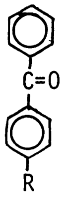
CHEMISTRY LETTERS, pp. 251-254, 1980. © The Chemical Society of Japan 1980

UNEXPECTED HIGH PHOTOOXIDIZING EFFICIENY OF BENZOPHENONE DERIVATIVES HAVING TETRAALKYLAMMONIUM SUBSTITUENTS[1]

Shigeo TAZUKE, Yasuhiro KAWASAKI, Noboru KITAMURA, and Takashi INOUE
Research Laboratory of Resources Utilization, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 227

Benzophenone derivatives having various tetraalkylammonium ion in the 4 position (II, III, IV, and V) were found to be much more efficient sensitizers than benzophenone(I) in photooxidation of Leuco Crystal Violet(LCV) to Crystal Violet(CV^+) in acetonitrile in air, which was interpreted in terms of the cationic atmosphere effect facilitating the primary electron transfer process from LCV to BP^{*3}.

In the course of investigating photochemical and photophysical behaviors of molecular aggregates in which benzophenone(BP) molecules are chemically bound, we found that BP derivatives having quarternary ammonium ion(II, III, IV, and V) revealed very much enhanced photosensitivity towards photooxidation of Leuco Crystal Violet(LCV) in acetonitrile[2].



I: R = H, II_a: R = $-CH_2\overset{+}{N}(C_2H_5)_3Cl^-$, II_b: R = $-CH_2\overset{+}{N}(C_2H_5)_3Br^-$,
III: R = $-CH_2\overset{+}{N}(C_8H_{17})_3Br^-$, IV: R = $-CH_2\overset{+}{N}(CH_3)_2(C_{12}H_{25})Br^-$,
V: R = $-OC_{10}H_{20}\overset{+}{N}(CH_3)_3Br^-$.

When dry acetonitrile solution containing LCV(10^{-4}M) and BP derivative(10^{-3}M) is irradiated with a Xenon lamp in the wavelength region between 340 and 420nm, the BP derivative is selectively excited and color development peaking at ~590nm is observed. Typical examples of the reaction profile are shown in Figure 1.

These differences in reactivity are obviously not attributable to absorption differences of the photosensitizers used. All BP derivatives show a $n-\pi^*$ transition band at ~335nm either as an independent peak or as a shoulder whose molar absorbance is constant at 150(±10%) in acetonitrile. Ordinary substituent effects on aromatic compounds could not explain the results as well, since inductive effect by ammonium ion remotely attached to BP(V) is hardly conceivable. Another approach to interprete the results on the basis of molecular aggregate formation(micellar effect) seems to be not appropriate[3]. Although molecular association of surfactant molecules in both polar and non-polar organic solvents has been demonstrated[4,5], comparable reactivities of II_b and III indicate that surfactant properties of sensitizers are not of importance.

A remaining possibility is neutral salt effect. By adding a variety of neutral salts to I, the rate of CV^+ formation increases as shown in Figure 2. This positive salt effect is not limited to tetraalkylammonium salts. Lithium chloride is equally effective. Apparently, heavy atom effect is responsible for the negative salt effect of iodide[6].

The finding that the reactivities of II_b, III, and IV are much higher than that of V while reactivities of I and p-methoxybenzophenone are almost identical suggests that the distance between

BP and the cation is a determining factor.

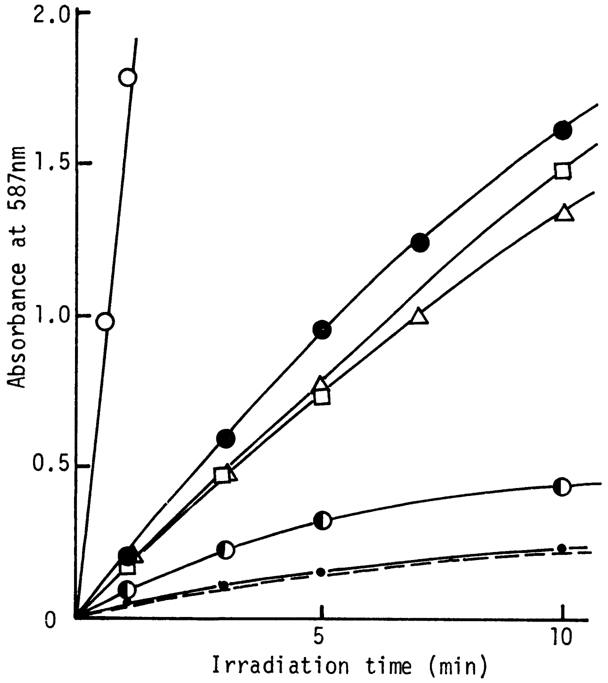


Figure 1. Photooxidation of LCV by BP derivatives. [LCV] = 1×10^{-4}M, [BP] = 1×10^{-3}M at r.t. in air, irradiation wavelength: 340-420nm.
• : I, ----: p-methoxybenzophenone,
○: II_a, ●: II_b, △ : III, □: IV,
◐: V.

