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Photochemical Reactions of *p*-Benzoquinone Complexes with Aromatic Molecules

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Electronic absorption spectra and ESR spectra have been measured for the photolyzed charge transfer complexes between *p*-benzoquinone and aromatic donors in low temperature matrices. When the *p*-benzoquinone complex with toluene or *p*-xylene was irradiated at 77°K, an electronic absorption spectrum attributable to the semiquinone radical was obtained together with that of the benzyl-type radical. The spectral shape and position of the former are somewhat different from those of the semiquinone radicals obtained by the photolysis of *p*-benzoquinone or hydroquinone. These differences indicate the presence of interaction between semiquinone and benzyl-type radicals. The ESR spectra obtained from these systems show that these radicals form pairs in the triplet ($S=1$) state. It is concluded that the radical pairs are produced as a result of intermolecular hydrogen atom transfer from the aromatic donor molecule to *p*-benzoquinone in the excited states of the CT complexes formed between them. The irradiations of various *p*-benzoquinone complexes were carried out in the wavelength regions corresponding to the lowest CT absorption bands at 77°K, and the reactivities were discussed in relation to the electronic structures and geometrical configurations of the CT complexes in the excited states. From the analysis of ESR spectra, the fine structure constant was evaluated for each of the radical pairs, from which the average distance between interacting unpaired electrons was calculated.

Studies on the chemical behaviors of charge transfer (CT) complexes have presented some informations for understanding the reaction paths in which CT complex are involved.[1] In view of the electronic nature of the CT interaction, it is understood that the complexes in the states are generally the precursors of ionic reactions. It was found by Leonhardt and Weller that flash illumination of a solution of peryline and *N*,*N*-dimethylaniline in a polar solvent leads to the formation of perylene anion.[2] Thereafter, it has been shown for

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[1] E. M. Kosower, *Prog. Phys. Org. Chem.*, **3**, 81 (1965); T. Nogami, K. Yoshihara, and S. Nagakura, *J. Phys. Chem.*, **73**, 2670 (1969); T. Nogami, T. Yamaoka, K. Yoshihara, and S. Nagakura, This Bulletin, **44**, 380 (1971); S. Tazuke, *J. Phys. Chem.*, **74**, 2390 (1970).

[2] H. Leonhardt and A. Weller, *Z. Phys. Chem. N. F.*, **29**, 277 (1961); *Ber. Bunsenges. Phys. Chem.*, **67**, 791 (1963).

aromatic donor-acceptor systems that the formation of ionic species *via* the CT complexes in the excited states is a general phenomenon.[3] Recently, the ionic dissociation processes of excited CT complexes were studied by the nano-second laser photolysis.[4]

We have found that the photoreduction of benzophenone proceeds easily in low temperature rigid matrices containing aniline derivatives, leading to the formation of radical-pair between ketyl and aromatic amine radicals in the triplet state.[5] Since the photoreduction of benzophenone does not take place appreciably in ordinary organic matrices at 77° K, we have proposed that the formation of electron donor-acceptor complexes of benzophenone with aromatic amines enhances the photoreduction of benzophenone. In order to obtain further information on the roles of CT interactions in such chemical reactions, we have made a detailed study on the photochemistry of *p*-benzoquinone complexes in low temperature rigid matrices.

It is well known that *p*-benzoquinone forms stable CT complexes with various aromatic compounds.[6] Photoreductions of *p*-benzoquinone and its derivatives yield the semiquinone radicals in the hydrogen-donating solvents.[7] In the present paper, we have examined the photo-chemical reactivity of *p*-benzoquinone complexed with various electron donors. The electronic absorption and emission spectra of these complexes and the ESR spectra of the photolysis products have also been studied.

