Retardation of Autoxidation in the Presence of Water, Alcohols and Carboxylic Acids

Koji Ukegawa and Yoshio Kamiya*
National Research Institute for Pollution and Resources, Kawaguchi, Saitama 332
**Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113*

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The oxidation of alcohols and α-substituted toluenes in water, methanol and acetic acid was studied at 60—70 °C in the presence of 0.040 M AIBN. The rate of oxidation of alcohol, $k_p/(2k_t)^{1/2}$, considerably increases when the alcohol is diluted with an inert solvent. The rate remarkably decreases with the addition of water, methanol or various carboxylic acids. However in the presence of tetralyl hydroperoxide, *viz.*, when the hydroperoxyl radical is replaced by the tetralyl peroxyl radical, no further inhibition effect due to water, methanol or carboxylic acids is observed. The rate of oxidation of 1,4-cyclohexadiene decreases with the addition of water or acetic acid. However in the presence of 0.20 M tetralyl hydroperoxide, no further inhibition effect is observed. The rate of oxidation of 1-phenylethanol decreases with the addition of benzoic acid but not with that of methylbenzoate. The rate of oxidation of (2-chloroethyl)benzene, ethylbenzene and isopropylbenzene does not decrease with the addition of 0.224 M acetic acid, but that of *N,N*-dimethylbenzylamine, *N,N*-diethylbenzylamine, benzyl alcohol, 1-phenylethanol and methyl benzyl ether decreases. It is concluded that hydroperoxyl and alkylperoxyl radicals with α-substituents such as hydroxyl, carbonyl, alkoxyl or amino groups undergo deactivation due to hydrogen bonding with water, alcohols and carboxylic acids.

Although the autoxidation of hydrocarbons has been studied thoroughly by a number of workers,[1–5] many points are still left unclarified. Hendry and Russell,[6] and Howard and Ingold[7] reported that the solvent effect on the rate of autoxidation can be correlated as a function of dielectric constant and neither π-complex formation nor hydrogen bonding of alkylperoxyl radical is observed.

Zaikov and Maizus[8] suggested that the deactivation of peroxyl radical occurrs owing to hydrogen bonding with water in the autoxidation of methyl ethyl ketone. Imamura *et al.*[9] reported that the autoxidation of acetaldehyde is considerably retarded in the presence of vaious carboxylic acids. Bimolecular interaction of hydroperoxyl radicals is known to be strongly retarded in the presence of water.

In the course of studies on the autoxidation of alcohols, we found that hydroperoxyl radicals can be deactivated by water, alcohol and carboxylic acids. Furthermore, peroxyl radicals with α-substituent containing nitrogen or oxygen atoms were found to be deactivated by hydroxyl compounds. The deactivation effect, which is hardly observed in the case of alkylperoxyl radicals, can be explained only in terms of hydrogen bonding.

Experimental

The technique of oxidation was described elsewhere.[10] All the experiments were carried out at 60—70 °C in the presence of α,α'-azobisisobutyronitrile as an initiator under atmospheric pressure of oxygen. Hydroperoxide produced was determined by iodometric titration, where hydroperoxide was treated with KI in 80% aqueous acetic acid at room temperature in the dark.

Tetralyl hydroperoxide obtained by the autoxidation of tetralin was purified several times by recrystallization from heptane. The other materials were used after distillation or recrystallization of extra pure reagents.

Results and Discussion

Peroxyl radicals formed in the autoxidation of alcohols decompose to ketones and a hydroperoxyl radical, the hydroperoxyl radical being the chain carrier in the autoxidation of alcohols.[11] However, the α-hydroxyperoxyl radical can also be the chain carrier in the oxidation of some alcohols.[12]

The oxidation of an alcohol initiated by AIBN (α,α'-azobisisobutyronitrile) proceeds according to the following mechanisms.

