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 \( ^3\text{C}_{60} \) 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, and they are also known to perform well as antioxidants and stabilizers. Intramolecular hydrogen bonding is recognized as playing an important role in the reactivity of the phenolic function. The hydrogen bonding in bisphenol derivatives can stabilize not only the phenol form but also the phenoxyl radical form. 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, which can be ascribed to the effects of intramolecular hydrogen bonding stabilization in the radical cations and also in the phenoxy radical. 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.

<table>
<thead>
<tr>
<th>No.</th>
<th>( R_1 )</th>
<th>( R_2 )</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>( t\text{-C}_4\text{H}_9 )</td>
<td>CH(_3)</td>
</tr>
<tr>
<td>2</td>
<td>( t\text{-C}_4\text{H}_9 )</td>
<td>( n\text{-C}<em>8\text{H}</em>{17} )</td>
</tr>
<tr>
<td>3</td>
<td>( t\text{-C}<em>5\text{H}</em>{11} )</td>
<td>( n\text{-C}<em>8\text{H}</em>{17}\text{OH} )</td>
</tr>
<tr>
<td>4</td>
<td>( t\text{-C}<em>5\text{H}</em>{11} )</td>
<td>( n\text{-C}<em>8\text{H}</em>{17}\text{OH} )</td>
</tr>
</tbody>
</table>

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 \( ^3\text{C}_{60} \). A deaerated benzonitrile (PhCN) solution of buckminsterfullerene (\( \text{C}_{60} \)) 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 \( (^3\text{C}_{60}) \) was observed at 740 nm, which is the maximum wavelength of \( ^3\text{C}_{60} \), in the presence of various concentrations (4.0 x 10\(^{-3}\) - 3.8 x 10\(^{-2}\) M) of the bisphenol derivatives.

\(^1\text{H} \) NMR spectra were measured on a JEOL GSX-400 (400 MHz) spectrometer at different temperatures. Chemical shifts of \(^1\text{H} \) NMR 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.

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, 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 \( \text{C}_{60} \)
When a deaerated PhCN solution of \( \text{C}_{60} \) is excited at 355 nm, the singlet excited state of \( \text{C}_{60} \), which is known to be efficiently converted to the triplet excited state by the fast intersystem
crossing, is initially produced.\(^9\) The transient \(^{3}\text{C}_{60}\) triplet-triplet (T-T) absorption at 740 nm is observed by the laser flash photolysis of a deaerated PhCN solution of \(^{3}\text{C}_{60}\) and the characteristic absorption spectrum of \(^{3}\text{C}_{60}\) decays to the spectral baseline on the microsecond time scale. The one-electron reduction potential of \(^{3}\text{C}_{60}\) is 1.14 V vs. SCE and can therefore be reduced by electron donors.\(^9,10\) Thus, \(^{3}\text{C}_{60}\) decays significantly faster in the presence of bisphenol derivatives in PhCN due to electron transfer from bisphenol derivatives to \(^{3}\text{C}_{60}\) (eq 1). The bimolecular rate constants (\(k_{\text{ET}}\)) of electron transfer from the bisphenol derivatives to \(^{3}\text{C}_{60}\) were determined under pseudo-first-order conditions by monitoring the decay of T-T absorption at 740 nm due to \(^{3}\text{C}_{60}\) following excitation at 355 nm as a function of excess bisphenol derivative concentration ([ArOH]). The kinetics plots for bisphenol derivatives to \(^{3}\text{C}_{60}\) derivatives show significant curvature at relatively low concentrations of ArOH, and the \(k_{\text{ET}}\) values approach the limiting values at concentrations above 0.03 M (see Figure 2).

\[
^{3}\text{C}_{60} + \text{ArOH} \xrightarrow{k_{\text{ET}}} ^{3}\text{C}_{60}^{-} + \text{ArOH}^{+} \quad (1)
\]

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

\[
1/(k_{\text{obs}} - k_0) = 1/k_{\text{ET}} + (1/k_{\text{ET}}k_{\text{ET}})(1/[\text{ArOH}]) \quad (3)
\]

Such saturation (asymptotic) behavior of \(k_{\text{obs}}\) 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 \(k_{\text{obs}}\) corresponds to the intrinsic first-order rate constant (\(k_{\text{ET}}\)) 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 (\(K_{\text{EC}}\)) and the intrinsic electron-transfer rate constant (\(k_{\text{ET}}\)) are extracted according to eq 3, where \(k_0\) is the decay rate constant of \(^{3}\text{C}_{60}\) without a bisphenol derivative.

\[
{^{3}\text{C}_{60} + \text{ArOH} \xrightarrow{K_{\text{EC}}} ^{3}\text{C}_{60}^{-} + \text{ArOH}^{+} \quad (2)
\]

The \(K_{\text{EC}}\) 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 (\(E_{\text{ox}}\) 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 \(^{3}\text{C}_{60}\) (\(\Delta G_{\text{et}}\) in eV unit) is given by eq 4, where \(e\) is the elementary charge, \(E_{\text{ox}}\) and \(E_{\text{red}}\) are the one-electron oxidation potentials of bisphenol derivatives (1.03 - 1.13 V vs. SCE) and the one-electron reduction potential of \(^{3}\text{C}_{60}\) (1.14 V vs. SCE),\(^9,10\) respectively. The \(\Delta G_{\text{et}}\) 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 \(K_{\text{EC}}\) values obtained by eq 3 are expected to give nearly maxima values of \(K_{\text{EC}}\) 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 \(k_{\text{ET}}\) 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 \(k_{\text{ET}}\) 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\(_3\)H\(_7\)OH) 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 \(^{1}\text{H}\) 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.

**Photographic Properties**

The developing rates of substituted bisphenol derivatives which have normal-alkyl 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-trimethylhexane, which was used as a standard developing agent, owing to tert-alkyl groups at the ortho position of aromatic rings. 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.

### References


### 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 is a member of the SPSTJ.