Experimental

Materials. Both *p*-benzoquinone (BQ) and hydroquinone were purified by repeated recrystallization from ethanol and sublimation in vacuum. Toluene, *p*-xylene, mesitylene, *p*-methylanisole, α-methylnaphthalene, and *N*,*N*-dimethyl-*p*-toluidine were purified by fractional distillation under ordinary or reduced pressure. β-Methylnaphthalene and *p*-toluidine were purified by vacuum sublimation. The organic solvents used in the present work, 2-methyltetrahydrofuran (2-MTHF), ether, ethanol, and isopentane, were purified by the methods described in our previous papers.[5,8]

Apparatus. Photolysis was carried out with a 500-W super high pressure mercury lamp combined with various Toshiba glass filters in order to select the excitation wavelengths corresponding to the first CT absorption band of BQ complexes. All samples examined in this work were degassed by the usual freeze-pump-thaw technique. All experiments were performed at the temperature of liquid nitrogen. The instruments used for the measurements of emission and absorption spectra in the ultraviolet and visible region, and the ESR spectra are the same as described in our earlier paper.

Results

Electronic Absorption and Emission Spectra of BQ Complexes. The electronic spectrum of BQ shows an (n,π^*) band in the visible region and the lowest (π,π^*) band in the near ultraviolet region.[9] Apart from these bands, the electron donor-acceptor interactions between BQ and aromatic donors cause CT absorption bands. Both the maxima and the onset positions for the CT bands observed in 2-MTHF matrix at 77° K are summarized in Table 1, showing clearly that they shift to lower frequencies with decreasing ionization potentials of donor molecules.

The emission spectra of BQ complexes with toluene, mesitylene, and *p*-methylanisole are shown in Fig. 1. In the low temperature rigid matrix containing only BQ, a weak emission was found visually by high intensity excitation, but the emission was so weak that no spectrum could be recorded. As is seen in Fig.1, the emission maximum shifts slightly to longer wavelength as the ionization potential of donor molecules decreases. The phosphorescence spectra of BQ and its complexes with toluene and mesitylene were measured at low temperature by Briegleb *et al.*[10] The results obtained in the present work agree well with theirs. Since the shapes and band positions of the emission spectra obtained for the CT complexes are very much similar to those of BQ, the phosphorescent states of these complexes are most probably the modified locally excited $^3(n,\pi^*)$ state of BQ. Similar phosphorescence spectra have been observed for the BQ complexes with *p*-xylene, α-methylnaphthalene, and β-methylnaphthalene. In the case of CT complexes with *p*-toluidine and *N*,*N*-dimethyl-*p*-toluidine, no emission could be observed.

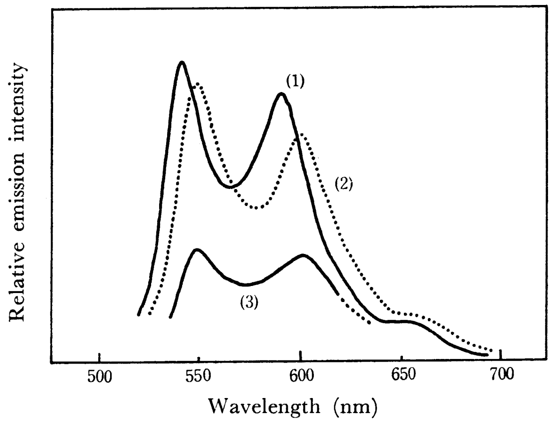

Fig. 1. Emission spectra of BQ complexes with aromatic donors in 2-MTHF at 77°K: 1) toluene; 2) mesitylene; 3) *p*-methylanisole.

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3) K. Kawai, N. Yamamoto, and H. Tsubomura, This Bulletin, **42**, 369 (1969); D. Rehen and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **73**, 839 (1970); T. Okada, H. Oohari, and N. Mataga, This Bulletin, **43**, 2750 (1970).

4) R. Potashnik and M. Ottolenghi, *Chem. Phys. Lett.*, **6**, 525 (1970); C. R. Goldschmidt and M. Ottolenghi, *ibid.*, **6**, 570 (1970); H. Masuhara and N. Mataga, *ibid.*, **6**, 608 (1970).

5) S. Arimitsu and H. Tsubomura, This Bulletin, **44**, 2288 (1971); *ibid.*, **45**, 1357 (1972).

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7) H. Linschitz, J. Rennert, and T. M. Kon, *J. Amer. Chem. Soc.*, **76**, 5839 (1954); N. K. Bridge and G. Porter, *Proc. Roy. Soc.*, **A244**, 259, 279 (1958); G. Porter and M. W. Windsor, *ibid.*, **A245**, 238 (1958).

