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A Study of the Decomposition Reaction of Cumene Hydroperoxide in the Presence of Triphenylsulfonium Chloride

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The homogeneous decomposition reaction of cumene hydroperoxide in cumene was studied by the use of triphenylsulfonium chloride over a low-temperature range (30—80°C). The hydroperoxide was decomposed remarkably in the presence of the sulfonium catalyst, whereas in the absence of the catalyst it was decomposed only a little. Among the homolytic decomposition products, acetophenone and dicumyl peroxide were found to be the main products, while α-cumyl alcohol was formed in only a small amount. Moreover, methyl alcohol was found in appreciable amounts. Traces of heterolytic reaction products, such as phenol and acetone, were also detected. After discussing the reaction mechanism and the nature of catalytic action, it is concluded that the partially-occupied *d* orbital of the sulfonium cation may play a role in breaking the oxygen-oxygen bond of the hydroperoxide homolytically. The counter chloride anion seems to take part in the heterolytic reaction to some extent.

The thermal decomposition of cumene hydroperoxide (CHP) above 100°C in various kinds of solvents has been studied by several authors.[1-7] Most of these studies have been based on kinetic methods. However, there are some discrepancies in their results,[2,3] particularly in the kinetic order of decomposition reaction. These discrepancies may be attributed to the distribution of the decomposition products which depends on the polarity of the solvents, the reaction temperature, and the presence or absence of catalysts.

CHP itself is thermally stable in hydrocarbons up to 130—140°C,[3] but by catalysts such as ferrous salt[4] and peroxides[4] it is decomposed even below 80°C. We found that sulfonium salts also decompose CHP at low temperatures (below 80°C), even though the character of the catalytic action is different from that of the above catalysts.

In the low-temperature decomposition of CHP by the use of triphenylsulfonium chloride, the main decomposition products are homolytic products: acetophenone (AP), dicumyl peroxide (DCP), and α-cumyl alcohol (CA). It is noticeable that the sulfonium salt catalyses the formation of methyl alcohol, which is scarcely at all found in the usual thermal decomposition of CHP in cumene.[1-3] This decomposition reaction is of a heterolytic nature because of the formation of phenol and acetone. Such processes of a heterolytic nature may be caused by an action of the counter chloride anion of the sulfonium catalyst. A presumption is made that the partially-occupied *d* orbitals[8] of the sulfonium cation might play an important role in the decomposition of CHP.

Experimental

Reagents. Commercial cumene hydroperoxide (CHP) (purity below 70%) was distilled in order to collect a fraction, 60°C/0.1 mmHg. In order to free it from traces of impurities, the fraction was extracted with sodium bicarbonate, filtered chromatographically through activated alumina (200—300 mesh), and stored in a nitrogen atmosphere at 0°C. The cumene was purified as has previously been described.[8,9] The sample of α-cumyl alcohol (CA) used (free from acetophenone) was recrystallized several times from ligroin. The dicumyl peroxide (DCP) and hydroquinone employed were of a commercially pure grade. The triphenylsulfonium chloride was prepared by the method described in a previous report.[10]

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[1] J. W. Forgham and H. L. Williams, *Can. J. Res.*, **B27**, 943 (1949).

[2] V. Stannett and R. B. Mesrobian, *J. Amer. Chem. Soc.*, **72**, 4125 (1950).

[3] M. S. Kharasch, A. Fono and W. Nudenberg, *J. Org. Chem.*, **16**, 113 (1951).

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

[9] K. Ohkubo, T. Yamabe and K. Fukui, *ibid.*, **42**, 2220 (1969).

[10] K. Fukui, K. Kanai, T. Takezono and H. Kitano, *Kogyo Kagaku Zasshi*, **67**, 1131 (1964).

Analysis of Reaction Products. The CHP, DCP, AP, and CA were determined in a way previously described.[9] The gaseous reaction products were collected by condensation at −76°C and were determined by gas chromatography as well as by an Orsat apparatus. For oxygen absorption, Fieser's solution[11] and a pyrogallol solution were used. The determination of the products obtained in trace amounts was also performed. The phenol was converted to tribromophenol.[12] The acetone was estimated on the basis of the iodoform equivalent.[13]

Reaction Procedure. The decomposition reaction of CHP in the presence of triphenylsulfonium chloride was carried out as follows. Triphenylsulfonium chloride was introduced into a reaction vessel containing CHP (22.5 mmol) and cumene (20 m*l*). The homogeneous reaction mixture was stirred with a magnetic stirrer at the desired temperature. The evolved gas was then collected at −76°C by a gas trap attached to an Orsat apparatus. The decomposition of CHP in cumene was followed by iodometric titration.