Initiation reaction:

$$\mathrm{AIBN + RH + O_2 \xrightarrow{R_i} RO_2\cdot(HO_2)}$$

Propagation reaction:

$$\mathrm{RO_2\cdot + RH \xrightarrow{k_p} ROOH + R\cdot}$$

$$\mathrm{(HO_2\cdot + RH \longrightarrow HOOH + R\cdot)}$$

$$\mathrm{R\cdot + O_2 \xrightarrow{fast} RO_2\cdot}$$

Termination reaction:

$$\mathrm{2RO_2\cdot(2HO_2\cdot) \xrightarrow{k_t} non\text{-}radical\ products}$$

When the concentration of oxygen is sufficiently high, the rate of oxidation can be expressed by

$$-\mathrm{d}O_2/\mathrm{d}t = (\mathrm{RH})R_i^{1/2}k_p/(2k_t)^{1/2}$$

where k_p and k_t are the rate constants of chain propagation reaction and chain termination reaction, respectively, and R_i is the rate of initiation reaction. When (RH) and R_i are given, $k_p/(2k_t)^{1/2}$ can be calculated by measuring the rate of oxidation:

$$k_p/(2k_t)^{1/2} = -\mathrm{d}O_2/\mathrm{d}t/(\mathrm{RH})R_i^{1/2}.$$

It has been reported[13] that the value of $k_p/(2k_t)^{1/2}$ of hydrocarbon solution remains constant when the substrate is diluted with an inert solvent having a dielectric constant similar to that of the hydrocarbon.

$k_p/(2k_t)^{1/2}$ was not constant in the oxidation of 1-phenylethanol, when the alcohol was diluted chlorobenzene having a dielectric constant similar to that of the alcohol. As shown in Fig. 1, $k_p/(2k_t)^{1/2}$ of 1-phenylethanol decreases markedly with the increase in the concentration of alcohol. This does not seem to have been reported in the autoxidation of hydrocarbons.

$k_p/(2k_t)^{1/2}$ increased with decreasing substrate concentration when other alcohols such as benzyl alcohol

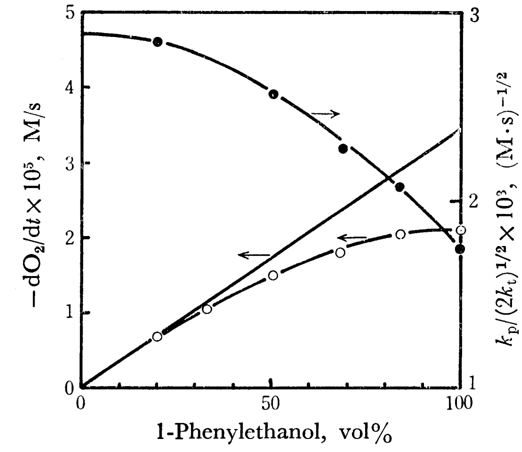

Fig. 1. The rate of oxidation of 1-phenylethanol as a function of alcohol concentration, 70 °C, $P_{O_2}=760$ mmHg, (AIBN) = 0.040 M, Solvent: chlorobenzene.

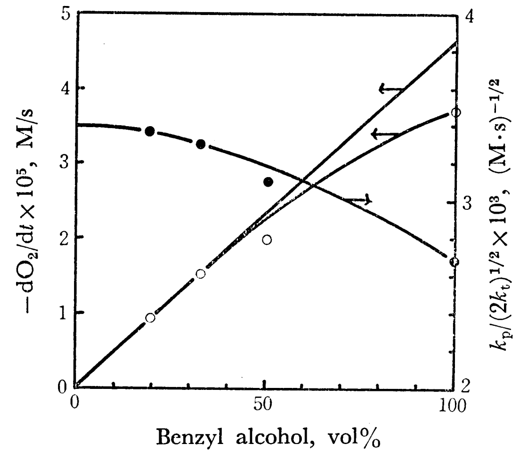

Fig. 2. The rate of oxidation of benzyl alcohol as a function of alcohol concentration, 70 °C, $P_{O_2}=760$ mmHg, (AIBN) = 0.040 M, Solvent: chlorobenzene/acetophenone = 1/2 by vol.

