Electron Spin Resonance and Kinetic Studies on the Liquid-phase Decomposition of Cumene Hydroperoxide by Lead Dioxide

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The kinetics of liquid-phase decomposition of cumene hydroproxide by lead dioxide have been studied by e.s.r. The concentration of cumylperoxyl radical in the reaction solution was determined. The e.s.r. and kinetic results as well as the product distribution lead to the conclusion that hydroperoxide decomposition by lead dioxide is a radical chain reaction. The hydroperoxide forms a surface complex on lead dioxide and the complex dissociates to the peroxyl radical which desorbs into the homogeneous phase, where chain propagation and termination proceed. The formation of a complex between hydroperoxide and peroxyl radical is suggested. The rate constants for the elementary reactions have been determined.

THE presence of heterogeneous catalysts, especially metal oxides, has a significant influence on the autoxidation of hydrocarbons in the liquid phase.[1-9] In the case of autoxidation of cumene over manganese dioxide, nickel oxide, silver oxide, *etc.*[1,2,4] the decomposition of cumene hydroperoxide over heterogeneous catalysts is considered to be the initial step of the autoxidation reaction, *i.e.*, the major source of radicals. However, few studies on the decomposition of hydroperoxides over heterogeneous catalysts have been performed,[3,10] and the initial steps on the solid surface are not clear. Therefore, in order to elucidate the mechanism of autoxidation of cumene with heterogeneous catalysts, it seemed of primary importance to investigate the decomposition of the hydroperoxide over solid catalysts.

In the preceding paper,[11] we reported the liquid-phase decay of cumylperoxyl radical, produced on solid catalysts (manganese dioxide and cobalt oxide supported on silica) by use of a flow technique. It has been found that cumylperoxyl radicals decay with first-order kinetics though it has often been assumed that the decay of cumylperoxyl radical is second order.[12]

We report here the decomposition of cumene hydroperoxide by lead dioxide. The concentration of the peroxyl radical during the decomposition was monitored by e.s.r. and was correlated with the rate of oxygen generation. This study also provides evidence for the first-order decay of cumylperoxyl radical in the liquid phase. A mechanism is proposed.

EXPERIMENTAL

Reagents.—Commercial lead dioxide calcinated at various temperatures (373—773 K) was used as catalyst. The surface area was 17.6 m^2 g^{-1} determined by the BET method. Cumene hydroperoxide was obtained from Nakarai Chem. Ltd.

E.s.r. Measurements.—The concentration of peroxyl radical was determined by carrying out the decomposition of the hydroperoxide in a quartz ampoule placed in the

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e.s.r. cavity. At high concentrations of hydroperoxide, the lead dioxide powder is suspended uniformly in the liquid by the generation of oxygen. At low concentrations, the oxygen is flowed through a small capillary in order to keep the catalyst well suspended. The concentration of peroxyl radical was also determined by simultaneous determination of the rate of oxygen generation.

The reaction was carried out in 50 or 100 cm^3 flasks. The part of the solution containing the catalyst powder was circulated by a roller pump through the e.s.r. cavity. The intensity of the e.s.r. signal was independent of the feed rate of the roller pump over the range 50—200 cm^3 min^{-1}. A JEOL X-band e.s.r. spectrometer (JES-PE-1X) with 100 kHz magnetic modulation was used. The concentration of radicals was determined by using 1,1-diphenyl-2-picrylhydrazyl in benzene as reference.

Rate of Oxygen Generation.—The rate of oxygen generation was measured with a gas burette or a wet-gasometer. Solutions of the hydroperoxide with lead dioxide powder were placed in a 100 cm^3 flask which was immersed in a temperature controlled bath, stirred magnetically, and attached to the gas burette or wet-gasometer. In preliminary experiments, it was established that mass transfer processes do not affect the reaction rate.

Analytical Procedure.—After the oxygen generation ceased completely, the products were analysed for the decomposition of cumene hydroperoxide. When unchanged hydroperoxide was present, part of the sample was titrated for cumene hydroperoxide by the iodimetric method,[13] and the rest was treated with sufficient triphenyl phosphine to convert cumene hydroperoxide into 1,1-dimethyl-2-phenylethanol quantitatively.[14] The treated sample was then analysed for 1,1-dimethyl-2-phenylethanol and acetophenone by a chromatographic method.