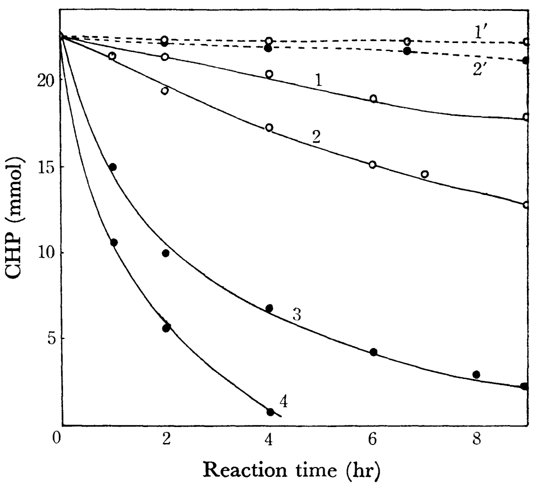

Fig. 1. The decomposition of CHP in the presence of $(C_6H_5)_3SCl$.

—○—: at 65°C, 1. 0.27 mmol 2. 0.35 mmol
—●—: at 80°C, 3. 0.27 mmol 4. 2.12 mmol
---○---: at 65°C, 1′. None
---●---: at 80°C, 2′. None

Results and Discussion

It is worthy of emphasis that CHP in cumene decomposes appreciably in the presence of sulfonium salts at relatively low temperatures (below 80°C), even though CHP is thermally so stable that little decomposition takes places in 48 hr at 100°C.[14] These phenomena are indicated in Fig. 1, where the thermal decomposition is very little, while the catalytic reaction is accelerated with the increase in the amount of the sulfonium catalyst and in the reaction temperature. The decrease in catalytic ability for CHP decomposition with the reaction time, especially at 80°C, may be connected with the masking action[9] of the products and of CHP itself, since the kinetic order of the reaction rate to the amount of the catalyst gradually decreases with the reaction time considering a first-order cleavage of CHP[3,6,7] (from the 0.55th order at the initial step to the 0.51st order and 0.47th order at 2.0 hr and 3.0 hr respectively). Table 1 indicates the distribution of reaction products with the reaction time. The formation of AP, DCP, and CA suggests that the catalytic decomposition of CHP is homolytic, while the small quantities of

TABLE 1. THE DECOMPOSION OF CHP (22.4 mmol) BY $(C_6H_5)_3SCl$ (0.37 mmol) AT 65°C

Reaction time (hr)	CHP decomposed (mmol)	Products[c]					
		AP (%)	DCP[a] (%)	CA (%)	C_6H_5OH (%)	CH_3COCH_3 (%)	Gas[b] (%)
1.0	0.9	48.3	45.5	1.1	trace	trace	30.3
2.0	3.2	45.4	46.6	1.8	0.6	0.3	37.2
4.0	5.1 (0.05)*	42.0	40.8	5.9	—	—	—
7.0	7.8 (0.10)*	44.3	39.6	7.4	1.0	0.9	—
10.3	12.5 (0.50)*	41.2 (63.8)*	38.4 (21.4)*	9.6 (5.2)*	1.2 (0.0)*	1.1 (0.0)*	33.4 —

* Thermal decomposition of CHP.
a) Mol% was calculated from 2 × DCP formed(mol)/ CHP decomposed(mol).
b) The gas evolved in this experiment was not thoroughly analyzed, but contains mainly methane. Oxygen was not detected in appreciable amounts.
c) Products were presented by mol% on the basis of CHP decomposed.

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[11] L. F. Fieser, *J. Amer. Chem. Soc.*, **46**, 2639 (1924).

[12] R. L. Shriner, R. C. Fuson and D. Y. Curtin, "The Systematic Identification of Organic Compounds," John Wiley & Sons, New York (1956), p. 264.

[13] R. L. Shriner, R. C. Fuson and D. Y. Curtin, *ibid.*, John Wiley & Sons, New York (1956), p. 156.

[14] M. S. Kharasch, A. Fono and A. C. Poshkus, *J. Org. Chem.*, **15**, 775 (1950).

