Fine Control of Electron-Transfer Properties of Bisphenol Developing Agents for Silver Salt Photothermographic Materials by Hydrogen Bonding Substituents

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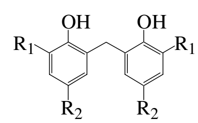
Abstract

The effects of hydrogen bonding substituents at the para position of aromatic rings of bisphenol derivatives on the electron-transfer properties of a series of bisphenol derivatives have been investigated in relation to their photothermographic properties. Rates of bimolecular electron transfer from a series of bisphenol derivatives to $^3C_{60}{}^*$ have been determined by laser flash photolysis. Intramolecular hydrogen bonding formed between hydrogen bonding substituents at the para position of aromatic rings plays an important role in the fine control of the oxidation properties of bisphenol derivatives.

Introduction

Social concerns over the protection of the environment have increasingly grown. At the same time, the digitization and networking of medical imaging information have made remarkable advances. Such social concerns together with the technological advances have led to the design and development of dry processing imaging systems using photothermographic materials. In recent years, a demand for excellent developing ability of the photothermographic materials of such systems has particularly mounted to meet network time constraints. To realize excellent developing ability without deterioration of fog, 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] In addition, it has recently been reported that bisphenol derivatives with *tert*-alkyl groups such as *tert*-butyl groups at the ortho position of aromatic rings exhibit high developing activity[1,6] which can be ascribed to the effects of intramolecular hydrogen bonding stabilization in the radical cations and also in the phenoxyl radicals.[1] However, the effects of intramolecular hydrogen bonding on the electron-transfer properties of bisphenol derivatives have yet to be examined.

We therefore decided to investigate the effects of the substituents, which can form intramolecular hydrogen bonding, on the electron-transfer properties of bisphenol derivatives in relation to their photothermographic properties such as developing ability and raw stock stability in silver salt photothermographic systems. Bisphenol derivatives with alcoholic OH groups at the *para* position of the phenol rings (R_2) used in this study are shown in Figure 1.



no.	R_1	R_2
1	t-C_4H_9	CH_3
2	t- C_4H_9	n-C_3H_7
3	t- C_4H_9	n-C_3H_6OH
4	t- C_5H_{11}	n-C_3H_6OH

***Figure 1**. Chemical structures of bisphenol derivatives.*

Experimental

Laser flash photolysis was used for the kinetic measurements of electron transfer from a series of bisphenol derivatives to $^3C_{60}{}^*$. A deaerated benzonitrile (PhCN) solution of buckminsterfullerene (C_{60}) was excited by a Nd:YAG laser (Quanta-Ray, GCR-130, 6 ns fwhm) at 355 nm with a power of 30 mJ. The decay of the triplet excited state ($^3C_{60}{}^*$) was observed at 740 nm, which is the maximum wavelength of $^3C_{60}{}^*$, in the presence of various concentrations (4.0×10^{-3} - 3.8×10^{-2} M) of the bisphenol derivatives.

^{1}H NMR spectra were measured on a JEOL GSX-400 (400 MHz) spectrometer at different temperatures. Chemical shifts of ^{1}H MNR were expressed in parts per million downfield from tetramethylsilane as an internal standard ($\delta = 0$).

Density functional theory (DFT) calculations were performed at the Becke3LYP/6-31G level with a Gaussian 98 program on a Compaq DS20E computer.[7]

The evaluation of photographic properties was performed following standard procedure: film samples comprising organic silver salts, silver halide grains, and other reagents were prepared according to the literature,[8] 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

Electron Transfer from a Series of Bisphenol Derivatives to Photoactivated C_{60}

When a deaerated PhCN solution of C_{60} is excited at 355 nm, the singlet excited state of C_{60}, which is known to be efficiently converted to the triplet excited state by the fast intersystem crossing, is initially produced.[9] The transient $^3C_{60}^*$ triplet-triplet (T-T) absorption at 740 nm is observed by the laser flash photolysis of a deaerated PhCN solution of C_{60}, and the characteristic absorption spectrum of $^3C_{60}^*$ decays to the spectral baseline on the microsecond time scale. The one-electron reduction potential of $^3C_{60}^*$ is 1.14 V *vs.* SCE and can therefore be reduced by electron donors.[9,10] Thus, $^3C_{60}^*$ decays significantly faster in the presence of bisphenol derivatives in PhCN due to electron transfer from bisphenol derivatives to $^3C_{60}^*$ (eq 1). The bimolecular rate constants (k_{et}) of electron transfer from the bisphenol derivatives to $^3C_{60}^*$ were determined under pseudo-first-order conditions by monitoring the decay of T-T absorption at 740 nm due to $^3C_{60}^*$ following excitation at 355 nm as a function of excess bisphenol derivative concentration ([ArOH]). The decay obeys first-order

$$^3C_{60}^* + \text{ArOH} \xrightarrow{k_{et}} C_{60}^{\bullet -} + \text{ArOH}^{\bullet +} \qquad (1)$$

kinetics, and the observed pseudo-first-order rate constants (k_{obs}) were plotted against the [ArOH]. The kinetics plots for bisphenol derivatives show significant curvature at relatively low concentrations of ArOH, and the k_{obs} values approach the limiting values at concentrations above 0.03 M (see Figure 2).