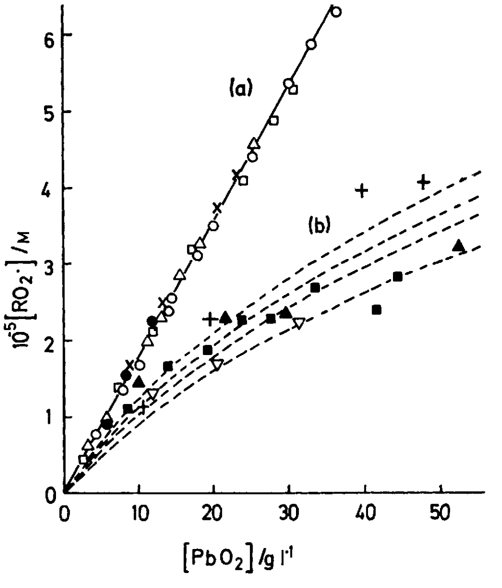

FIGURE 1 Initial concentration of cumylperoxyl radical as a function of catalyst weight to liquid volume ratio for different concentrations of cumene hydroperoxide at 291 K: (a) ○ 4.70M; × 3.53M; □ 3.14M; △ 2.35M; ● 1.57M; (b) + 0.474M; ▲ 0.237M; ■ 0.158M; ▽ 0.079M; (— — —) calculated

RESULTS

Concentration of Peroxyl Radical during Decomposition.—When lead dioxide powder was added to cumene hydroperoxide solution, the e.s.r. spectrum of cumylperoxyl radical (*g* 2.014 6—2.015 0) was observed. The concentration of the peroxyl radical was monitored with time.

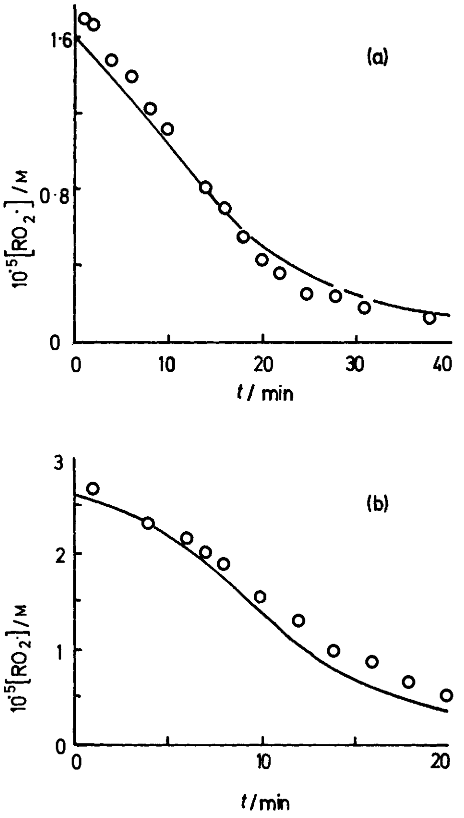

FIGURE 2 Concentration of cymylperoxyl radical as a function of reaction time at 291 K. Initial concentration of cumene hydroperoxide: (a) 0.078 4M; (b) 0.158M; catalyst weight to liquid volume ratio (a) 19.5 g l^{-1}; (b) 33.0 g l^{-1}; (——) calculated

For higher concentrations of hydroperoxide (1.57—4.70M), a steady state was observed for several tens of minutes. The steady concentration of the radical was proportional to the ratio of catalyst weight to liquid volume and independent of the initial hydroperoxide concentration as shown in curve (a) of Figure 1.

$$[RO_2^\cdot] = k_a[PbO_2][ROOH]^0 \qquad (1)$$

For lower concentrations of hydroperoxide (<0.474M), the radical concentration decreases with time as shown in Figure 2. The initial radical concentration obtained by extrapolation of the concentration–time curve to time zero depended on the hydroperoxide concentration and the catalyst ratio as shown in curves (b) of Figure 1. It should be noted here that the initial radical concentrations for lower hydroperoxide concentrations [curves (b)] are smaller than those for higher hydroperoxide concentrations [curve (a)]. The dependence of the radical concentration on the catalyst ratio is less than first order and is close to half order for the lower hydroperoxide concentrations.