8) S. Arimitsu, K. Kimura, and H. Tsubomura, This Bulletin, **42**, 1858 (1969).

9) J. W. Sidman, *J. Chem. Phys.*, **27**, 820 (1957); A. Kuboyama, This Bulletin, **35**, 295 (1962).

10) G. Briegleb, W. Herre, and D. Wolf, *Spectrochim. Acta*, **25**, 39 (1969).

Absorption Spectra of BQ Complexes Irradiated at 77°K. Electronic absorption spectrum obtained after the photolysis of BQ in an ethanol rigid matrix is shown by curve a in Fig.2. A similar spectrum was observed after the photolysis of hydroquinone in ethanol.[11] Therefore, it is unambiguously concluded that these absorptions are ascribed to the semiquinone radical, in agreement with the assignment of previous authors.[12] When hydroquinone in a mixed (1:1) solvent of toluene and ethanol was photolyzed at 77° K, the absorption spectrum of semiquinone radical as shown by curve b in Fig.2 was obtained. The spectrum is a little broader than that in pure ethanol at 77°K. When BQ-toluene complex was irradiated in the wavelength region corresponding to the CT absorption band at 77° K, a spectrum shown by curve c in Fig.2 was obtained, by subtracting the absorption before irradiation. It seems reasonable to attribute the visible absorption to the semiquinone radical and the near ultraviolet absorption to the benzyl radical.

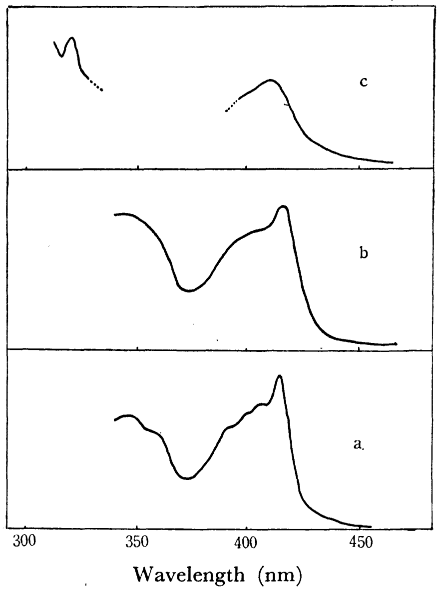

Fig. 2. Electronic absorption spectra of semiquinone radicals obtained after the photolysis of BQ and hydroquinone in low temperature rigid matrices: a, BQ in ethanol at 77°K; b, hydroquinone in toluene and ethanol (1 : 1) at 77°K; c, BQ in toluene and ethanol (1 : 1) at 77°K.

BQ-*p*-xylene complex shows a CT absorption maximum at 360 nm in an EPA (5 parts ether, 5 parts isopentane, 2 parts ethanol) rigid matrix. When it was subjected to irradiation in the range from 350 to 400 nm at 77° K, the absorption of semiquinone radical appeared gradually. At the same time, the CT absorption faded and the absorption attributable *p*-methylbenzyl radical also appeared. No spectral change was detected by the illumination of *p*-xylene in an EPA solution at the same wavelength region at 77° K.

ESR Spectra of BQ Complexes Irradiated at 77°K. A typical ESR spectrum obtained after the photolysis of the CT complex of BQ and *p*-methylanisole is shown in Fig.3. The spectrum consists of a weak band at a low magnetic field and stronger bands showing large splittings centered at a magneitc field twice as large as that for the weak one. In our previous study on the photochemistry of benzophenone in aromatic amine solutions, we found that the ESR spectra obtained after the irradiation of benzophenone–aromatic amine systems can be attributed to the radical pair in the triplet state ($S=1$).[5] The ESR spectrum shown in Fig. 3, together with those obtained from other BQ complexes, agrees well with them, and unambigously indicates that similar radical pairs are produced.

