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Formation of a Charge-Transfer Complex between the 1-Methyl-1-phenylethylperoxyl Radical and Pyridine during Decomposition of 1-Methyl-1-phenylethyl Hydroperoxide

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The apparent rate constant for the self-reaction of 1-methyl-1-phenylethylperoxyl radicals ($\mathrm{RO_2^{\bullet}}$) in the presence of pyridine was determined from simultaneous measurements of the rate of oxygen generation and the concentration of the peroxyl radical during the decomposition of 1-methyl-1-phenylethyl hydroperoxide with lead dioxide. The apparent rate constant decreased markedly with an increase in the concentration of pyridine, which clearly demonstrates the low reactivity of $\mathrm{RO_2^{\bullet}}$ in the presence of pyridine. This behavior is taken as evidence that the charge-transfer complex between the peroxyl radical and pyridine is formed and that the reactivity of complexed peroxyl radicals is much lower than that of uncomplexed peroxyl radicals. The equilibrium constant for the formation of the charge-transfer complex has been determined to be 0.55 $\mathrm{M^{-1}}$ at 293 K and the values of $-\Delta H$ and $-\Delta S$ were found to be 31 kJ $\mathrm{mol^{-1}}$ and 109 J $\mathrm{mol^{-1}\,K^{-1}}$, respectively.

The effects of solvents on the reactivity of free radicals due to complex formation between the radicals and the solvents have been investigated by several authors.[1–10] Porter and Smith[1] have explained the influence of chaperon molecules on the recombination rate of iodine atoms in terms of a charge-transfer complex intermediate between the two species, spectroscopic support of which has also been reported.[2–4] Russell[5] has shown that the pronounced solvent effects on chlorine atom-substrate complexes of similar nature. Boozer and Hammond[6,7] have postulated the formation of charge-transfer complexes between alkylperoxyl radicals and inhibitors (aromatic amines and phenols) in the autoxidation of hydrocarbons. Thomas[8] has also examined the possibility of complex formation between the 1-methyl-1-phenylethylperoxyl radical and pyridine in a study on the autoxidation of cumene at 330 and 347 K, but no clear evidence was obtained. Thus, an inhibition mechanism involving charge-transfer between a chain propagating radical and the antioxidant has often been suggested,[6–8] but has rarely been identified with any certainty.

Previously, the present authors postulated the following complex formation between the 1-methyl-1-phenylethylperoxyl radical and 1-methyl-1-phenylethyl hydroperoxide as the result of electron spin resonance and kinetic studies of hydroperoxide decomposition with lead dioxide.[9]

$$\mathrm{RO_2^{\bullet}} + n\,\mathrm{ROOH} \rightleftarrows (\mathrm{RO_2^{\bullet}} \cdots n\,\mathrm{ROOH}).$$

The value $n=2$ was obtained from the change in the ESR line width of the peroxyl radical, as well as from kinetic results of the hydroperoxide decomposition. The reactivity of the complexed radicals was found to be much lower than that of uncomplexed radicals. Similar results indicating that complex formation between radicals and solvents leads to a decrease in the apparent reactivity of the radicals has been obtained in the case of the autoxidation of ethyl methyl ketone in aqueous solutions.[10] It was shown that equilibrium in the reaction

$$\mathrm{RO_2^{\bullet}} + m\,\mathrm{H_2O} \rightleftarrows (\mathrm{RO_2^{\bullet}} \cdots m\,\mathrm{H_2O})$$

is rapidly established in the system. In this case, the value, $m=1$, was obtained. Thus, there are cases in which the apparent reactivity of radicals decreases markedly as the results of complex formation between radicals and solvents, although these processes remain some of the least understood of all inhibition mechanism.[11]

Pyridine is known to form strong charge-transfer complexes with acceptors such as iodine.[12] Therefore, in the present study, the change in apparent reactivity of the 1-methyl-1-phenylethylperoxyl radical for the self-reaction in the presence of pyridine was investigated by electron spin resonance and kinetic methods, and evidence of the formation of charge-transfer complexes between the peroxyl radical and pyridine is presented. The equilibrium constant, K, and the values of ΔH and ΔS for complex formation are reported.