TABLE 2. THE EFFECT OF THE AMOUNT OF $(C_6H_5)_3SCl$ UPON THE DECOMPOSITION OF CHP (22.5 mmol)

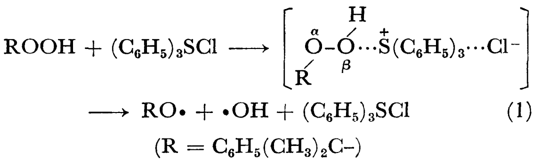
$(C_6H_5)_3SCl$ (mmol)	Reaction temp. (°C)	Reaction time (hr)	CHP decomposed (mmol)	Products[a)]						
				AP (%)	DCP (%)	CA (%)	CH_3OH[b)] (%)	C_6H_5OH (%)	CH_4[c)] (%)	O_2 (%)
0.27	65	9.0	4.50	50.6	37.4	11.1	12.1	—	30.4	0.0
0.27	65	13.0	7.2	57.8	30.2	9.2	18.2	1.7	—	0.0
0.37	65	9.0	10.1	52.6	30.3	8.0	12.8	—	32.0	0.0
0.50	65	13.0	12.40	58.8	21.1	10.1	17.4	2.0	—	—
0.27	80	9.0	20.47	51.4	32.8	14.5	—	—	32.1	—
2.12	80	5.0	22.39	59.3	24.7	15.6	11.7	1.2	—	—
7.03	80	4.0	21.80	48.8	38.2	8.8	13.2	1.5	—	0.0

a) Products were presented by mol% on the basis of CHP decomposed. But DCP (%) was calculated from 2 × DCP formed(mol)/CHP decomposed(mol).

b) This amount of methyl alcohol was determined from that of CH_3OH in the gas trap and its amount in the reaction mixture was negletced.

c) Gaseous products were not analyzed but tentatively assumed as methane.

phenol and acetone produced imply that this reaction might include the heterolytic cleavage of CHP. Moreover, as is shown in Table 2, one of the products of this reaction is an appreciable amount of methyl alcohol, which is hardly ever found in a usual homolytic thermal decomposition reaction in such non-polar solvents as cumene. From these results, the mechanism of this low-temperature reaction may be discussed.



$$ROOH + (C_6H_5)_3SCl \longrightarrow \left[\overset{\alpha}{O}\text{–}\underset{\beta}{\overset{H}{O}}\cdots\overset{+}{S}(C_6H_5)_3\cdots Cl^-\right] \longrightarrow RO\bullet + \bullet OH + (C_6H_5)_3SCl \qquad (1)$$

$$(R = C_6H_5(CH_3)_2C\text{–})$$

In the first step of this reaction, sulfonium salt may cleave the oxygen-oxygen bond of CHP into two parts, α-cumyloxy and hydroxy radicals. In all the bonds of CHP, the oxygen-oxygen bond is the weakest in the sense that the dissociation energy of this bond is considerably smaller than those of the other bonds. Following a molecular orbital calculation by Fukui *et al.*,[15)] the lowest vacant orbitals of hydroperoxides are the $p\sigma$-type anti-bonding orbitals of the O–O bond. In the catalytic process, the electron of the partially-occupied *d* orbital[8)] of the central sulfur atom of the sulfonium cation may be transferred to this lowest vacant orbital. The interaction of this orbital with electron-donor molecules would take place in the direction of the bond axis from the β-oxygen side, since the partial population of the β-oxygen of this vacant orbital is larger than that of the α-oxygen.[15)] The charge transferred from the sulfonium moiety to the oxygen-oxygen bond may increase the antibonding character of the bond and promote the scission. This circumstance is portrayed in Fig. 2. In this figure, the structure of the triphenylsulfonium ion is assumed to be a propeller-like D_3 symmetry, like the triphenylcarbonium cation.[16)] In this connection the mode of the interaction between the $p\sigma$-orbital of the O–O bond and the "partially occupied" *d*-orbital[8)] on the sulfonium sulfur atom comes into question. From both energetic and steric points of view, the d_{z^2}-orbital seems to the most probable *d*-orbital interacting with CHP. Several reasons for this can be mentioned: (1) d_{xy} and $d_{x^2-y^2}$ orbitals in the field of the sp^2-hybridized S atom[8)] are energetically unstable because of the interaction with three sulfur-phenyl bonds; (2) the interaction of the *d*-orbitals (d_{xy} and $d_{x^2-y^2}$) with CHP will be sterically hindered by phenyl groups; (3) d_{xy} and d_{yz} orbitals become somewhat unstable by the interaction, through d-π-type conjugation, with π-orbitals of phenyl groups,[17–19)] while phenyl rings also sterically hinder the interaction with CHP to some extent (see Fig. 2), and (4) the d_{z^2}-orbital is most acceptable because it has no conjugation with the π orbitals of phenyl groups and because it has only a small interaction with sulfur-phenyl bonds.