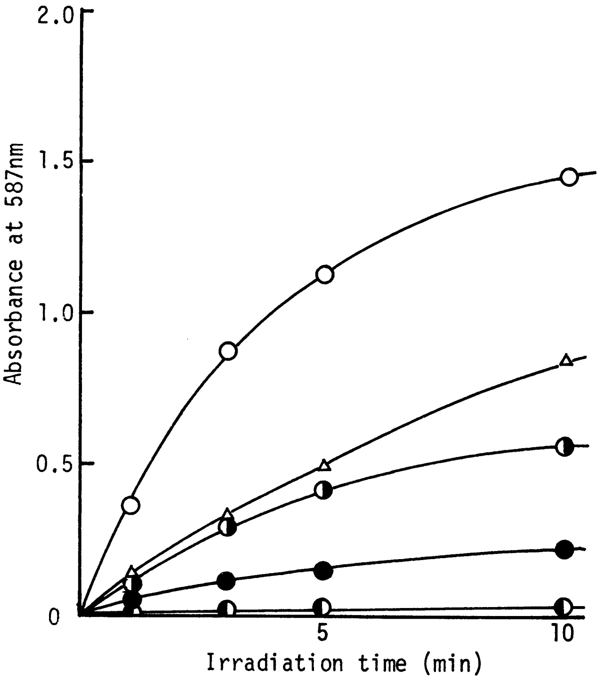


Figure 2. Neutral salt effect on photooxidation of LCV by I. Conditions are same as those in Figure 1. $[M^+X^-] = 10^{-3}$M.
$M^+ = (n\text{-}C_4H_9)_4N^+$
$X^- = Cl^-$(○), Br^-(◑), I^-(◐), ClO_4^-(●).
M^+X^- = LiCl(△).

Photoreaction between I and tertiary amines is a well established process which proceeds via electron transfer from amine to I in polar media[7]. On the condition that the primary process of

$$I^* + R_3N \longrightarrow I^{\overline{\cdot}} + R_3N^{+\cdot} \qquad (1)$$

photooxidation of LCV by benzophenone derivatives is electron transfer, the salt effects mentioned above are well understood. Under the influence of cationic atmosphere, $LCV^{+\cdot}$ is repelled and consequently, back electron transfer will be suppressed[8]. As a matter of course, closer the ammonium ion to BP, more efficient the electron transfer process. Addition of neutral salts also facilitates dissociation of $LCV^{+\cdot}$ from $BP^{\overline{\cdot}}$.

Following elementary processes give a kinetic expression in the form of Stern-Volmer equation.[9]

$$BP \longrightarrow BP^{*1} \xrightarrow{\phi_{isc} = 1} BP^{*3} \qquad (2)$$

$$BP^{*3} \xrightarrow{k_d} BP \qquad (3)$$

$$BP^{*3} \xrightarrow{k_p} BP + h\nu_p \qquad (4)$$

$$BP^{*3} + O_2 \xrightarrow{k_o} BP + {}^1O_2 \qquad (5)$$

$$BP^{*3} + LCV \xrightarrow{k_r} \underset{X}{(BP^{\overline{\cdot}} \cdots LCV^{+\cdot})} \qquad (6)$$

$$X \xrightarrow{k_q} BP + LCV \qquad (7)$$

$$X \xrightarrow{k_1} BP^{\overline{\cdot}} + LCV^{+\cdot} \qquad (8)$$

$$X + O_2 \xrightarrow{k_q'} BP + O_2^{\overline{\cdot}} + LCV^{+\cdot} \qquad (9)$$

$$LCV^{+\cdot} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} CV\cdot + H^+ \qquad (10)^{10}$$

$$LCV^{+\cdot} + CV\cdot \xrightarrow{k_3} CV^+ + LCV \qquad (11)^{10}$$

Assuming photostationary state for X, BP^{*3}, $LCV^{+\cdot}$, and CV·, we obtained (12) where $\tau^{-1} = k_d + k_p + k_o[O_2]$. The plots fall on straight lines as shown in Figure 3. Remarks should be made on the intrinsic $\emptyset_{CV^+}$ value for II_a. Since the maximum value of $\emptyset_{CV}^+$ is expected to be 0.5 as shown by (12), the result indicates complete utilization of BP^{*3} to the formation of CV^+ if X is once formed. Then, $k_q'[O_2] + k_1 >> k_q$ is concluded. The cationic atmosphere at BP would bring about suppression of process (7) and acceleration of process (8) and possibly of process (9) as well.