Rate of Oxygen Generation.—The rate of oxygen generation was examined for 0.039 5—4.70M-hydroperoxide.

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The rate was constant for several tens of minutes for higher concentrations of hydroperoxide (>1.57M), but decreased with time for lower concentrations (Figure 3). The initial rate was plotted as a function of the ratio of catalyst weight to liquid volume (Figure 4). For higher concentrations of hydroperoxide [curves (a) and (b) of Figure 4] the rate of oxygen generation is found to be proportional to $[PbO_2]^2$. However, for low hydroperoxide concentrations [curve (c)] the rate is close to first order in $[PbO_2]$.

$$-d[O_2]/dt = k_b[PbO_2]^2 \qquad (2)$$

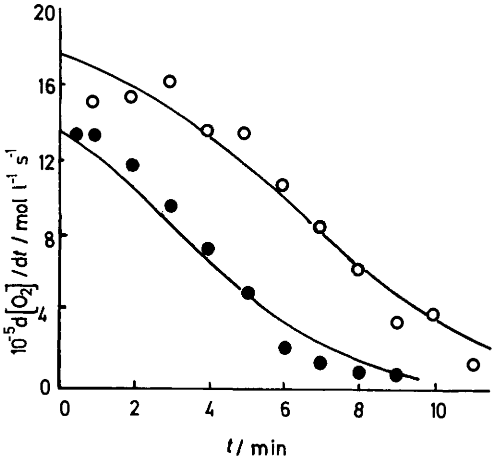

FIGURE 3 Rate of oxygen generation as a function of reaction time at 291 K; initial concentration of cumene hydroperoxide: ○ 0.158M; ● 0.0784M; catalyst weight to liquid volume ratio: ○, ● 33.8 g l^{-1}; (——) calculated

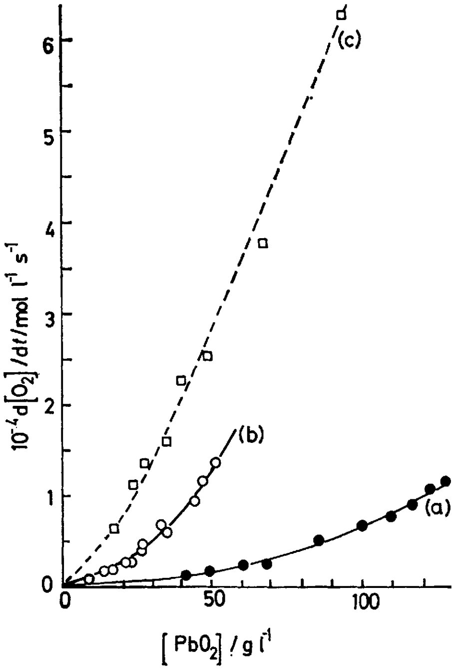

FIGURE 4 Initial rate of oxygen generation as a function of catalyst weight to liquid volume ratio at 291 K; initial concentration of cumene hydroperoxide: (a) ● 4.70M; (b) ○ 1.57M; (c) □ 0.158M; (— — —) calculated

As shown in Figure 5, at constant catalyst ratio, the rate of oxygen generation increases markedly with an increase in hydroperoxide concentration and reached a maximum. It should be noted that the rate decreases with concentration in the higher concentration region, retaining second-order dependence on $[PbO_2]$.

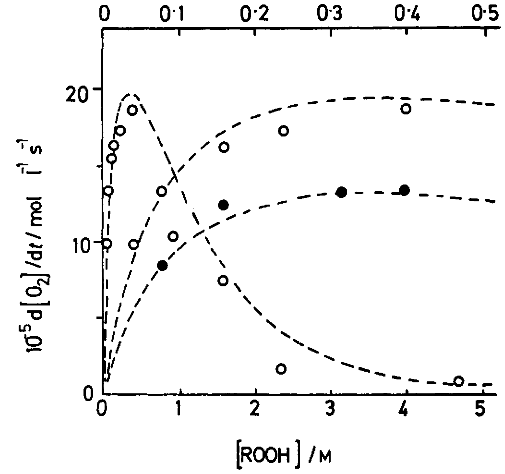

FIGURE 5 Initial rate of oxygen generation as a function of initial concentration of cumene hydroperoxide at 291 K; catalyst weight to liquid volume ratio; ○ 33.8 g l^{-1}, ● 25.0 g l^{-1}; (— — —) calculated