In the transition state shown in the scheme of reaction (1), the hydroxyl group may bear a somewhat ionic character in view of the large electron affinity of the HO radical (~136 kcal).[20)] At this stage, the partially-ionic hydroxyl group would exhibit a counter-anion like behavior.[*1] In conformity with the liberation of the OH radical, the

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[15)] T. Yonezawa, O. Yamamoto, H. Kato and K. Fukui, *Nippon Kagaku Zasshi*, **87**, 26 (1966).

[16)] D. W. A. Sharp and N. Sheppard, *J. Chem. Soc.*, **1957**, 674.

[17)] L. Goodman and R. W. Taft, *J. Amer. Chem. Soc.*, **87**, 4385 (1965).

[18)] R. W. Taft and J. W. Rokshys, Jr., *ibid.*, **87**, 4387 (1965).

[19)] C. C. Price and S. Oae, "Sulfur Bonding," The Ronald Press, New York (1962), p. 152.

[20)] N. Uri, *Chem. Rev.*, **50**, 375 (1952).

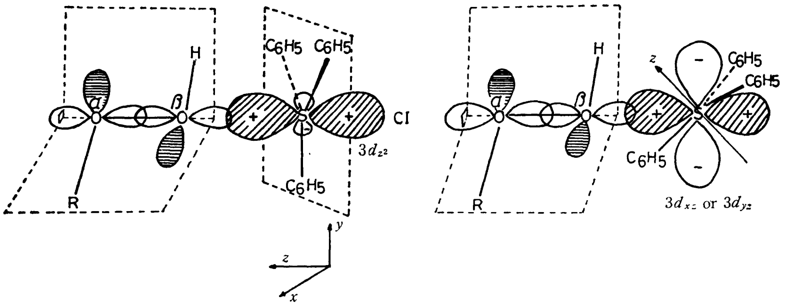

Fig. 2. Assumed mode of reaction between ROOH and $(C_6H_5)_3SCl$.

electron migration would take place, again through the central sulfur, to an opposite-side-lying chlorine atom, thus regenerating the triphenylsulfonium chloride. Actually, triphenylsulfonium hydroxide is never formed in the final system. The α-cumyloxy radicals primarily formed are then readily converted to the major reaction products (presented in Table 1) through reactions (2a), (2b), and (2c).

$$RO\cdot \xrightarrow{\beta\text{-scission}} AP + CH_3\cdot \qquad (2a)$$

$$RO\cdot \xrightarrow[RO\cdot]{\text{coupling}} DCP \qquad (2b)$$

$$RO\cdot \xrightarrow[RH]{\text{hydrogen abstraction}} ROH + R\cdot \qquad (2c)$$

$(R = \alpha\text{-cumyl})$

The reaction of the RO radical with ROOH is not presented because the reaction does not seem essential; the concentration of ROOH is much lower than that of RH.

Among the above products, DCP and AP are formed predominantly. The formation of such large amounts of the former may be attributed to its thermal stability in this temperature range. However, an accumulation of DCP causes gradual decomposition as the reaction proceeds, because DCP is decomposed by the sulfonium catalyst[9)] to some extent. The results are shown in Table 1. The remarkable formation of AP may be attributed to the ease of the β-scission of a carbon-methyl bond in the α-cumyloxy radical. After the α-cumyloxy radical is formed from the cleavage of the O–O bond of CHP, the odd electron may conjugate with the sigma electrons of a $C–CH_3$ bond through π-type orbital overlapping. This is a pi-participation of the oxygen *p*-electron in the β-methyl fission.

Interestingly, CA is formed only in small amounts. No such result was observed in the thermal decomposition at higher temperatures,[3,4)] where both CA and AP are produced in comparable amounts. The CA formation may be depressed at lower reaction temperatures by the steric hindrance of both bulky reactants (α-cumyloxy radical and cumene). The small quantity of CA formation will be discussed below.

