Decay Kinetics of Cumylperoxyl Radical produced by the Decomposition of Cumene Hydroperoxide

By **Shun-ichi Fukuzumi** and **Yoshio Ono**,* Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo, Japan 152

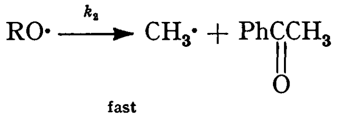
Cumylperoxyl radicals, produced by the decomposition of cumene hydroperoxide on heterogeneous catalysts (manganese dioxide and cobalt oxide supported on silica) at 300 and 295 K, have been detected in the liquid phase by use of e.s.r. spectroscopy. The decay kinetics of cumylperoxyl radicals have been investigated at various initial concentrations of the peroxyl radical (2.3×10^{-6}—1.12×10^{-5}M) over a range of the initial hydroperoxide concentration (0.74—4.70M). The decay of cumylperoxyl radicals strictly obeyed first-order kinetics with rate constant $k_t = 0.15 \pm 0.01\ \text{s}^{-1}$ at 300 K, irrespective of the initial hydroperoxide concentration, the solvent used as diluent (carbon tetrachloride, benzene, and cumene), and the catalyst (manganese dioxide and cobalt oxide supported on silica).

THE self-reaction of peroxyl radicals has been extensively studied because it is responsible for chain termination in hydrocarbon autoxidations. The rate of self-reaction of primary or secondary peroxyl radicals is generally accepted to obey second-order kinetics [reaction (1)].[1]

$$2R_2CHOO\cdot \longrightarrow R_2C{=}O + R_2CHOH + O_2 \qquad (1)$$

$$\begin{array}{ll} ROO\cdot + ROO\cdot \overset{K}{\rightleftharpoons} (RO_4R) \xrightarrow{k_{1a}} 2RO\cdot + O_2 & \\ \qquad\qquad\qquad\qquad\quad \xrightarrow{k_{1b}} ROOR + O_2 & (2) \end{array}$$

$(R = PhCMe_2)$



$$RO\cdot \xrightarrow{k_2} CH_3\cdot + PhC(=O)CH_3 \qquad (3)$$

$$CH_3\cdot + O_2 \xrightarrow{\text{fast}} CH_3OO\cdot \qquad (4)$$

$$CH_3OO\cdot + ROO\cdot \xrightarrow{k_4} CH_2O + O_2 + ROH \qquad (5)$$

$$RO\cdot + RH \xrightarrow{k_5} ROH + R\cdot \qquad (6)$$

$$RO\cdot + ROOH \xrightarrow{k_6} ROH + ROO\cdot \qquad (7)$$

$$CH_3OO\cdot + RH \xrightarrow{k_7} R\cdot + CH_3COOH \qquad (8)$$

The decay process of tertiary peroxyl radicals is more complicated. For example, in the case of cumylperoxyl radicals, mechanism (2)—(8) has been proposed by several authors.[1] Acceptance of this mechanism gives the rate expression (9) for termination of cumene

$$R_t = k_t[ROO\cdot]^2 \qquad (9)$$

autoxidation [2] with the definitions (10) and (11). The

$$k_t = k_{1b}F + k_{1a} \qquad (10)$$

$$F = \frac{k_2k_4[ROO\cdot]}{(k_2 + k_5[RH] + k_6[ROOH])(k_4[ROO\cdot] + k_7[RH])} \qquad (11)$$

inclusion of reactions (3)—(8) is based on the fact that appreciable amounts of acetophenone are observed among the products.[2-4]

While the mechanism demands second- or third-order decay of peroxyl radicals, the direct determination of the kinetics of the decay process by e.s.r. spectroscopy has led to the reaction being reported as of first, second,

---

[1] J. A. Howard, *Adv. Free Radical Chem.*, 1972, **4**, 49 and references therein.

[2] D. G. Hendry, *J. Amer. Chem. Soc.*, 1967, **89**, 5433.

[3] H. S. Blanchard, *J. Amer. Chem. Soc.*, 1959, **81**, 4548.