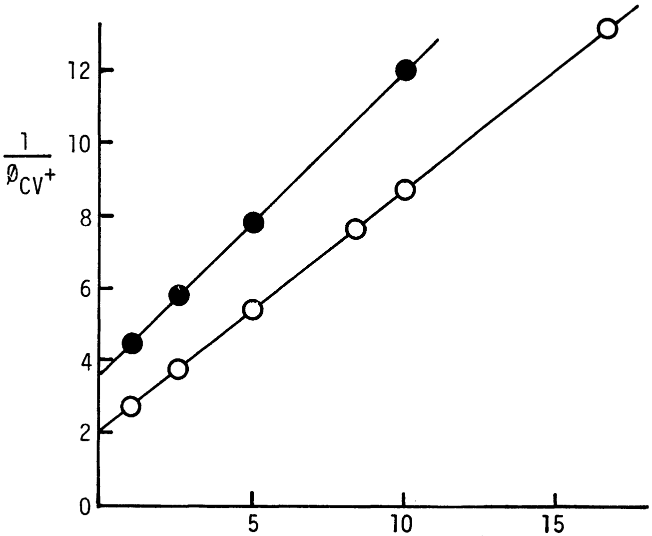
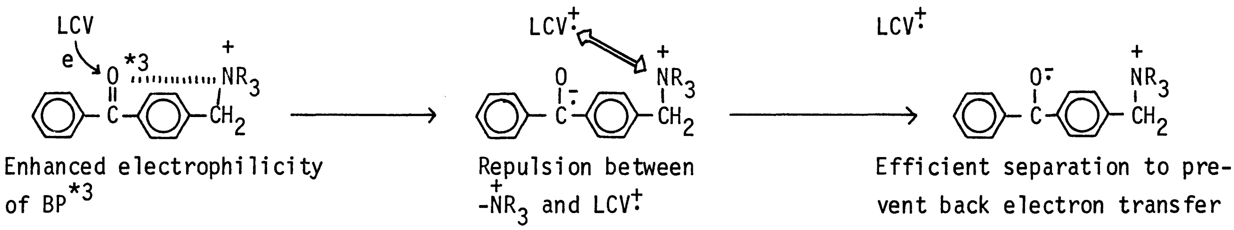


Figure 3. Stern-Volmer plots for CV^+ formation. [BP] = 1 x 10^{-3}M, irradiation at 365nm in air. solvent : acetonitrile.
○: II_a, ●: I + $(n\text{-}C_4H_9)_4N^+Cl^-$(1 x 10^{-2}M)

$$1/\emptyset_{CV^+} = 2\left(1 + \frac{k_q}{k_q'[O_2] + k_1}\right)\left(1 + \frac{1}{\tau\, k_r[LCV]}\right) \qquad (12)^{11}$$

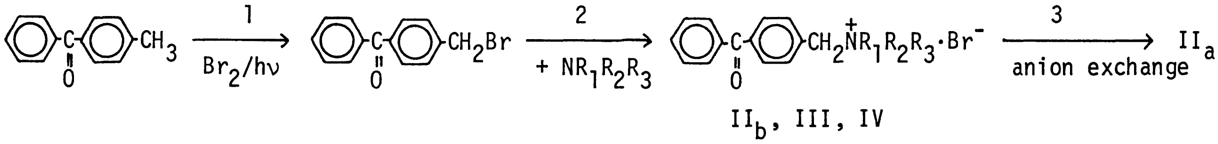
So far reactions in air concern, difference between II_a and I plus ammonium salt could be expressed by the difference in kinetic parameters using same kinetic expression. However, we are not yet sure whether the ion-bound sensitizers could be treated as the high concentration limit of neutral salt effect. These problems would be settled by more rigorous kinetic treatments in unaerobic conditions and transient spectroscopy.