Experimental

The apparatus has been described in detail elsewhere.[9,13] The decomposition of 1-methyl-1-phenylethyl hydroperoxide in $\mathrm{CCl_4}$ and pyridine in the presence of lead dioxide powder was carried out in a 50- or 100-$\mathrm{cm^3}$ flask immersed in a temperature-controlled bath, stirred magnetically and attached to a wet-gasometer. In order to determine the concentration of the peroxyl radical as well as the rate of oxygen generation under the same conditions, simultaneous measurements of the radical concentration and the rate of oxygen generation were performed as follows. While the rate of oxygen generation was measured with a wet-gasometer, the part of the solution involving the catalyst powder was circulated, using a roller pump, through the ESR cavity where the ESR measurements were carried out. The intensity of the ESR signal was confirmed to be independent of the feed rate of the roller pump over the range from 50—200 $\mathrm{cm^3/min}$. A JEOL-X-band spectrometer (JES-PE-1X) with 100-kHz magnetic modulation was used to detect the radicals. The radical concentration was determined by comparing the absorption area of the radical with that of 1,1-diphenyl-2-picrylhydrazyl in benzene. The change in sensitivity of the spectrometer due to the decrease in the Q factor caused by introducing a polar solvent such as pyridine was calibrated using an ESR marker in the ESR cavity.

Results and Discussion

When lead dioxide powder is added to the hydroperoxide solution, the ESR spectrum of the 1-methyl-1-phenylethylperoxyl radical is observed and oxygen gas evolves. The ESR spectrum consists of a single symmetrical line with no detectable hyperfine structure and an isotropic *g*-factor of 2.0148±0.0004, which is in good agreement with the values reported previously.[9,13–15] No ESR signal was obtained and no oxygen gas evolved unless lead dioxide powder was added. Simultaneous measurements of the radical concentration and the rate of oxygen generation were carried out both in the absence of and in the presence of pyridine. All the experiments were performed in hydroperoxide concentrations below 0.3 M, for which complex formation between the peroxyl radical and the hydroperoxide is negligible.[9]

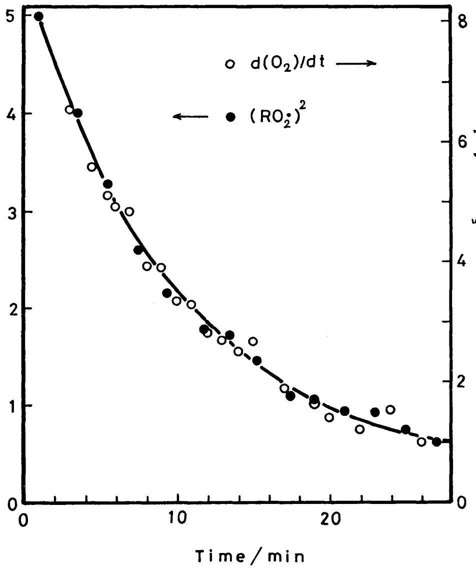

Fig. 1. The square of the 1-methyl-1-phenylethylperoxyl radical concentration and the rate of oxygen generation are plotted against time for the decomposition of 1-methyl-1-phenylethyl hydroperoxide with lead dioxide in the presence of pyridine at 303 K.
Initial concentration of the hydroperoxide: 0.254 M, initial ratio of PbO_2 weight to liquid volume: 40.5 g/l, pyridine concentration: 1.70 M, solvent: CCl_4.

