# Oxidation of Lipids. II. Rate of Inhibition of Oxidation by α-Tocopherol and Hindered Phenols Measured by Chemiluminescence

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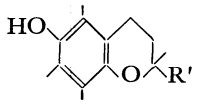
The rate constants for the interactions of peroxyl radicals with α-tocopherol and hindered phenols were determined by chemiluminescence method. The thermal decomposition of di-*t*-butyl diperoxyoxalate in *o*-dichlorobenzene with and without ethylbenzene was found to give chemiluminescence under oxygen. 9,10-Dibromoanthracene was an effective activator. The addition of 1-tetralyl hydroperoxide gave chemiluminescence both in the presence and absence of oxygen, while the addition of *t*-butyl hydroperoxide suppressed the chemiluminescence almost completely even under oxygen. The addition of α-tocopherol and phenols also diminished the chemiluminescence, but after reaching the minimum intensity it again increased as the inhibitors were consumed. The rate constants for the scavenging of 1-phenylethylperoxyl radical by α-tocopherol, 2,4,6-tri-*t*-butylphenol and 2,6-di-*t*-butyl-4-methylphenol were obtained as $1.5\times10^5$, $1.2\times10^4$, and $1.0\times10^4$ $M^{-1}$ $s^{-1}$ (1 M= 1 mol $dm^{-3}$) respectively.

α-Tocopherol **1**, the major component of vitamin E, is known to contribute in biological systems as an inhibitor of lipid peroxidation.[1,2] α-Tocopherol is

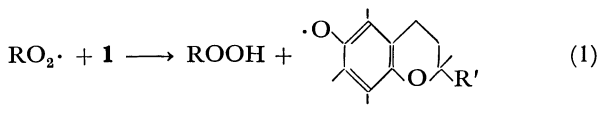


**1**

R′: $(CH_2CH_2CH_2\underset{\displaystyle CH_3}{\underset{|}{C}}H)_3CH_3$

also used as an added antioxidant for foods and oils. It has been reported that α-tocopherol scavenges not only peroxyl radicals but also singlet oxygen[3-7] and superoxide anion radical.[8-12] However, trapping of peroxyl radicals must be the most important function of vitamin E, and to know the reactivity of α-tocopherol toward peroxyl radicals is important in understanding the antioxidizing behavior of vitamin E.

The rate constant for the interaction of α-tocopherol with peroxyl radicals has been determined recently.[13-15] The reported values range from $2\times10^5$ to $5\times10^8$ $M^{-1}$ $s^{-1}$. Kharitonova *et al.*[13] obtained $k_{inh}$ as $2\times10^5$



$RO_2\cdot + 1 \longrightarrow ROOH +$ **2** (1)

$M^{-1}$ $s^{-1}$ at 60 °C from the rate of inhibited oxidation of cumene. Ingold and his coworkers[15] also determined $k_{inh}$ as $2.3\times10^6$ $M^{-1}$ $s^{-1}$ from the rate of inhibited oxidation of styrene. On the other hand, Packer, Slater, and Willson[14] obtained $k_{inh}$ for trichloromethylperoxyl radical as $5\times10^8$ $M^{-1}$ $s^{-1}$ spectrometrically.

We have measured this rate constant $k_{inh}$ for **1** by the chemiluminescence method. Since the first finding by Vassilev and Vichutinskii[16] that the oxidation of organic compounds is accompanied by the emission of weak chemiluminescence, the rate constants for autoxidation have been determined by measuring the chemiluminesence intensity.[17,18] This chemiluminescence method has been also applied recently to estimate the extent of oxidation of fats, oils and biological systems.[19-26]

## Experimental

*Materials.* Natural *d*-α-tocopherol was kindly supplied from Eisai Co. Ltd. 2,4,6-Tri-*t*-butylphenol (TBP) and 2,6-di-*t*-butyl-4-methylphenol (BMP) were recrystallized from methanol. 2,6-Di-*t*-butylphenol was used as received. Di-*t*-butyl diperoxyoxalate (DBPO) was synthesized from *t*-butyl hydroperoxide and oxalyl chloride by the method of Bartlett *et al.*[27] Commercial 9,10-dibromoanthracene was recrystallized from methanol. 1-Tetralyl hydroperoxide (TOOH) was prepared by the air oxidation of tetralin in the presence of azobisisobutyronitrile, followed by recrystallization from heptane. Commercial *t*-butyl hydroperoxide was distilled under reduced pressure prior to use 42 °C/24 Torr (1 Torr≈133.322 Pa). Ethylbenzene was washed with acid, water, alkaline and water, dried and distilled. *o*-Dichlorobenzene was used as received.