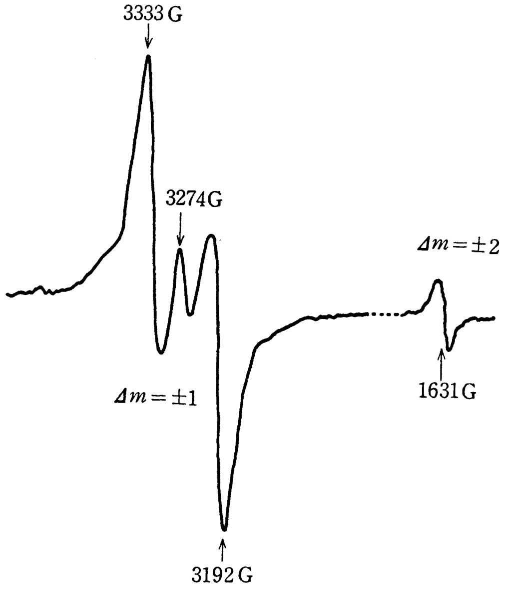

Fig. 3. An ESR spectrum of BQ-*p*-methylanisole complex in 2-MTHF irradiated at 77°K. ($\nu=9147$ MHz.)

When BQ was irradiated at 77° K, the ESR spectrum obtained shows only the absorption signals due to free radicals at the $g=2$ region, attributable to the semiquinone and solvent radicals. From these experimental results, it is established that the absorption spectra are due to radical pairs produced by the intermolecular hydrogen transfer from donors to BQ. Photolysis of the BQ complexes with toluene, *p*-xylene, mesitylene, and α-methylnaphthalene also showed similar ESR spectra. In the case of BQ-β-methylnaphthalene, it has been suggested by the ESR measurement that the hydrogen transfer reaction does not take place appreciably, only radical absorption appearing at the $g=2$ region. In BQ-*p*-toluidine and BQ-*N*,*N*-dimethyl-*p*-toluidine systems, no ESR signal could be found by excitation of the lowest CT absorption band, indicating no photochemical reaction. From the electronic absorption measurements, it was also established that

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[11] K. Kimura, K. Yoshinaga, and H. Tsubomura, *J. Phys. Chem.*, **71**, 4485 (1967).

[12] G. Porter and E. Strachan, *Trans, Faraday Soc.*, **54**, 1595 (1958); G. Porter and F. Wilkinson, *Proc. Roy. Soc.*, **A264**, 1(1961); G. Porter, and P. Suppan, *Trans. Faraday Soc.*, **61**, 1664 (1965).

[13] Y. Kurita, H. Ohigashi, and M. Kashiwagi, *Bussei*, **9**, 87 (1968).

Table 1. CT spectral characteristics of the complexes of *p*-benzoquinone and various aromatic donors at 77°K and the appearance of the ESR spectra of their irradiation products

Donor	CT band maxima, $\times 10^3$ cm^{-1}	CT band onset $\times 10^3$ cm^{-1}	Phosphorescence onset, $\times 10^3$ cm^{-1}	Donor I_p[15] eV	Total spin	D, gauss	*R*, Å
Toluene	∼31.3	∼25.0	18.5	8.82	1	135	5.9_1
p-Xylene	29.4	∼23.8		8.45	1	142	5.8_1
Mesitylene	28.6	∼22·7	18.3	8.39	1	137	5.8_8
α-Methylnaphthalene	25.3	∼19.2		7.96	1	118	6.1_8
p-Methylanisole	24.6	∼19.2	18.2		1	141	5.8_2
p-Toluidine	19.3	∼14.3			—		
N,N-Dimethyl-*p*-toluidine	18.7	<14.3			—		

the absorption intensity of the CT bands of these systems did not change detectably throughout the irradiation.