On the other hand, the hydroxy radical primarily formed from CHP readily undergoes conversion to CH_3OH and H_2O through hydrogen abstraction or through coupling with the methyl radical.

$$\cdot OH \xrightarrow{RH} H_2O + R\cdot \qquad (3a)$$

$$\cdot OH \xrightarrow{ROOH} H_2O + RO_2\cdot \qquad (3b)$$

$$\cdot OH \xrightarrow{\cdot CH_3} CH_3OH \qquad (3c)$$

Reactions (3a) and (3c) are probable because water[*2] and methyl alcohol are found in the products in appreciable amounts (see Tables 2 and 3). Reaction (3b) seems not very likely to occur since the oxygen evolution expected from the recombination of the cumylperoxy radical[*3] was not observed. Kharasch[3)] also argued the difficulty of reaction (3b) from the kinetic point of view. The coupling and disproportionation of the OH radical must also be mentioned.

$$\cdot OH + \cdot OH \rightleftarrows H_2O_2 \qquad (3d)$$

$$\cdot OH + \cdot OH \longrightarrow H_2O + \cdot O\cdot \qquad (3e)$$

However, these reactions are obviously much less important than (3a) and (3c). In reaction (3d), the reverse reaction is dominant in the present case. Reaction (3e) may be difficult energetically; actually, no evolution of gaseous oxygen was observed.

[*1] This is expected from the fact that triphenylsulfonium chloride is actually very hygroscopic and that an air-polluted sample shows an appreciable OH peak in the infrared region. It should here be stressed, however, that in spite of such a strong affinity to OH groups, triphenylsulfonium salt does not decompose easily in polar sovents containing OH groups, such as water, hydroperoxides and various kinds of alcohols, and can even be recrystallized from them. It should further be emphasized that no products formed by the coupling of R· or CH_3· with the chlorine atom, such as α-cumyl chloride and methyl chloride, result from this decomposition reaction.

[*2] The quantitative determination of the amount of water was not performed in our experiments.

[*3] Cumylperoxy radicals ($RO_2\cdot$) easily combine with each other to evolve gaseous oxygen: $2RO_2\cdot \rightarrow [RO_4R] \rightarrow 2RO\cdot + O_2$

Radicals produced secondarily by dismutation or by reaction with the solvent (RH) may take part in the decomposition of CHP.[1,2] In the first place, the methyl radical formed mainly from the β-scission of the α-cumyloxy radical contributes to the formation of methyl alcohol reaction (4a) as well as to the formation of gaseous products through reactions (4b) and (4c):

$$\cdot\mathrm{CH_3} - \left| \begin{array}{lr} \xrightarrow{\mathrm{ROOH}} \mathrm{CH_3OH + RO\cdot} & \text{(4a)} \\ \xrightarrow{\mathrm{RH}} \mathrm{CH_4 + \cdot R} & \text{(4b)} \\ \xrightarrow{\mathrm{RO\cdot}} \mathrm{C_2H_6 + AP} & \text{(4c)} \end{array} \right.$$

Reaction (4a) may be promoted by the sulfonium catalyst for the same reasons as is the decomposition of CHP (see reaction (1)). Reactions (4b) and (4c) appear to take place more readily than (4a), since gaseous products are actually formed in larger amounts than methyl alcohol[*4] (see Tables 2 and 3).

In the second place, the slight CA formation, compared with that of AP, would be explained by the behavior of the α-cumyloxy radicals (RO•) formed in the primary step (1) and in the secondary step (4a). The possible reactions of CA formation may be reactions (2c), (5a), and (5b):

$$\mathrm{RO\cdot} - \left| \begin{array}{lr} \xrightarrow{\mathrm{RH}} \mathrm{ROH + R\cdot} & \text{(2c)} \\ \xrightarrow{\mathrm{ROOH}} \mathrm{ROH + RO_2\cdot} & \text{(5a)} \\ \xrightarrow{\mathrm{H_2O}} \mathrm{ROH + HO\cdot} & \text{(5b)} \end{array} \right.$$

If the ease of the hydrogen abstraction of the RO radical depends mainly on the bond-dissociation energy in hydrogen donors, reactions (2c) and (5a) will be more predominant than (5b), because the dissociation energies of R–H (~85 kcal) and ROO–H (~89.5 kcal)[*5] are considerably lower than HO–H (~120 kcal[10]). However, reaction (5a) is unlikely, like (3b), because of the low concentration of ROOH compared with RH; the absence of reaction (5a) can be ascertained from the lack of any evolution of oxygen, even though ROOH is as good a hydrogen donor as RH. Hence, it may be reasonable to conclude that CA is formed predominantly through the reaction path (2c). At any rate, the small amount of CA may be attributed to the prevalence of the intramolecular reaction (2a) over the intermolecular one (2c).