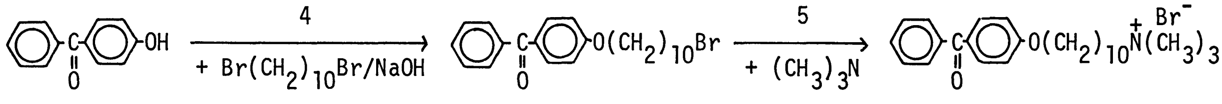
Ionic atmosphere effects are often considered as a characteristic of micellar systems. When sensitizers bearing ionic atmosphere are used, an isolated sensitizer molecule in organic solvents could exhibit ionic atmosphere effects. Molecular aggregate formation is consequently not a necessary condition to utilize ionic atmosphere effects in redox processes as shown below.



Experimental

Outlines of sample preparation are shown below.





V

1 Photobromination in CCl_4 for 1.5h under reflux. Light source: a 300W high pressure Hg lamp with a filter solution($CuSO_4$ 30g in 300ml of water). Recrystallization from ethanol. Y = 56%.

2 Reaction in ethanol for 7h under reflux. Y = 50～80%.

3 Exchange of bromide ion with chloride ion over an ion exchanger(Diaion resin SA-10, Mitsubishi Chem. Co.). Recovery ≒ 50%.

4 Reaction with an excess amount of the bromide in alkaline(aq. NaOH) condition for 8h under reflux. Recrystallization from n-hexane/benzene(10/1). Y = 33%.

5 Reaction in ethyl ether in a sealed tube at room temperature for 20 days. Y = 61%.

Table 1. Analytical Data of BP Derivatives.

BP derivative	m.p. °C (recrystallizing solvents)	C% obs.(calcd)	H% obs.(calcd)	N% obs.(calcd)	halogen% obs.(calcd)
II_a	188-191(acetone)	71.68(72.38)	8.06(7.90)	4.33(4.22)	12.46(10.68)
II_b	192-194(acetone/ethanol)	63.11(63.83)	6.98(6.96)	3.85(3.72)	20.51(21.12)
III	70- 78(n-hexane/benzene)	71.43(72.58)	10.21(9.94)	2.35(2.23)	12.85(12.70)
IV	124-127(n-hexane/acetone)	68.83(68.70)	8.67(8.89)	2.87(2.91)	16.38(16.71)
V	160-162(benzene/ethanol)	65.88(65.53)	8.32(8.04)	2.94(2.94)	17.83(16.77)

References and Notes

1) A part of this report was presented at Symposium of Photochemistry, Kyoto(1978).

2) Recently, Breslow et.al. also reported photoreactions of benzophenone having quarternary ammonium ion. R. Breslow, S. Kitabatake, and J. Rothbard, J. Am. Chem. Soc., 100, 8156(1978).

3) J. H. Fendler and E. J. Fendler, "Catalysis in Micellar and Macromolecular Systems", Academic Press, New York(1975).

4) B. Siegel and R. Breslow, J. Am. Chem. Soc., 97, 6869(1975).

5) U. Herrmann and Z. A. Shelly, J. Am. Chem. Soc., 101, 2665(1979).

6) The sequence of salt effect, $I^- < ClO_4^- <$ no salt $< Br^- < Cl^-$, cannot be explained only by heavy atom effect. Probably, the order of nucleophilicity of anion, $Br^- \sim Cl^- > I^- > ClO_4^-$, is also relevant for this problem.. Further discussions are left for future publications.

7) N. J. Turro, "Modern Molecular Photochemistry", Benjamin/Cummings Publ., Menlo Park(1978), p373.

8) B. Katusin-Rozem, M. Wong, and J. K. Thomas, J. Am. Chem. Soc., 100, 1679(1978); Y. Waka, K. Hamamoto, and N. Mataga, Chem. Phys. Lett., 53, 242(1978).

9) To obtain a plottable kinetic equation, some of possible elementary processes are omitted. These include oxidation of CV· to CV^+ by oxygen, hydrogen abstraction by $O_2^{\cdot-}$ from LCV. The kinetic expression should therefore be considered tentative.

10) A. MacLachlan, J. Phys. Chem., 71, 718(1967); S. Tazuke, H. Tomono, N. Kitamura, K. Sato, and N. Hayashi, Chem. Lett., 85(1979).

11) Two photons are required to give a CV^+ as indicated by eq.(10) and (11). See also ref. 10).

(Received October 11, 1979)