(Fig. 2) and 2-propanol were diluted with inert solvents whose dielectric constants were approximately equal to those of alcohols.

The values indicate that the hydrogen abstraction of alcohols is retarded by the hydrogen bonding between two hydroxyl compounds or by the hydrogen bonding of peroxyl radical with hydroxyl compound. The hydrogen bonding between alcohol molecules has no significant effect on the rate of hydrogen abstraction, since water no more retards the oxidation when a hydroperoxyl radical is replaced by a tetralylperoxyl radical.

The extrapolated values of $k_p/(2k_t)^{1/2}$ to zero alcohol concentration are given in Table 1. The ratio of $k_p/(2k_t)^{1/2}$ at 0% alcohol to $k_p/(2k_t)^{1/2}$ at 100% alcohol is between 2.0 and 1.3.

The effect of hydroxyl compounds on the rate of oxidation of 1-phenylethanol is shown in Fig. 3. *t*-Butyl alcohol accelerated the rate of oxidation, but water and methanol strongly retarded it; methanol did not retard the oxidation of tetralin (Table 2). The result of *t*-butyl alcohol is probably due to steric hindrance for hydrogen bonding. Similarly, the rate of oxidation of 2-propanol was inhibited in the presence of water, but the rate of oxidation of *p*-isopropyltoluene (Fig. 4) was not affected by the addition of methanol and water.

TABLE 1. EFFECT OF ALCOHOL CONCENTRATION ON THE RATE OF OXIDATION OF ALCOHOL
70 °C, $P_{O_2}=760$ mmHg, (AIBN) = 0.040 M

Alcohol	Solvent	$\dfrac{(k_p/(2k_t)^{1/2})(RH)=0\%}{(k_p/(2k_t)^{1/2})(RH)=100\%}$
2-Propanol	Chlorobenzene	2.0
1-Phenylethanol	Chlorobenzene	1.6
Benzyl alcohol	Chlorobenzene + acetophenone	1.3

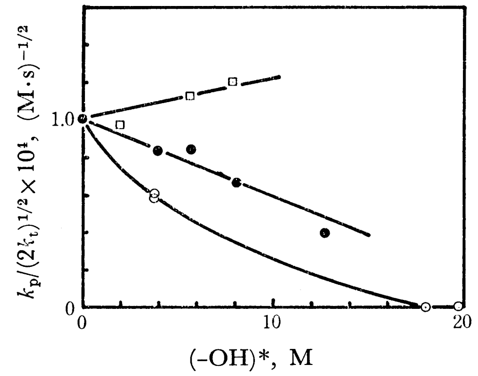

Fig. 3. Oxidation of 1-phenylethanol in the presencs of H_2O (○), methanol (●) or *t*-butyl alcohol (□), 60 °C, $P_{O_2}=760$ mmHg, (AIBN) = 0.040 M, * (-OH) = $(H_2O) \times 2$.

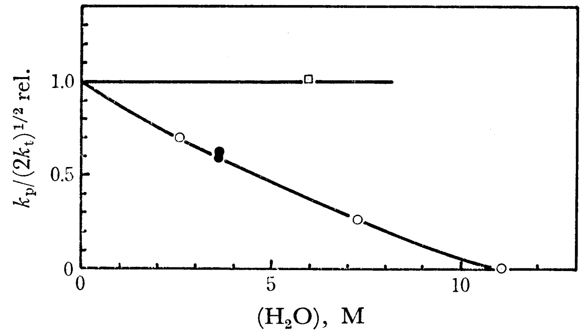

Fig. 4. Oxidation of 2-propanol, 1-phenylethanol or *p*-isopropyltoluene in the presence of H_2O.
○: 2-propanol at 60 °C, (AIBN) = 0.040 M. ●: 1-phenylethanol at 60 °C, (AIBN) = 0.040 M, H_2O/*t*-butyl alcohol = 1/2 by vol. □: *p*-isopropyltoluene at 70 °C, (AIBN) = 0.040 M, H_2O/*t*-butyl alcohol = 3/20 by vol.

