Electron Spin Resonance and Kinetic Studies on the Liquid-phase Autoxidation of Cumene with Lead Dioxide

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The autoxidation of cumene with lead dioxide has been studied over the range 291—323 K. By use of e.s.r. the concentration of cumylperoxyl radical (a chain-propagating agent) was monitored during autoxidation. The kinetics of this reaction were determined by measuring the concentration of cumylperoxyl radical and the rate of oxygen consumption under the same conditions. Both the radical concentration and the rate of oxygen consumption were constant with time and were independent of the catalyst weight : liquid volume ratio. The variation in radical concentration was first order in cumene concentration, while the rate of oxygen consumption was second order. Chain initiation involves the formation of cumylperoxyl radical from decomposition of the hydroperoxide over the catalyst surface and desorption into the homogeneous phase where chain propagation and termination proceed. Rate equations derived from the proposed reaction mechanism explain quantitatively the experimental observations. Values of the rate constants have been determined.

THE autoxidation of liquid hydrocarbons with heterogeneous catalysts has been studied by several investigators.[1-10] This reaction is considered to proceed by a radical chain; chain initiation involves the formation of free radicals on the solid surfaces and their desorption into the homogeneous phase, where chain propagation and termination proceed.[5] The presence of peroxyl radical (a chain-propagating agent) in the homogeneous phase has been confirmed in the autoxidation of cumene with manganese dioxide, nickel oxide, silver oxide, *etc.*, by use of e.s.r.[5,7,9] However, e.s.r. has not been applied to the study of the kinetics of autoxidation of hydrocarbons with heterogeneous catalysts.

We have measured the concentration of cumylperoxyl radical during the autoxidation of cumene (RH) with lead dioxide. Simultaneous measurements of the radical concentration and the rate of oxygen consumption have permitted the mechanism for the elementary reactions and the rate constants to be determined directly.

The major source of radicals in the cumene oxidation with metal oxides is considered to be the decomposition of cumene hydroperoxide on the solid surface.[5,8] In the preceding paper,[11] we reported the decomposition of cumene hydroperoxide with lead dioxide studied by e.s.r. spectroscopy. A mechanism for hydroperoxide decomposition was proposed, consistent with the kinetics of the variation of radical concentration [$RO_2^{\bullet}$] and the

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[10] H. J. Neuburg, M. J. Phillips, and W. F. Graydon, *J. Catalysis*, 1975, **38**, 33.
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rate of oxygen generation as well as the product distribution. In this paper, we show that the mechanism for hydroperoxide decomposition can be applied to the autoxidation of cumene with lead dioxide.

EXPERIMENTAL

Materials.—Cumene (reagent grade), obtained from commercial sources, was distilled and percolated through an activated alumina column prior to use. The other reagents (reagent grade) were used without further purification. The surface area of lead dioxide was 17.6 $m^2 g^{-1}$, as determined by the BET method.

E.s.r. Measurements.—Free radical concentration was determined by carrying out autoxidation in a tube (3 mm i.d.) placed in the e.s.r. cavity. Oxygen was bubbled into the solution through a capillary. Simultaneous measurements of the radical concentration and the rate of oxygen consumption were performed as follows. The reaction was carried out in 50 or 100 cm^3 flasks at various temperatures. Part of the solution containing the catalyst powder was circulated with the use of a roller pump through the e.s.r. cavity where the e.s.r. measurements were carried out. At the same time, the rate of oxygen consumption was measured with a gas burette or a wet-gasometer. Cumene in CCl_4 with lead dioxide powder added was placed in a flask immersed in a temperature controlled bath stirred magnetically, and attached to a gas burette or a wet-gasometer.

Measurements of Hydroperoxide Concentration and Product Analysis.—The initial hydroperoxide concentration in cumene varied over the range $0(<10^{-3}$M)—0.079M, by adding cumene hydroperoxide to cumene solution. The concentration of cumene hydroperoxide was determined by an iodimetric method.[12] The concentrations of the hydroperoxide and the other products during the reaction were determined as follows. On stopping the reaction, the solution containing the catalyst powder was filtered immediately and the sample was titrated for hydroperoxide by the iodimetric method. Part of the filtered solution was treated with sufficient triphenylphosphine to convert the hydroperoxide into 1,1-dimethyl-2-phenylethanol quantitatively.[13] The treated sample was then analysed for 1,1-dimethyl-2-phenylethanol and acetophenone by chromatography.

