a reason to be discussed later.

AP Formation. Acetophenone (AP) is formed through a β-scission of the methy radical, (4b). Reaction (4b) is predominant rather than reaction (4a), as is indicated in Table 4. The difference in activation energies (about 7.3 kcal) between (4a) and (4b) was also reported by Bailey and Godin.16)

Formation of DCP. Under the conditions of low-temerature oxidation, a chain-terminating step by coupling, (4c), is also to be taken into account. DCP is thermally stable at 70—85°C, but it should be noticed that the scission of the O–O linkage of common peroxides is easier than that of hydroperoxides. The activation energy of the O–O bond fission of dialkyl peroxides (~36.2 kcal17)) is smaller than that of alkyl hydroperoxide (~38.5 kcal18)). Actually, the rate of the thermal decomposition of DCP is found to be appreciably faster than that of CHP.18) As is shown in Table 3, the amount of DCP decreases as the reaction proceeds, corresponding to the decomposition of DCP accumulated.

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14) C. Walling, "Free Radicals in Solution," John Wiley and Sons, New York, N. Y. (1957), p. 444.

15) S. W. Benson, *J. Am. Chem. Soc.*, **86**, 3922 (1964).

16) H. C. Bailey and G. W. Godin, *Trans. Faraday Soc.*, **52**, 68 (1956).

17) A. D. Kirk and J. H. Knox, *ibid.*, **56**, 1296 (1960).

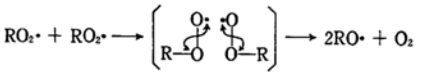
18) A. V. Tobolsky and R. B. Mesrobian, "Organic Peroxides," Interscience Publishers, New York (1954), pp. 88—89.

Table 4 indicates that the catalyst lessens the formation of DCP. Here it must be remarked that the catalyst accelerates the decomposition of CHP to produce RO·. Accordingly, it may rather be expected that the DCP formation would increase on that account, especially at a low temperature, provided that the catalyst does not force the decomposition of DCP. In reality, DCP is considerably decomposed by the catalyst in cumene without O_2 at 85°C, forming AP predominantly and also CA in an appreciable amount,[*6] whereas thermally the decomposition is far smaller.

$$\mathrm{ROOR} \xrightarrow{\text{sulfonium catalyst}} 2\mathrm{RO}\cdot \rightarrow \text{(4a) or (4b)} \qquad (8)$$

The decomposition of DCP is, therefore, one of the pathways to AP and CA.[*7] The thermal decomposition of DCP in cumene has been studied by Bailey and Godin,[14] who reported that the ratio of AP to CA varied from 0.68 to 1.95 in the range from 111.2°C to 160°C. This phenomenon may suggest that AP formation is more strongly accelerated by the temperature than is CA formation. This point will be discussed again later.

Formation of RO_4R. Mention should be made here of the possible coupling of cumylperoxy radicals ($RO_2\cdot$) to form unstable intermediates (RO_4R).[*8]



(9)

$$RO_2\cdot + RO_2\cdot \longrightarrow \left[R{-}O{-}O\cdot \;\; \cdot O{-}O{-}R \right] \longrightarrow 2RO\cdot + O_2 \qquad (9)$$

The RO· radical produced will undergo reactions according to the three schemes (4a), (4b), and (4c).

Besides the process (4c), there seems to be another direct route to ROOR possible, as has been pointed out by Russel[19] in the case of secondary alkyl tetroxide:

$$RO_4R \rightarrow ROOR + O_2 \qquad (10)$$

Boozer and his co-workers[21] suggested the following reaction in their study using deutrocumene at 65°C:

$$RO_4R \rightarrow ROOH + C_6H_5C(CH_3){=}CH_2 + O_2 \qquad (11)$$

This reaction is, however, doubtful in the present case because no α-methylstyrene is detected in our experiments. The unreliability of reaction (11) can also be concluded in view of the result of an ^{18}O-tracer study by Bartlett[3] of the recombination of the cumyloxy radical.