*Apparatus and Procedure.* The emission intensity of chemiluminescence was measured by the single photon counting apparatus, type OX-7, manufactured by Tohoku Elec-

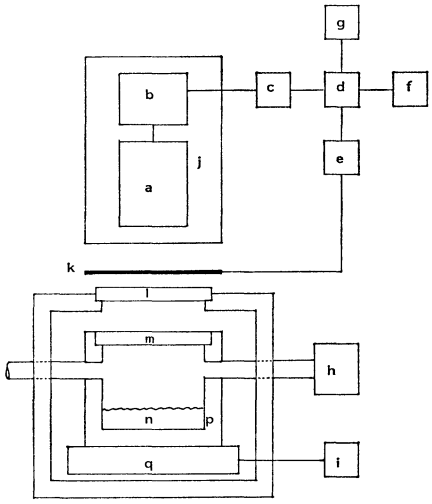



Fig. 1. Schematic diagram of the single photon counting apparatus, OX-7.
a: Photomultiplier, b: amplifier, c: gain thresh, d: counter, e: controller, f: printer, g: recorder, h: pump, i: temperature controller, j: cooler, k: shutter, l: filter, m: quartz window, n: sample, p: cell, q: heater.

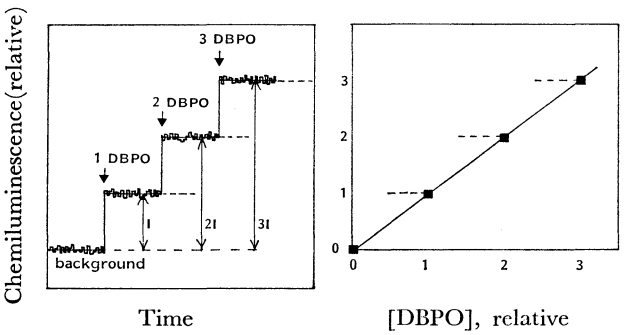



Fig. 2. Chemiluminescence intensity as a function of DBPO concentration.

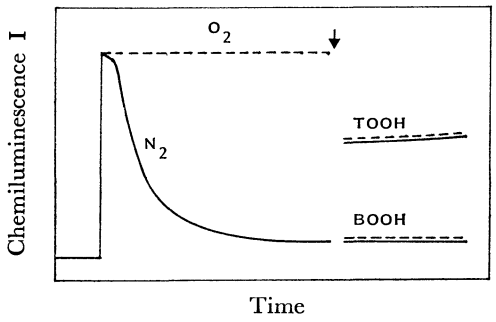



Fig. 3. Effect of atmosphere and addition of tetralyl (TOOH) and *t*-butyl (BOOH) hydroperoxides on the chemiluminescence, [DBPO]=0.10 M in *o*-dichlorobenzene at 25 °C.

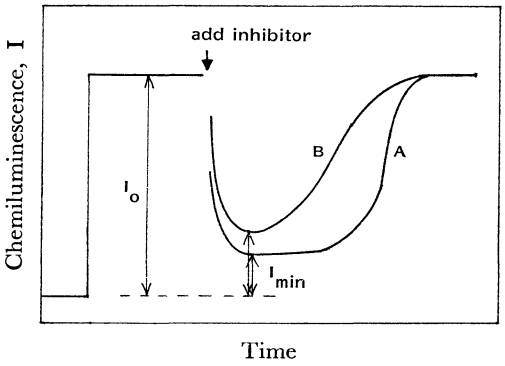



Fig. 4. Effect of addition of α-tocopherol (A) and TBP (B) on the chemiluminescence, [DBPO]=0.10 M in *o*-dichlorobenzene-ethylbenzene, 25 °C.

tronic Industries. The schematic diagram of the apparatus is shown in Fig. 1. The cell temperature was kept at 25 °C and the photomultiplier, Hamamatsu TV Co. type R878, was cooled to −20 °C.

