

Intramolecular Hydrogen Bonding of Oxidation Intermediates of Bisphenol Derivatives in Relation to Photothermographic Activity in Silver Salt Photothermographic Systems

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Abstract

The effects of intramolecular hydrogen bonding on the electron-transfer properties of a series of bisphenol derivatives, as compared with those of monophenol derivatives in which a hydroxy group is replaced with a methoxy group, have been investigated in relation to their photothermographic properties. The oxidation of bisphenol derivatives with one-electron oxidants occurs to give the radical cation, followed by deprotonation, to produce the phenoxyl radical. Both the radical cations and phenoxyl radicals have been detected by laser flash photolysis measurements. Rates of hydrogen-transfer reactions from a series of bisphenol derivatives to cumylperoxyl radicals have been determined by monitoring the decay of the ESR signal caused by the cumylperoxyl radical produced by the photoirradiation of an oxygen-saturated propionitrile solution of cumene and di-*t*-butylperoxide in the presence of bisphenol derivatives. Intramolecular hydrogen bonding plays an important role in determining overall oxidation reactivity in the two-electron oxidation process by decreasing the one-electron oxidation potentials and also through facilitating the deprotonation step from the bisphenol radical cation in producing a phenoxyl radical.

Introduction

Photothermographic materials have been widely used in dry processing imaging systems to protect the environment and to meet network time constraints. To optimize the photothermographic properties of such systems, it is essential to control the reactivity of the developer reagent, which is a main component of such systems. Bisphenol derivatives have recently merited particular interest as

efficient developers in photothermographic systems,^{1,2} and they are also known to perform well as antioxidants and stabilizers.^{3,4} Intramolecular hydrogen bonding is recognized as playing an important role in the reactivity of the phenolic function.⁴ The hydrogen bonding in bisphenol derivatives can stabilize not only the phenol form but also the phenoxyl radical form.⁵ However, to date there has been no systematic study of the effects of intramolecular hydrogen bonding on the electron-transfer properties of bisphenol derivatives.

This work therefore focuses on the effects of the intramolecular hydrogen bonding of oxidation intermediates on the electron-transfer properties of bisphenol derivatives in relation to their photothermographic activity in silver salt photothermographic systems. We examine the electron-transfer properties both of four bisphenol derivatives with different substituents (methyl, ethyl, *n*-propyl, and *t*-butyl groups) neighboring the hydroxy groups and of four monophenol derivatives in which a hydroxy group is replaced with a methoxy group (Fig. 1).

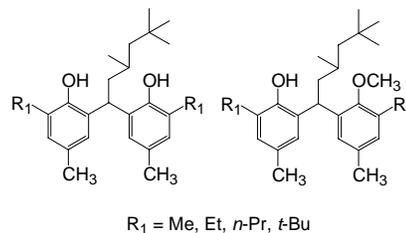
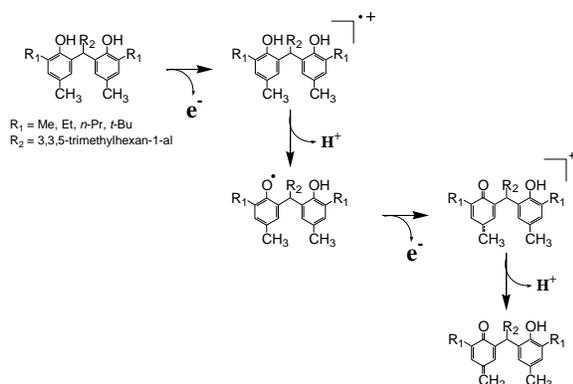


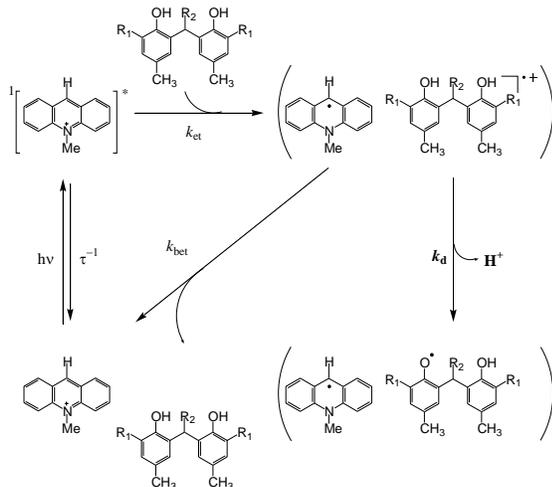
Figure 1. Chemical structures of bisphenol derivatives and monophenol derivatives.