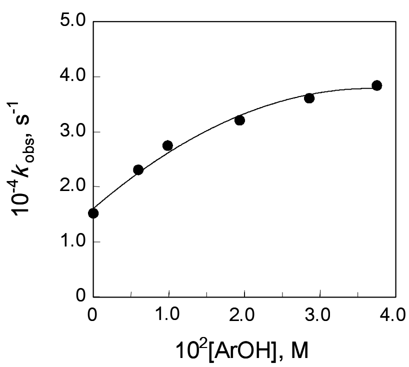


***Figure 2**. Plot of k_{obs} vs. concentration of a bisphenol derivative (R_1 = t-C_4H_9, R_2 = CH_3) [ArOH] for electron transfer from ArOH to $^3C_{60}^*$ in deaerated PhCN at 298 K.*

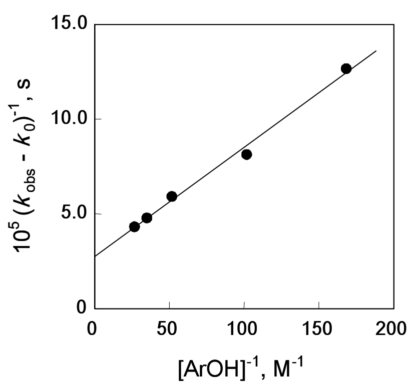


***Figure 3**. Double-reciprocal plot of $(k_{obs} - k_0)^{-1}$ vs. [ArOH]$^{-1}$ according to eq 3.*

Such saturation (asymptotic) behavior of k_{obs} has been reported in electron transfer from aromatic electron donors to the photoactivated quinones.[11,12] The saturation behavior is attributed to formation of an encounter complex prior to electron transfer (eq 2).[9] Thus, the limiting value of k_{obs} corresponds to the intrinsic

$$^3C_{60}^* + \text{ArOH} \underset{}{\overset{K_{EC}}{\rightleftharpoons}} \underset{\text{encounter complex}}{[^3C_{60}^*\text{---ArOH}]} \xrightarrow{k_{ET}} C_{60}^{\bullet -} + \text{ArOH}^{\bullet +} \qquad (2)$$

first-order rate constant (k_{ET}) of electron transfer within the encounter complex. Accordingly, the curved kinetics plot in Figure 2 is evaluated in a double-reciprocal plot in Figure 3, from which the equilibrium constant (K_{EC}) and the intrinsic electron-transfer rate constant (k_{ET}) are extracted according to eq 3, where k_0 is the decay rate constant of $^3C_{60}^*$ without a bisphenol derivative.

$$1/(k_{obs} - k_0) = 1/k_{ET} + (1/K_{EC}k_{ET})(1/[\text{ArOH}]) \qquad (3)$$

The K_{EC} values for complex formation of bisphenol derivatives in PhCN at 298 K were determined as in the range from 46 to 60 M^{-1}. The one-electron oxidation potentials of a series of bisphenol derivatives (E_{ox} *vs.* SCE) were determined in the range from 1.03 to 1.13 V by the electrochemical measurements. The free energy change of photoinduced electron transfer from bisphenol derivatives to $^3C_{60}^*$ (ΔG_{et} in eV unit) is given by eq 4, where e is

$$\Delta G_{et} = e(E_{ox} - E^*_{red}) \qquad (4)$$

the elementary charge, E_{ox} and E^*_{red} are the one-electron oxidation potentials of bisphenol derivatives (1.03 - 1.13 V *vs.* SCE) and the one-electron reduction potential of $^3C_{60}^*$ (1.14 V *vs.* SCE),[9,10] respectively. The ΔG_{et} values of a series of bisphenol derivatives thus evaluated by using eq 4 are in the range from -0.11 to -0.01 eV, indicating that the electron transfer is slightly exergonic. In such a case, the orbital interaction between electron donors and acceptors is maximized to form charge-transfer complexes.[11,12] Accordingly, the K_{EC} values obtained by eq 3 are expected to give nearly maxima values of K_{EC} for each bisphenol derivatives.