In general, 2 or 3 ml of appropriate solution was taken into the stainless steel cell and the chemiluminescence intensity was measured every 10 second and recorded. Neat *o*-dichlorobenzene or a mixture of *o*-dichlorobenzene and ethylbenzene (1/1 by v/v) was usually used as solvent. No filter was used.

## Results

A strong chemiluminescence was observed when DBPO was thermally decomposed in *o*-dichlorobenzene or *o*-dichlorobenzene–ethylbenzene at 25 °C under air. As shown in Fig. 2, the chemiluminescence intensity

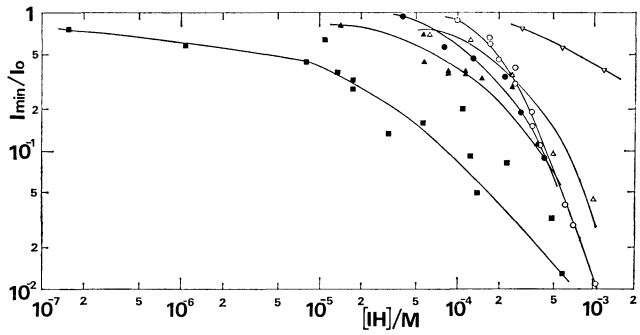



Fig. 5. Plot of $I_{min}/I_o$ as a function of inhibitor concentration in the thermal decomposition of DBPO at 25 °C in *o*-dichlorobenzene (open) and *o*-dichlorobenzene–ethylbenzene (solid).
■: α-Tocopherol, △,▲: TBP, ○,●: BMP, ▽: 2,6-di-*t*-butylphenol.

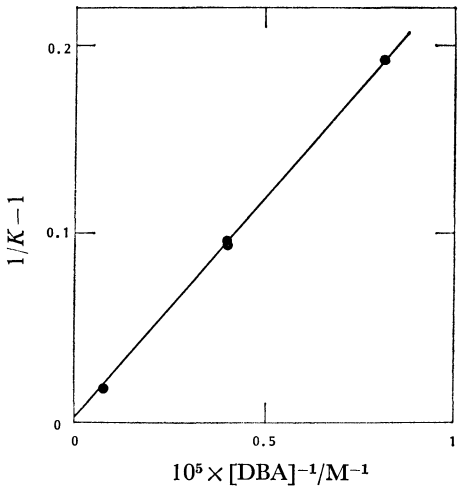



Fig. 6. Plot of $1/K-1$ against 1/[DBA] in the thermal decomposition of DBPO at 25 °C in *o*-dochlorobenzene.

*I* was proportional to the concentration of DBPO, or more strictly, to the absolute amount of DBPO. The concentration of DBPO was chosen so that the chemiluminescence intensity was several times larger than the background. Under nitrogen, however, little chemiluminescence was observed. Furthermore, as shown in Fig. 3, the addition of tetralyl hydroperoxide to the above solution gave chemiluminescence and its intensity was the same irrespective of the presence or absence of oxygen. On the other hand, the addition of *t*-butyl hydroperoxide did not give appreciable chemiluminescence even in the presence of oxygen.

Figure 4 shows that the addition of phenolic inhibitors to the DBPO solution diminished the chemiluminescence sharply and that, after reaching the minimum intensity $I_{min}$, it increased again as the inhibitors were consumed. Figure 5 shows the plot of $I_{min}/I_o$ as a function of inhibitor concentration. Similar phenomenon was observed when cobalt(II) acetylacetonate was added to the DBPO solution as observed by Gal and his colleagues.[18]

The addition of 9,10-dibromoanthracene (DBA) increased the chemiluminescence intensity markedly.

As shown in Fig. 6, the plot of $1/K-1$ as a function of 1/[DBA] gave a straight line, where $K=I_A/I_0$, and $I_A$ and $I_0$ are the chemiluminescence intensity in the presence and absence of 9,10-dibromoanthracene respectively.