RESULTS

Concentration of Cumylperoxyl Radical during Reaction.—When lead dioxide powder was added to the cumene solution, the e.s.r. spectrum of cumylperoxyl radical (g 2.015 0 ± 0.000 4) was observed. The g value is in good agreement with previous reports.[11,14,15] The radical concentration was almost constant for several hours during the reaction. The effect of the concentration of cumene and the catalyst weight : liquid volume ratio on the concentration of the peroxyl radical were investigated at 291 K as shown in Figures 1 and 2. The radical concentration is found to be independent of the catalyst weight : liquid volume ratio over the range 30—100 g l^{-1} and to be proportional to the cumene concentration [equation (1) where $k_a = (1.95 \pm 0.07) \times 10^{-6}$ g l^{-1}].

$$[RO_2^{\bullet}] = k_a[RH][PbO_2]^0 \quad (1)$$

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Rate of Oxygen Consumption.—Oxygen was absorbed when lead dioxide powder was added to a cumene solution and the rate of oxygen consumption was constant with time for several hours. The absorption of oxygen did not occur

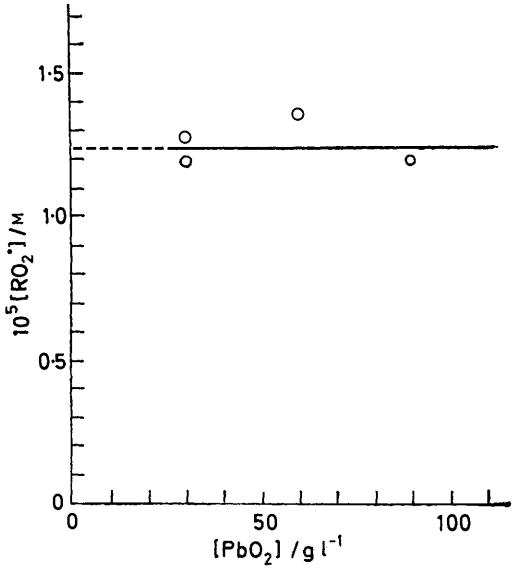

FIGURE 1 Concentration of cumylperoxyl radical during autoxidation of cumene with lead dioxide as a function of catalyst weight : liquid volume ratio at 291 K. Initial concentration of cumene 5.38M

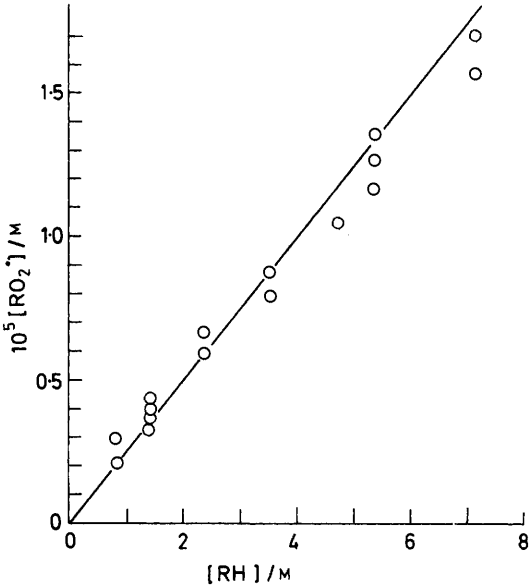

FIGURE 2 Concentration of cumylperoxyl radical during autoxidation of cumene with lead dioxide as a function of initial concentration of cumene at 291 K

unless lead dioxide was introduced. The effects of the catalyst weight : liquid volume ratio and cumene concentration on the rate of oxygen consumption were investigated at 291 K as shown in Figures 3 and 4. The rate of oxygen consumption is independent of the catalyst ratio and is

[14] M. Bersohn and J. R. Thomas, *J. Amer. Chem. Soc.*, 1964, **86**, 959.
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proportional to the square of the cumene concentration [equation (2) where $k_b = (9.5 \pm 0.2) \times 10^{-7}$ l^2 g^{-1} mol^{-1} s^{-1}].

$$d[O_2]/dt = k_b [RH]^2[PbO_2]^0 \quad (2)$$

Effect of Temperature on Radical Concentration and Rate of Oxygen Consumption.—Measurements of the radical