A typical example of the change in the rate of oxygen generation and the peroxyl radical concentration with reaction time is shown in Fig. 1, in which the ordinates are the square of the radical concentration and the rate of oxygen generation. The initial concentrations of the hydroperoxide and pyridine were 0.254 and 1.70 M, respectively, and the ratio of catalyst weight to liquid volume was 40.5 g/l. As shown in Fig. 1, by selecting appropriate ordinate scales, the square of the radical concentration and the rate of oxygen generation behave in exactly the same manner, that is, the rate of oxygen generation is proportional to the square of the radical concentration, thus

$$\frac{\mathrm{d}[\mathrm{O_2}]}{\mathrm{d}t} = k_6^{\mathrm{exp}}[\mathrm{RO_2^{\bullet}}]^2, \tag{1}$$

where k_6^{exp} is a constant. It is well accepted that 1-methyl-1-phenylethyl hydroperoxide undergoes induced decomposition as follows:[16–18]

$$\mathrm{RO_2^{\bullet}} + \mathrm{RO_2^{\bullet}} \xrightarrow{k_6} 2\mathrm{RO\cdot} + \mathrm{O_2}, \tag{2}$$

$$\mathrm{RO\cdot} + \mathrm{ROOH} \xrightarrow{k_5} \mathrm{ROH} + \mathrm{RO_2^{\bullet}}. \tag{3}$$

Equation 1 clearly indicates that the oxygen generation reaction involves a bimolecular reaction of $\mathrm{RO_2^{\bullet}}$ (2) and that most RO· radicals react with ROOH and thus regenerate $\mathrm{RO_2^{\bullet}}$; the fraction of RO· radicals which do not react with ROOH (*e.g.*, due to *β*-sission resulting in the absorption of O_2) is negligible.[9] In fact, the main product, ROH (90%), and only a small amount of acetophenone (7%) were obtained by decomposition of the hydroperoxide with lead dioxide. Furthermore, it was confirmed that the molar ratio of the ROH produced to the oxygen evolved was very close to 2.[9] Then, it should be obvious that the proportionality constant, k_6^{exp}, gives the rate constant of the bimolecular reaction for the peroxyl radicals, Reaction 2.

In the same manner for the case shown in Fig. 1, the proportionality constant, k_6^{exp}, was determined for various pyridine concentrations. Figure 2 shows the relation between k_6^{exp} and the pyridine concentration at various reaction temperatures from 293—313 K. As is shown in Fig. 2, k_6^{exp} decreases with increasing pyridine concentration. This clearly demonstrates the decrease in the $\mathrm{RO_2^{\bullet}}$ reactivity for the $\mathrm{RO_2^{\bullet}}$ self-reaction, Reaction 2, with increasing pyridine concentration. It should be noted that complex formation between the hydroperoxide and pyridine, if occurs, cannot have any influence on k_6^{exp} since the rate-determining step for chain propagation is Reaction 2 and relation 1 is valid.

Solvent effects on the rate constants for reactions involving polar solvents have frequently been described using Kirkwood's equation:[19]

$$\log k_6 = \log k_6{}^0 - \frac{1}{kT}\,\frac{\varepsilon-1}{2\varepsilon+1}\left(\frac{\mu_1{}^2}{r_1{}^3}+\frac{\mu_2{}^2}{r_2{}^3}+\frac{\mu_3{}^2}{r_3{}^3}\right), \tag{4}$$

where $k_6{}^0$ is the rate constant at $\varepsilon=1$, k is the Boltzmann constant, μ_1, μ_2, r_1, and r_2 are the dipole moments and effective radii of the reactants, and μ_3 and r_3 refer to those of the activated complex. According to Kirkwood's equation, the rate constant should increase with increasing polarity of the solvent. This has been reported to be the case for the oxidation of ethyl methyl ketone in benzene solutions.[10] In the present case, however, the apparent rate constant, k_6^{exp}, decreases with the pyridine concentration even though the polarity of the medium increases. Then, the following complex formation between the peroxyl radical and pyridine is postulated in order to explain the experimental observations in Fig. 2;

$$\mathrm{RO_2^{\bullet}} + n\,\mathrm{Py} \overset{K}{\rightleftarrows} (\mathrm{RO_2^{\bullet}}\cdots n\,\mathrm{Py}). \tag{5}$$

Two types of peroxyl radicals, uncomplexed ($\mathrm{RO_2^{\bullet}}$) and complexed ($\mathrm{RO_2^{\bullet}}\cdots n\mathrm{Py}$), are in equilibrium in the system. The peroxyl radical concentration $(\mathrm{RO_2^{\bullet}})_t$ measured using ESR is equal to the sum of the concentration of the two species, thus