In the third place, it should be noted that the coupling product of α-cumyl radicals (R•), namely, bi-α-cumyl (R–R), is not found in any appreciable amount. From the facts that the R radicals formed tend to be easily deactivated by the trapping of the RH solvent or of other solvents (ROOH and H_2O), and that the amount of active R radicals may be small, the chance of coupling may be small.

In the thermal decomposition of CHP in cumene at the temperatures of 128°C and 158°C, Kharasch and his co-workers[3] confirmed the negligible amount of bi-α-cumyl in spite of the remarkable formation of R radicals. They attributed this result to the reaction of the R radical with ROOH, which contributes to the CA formation through the following path:

$$\mathrm{ROOH + R\cdot} \rightleftarrows \text{Complex A}$$

$$\text{Complex A} + \mathrm{RH} \longrightarrow \mathrm{2ROH + R\cdot}$$

However, such a complex was not confirmed. As for the explanation of the negligible formation of bi-α-cumyl, the difficulty of R–R formation must first of all be mentioned, especially in the low-temperature reaction of our experiments.

The homolytic nature of the low-temperature decomposition by the sulfonium chloride may have been clarified in the above discussions. However, the reaction seems to involve a somewhat heterolytic part. The formations of phenol and acetone in measurable amounts (as is shown in Tables 1 and 2) should be regarded as the result of heterolytic decomposition. In this connection, the role of the chloride anion of sulfonium salt should be noticed. It may be reasonable to presume, as was indicated in the works by Barb and his co-workers,[23,24] by Kolthoff and Medals,[25,26] by Taube and Bray,[27] and by Allen,[28] that the chloride anion is converted to the chlorine atom through charge-transfer to the hydroxy radical:

$$\mathrm{Cl^- + \cdot OH \longrightarrow Cl\cdot + OH^-} \qquad \text{(6a)}$$

$$\underset{\text{(or ROOH)}}{\mathrm{Cl\cdot + RH}} \longrightarrow \underset{\text{(or RO}_2\text{)}}{\mathrm{HCl + R\cdot}} \qquad \text{(6b)}$$

$$\mathrm{C_6H_5C(CH_3)_2O_2H \xrightarrow{H^+(HCl)} C_6H_5OH + (CH_3)_2CO + H^+(HCl)} \qquad \text{(6c)}$$

The possibility of (6a) is also supported by the fact that reaction (6a) has the very small activation energy of 3 kcal.[20] The chlorine atom thus formed

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[*4] The methane formation should be ascribed to the hydrogen abstraction of $CH_3\cdot$. The activation energy of the reaction $CH_3\cdot + ROOH$ (R=*t*-butyl) → $CH_4 + RO_2\cdot$ is 8.1 kcal, while that of $CH_3\cdot + RH$(*n*-hexane)→ $CH_4 + R\cdot$ is 11.7 kcal.[21]

21) A. F. Trotman-Dickenson, "Gas Kinetics," Butterworth Scientific Publications, London (1955).

[*5] The dissociation energy of ROO–H is assumed to be the same as that of HOO–H (89.5 kcal).[22]

22) S. W. Benson, *J. Amer. Chem. Soc.*, **86**, 3922 (1964).

23) W.G. Barb, J.H.P. Baxendale, P. George and K.R. Hargrave, *Trans. Faraday Soc.*, **47**, 462 (1951).

24) W.G. Barb, J.H.P. Baxendale, P. George and K.R. Hargrave, *ibid.*, **47**, 591 (1951).

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26) I. M. Kolthoff and A. I. Medala, *ibid.*, **71**, 3784 (1949).

27) H. Taube and W. C. Bray, *ibid.*, **62**, 3357 (1940).

28) A. O. Allen, *J. Phy. & Colloid Chem.*, **52**, 479 (1948).

TABLE 3. TEMPERATURE EFFECT UPON THE DECOMPOSITION OF CHP (22.5 mmol) BY TRIPHENYLSULFONIUM CHLORIDE

$(C_6H_5)_3SCl$ (mmol)	Reaction temp. (°C)	Reaction time (hr)	CHP decomposed (mmol)	Products[a)]					
				AP (%)	DCP (%)	CA (%)	CH_3OH (%)	CH_4[b)] (%)	O_2 (%)
none	80	9.0	1.20	42.9	40.0	9.65	trace	33.0	0.0
0.27	80	9.0	20.47	51.4	32.8	14.5	—	32.1	0.0
0.27	65	9.0	10.1	52.6	37.3	8.0	12.8	35.0	0.0
3.35	55	4.0	5.50	41.6	41.3	8.2	9.8	—	—
2.12	30	4.0	0.00						

a) Products were presented by mol% on the basis of CHP decomposed.
But DCP (%) was calculated from 2 × DCP formed(mol)/CHP decomposed(mol).
b) The gase evolved in this experiment was not fully analyzed, but contained mainly methane.