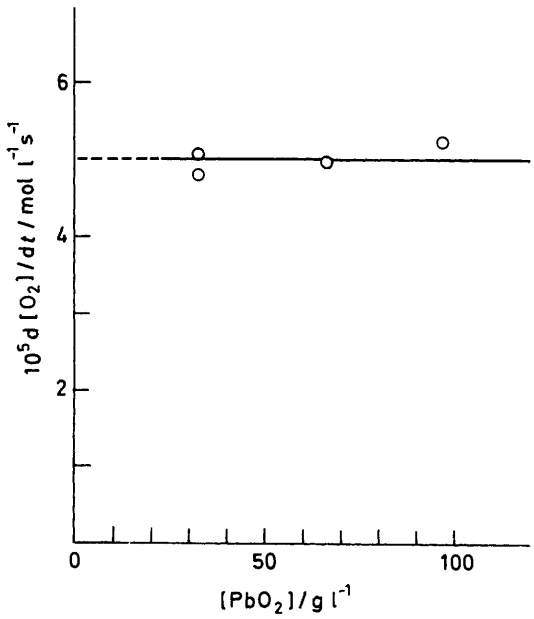

FIGURE 3 Rate of oxygen consumption as a function of catalyst weight : liquid volume ratio at 291 K. Initial concentration of cumene 7.18M

concentration and the rate of oxygen consumption were done simultaneously in the tenperature range 291—323 K. The results are shown in Figure 5. In each case, experiments were started with the same initial hydroperoxide and cumene concentrations and the same catalyst weight : liquid volume ratio. By assuming the kinetics of equations (1)

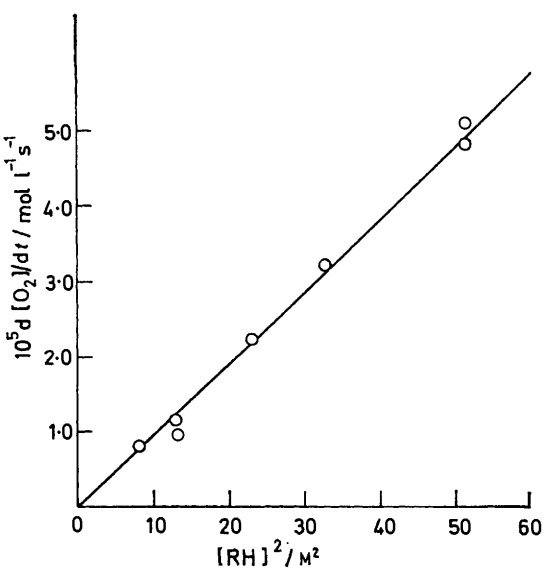

FIGURE 4 Rate of oxygen consumption plotted against squared concentration of cumene at 291 K

and (2) are operative throughout the temperature range, the activation energy for k_a and k_b were determined and found to be 0.0 and 30 kJ mol^{-1}, respectively.

Hydroperoxide Concentration during the Reaction.—The hydroperoxide concentration during the reaction was measured at various times and was almost constant for several tens of minutes. The effects of the initial hydroperoxide and cumene concentrations and the catalyst weight : liquid volume ratio on the hydroperoxide concentration during the reaction were investigated at 291 K. The results are summarized in Table 1. The hydroperoxide

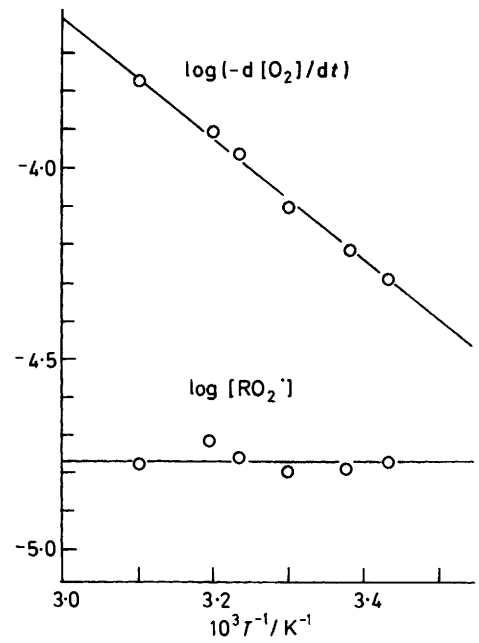

FIGURE 5 Arrhenius plots of rate of oxygen consumption and concentration of cumylperoxyl radical for autoxidation of cumene with lead dioxide