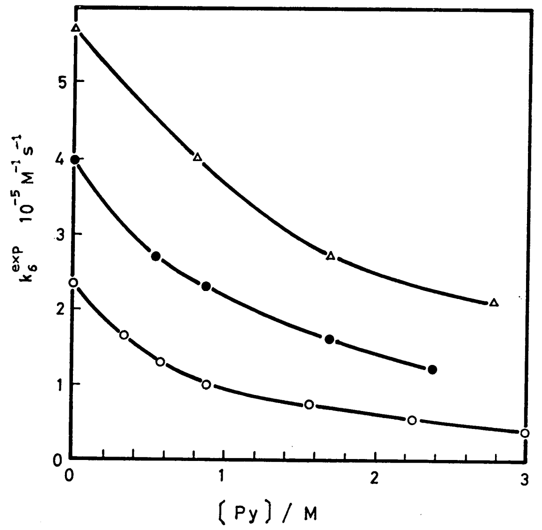

Fig. 2. k_6^{exp} as a function of the pyridine concentration for different temperatures.
○ 293 K, ● 303 K, △ 313 K.

$$[RO_2^{\bullet}]_t = [RO_2^{\bullet}] + [RO_2^{\bullet} \cdots n\,Py]. \tag{6}$$

The peroxyl radical self-reactions may be represented as

$$RO_2^{\bullet} + RO_2^{\bullet} \xrightarrow{k_6} O_2 + 2RO\cdot, \tag{7}$$

$$RO_2^{\bullet} + (RO_2^{\bullet} \cdots n\,Py) \xrightarrow{k_6'} O_2 + 2RO\cdot + n\,Py, \tag{8}$$

$$(RO_2^{\bullet} \cdots n\,Py) + (RO_2^{\bullet} \cdots n\,Py) \xrightarrow{k_6''} O_2 + 2RO\cdot + 2n\,Py. \tag{9}$$

From Eqs. 5—9, the rate of oxygen generation is given by

$$\frac{d[O_2]}{dt} = \frac{k_6 + k_6'K[Py]^n + k_6''K^2[Py]^{2n}}{(1+K[Py]^n)^2}[RO_2^{\bullet}]_t^2. \tag{10}$$

Thus, the experimental rate constant, k_6^{exp}, is expressed as

$$k_6^{exp} = \frac{k_6 + k_6'K[Py]^n + k_6''K^2[Py]^{2n}}{(1+K[Py]^n)^2} \tag{11}$$

If one assumes that the reactivity of the complexed peroxyl radical is much lower than that of the uncomplexed radical, that is, that k_6' and $k_6'' \ll k_6$, then, Eq. 11 reduces to

$$k_6^{exp} = \frac{k_6}{(1+K[Py]^n)^2}. \tag{12}$$

Equation 12 can be rewritten as

$$\log\left(\left(\frac{k_6}{k_6^{exp}}\right)^{1/2} - 1\right) = n \log[Py] + \log K. \tag{13}$$

In Fig. 3, the plot of log $((k_6/k_6^{exp})^{1/2} - 1)$ as a function of log [Py] is a straight line for each temperature, which indicates the validity of the above mechanism. The value $n=1$ is obtained from the slopes of these lines. This indicates the association of one pyridine molecule with a single peroxyl radical.

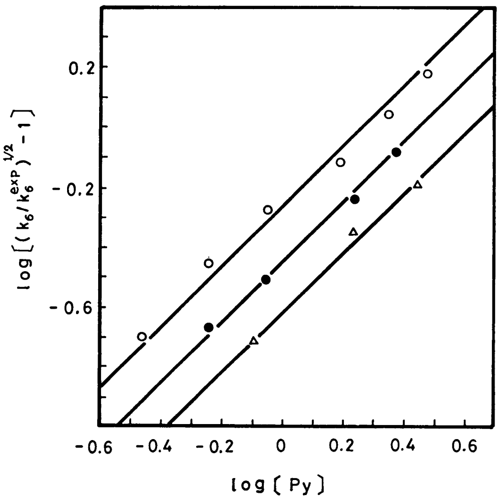

Fig. 3. log $[(k_6/k_6^{exp})^{1/2} - 1]$ as a function of log [Py] for different temperatures.
○ 293 K, ● 303 K, △ 313 K.