We can evaluate the fine structure constants (D) from the spin-spin splittings of the $\Delta m = \pm 1$ transitions of the ESR spectra obtained. The fine structure constants obtained from the separation corresponding to D are listed in Table 1, together with the average distance (R) between two unpaired electrons, calculated from these constants by using a point-charge-density approximation.[13]

Discussion

It can be seen in Table 1 that the frequencies of the charge-transfer bands arising from the interaction between the aromatic donor and BQ shift to the longer wavelength with decreasing ionization potentials of the donor molecules. As to the photochemical behaviors, the CT complexes of BQ can be classified into two groups. The complexes with toluene, *p*-xylene, mesitylene, α-methylnaphthalene, and *p*-methylanisole belong to group A and those with *p*-toluidine and *N,N*-dimethyl-*p*-toluidine to group B. The photoreduction of BQ takes place in group A, but not in group B. In group A, the CT state is higher than the lowest triplet state in each system, characterized as the locally excited $^3(n,\pi^*)$ state of BQ, as indicated by the measurements of emission spectra. The lowest excited singlet states of BQ complexes in group A have mainly the nature of either the CT state or the locally excited $^1(n,\pi^*)$ state of BQ. In group B, on the other hand, the lowest triplet state is not the $^3(n,\pi^*)$ state of BQ but mostly of the CT nature, as suggested by the emission spectral measurements, and the lowest excited singlet state is also the CT state. Therefore, it can safely be concluded that the distinction between photochemical behaviors of group A and B can be explained on the basis of the different electronic structures in the lowest triplet states of these complexes. Consequently, it is concluded that the hydrogen trasnfer reaction of BQ complexes occurs in the lowest triplet states of the CT complexes characterized by the (n,π^*) state of BQ.

Another possible alternative for the photochemical reaction mechanism for the BQ complexes is the initial electron transfer from the donor molecule to BQ, followed by the proton transfer. This seems unlikely, however, because such a reaction should be favorable in the cases of stronger CT complexes such as BQ–*p*-toluidine and BQ–*N,N*-dimethyl-*p*-toluidine systems, contrary to our experimental results.

As shown in Table 1, the fine structure constants of radical pairs are different from complex to complex. It can be concluded from these results that the intermolecular hydrogen transfer occurs from the donors, not from the solvent, to BQ in the low temperature matrices, leading to the formation of the radical pair in the triplet spin state, because, if the hydrogen transfer reaction were to occur from the solvent molecule to BQ, the fine structure constant should be the same in all cases.

It is interesting to note that the photochemical reaction of these complexes is affected critically by the position of the methyl-group in the donor molecules. For example, the CT complex of BQ–α-methylnaphthalene excited in the wavelength region of the CT absorption band shows an ESR spectrum arising from the triplet radical pair, but the spectrum attributable to the semiquinone and solvent radicals were obtained from the photolysis of BQ–β-methylnaphthalene system. Therefore, no hydrogen atom transfer reaction from the donor to BQ is shown to take place in the latter system. The distinction in the photochemical reaction between the above two complexes is not explained by the electronic natures of the lowest excited triplet states, since they have both the locally excited $^3(n,\pi^*)$ levels of BQ as the lowest triplet level as suggested by the emission measurements. Thus it seems more reasonable to conclude that the distinction is caused by the different geometric conditions between the two complexes, leading probably to the changes of $CH_3 \cdots O$ distance, there are some theoretical arguments on the geometrical configuations of molecular complexes in the excited states.[14] The present results and those of the similar studies might provide bases for

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[14] T. Kobayashi, S. Iwata, and S. Nagakura, This Bulletin, **43**, 713 (1970); T. Kobayashi, K. Yoshihara, and S. Nagakura, *ibid.*, **44**, 2603 (1971); H. Masuhara and N. Mataga, *Z. Phys. Chem. N. F.*, to be published.

[15] K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectrosc. Radiat. Transfer*, **2**, 369 (1962).

the elucidation of the geometries of CT complexes in the excited states as well as in the ground states.

In conclusion, it has been established in the present work that the photochemical hydrogen abstraction reaction of BQ in the complexes with aromatic donors occurs in low temperature rigid matrices, only in cases where the lowest triplet state is mainly of the $^3(n,\pi^*)$ character of BQ. In cases where the donor is so strong that the ^{3}CT state is lower than the $^3(n,\pi^*)$ state of BQ, no hydrogen abstraction takes place. These results indicate that the reactions proceed from such states as those in which the oxygen atom has an unpaired electron in its non-bonding atomic orbital. These results also clearly indicate that the initial electron transfer followed by proton tunnelling is not the route for the hydrogen abstraction reaction irrespective of the strengths of the donor-acceptor interactions.