The rate of oxidation of 2-propanol in the presence of 0.20 M tetralyl hydroperoxide is plotted against water concentration (Fig. 5). The hydroperoxide method was proposed by Howard *et al.*[14] In the presence of tetralyl hydroperoxide, the chain carrier completely changes from the hydroperoxyl radical to the tetralylperoxyl radical at hydroperoxide concentrations above 0.1 M (Fig. 6). In the presence of tetralyl hydroperoxide, *viz.*, when the hydroperoxyl radical

TABLE 2. EFFECT OF METHANOL ON THE RATE OF OXIDATION OF TETRALIN

60 °C, P_{O_2} = 760 mmHg, (AIBN) = 0.040 M

(Tetralin) M	(Methanol) M	$-dO_2/dt$ $\times 10^5$, M/s	$k_p/(2k_t)^{1/2}$ $\times 10^3$, $(M \cdot s)^{-1/2}$
6.58	0.0	3.13	6.23
5.06	5.70	2.86	7.41
4.39	8.23	2.61	7.79

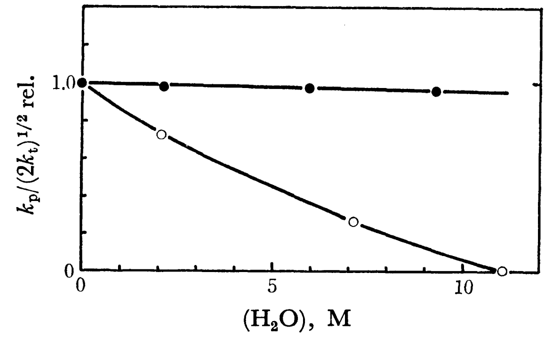

Fig. 5. Effect of water concentration in the autoxidation of 2-propanol.
○: Hydroperoxyl radical, in the presence of H_2O, 60 °C, (AIBN) = 0.040 M. ●: Tetralylperoxyl radical, in the presence of THP and H_2O, 50 °C, (AIBN) = 0.040 M, (THP) = 0.20 M.

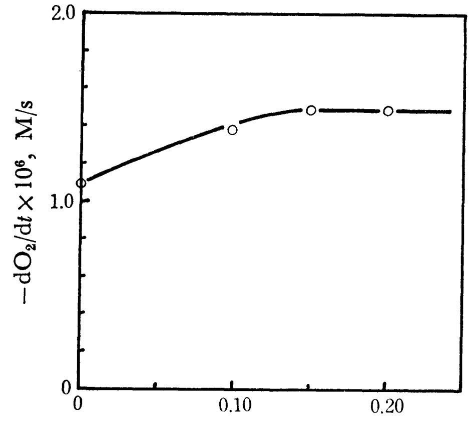

Fig. 6. Oxidation of 2-propanol in the presence of tetralyl hydroperoxide.
50 °C, (AIBN) = 0.040 M, P_{O_2} = 760 mmHg, (2-propanol) = 13.1 M.

is replaced by the tetralylperoxyl radical, no further inhibition effect due to water is observed.

Thus it can be concluded that hydroxyl compounds such as water and alcohols except *t*-butyl alcohol, deactivate by hydrogen bonding only hydroperoxyl and α-hydroxyalkylperoxyl radicals and not ordinary alkylperoxyl radical.

The hydrogen bonding of peroxyl radical with hydroxy compound lowers both k_p and k_t. It is suggested that $k_p/(2k_p)^{1/2}$ decreases because the extent of decrease of k_p is greater than that of $\sqrt{2k_t}$.