Behavior of the Methyl Radical. Methyl radicals are produced through the β-scission of RO·. They are converted to the peroxy radical in the following way:

$$CH_3\cdot + O_2 \rightarrow CH_3OO\cdot \qquad (12)$$

Other possibilities for the disappearance of $CH_3\cdot$ involve various chain-transferring and chain-terminating reactions:

$$CH_3\cdot + RH \rightarrow CH_4 + R\cdot \qquad (13a)$$

$$CH_3\cdot + ROOH \rightarrow CH_4 + RO_2\cdot \qquad (13b)$$

$$CH_3\cdot + CH_3\cdot \rightarrow C_2H_6 \qquad (14)$$

$$CH_3\cdot + RO\cdot \rightarrow CH_3OR \qquad (15)$$

$$CH_3\cdot + RO_2\cdot \rightarrow CH_3OOR \qquad (16)$$

Of these, (15) and (16) are not likely in the present low-temperature oxidation since neither cumylmethyl ether nor cumylmethyl peroxide was detected. Also, reaction (14) may be discarded in this case because of the low concentration of $CH_3\cdot$ radicals. Consequently, the hydrogen abstraction reactions, (13a) and (13b), seem to be almost the only pathway of $CH_3\cdot$ consumption.

The activation energy of (13a) is relatively small.[*9] Actually, methane is detected in the decomposition of CHP by triphenylsulfonium chloride at 65°C.[*10] Also, reaction (13b) can not be disregarded. Kharasch and his co-workers have confirmed the methane formation from thermal decomposition of CHP in decane at 140°C. In that case, however, decane can not be a good hydrogen source. In the present case, (13a) seems to be preferable.

In the presence of an appreciable amount of molecular oxygen, however, reaction (12) might be preferable to (13). The behavior of methyl-

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[*6] 92% of the DCP (initial amount=22.5 mmol) in cumene is decomposed by triphenylsulfonium chloride (22.5 mmol) in about 11.0 hr at 85°C, thus forming AP (52.3%) and CA (36%), but thermally it decomposes only about 34% of the initial amount during the same reaction time.

[*7] DCP melts at 39°C and is less stable than CHP. The scission of the O-O bond of DCP has a smaller energy of activation (34.5 kcal/mol)[16] than that of CHP (∼38 kcal).

[*8] The formation of RO_4R was first proposed by Russell[19] for *s*-alkylperoxy radicals. The transitory existence of this intermediate has also been supported by Milas and Djokic[20] in their study of the ozonization of potassium *t*-perbutoxide. A crystalline solid isolated at −78°C, which might be expected to be di-*t*-butyl tetroxide, decomposed spontaneously at −30 to 0°C to give equivalent amounts of di-*t*-butyl peroxide and oxygen molecules. The possibility of the presence of RO_4R is suggested by a recent thermochemical calculation by Benson.[11]

19) G. A. Russell, *J. Am. Chem. Soc.*, **79**, 3781 (1957).

20) N. A. Milas and S. M. Djokic, *Chem. Ind. (London)*, **1962**, 405.

21) C. E. Boozer, B. W. Pounder, J. C. Trisler and C. E. Wightman, *J. Am. Chem. Soc.*, **78**, 1506 (1956).

[*9] We assume that $R=\alpha$-cumyl is almost equal to or less than $R=t$-butyl in reaction (13) and cite the value of 7.7 kcal after Tikhomirova.[22]

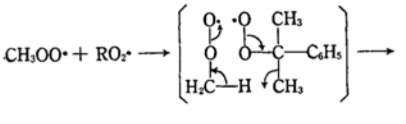
22) N. N. Tikhomirova and V. V. Voevodskii, *Chem. Abstr.*, **45**, 9940 (1951) (*Doklady Akad. Nauk S.S.S.R.*, **79**, 993 (1951)).

[*10] Some CHP (4.50 mmol) in cumene (20 m*l*) is decomposed by $(C_6H_5)_3SCl$ (0.27 mmol) for 9.0 hr to produce about 30 mol% of methane.

peroxy radicals thus formed is still obscure. Traylor and Russell[5] have proposed the following path:

$$CH_3OO\cdot + RO_2\cdot \rightarrow CH_2O + ROH(CA) + O_2 \quad (17)$$

In the low-temperature oxidation, however, CA formation is depressed remarkably, as has been reported by Blanchard,[11] while AP is produced dominantly. If all of the methyl radicals formed are converted to methylperoxy radicals according to reaction (12), the amount of CA should, stoichiometrically, be not less than that of AP. In reality, however, the quantity of CA is much less than that of AP. By means of scheme (17) only, this fact can not be explained. Another route to AP may, for instance, be of the following type:



$$CH_2O + AP + CH_4 + O_2 \quad (18)$$

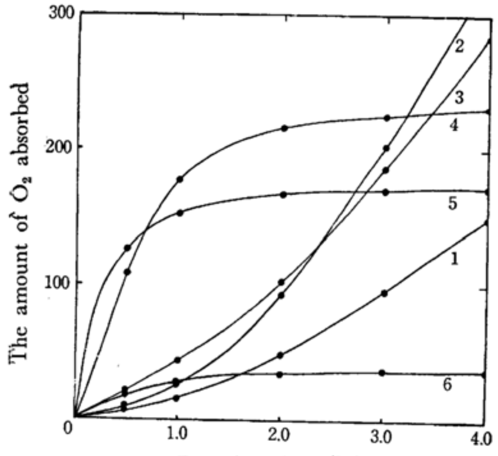


Fig. 3. temperatuee effect on oxygen absorption by the use of $(C_6H_5)_3SCl$ (16.65×10^{-3} mmol/ml). 1: 55°C; 2: 65°C; 3: 70°C; 4: 80°C; 5: 100°C; 6: 120°C

Such a concerted, complicated process may be possible in the solvent cage, just as in the case of Eq. (9).

Temperature Effect. The present experiment was carried out in the temperature range from 55 to 85°C; in this range sulfonium catalysts are relatively stable. In order to specify the influences of temperature on the oxidation process, a higher-temperature range up to 120°C was also employed. Figure 3 indicates that the reactions below 70°C are clearly autocatalytic, while those above 80°C are auto-retarding. The latter ones may be ascribed to the deoxygenation of the catalyst-oxygen complex according to the increase in the temperature[*11] and by means of the masking action of products. The variation in the products with the reaction temperature is indicated in Table 5. The decrease in CHP with the temperature is remakable, while AP and CA apparently increase as the temperature rises, the former more than the latter. Such a difference in the temperature effect of AP and CA is reasonable. The former arises from an intramolecular reaction of RO· in which the vibrational cleavage of the carbon-methyl bond takes place as a result of the participation of adjacent π orbitals. The latter is produced by an intermolecular hydrogen abstraction from RH; the rate of such a process may be controlled by the steric hindrance of two bulky reactants. The temperature dependence of the (AP/CA) ratio has been found to be 7.3 kcal.[16] In the present catalytic process, it is noted that the CA formation through reaction (6) is also depressed with the increase in the temperature as a result of the deoxygenation of the catalyst complex.

Additive Effect. The deactivation of the sulfonium catalyst, possibly caused by a masking action of oxidation products, is deduced from the effect of various additives on the rate of oxygen absorption. Table 6 displays the decrease in the initial maximum rate[2] of oxygen absorption and the lengthening of the induction period. The decrease in the rate is particularly remarkable in

TABLE 5. EFFECT OF TEMPERATURE UPON PRODUCT COMPOSITION
(catalyst amount: 16.65×10^{-3} mmol/ml; reaction time: 4.0 hr)

Reaction temperature (°C)	O_2 absorbed (mmol)	Weight increase (mg)	CHP (%)*	DCP (%)*	AP (%)*	CA (%)*
55	6.26	166.9	78.3	6.37	8.10	7.8
65	13.1	247.8	60.7	5.42	21.1	12.6
80	9.46	315.4	38.47	11.7	34.4	20.8
100	6.58	—	4.57	—	56.0	28.5
120	1.25	13.1	1.44	17.0	63.2	26.2

* Per cents of CHP, AP and CA are defined by (mol of compound found)/(mol O_2 absorbed), DCP (%) is defined by 2×(mol of DCP found)/(mol of O_2 absorbed).

[*11] The large optical density of the absorption band of a possible methyl-cyclohexane-oxygen complex is observed at lower temperatures (H. Tsubomura and R. P. Lange, *J. Chem. Phys.*, **36**, 2155 (1962)).

the case of CA. The reason may be the masking action of the additives through their shielding of *d* orbitals of the catalyst, as has been described previously.[1,2] It has been ascertained that the sulfonium catalysts are not decomposed by these reaction products.[1]

TABLE 6. THE EFFECT OF ADDITION OF PRODUCT MOLECULES UPON INITIAL MAXIMUM RATE[a] AND THE LENGTH OF INDUCTION PERIOD AT 70°C (catalyst amount 3.35×10^{-4} mmol/m*l*)