## Discussion

Upon thermal decomposition, DBPO gives two molecules each of *t*-butoxyl radical and carbon dioxide. The rate constant for unimolecular decomposition of DBPO is $k_d=1.6\times10^{-5}$ s$^{-1}$ at 25 °C and its half life is $\tau_{1/2}=12$ h.[27] Therefore, it may be safely considered that DBPO gives *t*-butoxyl radical at constant rate under the present reaction conditions.

$$\mathrm{DBPO} \xrightarrow{k_d} 2(\mathrm{CH_3})_3\mathrm{CO}\cdot + 2\mathrm{CO_2} \quad (1)$$

$$(\mathrm{CH_3})_3\mathrm{CO}\cdot \longrightarrow (\mathrm{CH_3})_2\mathrm{CO} + \mathrm{CH_3}\cdot \quad (2)$$

$$\mathrm{CH_3}\cdot + \mathrm{O_2} \longrightarrow \mathrm{CH_3O_2}\cdot \quad (3)$$

$$2\mathrm{CH_3O_2}\cdot \xrightarrow{k_t} \mathrm{CH_3OH} + {}^3\mathrm{CH_2O}^* + {}^1\mathrm{O_2} \quad (4)$$

$${}^3\mathrm{CH_2O}^* \longrightarrow {}^1\mathrm{CH_2O} + h\nu \quad (5)$$

$${}^1\mathrm{O_2} \longrightarrow {}^3\mathrm{O_2} + h\nu \quad (6)$$

Chemiluminescence arises at the expense of the energy released by exothermic reaction and in the liquid phase oxidation only the chain terminating recombination of peroxyl radicals are sufficiently exothermic for ensuring luminescence in the visible region.[17] About 100 kcal/mol of energy is liberated in the recombination of peroxyl radicals and it is distributed among the products. It has been known that the bimolecular interactions of primary and secondary peroxyl radicals yield triplet carbonyl compound and singlet oxygen[17,28-31] and that these two species emit the chemiluminescence.

Thus, the chemiluminescence observed in the decomposition of DBPO must arise from triplet formaldehyde and/or singlet oxygen formed in Reaction 4. That there was little chemiluminescence in the absence of oxygen suggests that acetone formed in Reaction 2 does not give chemiluminescence.

The steady state treatment for Reactions 1 to 6 gives

$$[\mathrm{CH_3O_2}\cdot] = (k_d[\mathrm{DBPO}]/k_t)^{1/2}. \quad (7)$$

Therefore, the chemiluminescence intensity $I$ is directly proportional to the concentration of DBPO as observed experimentally (Fig. 2).

$$I = a[\mathrm{CH_3O_2}\cdot]^2 = ak_d[\mathrm{DBPO}]/k_t \quad (8)$$

It has been reported that species such as oxygen[31,32] and di-*t*-butyl peroxide[33,34] quench the chemiluminescence. Especially, the quenching by oxygen may be important since oxygen molecule is formed in the bimolecular termination reactions of peroxyl radicals in the close neighborhood of the excited product and may cause its deactivation. The effect of these adventitious quenchers must be small, however, when the ratio of intensity $I/I_0$ is considered rather than the absolute intensity. The luminescence yield is independent of the radical concentration.[35] Phenols are known as photoluminescence quencher, but it was established that the chemical reaction between phenols and peroxyl radicals is of major importance and the physical effect, if any, is negligibly small.[17]

The effect of addition of tetralyl and *t*-butyl hydroperoxides supports the above conclusion. *t*-Butoxyl radical formed from DBPO abstracts readily the hydroperoxidic hydrogens to yield peroxyl radicals. The bimolecular interactions of tetralylperoxyl radicals are terminating and give tetralol, tetralone, and oxygen.

$$(\mathrm{CH_3})_3\mathrm{CO}\cdot + \mathrm{ROOH} \longrightarrow (\mathrm{CH_3})_3\mathrm{COH} + \mathrm{RO_2}\cdot \quad (9)$$

The triplet tetralone and/or singlet oxygen give chemiluminescence irrespective of the presence or absence of oxygen. On the other hand, the bimolecular interactions of *t*-butylperoxyl radicals proceed differently.[36] The *t*-butoxyl radical formed in Reaction 11 again reacts with added *t*-butyl hydroperoxide. Therefore, the addition of *t*-butyl hydroperoxie suppresses the formation of triplet carbonyl and singlet oxygen, and hence the chemiluminescence as well.