TABLE 3. EFFECT OF ACETIC ACID ON THE RATE OF TETRALIN

60 °C, P_{O_2} = 760 mmHg, (AIBN) = 0.040 M

(Tetralin) M	(Acetic acid) M	$-dO_2/dt$ $\times 10^5$, M/s	$k_p/(2k_t)^{1/2}$ rel.
7.35	0.0	3.13	1.00
6.68	1.59	2.80	0.984
5.65	4.04	2.50	1.04

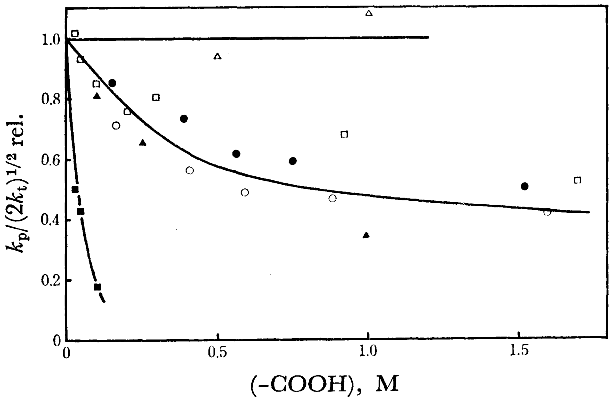

Fig. 7. Oxidation of 1-phenylethanol in the presence of carboxylic acids.
70 °C, P_{O_2} = 760 mmHg, (AIBN) = 0.040 M.
○: acetic acid, ●: monochloroacetic acid, □: benzoic acid, ■: *p*-nitrobenzoic acid, ▲: butyric acid, △: oxalic acid.

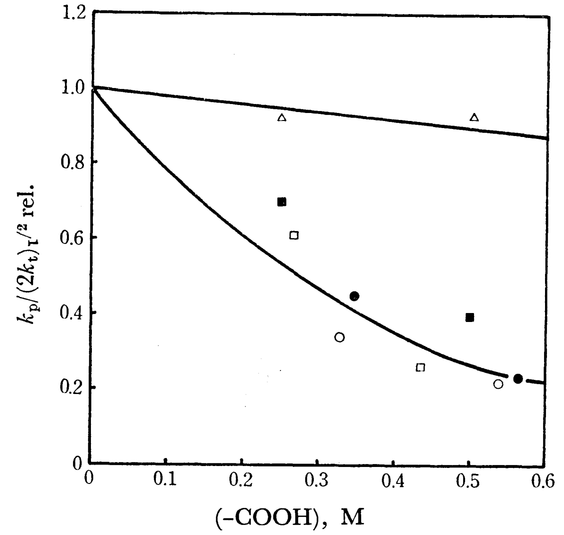

Fig. 8. Oxidation of 2-propanol in the presence of carboxylic acids.
60 °C, P_{O_2} = 760 mmHg, (AIBN) = 0.040 M.
●: Acetic acid, ○: monochloroacetic acid, □: propionic acid, ■: benzoic acid, △: oxalic acid.

The relative rate constant of oxidatikn of 1-phenylethanol, $k_p/(2k_t)^{1/2}{}_{rel.}$, is plotted against the concentration of carboxylic acids (Fig. 7). We see that the rate constant of oxidation of 1-phenylethanol, $k_p/(2k_t)^{1/2}{}_{rel.}$, is not affected by the addition of oxalic acid, decreasing remarkably by the addition of *p*-nitrobenzoic acid, decreasing to a similar extent by the addition of various carboxylic acids such as acetic, benzoic, butyric, chloroacetic acids. The effect of fatty acid and benzenecarboxylic acid seems to be independent of acid strength. The very small effect of oxalic acid may be due to intramolecular hydrogen bonding of oxalic acid. A similar solvent effect was observed in the oxidation of 2-propanol in the presence of carboxylic aicds (Fig. 8).

Acetic acid has no retardation effect on the hydrogen abstraction step by alkyl peroxyl radical (Table 3). This was confirmed by the hydroperoxide method, since the retardation effect due to acetic acid on the oxidation of 2-propanol is almost eliminated in the presence of tetralyl hydroperoxide (Fig. 9).