TABLE 1

Concentration of cumene hydroperoxide during autoxidation of cumene with lead dioxide

$[ROOH]_0$/ M	[RH]/ M	$[PbO_2]$/ g l^{-1}	$[ROOH]_\infty$/ M	$[RO_2\cdot]$/M Exp.	Calc.
0(<10^{-3})	7.18	63.2	0.0094	1.10	1.25
0.0135	7.18	66.7	0.0090	1.10	0.88
0.0135	7.18	47.4	0.0119	1.10	1.16
0.0790	7.18	47.4	0.0120	1.10	1.16
0.0790	7.18	16.7	0.0333	1.10	0.89
0.0135	7.18	33.3	0.0132	1.10	0.88
0.0135	7.18	133.0	0.0038	1.10	1.19
0.0135	4.70	47.4	0.0058	0.72	0.71
0.0135	3.59	47.4	0.0028	0.55	0.40

concentration during the reaction is independent of the initial hydroperoxide concentration and depends only on the cumene concentration and the catalyst weight : liquid volume ratio.

Product Distribution.—The product distribution as well as the steady state concentration of cumene hydroperoxide were determined. The results are summarized in Table 2, where the amount of oxygen absorbed during the reaction is also presented. 1,1-Dimethyl-2-phenylethanol is found to be the major product and the small amount of acetophenone is also produced. Since the cumene hydroperoxide introduced initially is considered to be converted into 1,1-

TABLE 2

Product distribution of cumene oxidation with lead dioxide

$[RH]_0$/M	$[PbO_2]_0$/g l^{-1}	$[ROOH]_0$/M	$[ROOH]_\infty$/M	[PhCOMe]/M	[ROH]/M	$[O_2]$/M	[ROH]* : $[O_2]$
7.18	133.0	0.0135	0.0050	0.0025	0.090	0.037	2.05
7.18	47.4	0.0135	0.0120	0.0055	0.103	0.054	1.65
3.59	47.4	0.0068	0.0028	0.0188	0.185	0.099	1.80
7.18	47.4	0.0919	0.0120	0.0043	0.163	0.033	2.14
7.18	47.4	0($<10^{-3}$)	0.0094	0.0018	0.048	0.021	2.28
7.18	33.3	0.0135	0.0117	0.0040	0.081	0.036	1.87
7.18	33.3	0.0135	0.0120	0.0063	0.114	0.048	2.10
7.18	66.7	0.0135	0.0090	0.0054	0.094	0.045	1.80
7.18	133.0	0.0135		0.0121	0.195	0.093	1.94

$[ROH]^* = [ROH] - [ROOH]_0$.

dimethyl-2-phenylethanol almost quantitatively,[11] the concentration of 1,1-dimethyl-2-phenylethanol produced by the autoxidation of cumene, [ROH]*, is represented by equation (3). The ratio of [ROH]* to the amount of

$$[ROH]^* = [ROH] - [ROOH]_0 \quad (3)$$

oxygen absorbed $[O_2]$ is 1.96 ± 0.07 (Table 2). It should be noted that this ratio is almost the same as that of the concentration of 1,1-dimethyl-2-phenylethanol to the amount of oxygen generated in the decomposition of cumene hydroperoxide with lead dioxide.[11]

DISCUSSION

Reaction Mechanism.—From equations (1) and (2) equation (4) is obtained where k_c is 0.49 l mol^{-1} s^{-1} at

$$-d[O_2]/dt = k_c[RH][RO_2\cdot] \quad (4)$$

291 K. Equation (4) suggests that the chain propagation reactions (5) and (6) proceed. The radical R·

$$RO_2\cdot + RH \xrightarrow{k_3} ROOH + R\cdot \quad (5)$$

$$R\cdot + O_2 \xrightarrow{k_4} RO_2\cdot \quad (6)$$

reacts with a molecule of oxygen and is converted into the peroxyl radical, which in turn reacts with the substrate resulting in the formation of the hydroperoxide and the alkyl radical. The propagation reactions (5) and (6) have been assumed in the autoxidation of hydrocarbons. However, a direct experimental proof has never been reported. In this study, the proportionality between the rate of oxygen consumption and the concentration of the peroxyl radical was confirmed experimentally.