will react with RH or ROOH to produce HCl, which behaves as a catalyst for reaction (6c). However, in the sulfonium chloride, the supply of free Cl^- can not be expected because of the appreciable covalent nature[8)] of the bond between the sulfonium cation and the counter-anion. Actually, more than 70% of the triphenylsulfonium chloride can be recovered from the reaction mixture, even after a 13-hr reaction. Hence, the contribution of the chloride anion is limited, even if it takes part in the heterolytic decomposition. This is reflected in the very small amounts of phenol and acetone formed.

Another possibility for the heterolytic decomposition of CHP has been postulated by Kharasch and his co-workers[3)] in the following self-decomposition of CHP ((7) and (8)):

$$C_6H_5(CH_3)_2COOH \xrightarrow{\text{heterolytic cleavage}} C_6H_5(CH_3)_2CO^+ + OH^- \qquad (7)$$

$$C_6H_5(CH_3)_2CO^+ \xrightarrow{\text{rearrangement}} C_6H_5O(CH_3)_2C^+ \qquad (8)$$

The cation formed is capable of further conversion to give phenol and acetone. However, it seems difficult for reaction (7) to occur without traces of acidic impurities; therfore, the small amounts of phenol and acetone formed may be ascribed to the contribution of the chloride anion.

The temperature effect on the catalytic decomposition of CHP is shown in Table 3. As the table shows, the homolytic decomposition proceeds even at 55°C, but it disappears at 30°C. The increase in the temperature depresses the DCP formation, implying the thermal decomposition of DCP, whereas AP and CA increase to some extent.

It is necessary to investigate the effect of the decomposition products on the reaction in order to clarify the mechanism. Table 4 indicates the additive effect of CA, DCP, and hydroquinone. Hydroquinone is employed as an additive of the hydrogen donor. At first, the reaction system initially containing CA as an additive evolves gaseous oxygen, which is undetectable in the absence of the alcohol. This phenomenon may be attributed to the heterolytic decomposition of CHP, as was first pointed out by Kharasch and his co-workers.[3),*6] It is obvious that the catalytic decomposition is markedly prevented by the addition of CA. This fact may be directly connected with the masking action[9)] of the additive. Such a masking action of CA depresses the catalytic activity on the homolytic decomposition of CHP, leading to the heterolytic decomposition.

Secondary, the effect of DCP addition is apparently confirmed in the remarkable formation of AP and CH_3OH. This result suggests that the growth of the RO• concentration caused by the DCP decomposition promotes reaction (2a) and subsequently (4a).

Thirdly, it is well known that hydroquinone is a good hydrogen donor as well as a radical scavenger. The remarkable effect of its addition appears to be the reaction with RO radicals to give ROH. Furthermore, hydroquinone depresses the catalytic activity through the masking action caused by the hydrogen bonds of hydroquinone molecules and disturbs the dismutation or recombination of RO radicals by the exclusive formation of ROH.

In connection with the CHP decomposition by triphenylsulfonium chloride, the reactions of CHP with such other sulfur compounds as sulfide and thiophene were also carried out. Diphenyl sulfide produced CA mainly, while thiophene formed AP predominantly, as is shown in Table 5. The sulfides have no electron in *d*-orbitals, but have lone-pair

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[*6] They have suggested the following mechanism of the oxygen evolution:

$$\underset{}{ROOH + ROH} \rightleftarrows \underset{\text{(conjugate base)}}{ROO^-} + \underset{\text{(conjugate acid)}}{ROH_2^+}$$

$$ROO^- + ROOH \longrightarrow ROH + O_2 + RO^-$$

$$RO^- + ROH_2^+ \longrightarrow 2ROH$$

(R=α-cumyl)

TABLE 4. THE EFFECT OF ADDITIVES UPON THE DECOMPOSITION OF CHP (22.5 mmol) BY TRIPHENYLSULFONIUM CHLORIDE (0.37 mmol) AT 80°C FOR 9.0 hr