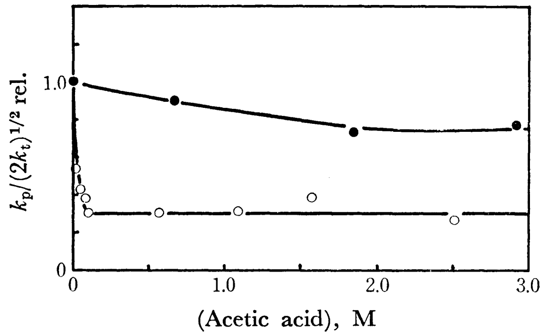

Fig. 9. Effect of acetic acid in the oxidation of 2-propanol.
50 °C, P_{O_2}=760 mmHg, (AIBN)=0.040 M
○: in the presence of acetic acid, ●: in the presence of acetic acid and THP, (THP)=0.20 M.

Table 4. Effect of acetic acid on the rate of oxidation of 1,4-cyclohexadiene
40 °C, P_{O_2}=760 mmHg, (AIBN)=0.040 M
(1,4-cyclohexadiene)=0.964 M, solvent: chlorobenzene

(Acetic acid) M	$-dO_2/dt$ $\times 10^6$, M/s	$k_p/(2k_t)^{1/2}$ rel.
0.0	7.13	1.00
0.0223	4.89	0.686
0.0520	3.02	0.424

Denisov and Solyanikov[15] reported that the decreasing rate of formation of hydrogen peroxide during the oxidation of 2-propanol is attributable to decomposition of hydrogen peroxide by the carboxylic acid formed during the course of oxidation. However, from our results it can be concluded that the rate of oxidation of 2-propanol decreases due to the deactivation of peroxyl radicals.

The effect of acetic acid on the hydroperoxyl radical is also confirmed in the autoxidation of 1,4-cyclohexadiene (Table 4), because in this case the chain carrier is hydroperoxyl radical[16].

The rate of oxidation of 1,4-cyclohexadiene was remarkably decreased by the addition of acetic acid (Table 4). The effect of association of hydroxyl compounds on the rate of oxidation of alcohol can be disregarded since 1,4-cyclohexadiene does not associate with acetic acid.

The rate of oxidation of 1-phenylethanol in the presence of phthalic acid or isophthalic acid is given in Table 5. It is clear that the rate of oxidation of 1-phenylethanol in the presence of isophthalic acid is smaller than that in the presence of phthalic acid. Phthalic acid has a greater dissociation constant than isophthalic acid, and the stability of intramolecular hydrogen bonding of phthalic acid should be higher than that of isophthalic acid.[17]

The relative rate constant of oxidation of 1-phenylethanol in the presence of 0.05 M isophthalic acid (0.815) is nearly equal to that in the presence of 0.1 M benzoic acid (0.798). It is concluded that the rate of oxidation of alcohols in the presence of dicarboxylic acid, which can form an intramolecular hydrogen bond, is greater than the rate in the presence of dicarboxylic acid, which has difficulty to form an intramolecular hydrogen bond.

The very small effect of oxalic acid on the autoxidation of 1-phenylethanol can be explained on the basis of intramolecular hydrogen bonding (Fig. 7).

Table 5. Effect of phthalic acid or isophthalic acid on the rate of oxidation of 1-phenylethanol
60 °C, P_{O_2}=760 mmHg, (AIBN)=0.040 M, solvent: *t*-butyl alcohol

(1-Phenylethanol) M	(Phthalic acid) M	(Isophthalic acid) M	$-dO_2/dt$ $\times 10^5$, M/s	$k_p/(2k_t)^{1/2}$ rel.
3.32	0.00	0.00	4.26	1.00
3.32	0.10	0.00	3.34	0.784
3.32	0.00	0.10	2.03	0.475