The initiation step of the autoxidation of cumene with lead dioxide is considered to be the hydroperoxide decomposition on the dioxide surface. Previously we have studied the decomposition of cumene hydroperoxide with lead dioxide and the decay of cumylperoxyl radical in the liquid phase,[11,16] where a mechanism for the decomposition was proposed. Thus, as far as the initiation and the termination steps are concerned, the reaction mechanism for the autoxidation of cumene with lead dioxide is considered to be known. Hence the whole reaction mechanism can be written by simply combining the mechanism for hydroperoxide decomposition with the propagation reactions (5) and (6) as equations (7)—(13). Here, we denote the rate of the hydroperoxide decomposition on the surface by R_i and the complex formation of the peroxyl radical with the hydroperoxide, proposed previously,[11] was eliminated

$$\text{Initiation } ROOH + PbO_2 \xrightarrow{R_i} RO_2\cdot \quad (7)$$

$$\text{Propagation } RO_2\cdot + RH \xrightarrow{k_3} R\cdot + ROOH \quad (8)$$

$$R\cdot + O_2 \xrightarrow{k_4} RO_2\cdot \quad (9)$$

$$RO\cdot + ROOH \xrightarrow{k_5} ROH + RO_2\cdot \quad (10)$$

$$RO_2\cdot + RO_2\cdot \xrightarrow{k_6} 2RO\cdot + O_2 \quad (11)$$

$$\text{Termination } RO_2\cdot \xrightarrow{k_7} PhCOMe + MeO\cdot \quad (12)$$

$$MeO\cdot + RO_2\cdot \xrightarrow{\text{fast}} \text{stable products} \quad (13)$$

since complex formation is negligible under the present experimental conditions (low hydroperoxide concentrations, <0.1M).

The peroxyl radical is formed on the catalyst surface by the decomposition of hydroperoxide and then desorbs into the homogeneous phase, where the chain propagation and chain termination proceed. According to this mechanism, the rate equations (14)—(17) follow. Applying the steady state approximation to [RO·] and $[RO_2\cdot]$,

$$d[RO_2\cdot]/dt = R_i - 2k_7\,[RO_2\cdot] \quad (14)$$

$$d[RO\cdot]/dt = -k_5[RO\cdot][ROOH] + 2k_6[RO_2\cdot]^2 \quad (15)$$

$$-d[O_2]/dt = -k_4[R\cdot][O_2] + k_6[RO_2\cdot]^2 \quad (16)$$

$$d[ROOH]/dt = -R_i - k_5[RO\cdot][ROOH] + k_3[RO_2\cdot][RH] \quad (17)$$

equation (17) can be rewritten as (18). The second term of the right hand side of (18) is negligiblly small compared

$$d[ROOH]/dt = -2k_7[RO_2\cdot] - 2k_6[RO_2\cdot]^2 + k_3[RO_2\cdot][RH] \quad (18)$$

with the first term, since our previous work [11,16] determined the values of $2k_6$ and $2k_7$ as 5.0×10^5 l mol^{-1} s^{-1} and 0.042 s^{-1}, *i.e.*, $k_6\,[RO_2\cdot]/k_7 \gg 1$ even if the minimum value of the radical concentration in Figure 1 is used. Thus, equation (18) reduces to (19).

$$d[ROOH]/dt = -2k_6[RO_2\cdot]^2 + k_3[RO_2\cdot][RH] \quad (19)$$

The concentration of hydroperoxide during the reaction was found to be steady, *i.e.*, $d[ROOH]/dt = 0$.

[16] S. Fukuzumi and Y. Ono, *J.C.S. Perkin II*, 1977, 622.

The concentration of peroxyl radical is then given by equation (2) which is consistent with the experimental

$$[RO_2^{\bullet}] = k_3[RH]/2k_6 \quad (20)$$

observation that the radical concentration is proportional to the concentration of cumene, but independent of the catalyst weight : liquid volume ratio. The rate of oxygen consumption can be rewritten as equation (21) which also agrees with the experimental observation that

$$-d[O_2]/dt = k_3[RO_2^{\bullet}][RH] - k_6[RO_2^{\bullet}]^2 = k_3^2[RH]^2/4k_6 \quad (21)$$

the rate of oxygen consumption is proportional to the square of the cumene concentration and independent of the catalyst weight : liquid volume ratio.