$$2(\mathrm{CH_3})_3\mathrm{CO_2}\cdot \longrightarrow [(\mathrm{CH_3})_3\mathrm{COOOOC}(\mathrm{CH_3})_3]$$

$$\longrightarrow (\mathrm{CH_3})_3\mathrm{COOC}(\mathrm{CH_3})_3 + \mathrm{O_2} \quad (10)$$

$$\longrightarrow 2(\mathrm{CH_3})_3\mathrm{CO}\cdot + \mathrm{O_2} \quad (11)$$

The activation of chemiluminescence by 9,10-dibromoanthracene (DBA) in DBPO–ethylbenzene system may be explained by the following scheme, where A represents DBA. *t*-Butoxyl radical attacks ethylbenzene to give 1-phenylethyl radical, which reacts with oxygen and then gives 1-phenylethanol, acetophenone, and oxygen.

$$\mathrm{DBPO} \longrightarrow 2(\mathrm{CH_3})_3\mathrm{CO}\cdot + 2\mathrm{CO} \quad (1)$$

$$(\mathrm{CH_3})_3\mathrm{CO}\cdot + \mathrm{PhCH_2CH_3} \longrightarrow (\mathrm{CH_3})_3\mathrm{COH} + \mathrm{PhC}\dot{\mathrm{H}}\mathrm{CH_3} \quad (12)$$

$$\mathrm{PhC}\dot{\mathrm{H}}\mathrm{CH_3} + \mathrm{O_2} \longrightarrow \mathrm{PhCH(OO}\cdot)\mathrm{CH_3} \quad (13)$$

$$2\mathrm{PhCH(OO}\cdot)\mathrm{CH_3} \xrightarrow{k_t'} \mathrm{PhCH(OH)CH_3} + \mathrm{PhC(=O)CH_3}^* + \mathrm{O_2} \quad (14)$$

$$\mathrm{PhC(=O)CH_3}^* \xrightarrow{f_P} \mathrm{PhC(=O)CH_3} + h\nu \quad (15)$$

$$\mathrm{PhC(=O)CH_3}^* + \mathrm{A} \longrightarrow \mathrm{PhC(=O)CH_3} + \mathrm{A}^* \quad (16)$$

$$\mathrm{A}^* \xrightarrow{f_A} \mathrm{A} + h\nu \quad (17)$$

Under these circumstances, Eq. 18 holds,[17]

$$\frac{1}{K-1} = \frac{\eta_P}{\eta_A-\eta_P} + \frac{1}{\eta_A-\eta_P}\cdot\frac{f_P}{k_{PA}}\cdot\frac{1}{[\mathrm{DBA}]} \quad (18)$$

where $\eta_P$, $\eta_A$, $f_P$, and $k_{PA}$ represent, respectively, quantum yields for chemiluminescence of activated acetophenone and activator, probability of radiative transitions and the rate constant for energy transfer from triplet carbonyl to activator. From the intercept of Fig. 6, $\eta_P/(\eta_A-\eta_P)=1.09\times10^{-3}$, and hence, $\eta_A/\eta_P\approx10^3$, suggesting that 9,10-dibromoanthracene has much higher quantum yield than excited acetophenone.

In the presence of phenolic inhibitors IH, the reaction proceeds by the steps 1, 12, 13, 14, 15, 19, and 20, where $\mathrm{RO_2}\cdot$ denotes the 1-phenylethylperoxyl radical.

$$\mathrm{RO_2}\cdot + \mathrm{IH} \xrightarrow{k_{inh}} \mathrm{ROOH} + \mathrm{I}\cdot \quad (19)$$

$$\mathrm{RO_2}\cdot + \mathrm{I}\cdot \xrightarrow{k_0} \mathrm{ROOI} \quad (20)$$