Table 6. Effect of benzoic acids on the rate of oxidation of 1-phenylethanol
60 °C, P_{O_2}=760 mmHg, (AIBN)=0.040 M, (-COOH)=0.10 M

Substituted benzoic acid	σ^+ [18]	1-Phenylethanol M	$-dO_2/dt$ $\times 10^6$, M/s	$k_p/(2k_t)^{1/2}$ $\times 10^3$, $(M\cdot s)^{-1/2}$	$k_p/(2k_t)^{1/2}$ rel.
p-CH_3O	−0.778	8.30	6.23	0.983	0.793
p-CH_3	−0.311	8.30	6.36	1.01	0.811
p-H	0.00	8.30	6.26	0.989	0.798
p-Cl	+0.114	8.30	6.54	1.03	0.834
m-COOH	+0.322	3.32	3.46	1.37	0.815
p-NO_2	+0.790	8.30	0.36	0.057	0.046

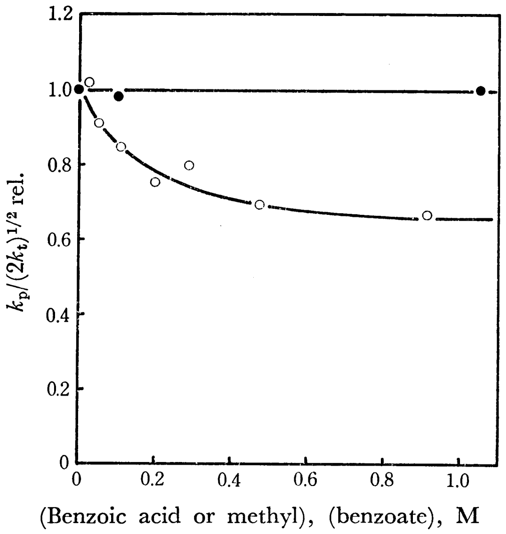

Fig. 10. The rate of oxidation of 1-phenylethanol in the presence of benzoic acid (○) or methyl benzoate (●).
70 °C, $P_{O_2}=760$ mmHg, (AIBN) = 0.040 M.

TABLE 7. AUTOXIDATION OF *N*,*N*-DIMETHYLBENZYLAMINE AND DIBENZYL ETHER IN THE PRESENCE OF WATER IN *t*-BUTYL ALCOHOL
70 °C, $P_{O_2}=760$ mmHg, (AIBN) = 0.040 M

Substrate M	H_2O M	$-dO_2/dt$ $\times 10^6$, M/s	$k_p/(2k_t)^{1/2}$ rel.
N,*N*-Dimethylbenzylamine			
4.51 (in *t*-butyl alcohol)	0.0	73.1	1.00
4.51 (in *t*-butyl alcohol)	3.71	10.3	0.14
Dibenzyl ether			
3.48 (in *t*-butyl alcohol)	0.0	98.3	1.00
3.48 (in *t*-butyl alcohol)	1.68	77.3	0.79

The effect of substituent on the benzene nucleus was studied using substitued benzoic acid in the autoxidation of 1-phenylethannol (Table 6). Except for the nitro group, no significant difference was observed in the retardation effect of benzoic acids.

The rate of oxidation of 1-phenylethanol, plotted against the concentration of benzoic acid or methyl benzoate (Fig. 10) apparently decreases with carboxylic acid and not ester. It can be said that carboxylic acids deactivate the chain carrier of alcohol, *viz.*, hydroperoxyl and α-hydroxyalkylperoxyl radicals, due to a hydrogen bonding, but not alkylperoxyl radicals.

The effect of α-substituent of toluene on the rate of autoxidation in the presence of hydroxyl compounds should be investigated.

Addition of water to *N*,*N*-dimethylbenzylamine and benzyl ether decreased the rate of oxidation by factors of 0.14 and 0.79, respectively (Table 7).

The effect of acetic acid in the autoxidation of ten kinds of α-substituted toluenes is given in Table 8.