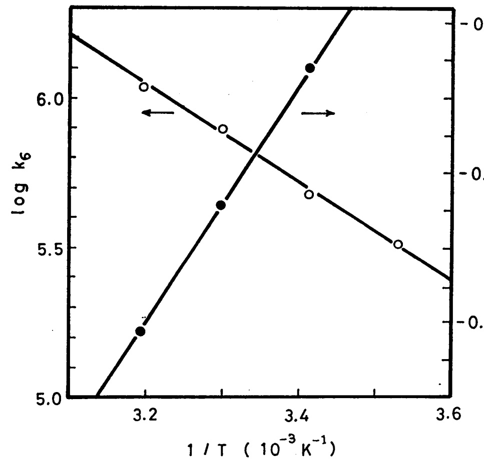

Fig. 4. The dependence of log K and log k_6 on $1/T$.

TABLE 1. ACTIVATION PARAMETERS FOR THE SELF-REACTION OF 1-METHYL-1-PHENYLETHYLPEROXYL RADICALS AND COMPLEX FORMATION BETWEEN THE 1-METHYL-1-PHENYLPEROXYL RADICAL AND PYRIDINE

Log A_6/M^{-1} s^{-1}	E_6 kJ mol^{-1}	$-\Delta H$ kJ mol^{-1}	$-\Delta S$ J mol^{-1} K^{-1}	Ref.
11.2	31	31	109	This study
10.9[a]	30[a]			13
		33[b]	65[b]	12

a) Obtained for the autoxidation of cumene with lead dioxide. b) Activation parameters for the charge-transfer complex between pyridine and iodine.

The temperature dependence of k_6 and K obtained from Fig. 3 is shown in Fig. 4. The values of the activation parameters for the radical self-reaction, A_6 and E_6, as well as ΔH and ΔS for the complex formation derived from Fig. 4, are summarized in Table 1 together with the activation parameters, A_6 and E_6, obtained from the autoxidation of cumene with lead dioxide.[13] The Arrhenius parameters of the peroxyl radical self-reaction in hydroperoxide decomposition are in good agreement with those obtained for the autoxidation of cumene. The high ΔH value, 31 kJ mol^{-1}, explains why Thomas[8] was unable to estimate the equilibrium constant K

for the $\mathrm{RO_2^{\bullet}}$–pyridine complex in the autoxidation of cumene; his experiments were carried out at higher temperatures (330 and 347 K) since he used the thermal initiator AIBN. The equilibrium constant K has the small values 0.14 $\mathrm{M^{-1}}$ at 330 K and 0.08 $\mathrm{M^{-1}}$ at 347 K, as estimated from the ΔH and ΔS values given in Table 1. These K values are consistent with the estimation of Thomas that K cannot have a value in excess of 0.4 $\mathrm{M^{-1}}$. Since pyridine is known to form strong charge-transfer complexes with acceptors such as iodine,[12] the values of ΔH and ΔS for the formation of the charge-transfer complex between pyridine and iodine are compared with those for the present case in Table 1. The ΔH value for the $\mathrm{RO_2^{\bullet}}$–pyridine complex is in good agreement with that for the charge-transfer complex between pyridine and iodine. Hence, the complex formation between 1-methyl-1-phenylethylperoxyl radical and pyridine can be considered to follow a charge-transfer process analogous to the pyridine–iodine complex, *i.e.*,

$$\mathrm{RO_2^{\bullet}} + \mathrm{Py} \rightleftharpoons (\mathrm{RO_2^{\bullet\delta-}}\ \mathrm{Py^{\delta+}}). \tag{14}$$

Thus, the 1-methyl-1-phenylethylperoxyl radical is an electron acceptor in complex formation with pyridine.

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