Product Distribution.—Product analyses for the decomposition of cumene hydroperoxide were performed after generation of oxygen ceased completely. The results are summarized in Table 1. The major product was 1,1-dimethyl-2-phenylethanol and a small amount of acetophenone was also produced. Analyses of these products accounted for >95% of cumene hydroperoxide reacted in each run. The ratio of the concentration of 1,1-dimethyl-2-phenylethanol to the amount of oxygen generation ([ROH] : $[O_2]$) is 2.0 (mean value).

Catalyst Deactivation.—For the higher hydroperoxide concentrations, there is evidence that the reaction ceased completely though unchanged hydroperoxide is still present,

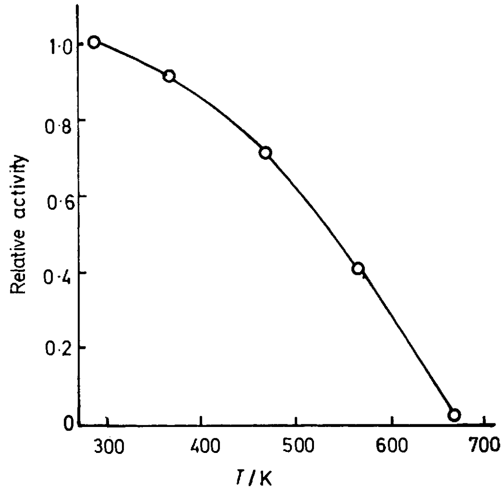

FIGURE 6 Effect of temperature of calcination of catalyst on rate of oxygen generation. Relative activity is taken as rate of oxygen generation with calcinated catalyst divided by that with uncalcinated catalyst

indicating catalyst deactivation. When the catalyst was carefully recovered after a reaction ceased completely and then used again with fresh hydroperoxide solution, the recovered catalyst showed no activity. Even when the reaction went to completion, the recovered catalyst showed lower activity. Therefore, it can be concluded that the lead dioxide used is deactivated in the course of the reaction.

Effect of Calcination of Catalyst.—Lead dioxide powder was heated in air at various temperatures (373—773 K) for 5 h and the effect of calcination on the relative activity was investigated by measuring the initial rate of oxygen generation with the calcinated catalyst. The results are shown in Figure 6, where the initial rate of oxygen generation with uncalcinated catalyst is taken as 1.0. With an increase of the calcinating temperature, the activity of the catalyst decreases, and is zero above 673 K.

DISCUSSION

Reaction Mechanism.—On the basis of the previous experimental results, the elementary reactions (3)—(11) are considered as the main steps for the decomposition of cumene hydroperoxide with lead dioxide where

$$\text{Initiation}\ \mathrm{ROOH} + \mathrm{PbO_2}^* \overset{K_1}{\rightleftharpoons} (\mathrm{ROOH})_a \cdots \mathrm{PbO_2}^* \qquad (3)$$

$$(\mathrm{ROOH})_a \cdots \mathrm{PbO_2}^* \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{PbO(OH)}^* + \mathrm{RO_2}\cdot \qquad (4)$$

$$\mathrm{ROOH} + \mathrm{PbO(OH)}^* \overset{K_2}{\rightleftharpoons} (\mathrm{ROOH})_a \cdots \mathrm{PbO(OH)}^* \qquad (5)$$

$$(\mathrm{ROOH})_a \cdots \mathrm{PbO(OH)}^* \xrightarrow{k_2} \mathrm{Pb(OH)_2}^* + \mathrm{RO_2}\cdot \qquad (6)$$

$$\text{Propagation}\ \mathrm{RO_2}\cdot + \mathrm{RO_2}\cdot \xrightarrow{k_6} 2\mathrm{RO}\cdot + \mathrm{O_2} \qquad (7)$$

$$\mathrm{RO}\cdot + \mathrm{ROOH} \xrightarrow{k_5} \mathrm{ROH} + \mathrm{RO_2}\cdot \qquad (8)$$

$$\text{Complex formation}\ \mathrm{RO_2}\cdot + 2\mathrm{ROOH} \overset{K}{\rightleftharpoons} (\mathrm{RO_2}\cdot \cdots 2\mathrm{ROOH}) \qquad (9)$$

$$\text{Termination}\ \mathrm{RO_2}\cdot \xrightarrow{k_7} \mathrm{R'C{=}O} + \mathrm{CH_3O}\cdot \qquad (10)$$

$$\mathrm{CH_3O}\cdot + \mathrm{RO_2}\cdot \xrightarrow{\text{fast}} \text{stable molecules} \qquad (11)$$