[4] T. G. Traylor and C. A. Russell, *J. Amer. Chem. Soc.*, 1965, **87**, 3698.

or intermediate order. Ingold and Morton[5] found that t-butylperoxyl radicals formed by the photolysis of di-t-butyl peroxide decayed with first-order kinetics in a variety of solvents. Zwolenik[6] reported that cumylperoxyl radicals produced by the photolysis of neat cumene hydroperoxide decayed with second-order kinetics. Maguire and Pink[7] found the decay kinetics of peroxyl radicals varied between first and second order depending on the experimental conditions. Thomas[8] produced t-butylperoxyl radicals by the reaction of t-butylperoxide with ceric ions, and found that the decay of the radical was second order at low radical concentrations ($4—8 \times 10^{-5}$M), and that over a higher concentration range (10^{-3}M) it was no longer second order but was represented more accurately as a combination of first- and second-order processes. Bennett *et al.*[9] reported that tertiary alkylperoxyl radicals derived from 2-methylpentane and 2,2,3-trimethylbutane decayed with good second-order kinetics over the temperature ranges 213—283 and 243—293 K, respectively.

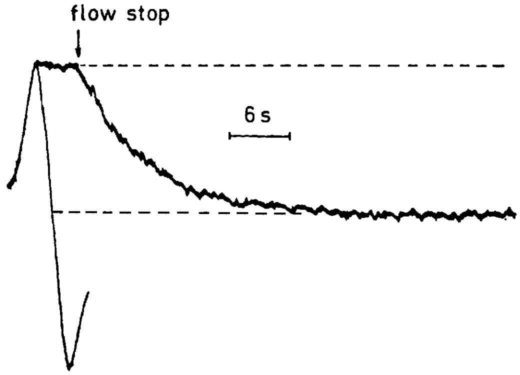
In most of these reports, peroxyl radicals are formed by the photolysis of hydroperoxides or peroxides and there is the possibility that the measured kinetics might be complicated by the involvement of the reaction of peroxyl radicals with other products of photolysis. We have recently reported that free radicals can be generated by flowing the substrate through a plug of manganese dioxide.[10,11] In this work, we have applied this technique to the formation of peroxyl radicals. A solution of cumene hydroperoxide was passed through the column of manganese dioxide, the exit of which led directly to the e.s.r. cavity. By changing the flow rate of the solution or the concentration of the hydroperoxide, the concentration of cumylperoxyl radical could be systematically controlled. Then, by stopping the flow suddenly, the decay kinetics of cumylperoxyl radicals can be measured under conditions very close to those of the autoxidation reaction.

EXPERIMENTAL

The method of radical generation was essentially that described previously.[10,11] Cumylperoxyl radical was prepared by passing a cumene hydroperoxide solution through tubing (i.d. 6 mm) packed with manganese dioxide (1.0 g; 20—30 mesh) or cobalt oxide supported on silica. The cumene hydroperoxide solution (0.74—4.70M) was added with a flow rate of 5—200 $cm^3 min^{-1}$. Carbon tetrachloride, benzene, or cumene were used as solvent. The outlet of the column led directly to the e.s.r. cavity. When the flow rate of the solution was kept constant, a steady concentration of cumylperoxyl radical was observed. The decay rate of the radical was measured by stopping the flow and by monitoring the decrease of the e.s.r. signal intensity. The response time of the e.s.r. recording system was kept far shorter than the life time of the radical. The e.s.r. measurements were carried out with a JEOL X-band spectrometer (JES-PE-1X) with a 100 kHz magnetic field modulation. The radical concentration was determined by calibration with a standard solution of 1,1-diphenyl-2-picrylhydrazyl in benzene. The change in sensitivity of the spectrometer due to the decrease in the Q factor by introducing a polar substrate such as cumene hydroperoxide was calibrated by use of an e.s.r. marker included in the e.s.r. cavity.

RESULTS AND DISCUSSION

Kinetics of Radical Decay.—When cumene hydroperoxide in carbon tetrachloride was passed through manganese dioxide column, a symmetric singlet signal was observed. The line width of the signal (0.65—1.53 mT) and the g value (2.014 6—2.015 0) depended on the initial concentration of cumene hydroperoxide. This g value is consistent with the one reported for cumylperoxyl radical,[6,12] and is clearly different from ones for alkoxyl radicals.[13] Thus, it is concluded that the observed signal is ascribed to cumylperoxyl radicals.