A proposed mechanism for the two-electron oxidation of this compound is shown in Scheme 1

Scheme 1



Scheme 2



Experimental

Laser flash photolysis was used to measure the transient absorption spectra of oxidation intermediates of the bisphenol derivatives. A deaerated MeCN solution containing a bisphenol derivative and 10-methylacridinium cation (AcrH^+) was excited by a Nd:YAG laser (Quanta-Ray, GCR-130, 6 ns fwhm) at 355 nm with a power of 30 mJ at 298 K.

The kinetic measurements of hydrogen-transfer reactions from a series of bisphenol derivatives to cumylperoxyl radicals were obtained by monitoring the ESR signal decay caused by cumylperoxyl radicals produced by the photoirradiation of an oxygen-saturated propionitrile solution of cumene and di-*t*-butylperoxide in the presence of bisphenol derivatives with a 1000 W Mercury lamp at 193 K.

Density functional theory (DFT) calculations were performed at the Becke3LYP/6-31G level with a Gaussian 98 program on a Compaq DS20E computer.

Photographic properties were evaluated following standard procedure: film samples comprising organic silver salts, silver halide grains, and other reagents were prepared according to the literature⁶, and the samples were uniformly exposed with an 810 nm laser diode and developed at a typical thermal development temperature of 399 K.

Results and Discussion

Detection of the Oxidation Intermediates of a Series of Bisphenol Derivatives and Monophenol Derivatives

The oxidation intermediates of a series of bisphenol derivatives, i.e., the radical cation species in Scheme 1, were produced by photoinduced electron transfer from bisphenol derivatives to AcrH^+ (*vide infra*). The laser excitation (355 nm from a Nd:YAG laser) of AcrH^+ in deaerated MeCN containing a bisphenol derivative gives the transient absorption of the radical cation of a bisphenol derivative (Fig. 2). Subsequently, an increase in absorbance due to the phenoxyl radical of the bisphenol derivative is accompanied by a concomitant decrease in absorbance due to the radical cation.

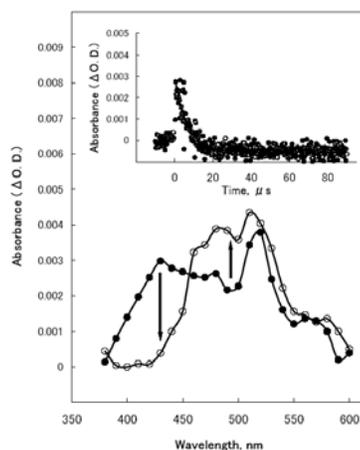


Figure 2. Transient absorption spectra measured at 2 ms (●) and 40 ms (○) after laser excitation (355 nm, 30mJ) of AcrH^+ ($2.8 \times 10^{-5} \text{ M}$) in deaerated MeCN containing a bisphenol derivative ($R_1 = \text{Me}$, 6.0 mM) at 298K. Inset shows time dependence of absorbance at 420 nm (●).

Absorption due to the radical cation of the bisphenol derivatives decays obeying first-order kinetics (inset, Fig. 2). The rate constants for deprotonation of the radical cations of bisphenol and monophenol derivatives are virtually the same. Recently, in contrasting bisphenol and monophenol derivatives, we demonstrated a clear correlation between a decrease in the logarithmic values of the observed second-order rate constants of the two-electron oxidation of those derivatives ($\log k_{\text{obs}}$) and an increase in their one-electron oxidation potentials (E^0_{ox}) (Fig. 3).¹

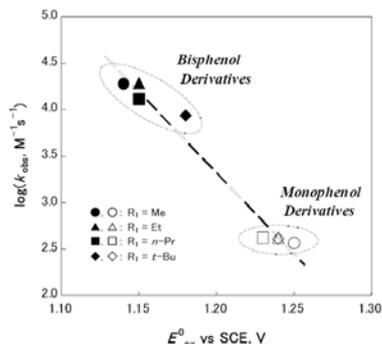


Figure 3. Plots of $\log k_{\text{obs}}$ versus E^0_{ox} ; the correlation between logarithm of the observed second-order rate constants for the two-electron oxidation of the bisphenol and monophenol derivatives and the one-electron oxidation potential in MeCN.