Product	Amount (mmol)	Rate (max.) ($\mathrm{mol}\ l^{-1}\,\mathrm{sec}^{-1}\times10^4$)	Induction period[b] (sec)
None	—	1.76	0
		(0.29)*	(450)*
CHP	6.75	1.12	70
		(0.31)*	(300)*
	9.00	1.04	75
	18.0	0.64	180
DCP	6.75	1.54	40
		(0.33)*	(270)*
	18.0	1.50	60
AP	1.70	0.894	30
		(0.26)*	(480)*
	4.28	0.745	70
	8.55	0.706	120
	17.0	0.297	190
CA	1.70	0.12	360
		(0.19)*	(600)*
	4.28	0.00	—

a) The maximum rate appeared at the initial step in the oxidation[2] using $(C_6H_5)_3SCl$.
b) The period was determined as the time passed from the start of oxygen absorption.
* The values in the parentheses were those obtained without use of catalyst. In this case, the maximum rate was calculated from the oxygen absorption curve at the reaction time of 1.0 hr.

TABLE 7. THE AMOUNT OF OXYGEN ABSORBED AND CUMENE HYDROPEROXIDE CONTENT IN THE OXIDATION OF CUMENE SATURATED WITH VARIOUS CHLORIDES (reaction temperature: 70°C; reaction time: 8.0 hr)

Catalyst (MCl) (M)	O_2 absorbed (mmol)	CHP (%)[a]
Li	18.2	35.6
Na	0.64	98.7
K	1.27	100
Rb	1.36	98.5
Cs	1.48	96.6
NH_4	0.43	100
$(C_6H_5)_3S$	18.6	50.6
None	5.73[b]	98.2

a) Calculated as mol CHP per 100 mol oxygen absorbed.
b) Reaction time was 17.5 hr.

It should be taken into account that the effect of product addition appears even in autoxidation without a catalyst. The promoting effect observed in the cases of CHP and DCP might be attributed to their action as initiators. Inhibitory action of CA (and, less remarkably, of AP) in thermal processes is observed, but the extent never exceeds the usual alcohol effect.[23] It is of interest that the catalyst activity of triphenylsulfonium chloride is almost independent of the chloride anion concentration. Table 7 compares the catalytic activities of various alkali chlorides and triphenylsulfonium chloride in the oxidation of cumene saturated with them. The oxygen absorption is never in proportion to the content of the chloride anion, a proportion to be expected from Table 1.[*12]

Summarized Scheme of the Reaction. In conclusion, the reaction mechanism is summarized schematically in Fig. 4 for help in understanding it.

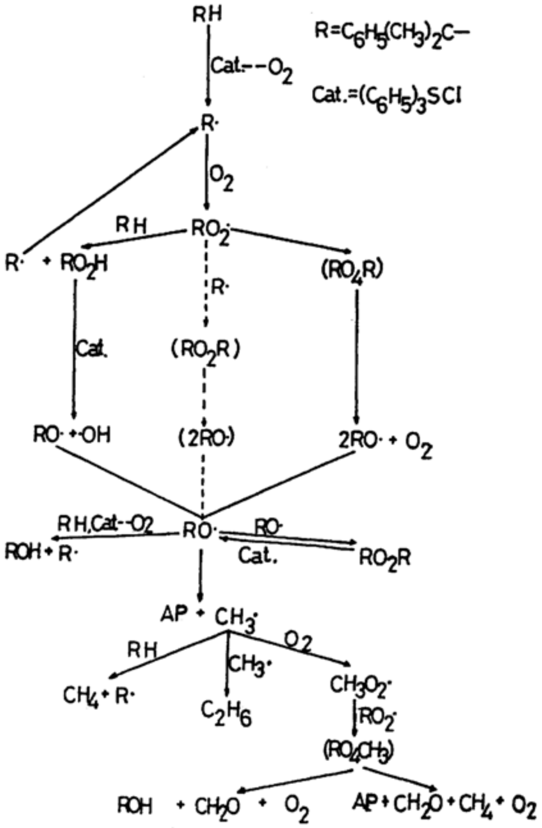


Fig. 6. A scheme for the mechanism of cumene oxidation by the use of $(C_6H_5)_3SCl$.

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23) For instance, see a) K. U. Ingold, *Chem. Revs.*, **61**, 563 (1961). b) K. Negoro and T. Sawada, *Kyogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*, **67**, 1105, 1172 (1964). c) J. Yamashita, K. Kurashima, M. Tobita and H. Hashimoto, *ibid.*, **67**, 1153 (1964).

[*12] The activity of lithium chloride will be discussed later.