Additive (mol% on basis of CHP)	CHP decomposed (mmol)	Products[a)]							
		AP (%)	DCP (%)	CA (%)	CH_3OH (%)	C_6H_5OH (%)	CH_3COCH_3 (%)	CH_4[b)] (%)	O_2 (%)
None	21.38	40.2	36.5	12.3	11.7	1.5	1.3	32.4	0.0
α-Cumyl alcohol (5.0%)	17.4	46.7	30.7	16.8	13.6	2.8	2.2	—	4.0
Dicumyl peroxide (5.0%)	22.5	54.9	—	9.4	19.3	—	—	—	0.0
Hydroquinone (10%)	14.0	32.6	25.0	35.5	15.8	3.0	2.5	—	0.0

a) Products were presented by mol% on the of basis of CHP decomposed.
But DCP (%) was calculaed from 2 × DCP formed(mol)/CHP decomposed(mol).

b) Gaseous products were not analyzed and assumed as methane because ethane may be produced only in negligibly small amounts.

TABLE 5. THE DECOMPOSITION PRODUCTS OF CHP BY THE USE OF SULFUR COMPOUNDS (initial amount of CHP: 22.5 mmol, reaction temperature: 80°C)

Compound	The amount of the compound (mmol)	Reaction time (hr)	The amount of CHP decomposed (mmol)	Products		
				AP (mmol)	DCP (mmol)	CA (mmol)
$(C_6H_5)_2S$	2.84	3.0	6.0	0.72	1.0	3.0
$(C_6H_5)_2S$	7.40	4.0	20.0	1.64	2.2	13.8
$(C_6H_5)_2S$	10.8	4.0[a)]	trace			
$(C_6H_5)_2S{=}O$	23.4	3.0	trace			
$\overline{CH(CH)_3S}$	6.0	3.0	4.6	4.0		
$\overline{CH(CH)_3S}$	23.8	4.0[b)]	15.6	13.6		

a) The reaction temperature was 25°C.
b) The reaction temperature was 65°C.

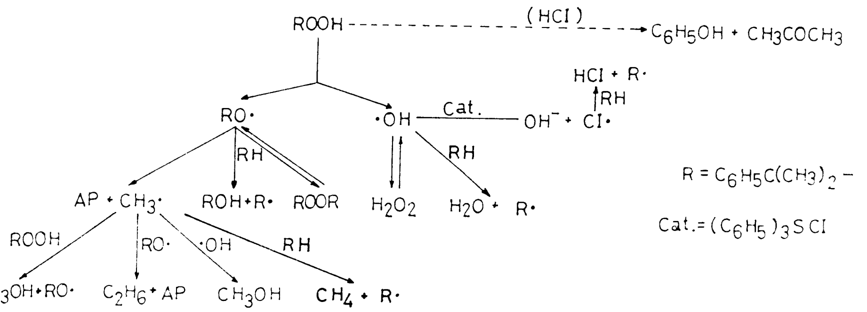

Fig. 3. A scheme for the mechanism of CHP decomposition by $(C_6H_5)_3SCl$.

electrons in the *p*-orbitals. They may act on CHP as nucleophiles and come to be sulfoxides themselves, which means that the hydrogen atom of CHP might migrate to the RO radical to form ROH in the transition state of the reaction. Detailed discussions will not be undertaken here, however, since the mechanism of the reaction of sulfides with hydroperoxide has been extensively discussed by many authors.[29–33]

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29) L. Bateman and K. R. Hargraue, *Proc. Roy. Soc.*, **A 224**, 389, 399 (1954).

30) L. Bateman and J. Cunneen, *J. Chem. Sec.*, **1955**, 1596.

31) L. Bateman and F. W. Sibley, *ibid.*, **1955**, 1996.

32) D. Barnard, *ibid.*, **1956**, 489.

33) K. R. Hargraves, *Proc. Roy. Soc.*, **A 225**, 55 (1956).

In conclusion, the decomposition mechanism of cumene hydroperoxide by triphenylsulfonium chloride is schematically illustrated in Fig. 3.

The features of the present experiments may be summarized thus:

a) In the low-temperature range (55—80°C), triphenylsulfonium chloride decomposes CHP remarkably. The partially-occupied $3d_{z^2}$ orbital of the central sulfur atom of the sulfonium salt may participate in the cleavage of the O–O bond of CHP.

b) The chloride anion of the sulfonium catalyst seems to be connected with the heterolytic decomposition of CHP.

c) Among the decomposition products, AP and DCP are mainly formed, while CA is found only in small quantities.

d) Methyl alcohol is formed in appreciable amounts. The catalyst is likely to aid its formation.

e) The hydroxy radicals primarily formed are consumed to produce H_2O and CH_3OH.