PbO_2^*, $PbO(OH)^*$, and $Pb(OH)_2^*$ designate the species on the dioxide surface.

The main features of the above mechanism are as follows. Initiation occurs on the surface. The hydroperoxide forms a complex with the surface species PbO_2^* and $PbO(OH)^*$ on lead dioxide, the complexes dissociate to the peroxyl radical which desorbs into the homogeneous phase, and PbO_2^* is reduced to inactive $Pb(OH)_2^*$. The initiation steps are consistent with the experimental results that lead dioxide is deactivated in the course of the reaction and that the activity of the catalyst decreases upon calcination suggesting that Pb^{IV} on the lead dioxide surface is active in the decomposition of the hydroperoxide since lead dioxide is known to be reduced to PbO by calcination above 573 K.[15]

Propagation proceeds through reactions (7) and (8), which give two ROH and one O_2 from two ROOH molecules as the major products, consistent with the product distribution in Table 1. We further assume that the complex formation between one peroxyl radical and two hydroperoxide molecules occurs and that only the free (uncomplexed) radical is active in the self-reaction of peroxyl radicals [reaction (7)] and in the decay on the surface [reverse reaction of (4)]. This assumption is introduced to account for the fact that the decomposition rate becomes smaller when the hydroperoxide concentration is higher (Figure 5). Termination of the chain results from the first-order reactions (10) and (11), as reported previously.[11]

Rate Equations.—The rate expression was derived from the above mechanism. The following assumptions were made. (a) $1 \ll K_2$ (ROOH), *i.e.*, most of the PbO(OH)* is complexed with the hydroperoxide. (b) The steady state approximation for $[RO_2\cdot]$, $[RO\cdot]$, $[CH_3O\cdot]$, and $[PbO(OH)^*]$ is operative. (c) The decay rates of free and complexed peroxyl radical are equal.

Thus, the observed concentration of the peroxyl radical, which is the sum of the uncomplexed and complexed forms, $[RO_2\cdot]_t = [RO_2\cdot] + [RO_2\cdot \cdots 2ROOH]$, is represented by equation (12). The rate of oxygen generation is then given by equation (14).

$$[\mathrm{RO_2}\cdot] = k_2(1 + K[\mathrm{ROOH}]^2)\{-1 + (1 + A)^{\frac{1}{2}}\}/2\,k_{-1} \qquad (12)$$

$$\mathrm{A} = \frac{4k_1k_{-1}K_1[\mathrm{ROOH}][\mathrm{PbO_2}^*]}{k_7k_2\{1 + K_1[\mathrm{ROOH}]\}\{1 + K[\mathrm{ROOH}]^2\}} \qquad (13)$$

$$\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t = \frac{k_6}{(1 + K[\mathrm{ROOH}]^2)^2}[\mathrm{RO_2}\cdot]_t^2 = k_6\left\{\frac{k_2}{2k_{-1}}[-1 + (1 + A)^{\frac{1}{2}}]\right\}^2 \qquad (14)$$

Equations (12) and (14) explain the observed dependence of peroxyl radical concentration and the rate of oxygen generation as follows. When the concentration of the hydroperoxide is so high that $A \ll 1$ and K_1[ROOH] $\gg 1$, equations (12) and (14) are reduced to (15) and (16) respectively. These are exactly the findings in equations (1) and (2) that the radical concentration is proportional to $[PbO_2]$ and independent of [ROOH], while the rate of oxygen generation is proportional to $[PbO_2]^2$ and decreases with increasing [ROOH].

$$[\mathrm{RO_2}\cdot]_t = k_1[\mathrm{PbO_2}^*]/k_7 \qquad (15)$$

$$\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t = \frac{k_1{}^2k_6}{k_7{}^2(1 + K[\mathrm{ROOH}]^2)^2}[\mathrm{PbO_2}^*]^2 \qquad (16)$$

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[15] M. C. Sneed and R. C. Brasted, ' Comprehensive Inorganic Chemistry,' Van Nostrand, New York, 1958, vol. VII, p. 238.