E.s.r. decay curve at 301 K; initial concentration of cumylperoxyl radical 8.0×10^{-6}M

Metal oxides such as manganese dioxide are often used as catalysts for hydrocarbon autoxidation and their role in the oxidation is postulated to be in initiating the radical chain mainly by the decomposition of hydroperoxides.[14,15] The observation of peroxyl radicals with the present method supports the idea of heterogeneous initiation of chain reactions.

On stopping the flow of the solution, a decrease in radical concentration was observed as shown in the Figure, and in several tens of seconds, the e.s.r. signal disappeared completely. Though the line width of the

---

[5] K. U. Ingold and J. R. Morton, *J. Amer. Chem. Soc.*, 1964, **86**, 3400.

[6] J. J. Zwolenik, *J. Phys. Chem.*, 1967, **71**, 2464.

[7] W. J. Maguire and R. C. Pink, *Trans. Faraday Soc.*, 1967, **63**, 1097.

[8] J. R. Thomas, *J. Amer. Chem. Soc.*, 1965, **87**, 3935.

[9] J. E. Bennett, D. M. Brown, and B. Mile, *Trans. Faraday Soc.*, 1970, **66**, 397.

[10] S. Fukuzumi, Y. Ono, and T. Keii, *Bull. Chem. Soc. Japan*, 1973, **46**, 3353.

[11] S. Fukuzumi, Y. Ono, and T. Keii, *Internat. J. Chem. Kinetics*, 1975, **7**, 535.

[12] M. Bersohn and J. R. Thomas, *J. Amer. Chem. Soc.*, 1964, **86**, 959.

[13] S. Weiner and G. S. Hammond, *J. Amer. Chem. Soc.*, 1969, **91**, 2182.

[14] Ya. B. Gorokhovatsky, Proceedings 5th International Congress on Catalysis, Amsterdam, 1972, Preprint, p. 621.

[15] A. D. Vreugdenhil, *J. Catalysis*, 1973, **28**, 493.

peroxyl radical depended on the concentration of cumene hydroperoxide, it did not change during the decay process. So, one can follow the change in the concentration simply by monitoring the peak amplitude of the signal.

The radical decay was found to be first order, plots of the logarithm of the concentration of cumylperoxyl radical *versus* time giving straight lines. It was also confirmed that the slope does not depend on the initial concentration of the peroxyl radical (the concentration when the flow is stopped), which was varied by changing the amount of catalyst or the feeding rate of the solution. In Table 1, the values of the first-order decay constant calculated from the slope of the plots are listed as a function of the initial concentration of cumene hydroperoxide. The constant does not depend on the concentration of cumene hydroperoxide. The results can definitely not be accounted for satisfactorily by a second-order rate law. When the reciprocal of the e.s.r. intensity was plotted against time, the plots substantially deviate over the second half of the decay though the initial parts of the plots seem to follow second-order kinetics. The apparent second-order rate constant, calculated from the initial straight part of the plots, depended markedly on the initial concentration of cumylperoxyl radical.

TABLE 1

First-order rate constant for decay of cumylperoxyl radical at 301 K

$[ROOH]_0/M$	$10^6[RO_2]_0/M$	No. of runs	k_d/s^{-1}
0.74	4.4—5.4	5	0.15—0.16
1.45	2.3—6.2	10	0.13—0.16
2.82	3.3—4.8	10	0.15—0.16
4.70	4.6—11.2	10	0.13—0.16
		35	0.15 ± 0.01

Effect of Catalyst and Solvent.—To examine if the catalyst or the solvent (CCl_4) takes some part in the decay of cumylperoxyl radical, the following experiments were carried out. Though the catalyst was outside the e.s.r. cavity, there may be a possibility that metal cations eluted from the catalyst react with the peroxyl radicals, but there was no sign of manganese or cobalt ions in the e.s.r. spectrum. Thus the results do not depend on the catalyst used (Table 2). The effect of the solvent on the decay rate was determined and the results are listed in Table 2. Replacement of carbon tetrachloride by cumene does not influence the rate constant, indicating that the decay constant obtained here can also be applied to the decay of peroxyl radicals during the autoxidation of cumene. This also means that the termination reactions (12) and (13) are not important for radical decay. The decay of the radicals in benzene proceeded a little more rapidly than in carbon tetrachloride, again with first-order kinetics. These results indicate that the solvents do not take any positive role in the decay of cumylperoxyl radicals.