Comparing the derived equations [(20) and (21)] with the experimental ones [(1) and (2)] the absolute rate constants, k_3 and $2k_6$, are obtained as $k_3 = 2k_b/k_a = 0.98$ l mol^{-1} s^{-1}, $2k_6 = 2k_b/k_a^2 = 5.0 \times 10^5$ l mol^{-1} s^{-1} at 291 K. The rate constant $2k_6$ for the bimolecular reaction of the peroxyl radicals obtained in this study (the autoxidation of cumene) is the same as that found previously [11] (Table 3).

TABLE 3

Rate constants for decomposition of cumene hydroperoxide with lead dioxide [11]

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

The mechanism for cumene oxidation presented above is the same as that proposed for the decomposition of cumene hydroperoxide except for two elementary reactions [(8) and (9)] which do not affect the concentration of peroxyl radical during the autoxidation. Therefore, the concentration of peroxyl radical can be expressed as a function of the hydroperoxide concentration and the catalyst weight : liquid volume ratio as expressed in the case of the hydroperoxide decomposition. This gives equation (22) {equation (17) of ref. 11

$$[RO_2^{\bullet}] = \frac{k_2}{2k_{-1}}\left\{-1 + \sqrt{1 + \frac{4k_1k_{-1}K_1[ROOH][PbO_2^*]}{k_7k_2(1 + K_1[ROOH])}}\right\} \quad (22)$$

given the assumption $K[ROOH] \ll 1$}. The rate constants in equation (22) are presented in Table 3. Thus, the concentration of the peroxyl radical during the autoxidation can be predicted from the observed concentration of hydroperoxide and the catalyst weight : liquid volume ratio used. The radical concentrations calculated are listed in Table 1, in which the observed concentrations of peroxyl radical are also given. The agreement between the observed and the calculated radical concentration is fairly good, supporting our mechanism for the autoxidation and for the decomposition of the hydroperoxide.

Product Distribution.—The proposed reaction mechanism can also explain the product distribution. The propagation reactions (8) and (9) yield the hydroperoxide, most of which decomposes into 1,1-dimethyl-2-phenylethanol by the consecutive chain reactions (10) and (11); a small amount of acetophenone is produced by the termination reactions (12) and (13). From equations (20) and (21), the rate of oxygen consumption is given by (23). On the other hand, the rate of the alcohol formation is given by (24). From equations (23) and (24), relation (25) is obtained. Equation (25)

$$-d[O_2]dt = k_6[RO_2^{\bullet}]^2 \quad (23)$$

$$d[ROH]^*/dt = k_5[RO^{\bullet}][ROOH] = 2k_6[RO_2^{\bullet}]^2 \quad (24)$$

$$-d[ROH]^*/d[O_2] = 2 \quad (25)$$

also agrees with the experimental observation in Table 2, $[ROH]^*/[O_2] = 1.96 \pm 0.07$.

Absolute Rate Constants for Cumene Oxidation.—The temperature dependence of the apparent rate constants k_a and k_b gives the activation energies E_3 and E_6 and the frequency factors A_3 and A_6 for the rate constants of propagation (k_3) and the interaction of the peroxyl radicals (k_6) shown in Table 4. Arrhenius parameters from the literature [17-21] are also given in Table 4. A number of techniques have been used in order to evaluate the rate constants for the elementary steps in the cumene autoxidation, the rotating sector technique,[17,18] the pre- and after-effect methods,[19,20] and the chemiluminescence method.[21] In the present study, the simultaneous measurements of the radical concentration and the rate of oxygen consumption permitted easy and accurate evaluation of the absolute rate constants for the autoxidation of cumene. Moreover, we confirmed that the rate expressions and the product distribution are consistent with the proposed mechanism.

TABLE 4

Activation parameters for cumene oxidation

log (A_3/l mol^{-1} s^{-1})	E_3/ kJ mol^{-1}	log (A_6/l mol^{-1} s^{-1})	E_6/ kJ mol^{-1}	Ref.
5.3	30	10.9	30	This study
		11.2 *	31 *	17
	28		25	18
8.2	52	10.7	40	19
4.0	27	5.3	0	20
6.5	42	9.8 ± 1.0	29 ± 6	21
		6.2	10	22

* Determined in the decomposition of cumene hydroperoxide with lead dioxide.

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