Temperature Dependence of the Electron-Transfer Rate Constant

To amplify the electron-transfer properties of a series of bisphenol derivatives in relation to photothermographic reactivity in silver salt photothermographic systems, we examined the temperature dependence of the bimolecular electron-transfer rate constants for a series of bisphenol derivative. The value of k_{ET} for the series of bisphenol derivatives increased from six-fold to ten-fold in a range between 298 K and 373 K. The Arrhenius plots of ln k_{ET} *vs.* the reciprocal temperature yield the activation energies (E_A) of electron transfer (see Figure 4). The E_A values for bisphenol derivatives which have hydrogen bonding substituents at R_2 (in our study, R_2 are *normal*-alkyl alcoholic OH groups, *n*-C_3H_6OH) are appreciably larger than those for other bisphenol derivatives whose R_2 are *normal*-alkyl groups (see Table I). The formation of intramolecular hydrogen bonding between *normal*-alkyl alcoholic OH groups at R_2 is indicated by analysis of temperature dependence of ^{1}H NMR chemical shift of OH group at the *para* position and is also supported by Density functional theory (DFT) calculations at the Becke3LYP/6-31G level,[7] as shown in Figure 5. Thus, the larger E_A values for *para-normal*-alkyl alcoholic OH groups substituted bisphenol derivatives may be ascribed to intramolecular hydrogen bonding between OH groups at the *para* position of aromatic rings, which results in increase in the reorganization energy of electron transfer.

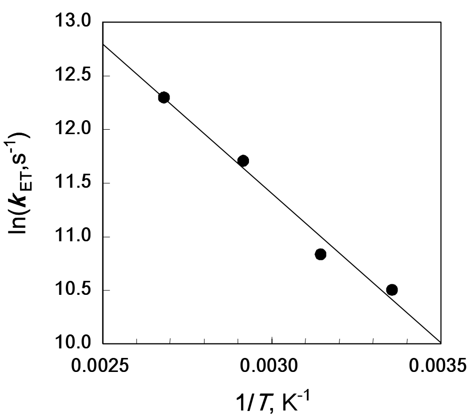


***Figure 4**. Temperature dependence of k_{ET} for electron transfer from a bisphenol derivatives (R_1 = t-C_4H_9, R_2 = CH_3) to $^3C_{60}^*$ in PhCN. The slope of the linear correlation affords the activation energy (E_A).*

Table I: Activation energies (E_A) of electron transfer from a series of bisphenol derivatives to $^3C_{60}^*$

no.	R_1	R_2	E_A, kcal mol^{-1}
1	t-C_4H_9	CH_3	5.5
2	t-C_4H_9	n-C_3H_7	5.5
3	t-C_4H_9	n-C_3H_6OH	6.6
4	t-C_5H_{11}	n-C_3H_6OH	7.0

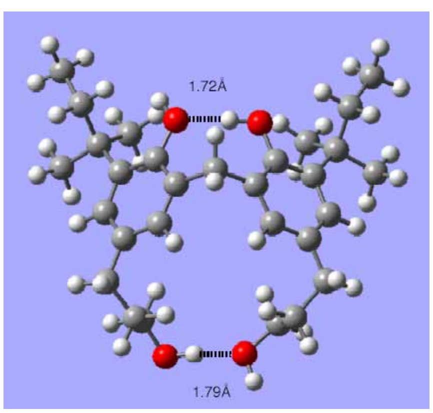


***Figure 5**. Optimized structure of a bisphenol derivative with hydrogen bonding subsituents (R_1 = t-C_5H_{11}, R_2 = n-C_3H_6OH) calculated using DFT at the Becke3LYP/6-31G level.*

Photographic Properties

The developing rates of substituted bisphenol derivatives which have *normal*-alky groups at the position of aromatic rings (R_2) were much faster than that of 1-bis(2-hydroxy-3,5-di-methylphenyl)-3,5,5-trimehylhexane, which was used as a standard developing agent, owing to *tert*-alkyl groups at the ortho position of aromatic rings.[1] However, the much higher developing ability brought about deterioration of fog under the present experimental conditions. In contrast, the bisphenol derivatives which have *normal*-alkyl alcoholic OH groups at R_2 showed the higher developing ability without deterioration of fog, particularly in the pre-exposure storage.

The hydrogen bonding substituents effects on the rates of photoinduced electron transfer of bisphenol derivatives are discussed and they are compared with those on the developing ability of bisphenol derivatives including storage stability. The intramolecular hydrogen bonding formed between *para-normal*-alkyl alcoholic OH groups is shown to play an important role in fine control of the oxidation properties of bisphenol derivatives.

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Author 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.