TABLE 2

Effect of catalyst and solvent on rate constant of decay of cumylperoxyl radical at 294 K

Catalyst	Solvent	[ROOH]/M	No. of runs	k_d/s^{-1}
MnO_2	CCl_4	2.79	3	0.041 ± 0.002
Co–SiO_2	CCl_4	1.70	4	0.042 ± 0.002
MnO_2	Cumene	0.944	4	0.044 ± 0.002
MnO_2	Benzene	0.944	3	0.051 ± 0.003

$$R\cdot + R\cdot \longrightarrow R{-}R \tag{12}$$

$$R\cdot + RO_2\cdot \longrightarrow ROOR \tag{13}$$

First-order Decay of Cumylperoxyl Radical.—It is clear from the results described above that the rate of the disappearance of cumylperoxyl radical is first order with respect to the radical concentration. However, it is often assumed that the decay is a second-order process, especially in the case of the autoxidation of cumene, and second-order rate constants have been calculated from the data by the rotating sector technique or pre- and after-effect methods.[1] But this would only reveal a 'second-order rate constant' for a specific set of conditions. Therefore, to determine the kinetics unambiguously, it is important to investigate the rate over a wide range of concentration of peroxyl radicals, though this presents difficulties because of experimental limitations. For example, in Zwolenik's work,[6] the initial concentration of the peroxyl radical was changed only over the range $1.6—2.7 \times 10^{-5}$M. In our work, the concentration ranged from 2.3×10^{-6} to 11.2×10^{-6}M and all 35 runs gave a first-order rate constant of $1.3—1.6 \times 10^{-1}\ s^{-1}$.

First-order decay of cumylperoxyl radical was also confirmed from measurements of the radical concentration during steady state decomposition of cumene hydroperoxide with lead dioxide.[16] The radical concentration was found to be proportional to the amount of lead dioxide and to be independent of the hydroperoxide concentration when the latter is reasonably high. It was reasonably assumed that free radical is formed exclusively by decomposition of the hydroperoxide on the surface of the solid, and the rate of the radical formation (R_i) is given by equation (14). If one

$$R_i = k_i[PbO_2][ROOH]^0 \tag{14}$$

expresses the radical decay rate (R_t) by equation (15)

$$R_t = k_t[RO_2\cdot]^n \tag{15}$$

then, in the steady state, one obtains equation (16).

$$k_i[PbO_2][ROOH]^0 = k_t[RO_2\cdot]^n \tag{16}$$

Thus, the experimental observation is explained readily only if $n = 1$.

In a forthcoming paper,[17] we shall show that the kinetics of the autoxidation of cumene is not incompatible with the first-order decay of the peroxyl radical.

---

[16] S. Fukuzumi and Y. Ono, *J.C.S. Perkin II*, following paper.

[17] S. Fukuzumi and Y. Ono, *J.C.S. Perkin II*, in the press.

The mechanism of the radical decay is not certain at this moment, but reactions (17) and (18) are compatible

$$PhCMe_2OO\cdot \longrightarrow PhCOMe + MeO\cdot \quad (17)$$

$$MeO\cdot + RO_2\cdot \xrightarrow{\text{fast}} \text{stable products} \quad (18)$$

with first-order decay kinetics. The unimolecular decomposition of cumylperoxyl radical has rarely been proposed, but it has been assumed for the decay process in the autoxidation of methyl ethyl ketone.[18] The

$$MeCOCH(Me)OO\cdot \longrightarrow MeCOCHO + MeO\cdot \quad (19)$$

proposed mechanism for the decay of cumylperoxyl radical also explains the production of acetophenone in the decomposition of the hydroperoxide. It should be noted that the well established decay process (2)—(8) was proposed originally to explain the formation of acetophenone. We have confirmed that the products of the decomposition of cumene hydroperoxide with lead dioxide are 90% 1,1-dimethyl-2-phenylethanol and 7.0% acetophenone.[17]

We thank Professor T. Keii for helpful discussions.

[6/657 *Received, 5th April,* 1976]

---

[18] G. E. Zaikov and Z. K. Maizus, Adv. Chem. Series, No. 75, Amer. Chem. Soc., 1968, p. 150.