In the low concentration range of ROOH, where $1 \gg K[\mathrm{ROOH}]^2$ holds, relations (17) and (18) are obtained. These equations explain the experimental

$$[\mathrm{RO}\cdot_2]_\mathrm{t} = \frac{k_2}{2k_{-1}}\left[-1 + \sqrt{1 + \frac{4k_1k_{-1}K_1[\mathrm{ROOH}][\mathrm{PbO_2}^*]}{k_7k_2(1 + K_1[\mathrm{ROOH}])}}\right] \quad (17)$$

$$\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t = k_6[\mathrm{RO_2}\cdot]_\mathrm{t}^{\,2} \quad (18)$$

observations in Figures 2(b) and 4(c); the radical concentration depends slightly on the hydroperoxide concentration and exhibits roughly one-half-order dependence on $[\mathrm{PbO_2}]$, while the rate of oxygen generation exhibits roughly first-order dependence on $[\mathrm{PbO_2}]$.

The values of the rate constants and equilibrium constants were determined from the experimental results and are listed in Table 2. The radical concentration and the rate of oxygen generation for the initial conditions are calculated by use of equations (12) and (14). The agreements between the experimental results and the calculated ones (dotted lines in Figures 1, 4, and 5) are fairly good. It should be noted that the numbers of unknown parameters are less than the number of experimental observations.

TABLE 1

Product distribution for decomposition of cumene hydroperoxide (ROOH) with lead dioxide

$[\mathrm{ROOH}]_0$/ M	[ROOH] */ M	[ROH]/ M	[PhCOMe]/ M	$[\mathrm{O_2}]$/ M	[ROH] : $[\mathrm{O_2}]$
0.039	0	0.035	0.003	0.018	1.94
0.078	0	0.070	0.006	0.034	2.06
0.118	0	0.103	0.009	0.056	1.84
0.157	0	0.141	0.010	0.082	1.72
1.567	0.043	1.476	0.076	0.683	2.16
2.351	0.068	2.017	0.159	0.987	2.04
3.135	0.113	2.900	0.179	1.290	2.25

* Unchanged cumene hydroperoxide.

TABLE 2

Rate constants for decomposition of cumene hydroperoxide with lead dioxide

T/K	$10^6k_1k_7^{-1}$/ l $\mathrm{g^{-1}}$	$10^4k_{-1}k_2^{-1}$	$2 \times 10^{-5}k_6$/ l $\mathrm{mol^{-1}\,s^{-1}}$	K_1/l $\mathrm{mol^{-1}}$	K/$\mathrm{l^2\,mol^{-2}}$
291	2.0	3.6	5.0	22	0.50

Spectral Evidence for Complex Formation.—We have introduced in the above mechanism complex formation between the peroxyl radical and cumene hydroperoxide to explain the rate decrease in the high concentration region of hydroperoxide. The e.s.r. spectrum of cumylperoxyl radical seems to give evidence for complex formation. The line width and g value of the cumylperoxyl radical depend on the concentration of cumene hydroperoxide as shown in Figure 7. The line width markedly decreases with increasing hydroperoxide concentration, while the g value decreases slightly with concentration. According to Thomas,[16] the line width of a peroxyl radical is determined by relaxation through the spin–rotation interaction and is expressed by (19)

$$\Delta H \propto 1/a^3 \quad (19)$$

where a is the mean diameter of the radical. When complex formation of a peroxyl radical occurs a increases and, accordingly, the line width decreases. As described previously, we assume equilibrium (9) exists in the solution. The actual line width of the radical (ΔH_t) is the average of the line width of the free peroxyl radical (ΔH_f) and the complexed radical (ΔH_c) [equation (20)].

$$\Delta H_\mathrm{t} = \frac{\Delta H_\mathrm{f} + \Delta H_\mathrm{c}K[\mathrm{ROOH}]^2}{1 + K[\mathrm{ROOH}]^2} \quad (20)$$

The observed change of the line width with the hydroperoxide concentration can be explained by assuming $\Delta H_\mathrm{f} = 1.45$ mT, ΔH_c 0.65 mT, and $K = 0.50\ \mathrm{l^2\,mol^{-2}}$ which agrees with the value in Table 2. The solid line in Figure 7(a) is the calculated change of line width, showing good agreement with the experimental results. It should be noted that a number of complexed hydroperoxide molecules other than two could not explain the observed change.