If the deprotonation of the radical cations of the bisphenol and monophenol derivatives (k_d) is the rate-determining step for the two-electron oxidation process, then the overall rate constant of two-electron oxidation (k_{obs}) can be expressed as

$$k_{\text{obs}} = 2kdK_{\text{et}} \quad (1)$$

where K_{et} is the equilibrium constant of the uphill electron transfer. Since the free energy change of electron transfer ($\Delta G_{\text{et}}^0 = -2.3RT \log K_{\text{et}}$) is obtained from the E^0_{ox} and E^0_{red} values (Eq. 2), as in

$$\Delta G_{\text{et}}^0 = F(E^0_{\text{ox}} - E^0_{\text{red}}) \quad (2)$$

where F is the Faraday constant, $\log k_{\text{obs}}$ is given as a function of E^0_{ox} :

$$\log k_{\text{obs}} = \log 2kd - (F/2.3RT)(E^0_{\text{ox}} - E^0_{\text{red}}) \quad (3)$$

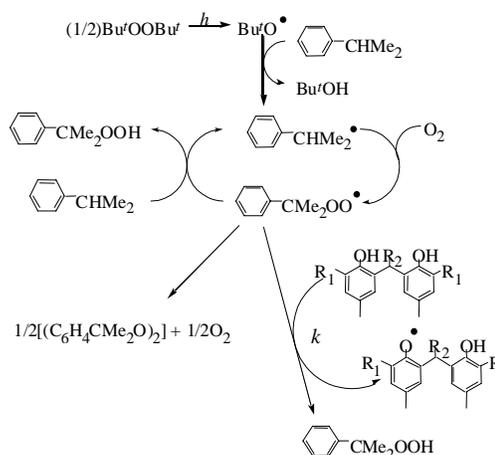
Thus, the plot of $\log k_{\text{obs}}$ versus E^0_{ox} would give a slope of $-(F/2.3RT)$, which corresponds to -17 at 298 K, provided that k_d remains constant.⁷ This plotted slope of -17 agrees well with the observed slope of -18 seen in Fig. 3. Moreover, the k_d values drawn from the k_{obs} values and the E^0_{ox} values using Eq. 3 agree with those determined independently from the first-order decay of the radical cations. This indicates that the difference in the electron transfer reactivity between the bisphenol and monophenol derivatives results mainly from the difference in their E^0_{ox} values. The lower E^0_{ox} values of the bisphenol derivatives can be ascribed to the hydrogen bonding stabilization in the radical cations. Thus, intramolecular hydrogen bonding in the radical cation presents itself as a main factor in controlling overall oxidation reactivity in the two-electron oxidation process by decreasing the one-electron oxidation potentials.

Hydrogen-Transfer Properties of a Series of Bisphenol Derivatives and Monophenol Derivatives

The rates of hydrogen-transfer reactions from a series of bisphenol derivatives in producing phenoxy radical species were measured using ESR. The cumylperoxyl radical is formed via a radical chain process with photoirradiation

(Scheme 3). The cumylperoxyl radical can abstract a hydrogen atom from cumene in the propagation step to yield cumene hydroperoxide, accompanied by regeneration of the cumyl radical. In the termination step, cumylperoxyl radicals decay via a bimolecular reaction to yield the corresponding peroxide and oxygen.⁸ When the light is cut off, the ESR signal intensity of the cumylperoxyl radical (Fig. 4a) decays obeying second-order kinetics due to the bimolecular reaction (Fig. 4b). In the presence of a bisphenol derivative, the decay rate of the cumylperoxyl radical after light cutoff is much greater than in the absence of a bisphenol derivative. The decay rate in the presence of a bisphenol derivative obeys pseudo-first-order kinetics rather than second-order kinetics (inset, Fig. 4b). Thus, the decay of the ESR signal due to the cumylperoxyl radical in the presence of a bisphenol derivative is ascribed to the hydrogen atom transfer from the bisphenol derivative to the cumylperoxyl radical (Scheme 3).

Scheme 3



The pseudo-first-order rate constant (k) exhibits first-order dependence with respect to concentration of bisphenol or monophenol derivatives (Fig. 5). The slope gives the second-order rate constant (k_{obs}) for the hydrogen-transfer process of bisphenol derivatives. It was found that the second-order rate constant for hydrogen-transfer of *t*-butyl substituted bisphenol derivative was about 2 times as great as those of the methyl, ethyl, and *n*-propyl substituted compounds. This indicates that the *t*-butyl substituent neighboring the hydroxyl groups has significant effects on intramolecular hydrogen bonding stabilization in both the radical cation and the phenoxy radical to facilitate the hydrogen-transfer step.