Table 1. Rate constants for the trapping of peroxyl radicals by inhibitors measured by chemiluminescence method, 25 °C

| Inhibitor | $k_{inh}/M^{-1}\,s^{-1}$ | | |
|---|---|---|---|
| | DBPO-IH | DBPO-IH-$PhC_2H_5$ | Literature values |
| BMP | $3.6\times10^4$ | $1.0\times10^4$ | $7.95\times10^3$,[a] $1.0\times10^4$,[b] $1.58\times10^4$,[c] $2.5\times10^4$,[d] |
| TBP | $3.1\times10^4$ | $1.2\times10^4$ | $7.30\times10^3$,[a] $6.8\times10^3$,[b] $1.3\times10^4$ [d] |
| 2,6-Di-*t*-butylphenol | $6.0\times10^3$ | | $2.25\times10^3$,[a] $9.5\times10^3$ [d] |
| α-Tocopherol | | $1.5\times10^5$ | $2.0\times10^5$,[e] $2.3\times10^6$,[f] $5\times10^8$ [g] |

a) From the rate of inhibited oxidation of styrene at 65 °C, Ref. 39. b) From the ESR method and extraporated to 25 °C, Ref. 40. c) From the rate of inhibited oxidation of styrene at 50 °C, Ref. 41. d) At 60 °C, Ref. 42. e) From the inhibited rate of oxidation of cumene at 60 °C, Ref. 13. f) From the rate of inhibited rate of oxidation of styrene at 30 °C, Ref. 15. g) From pulse radiolysis and spectrometrical determination for trichloromethylperoxyl radical, Ref. 14.

In the absence of inhibitor,

$$-d[RO_2\cdot]/dt = R_i - 2k_t'[RO_2\cdot]_0^2 \quad (21)$$

and hence,

$$[RO_2\cdot]_0 = (R_i/2k_t')^{1/2}, \quad (22)$$

where $R_i=2k_d[DBPO]$ is the rate of initiation and $[RO_2\cdot]_0$ is the steady state concentration of 1-phenylethylperoxyl radical in the absence of the inhibitor. When the inhibitor is added, the concentration of the inhibitor and so that of the peroxyl radical also changes with time, and the steady state treatment can not be applied. The concentration of the peroxyl radical is given by

$$d[RO_2\cdot]/dt = R_i - 2k_t'[RO_2\cdot]^2 - k_{inh}[RO_2\cdot][IH] - k_0[RO_2\cdot][I\cdot]. \quad (23)$$

Since $k_0 \gg k_{inh}$,

$$d[I\cdot]/dt = k_{inh}[RO_2\cdot][IH] - k_0[RO_2\cdot][I\cdot] = 0. \quad (24)$$

Therefore,

$$d[RO_2\cdot]/dt = R_i - 2k_t'[RO_2\cdot]^2 - 2k_{inh}[RO_2\cdot][IH]. \quad (25)$$

At the time when the chemiluminescence intensity is the minimum, $I_{min}$,

$$d[RO_2\cdot]/dt = R_i - 2k_t'[RO_2]_{min}^2 - 2k_{inh}[RO_2\cdot]_{min}[IH] = 0. \quad (26)$$

Then

$$\frac{I_{min}}{I_0} = \frac{[RO_2\cdot]_{min}^2}{[RO_2\cdot]_0^2} = \frac{R_i-2k_{inh}[RO_2\cdot]_{min}[IH]}{2k_t'}\frac{1}{(R_i/2k_t')} = 1 - \frac{2k_{inh}[IH]}{(2k_t'R_i)^{1/2}}\left(\frac{I_{min}}{I_o}\right)^{1/2}, \quad (27)$$

and

$$\frac{1}{Q} - Q = \frac{2k_{inh}}{(2k_t'R_i)^{1/2}}[IH], \quad (28)$$

where $Q=(I_{min}/I_o)^{1/2}$.[37] Similarly, in the system of DBPO and inhibitor in *o*-dichlorobenzene without ethylbenzene,

$$\frac{1}{Q} - Q = \frac{2k_{inh}}{(2k_tR_i)^{1/2}}[IH]. \quad (29)$$

Figures 7 and 8 show the plot of $Q^{-1}-Q$ as a function of inhibitor concentration for the systems DBPO–inhibitor and DBPO–inhibitor–ethylbenzene respectively. Some scatters are observed, but from the slope and the rate constants $k_t=10^8\ M^{-1}\,s^{-1}$ and $k_t'=2\times10^7\ M^{-1}\,s^{-1}$ from the literature,[36] the rate constants for the trapping of peroxyl radicals by an inhibitor are calculated as summarized in Table 1.