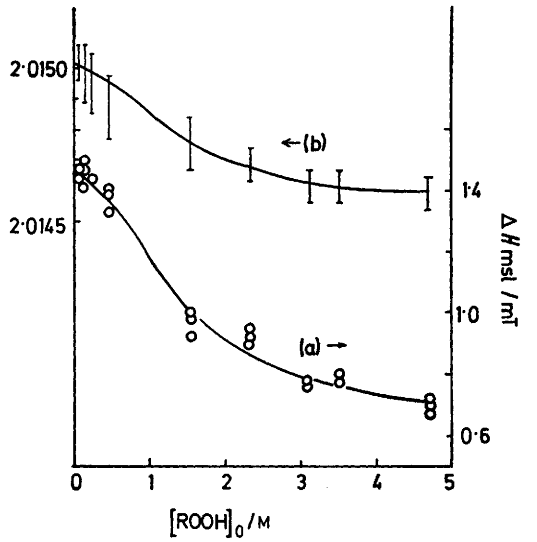

FIGURE 7 g Value and line width of cumylperoxyl radical as a function of initial concentration of cumene hydroperoxide; (——) calculated

The change in the g value of the peroxyl radical can be explained in a similar manner. The solid line in Figure 7(b) is calculated using the values g_f 2.015 00, g_c 2.014 54, and K 0.50 $\mathrm{l^2\,mol^{-2}}$. The reduction of the g value by complex formation through hydrogen bonding has been observed in other cases.[17-19]

Time Dependence of Radical Concentration and Rate of

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[16] J. R. Thomas, *J. Amer. Chem. Soc.*, 1966, **88**, 2064.

[17] T. Kawamura, S. Matsunami, T. Yonezawa, and K. Fukui, *Bull. Chem. Soc. Japan*, 1965, **38**, 1935.

[18] T. Kawamura, S. Matsunami, and T. Yonezawa, *Bull. Chem. Soc. Japan*, 1967, **40**, 1111.

[19] T. Yonezawa, T. Kawamura, M. Ushio, and Y. Nakao, *Bull. Chem. Soc. Japan*, 1970, **43**, 1022.

Oxygen Generation.—Since the values of the rate constants and the equilibrium constants are known, the change in the radical concentration and the rate of oxygen generation throughout the reaction can be predicted. The only limitation is the time dependence of $[PbO_2*]$ which changes to inactive $[Pb(OH)_2*]$. Therefore, we only treat cases in which the hydroperoxide concentration is so low that all the reactants decompose by the chain reactions (7) and (8) before an appreciable fraction of the surface sites is reduced. The rate of the hydroperoxide decomposition is given by equations (21) and (22). From equation (22), one can calculate the hydroperoxide concentration at any reaction time t by use of the values in Table 2. Then, using the values of the hydroperoxide concentration at time t the radical concentration and the rate of oxygen generation at t are obtained from equations (12) and (14), respectively. Thus, the time dependence of the radical concentration

$$-\mathrm{d}[\mathrm{ROOH}]/\mathrm{d}t = 2k_6[\mathrm{RO_2}\cdot]^2 = 2\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t \qquad (21)$$

$$-\mathrm{d}[\mathrm{ROOH}]/\mathrm{d}t = 2k_6\left\{\frac{k_2}{2k_{-1}}\left(-1 + \sqrt{1 + \frac{4k_1k_{-1}K_1[\mathrm{ROOH}][\mathrm{PbO_2}*]}{k_7k_2(1 + K_1[\mathrm{ROOH}])}}\right)\right\}^2 \qquad (22)$$

and the rate of oxygen generation are calculated from the initial conditions and are represented as the solid lines in Figures 2 and 3, respectively. The agreement between the experimental and calculated results is fair.

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