The rate of oxidation of *N*,*N*-dimethylbenzylamine, benzyl alcohol, *N*,*N*-diethylbenzylamine, 1-phenylethanol and methyl benzyl ether decreased with the addition of acetic acid. On the other hand, the rate of oxidation of (2-chloroethyl)benzene, ethylbenzene, cumene and diphenylmethane was unaffected.

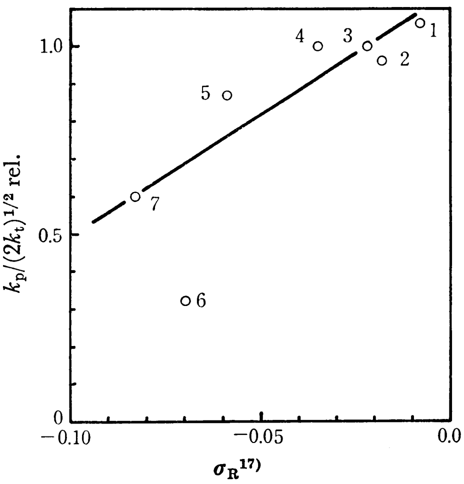

Fig. 11. Plots of $k_p/(2k_t)^{1/2}{}_{\text{rel.}}$ against σ_R.
1: (2-chloroethyl)benzene, 2: diphenylmethane, 3: ethylbenzene, 4: isopropylbenzene, 5: methyl benzyl ether, 6: benzyl alcohol, 7: 1-phenylethanol.

TABLE 8. $k_p/(2k_t)^{1/2}$ rel. OF AUTOXIDATION OF α-SUBSTITUTED TOLUENES IN THE PRESENCE OF ACETIC ACID
70 °C, $P_{O_2}=760$ mmHg, (AIBN) = 0.040 M
(acetic acid) = 0.224 M, solvent: chlorobenzene

Substrate	$\dfrac{\{k_p/(2k_t)^{1/2}\}(\text{AcOH})=0.224\text{ M}}{\{k_p/(2k_t)^{1/2}\}(\text{AcOH})=0.0\text{ M}}$
(2-Chloroethyl)benzene	1.06
Ethylbenzene	1.00
Isopropylbenzene	1.00
Diphenylmethane	0.96
Dibenzyl ether	0.93
Methyl benzyl ether	0.87
1-Phenylethanol	0.60
N,*N*-Diethylbenzylamine	0.60
Benzyl alcohol	0.32
N,*N*-Dimethylbenzylamine	0.19

It can be concluded that the hydroperoxyl radical and alkylperoxyl radicals with α-substituents such as hydroxyl, alkoxyl and amino groups are capable of forming hydrogen bonding with hydroxyl compounds.

We tried to correlate these results in terms of substituent effect. It is suggested that resonance effect takes part and increases the electron density of the peroxyl radical accelerating the formation of hydrogen bonding (Fig. 11).

According to Zaikov and Maizus,[8] the oxidation of methyl ethyl ketone is remarkably inhibited in the presence of water, and according to Imamura *et al.*[9] the rate of oxidation of acetaldehyde is retarded by the addition of various carboxylic acids.

Thus, alkylperoxyl radicals should have α-substituent such as hydroxyl, carbonyl, amino and alkoxyl groups for the formation of hydrogen bonding with water, alcohols and carboxylic acids. These results also indicate that the structure of hydrogen bonding of peroxyl radicals is very complex and it is difficult to present any quantitative explanation. Solvation of peroxyl radical and association of hydroxyl compounds should take part. However, a bridged cyclic structure involving nitrogen or oxygen atoms of α-substituents can be proposed for hydrogen bonding between water and peroxyl radicals.

It seems that the results[2)] showing that the termination rate constant of the hydroxyl radical is markedly affected by the solvent, *viz.*, 10^9 (l/mol·s) in neutral solvent but 10^6 in aqueous solution, and also that the hydroperoxyl radical is inactive in aqueous solution can be explained convincingly on the basis of hydrogen bonding effect.

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