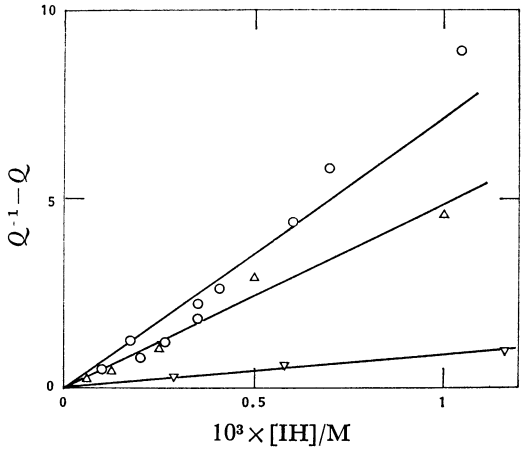



Fig. 7. Plot of $Q^{-1}-Q$ as a function of inhibitor concentration in *o*-dichlorobenzene.
△: TBP, ○: BMP, ▽: 2,6-di-*t*-butylphenol.

The rate constants measured in this study for hindered phenols are in reasonable agreement with literature values. The higher $k_{inh}$ in the absence of ethylbenzene must be ascribed to the contribution of faster interaction of *t*-butoxyl radical with phenols. The high $k_{inh}$, $5\times10^8\ M^{-1}\,s^{-1}$, for α-tocopherol toward trichloromethylperoxyl radical[14] must be due to a higher reactivity of trichloromethylperoxyl radical than normal alkylperoxyl radicals.[43] Those for α-tocopherol toward arylalkylperoxyl radicals are in fair agreement ranging from $1.5\times10^5$ to $2\times10^6\ M^{-1}\,s^{-1}$. The reason of this discrepancy is not clear at present. It may be in part due to the different attacking peroxyl radicals: The polymeric peroxyl radical in the oxidation of styrene may have higher reactivity toward α-tocopherol than simple alkylperoxyl radicals as it has toward hydrocarbons.[36,44]

In Figs. 7 and 8, $Q^{-1}-Q$ was plotted against the initial concentration of the inhibitor assuming the loss of inhibitor by the time the chemiluminescence intensity reached minimum was negligibly small. Ac-

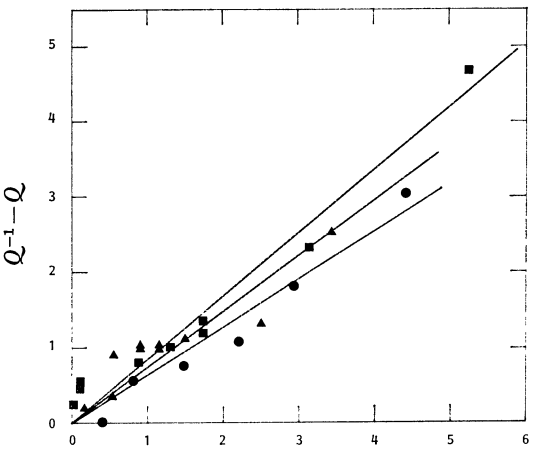



Fig. 8. Plot of $Q^{-1}-Q$ as a function of inhibitor concentration in *o*-dichlorobenzene–ethylbenzene.
■: α-Tocopherol, ▲: TBP, ●: BMP.

cordingly, the $k_{inh}$ we obtained for α-tocopherol may be lower slightly than it should be.

Figures 5 and 8 show that α-tocopherol has higher reactivity than TBP and BMP. Ingold and collaborators[15] argue that higher reactivity of α-tocopherol than simple hindered phenols toward peroxyl radicals arises from the fused chroman ring system that maintains a near-optimal orientation of the ethereal oxygen *p*-type lone pair with respect to the aromatic ring.

As reported previously,[45] the 6-chromanyloxyl radical **2** formed from α-tocopherol seems to have different reactivity toward peroxyl radical from the hindered phenoxyl radicals. We are currently extending our study on the antioxidizing behavior of tocopherols.

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