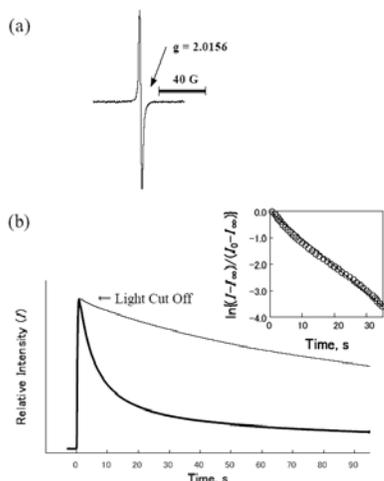


Figure 4. (a) ESR signal observed in photolysis of an O_2 -saturated EtCN solution of di-*t*-butylperoxide (1.0 M) and cumene (1.0 M) with a 1000 W mercury lamp at 193 K. (b) The decay profiles of the ESR intensity upon light cutoff without (fine line) and with (thick line) a bisphenol derivative ($R_1 = t\text{-Bu}$, 1.0×10^{-4} M) in O_2 -saturated EtCN at 193 K. Inset shows pseudo-first-order plot.

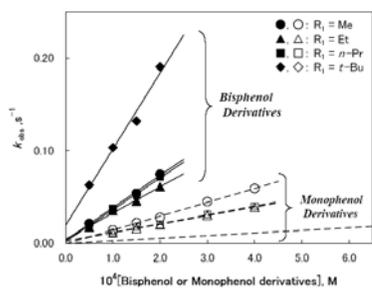


Figure 5. Plots of pseudo-first order rate constant (k) versus [bisphenol or monophenol derivatives] in the hydrogen transfer of bisphenol and monophenol derivatives in EtCN containing di-*t*-butylperoxide (1.0 M) and cumene (1.0 M) at 193 K.

Photographic Properties (Sensitometry) of a Series of Bisphenol Derivatives and Monophenol Derivatives

Fig. 6 shows the characteristic curves of the film samples to which various bisphenol derivatives and monophenol derivatives were added. The developing rate of substituted bisphenol derivatives decreases slightly according to the substituents in this order: methyl, ethyl, and *n*-propyl. In contrast, the developing rate of the bisphenol derivative with the *t*-butyl group was the highest among the examined bisphenol derivatives. The developing rates of the monophenol derivatives were significantly low as compared with those of the bisphenol derivatives, regardless of the substituent neighboring the hydroxy group.

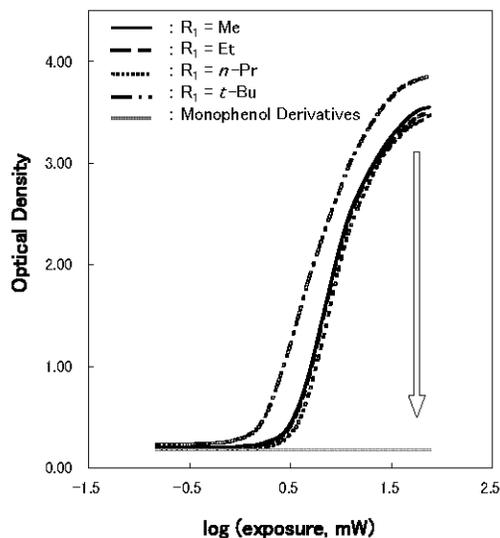


Figure 6. Effects of substituents of bisphenol derivatives and intramolecular hydrogen bonding on photothermographic characteristic curves obtained in the developing process at 399 K.

The high oxidation reactivity of a *t*-butyl-substituted bisphenol derivative can be ascribed to the effects of intramolecular hydrogen bonding stabilization in the radical cation, as well as to the phenoxyl radical. Thus, the presence of intramolecular hydrogen bonding is a main factor in controlling the reactivity of bisphenol derivatives during the oxidation process in silver salt photothermographic systems.

Conclusion

The electron-transfer properties of a series of bisphenol derivatives have been systematically examined. The decay time profiles both of the radical cations of bisphenol and monophenol derivatives and of the hydrogen-transfer of bisphenol and monophenol derivatives were measured. This revealed the effects of intramolecular hydrogen bonding on the electron-transfer properties, and, in turn, on the developing properties of bisphenol derivatives in silver salt photothermographic systems.

Two central conclusions stand:

1. The intramolecular hydrogen bonding of radical cations is a main factor in controlling the oxidation of bisphenol derivatives, and
2. The high oxidation reactivity of a *t*-butyl-substituted bisphenol derivative can be ascribed to the effects of intramolecular hydrogen bonding stabilization in the radical cation and also in the phenoxyl radical.

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Biography

Hiromi Akahori received her M.S. degree in Applied Chemistry from Keio University, Kanagawa, Japan, in 1994. Since then, she has been engaged in the research and development of medical film at the R&D Center of Konica Minolta Medical & Graphic, Inc. in Hino, Tokyo, Japan. Ms. Akahori a member of the SPSTJ.