

Reactions of Leuco Bindschedler's Green with Some *p*-Benzoquinones in Acetone

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The rate of reaction between Leuco Bindschedler's Green (BGH) and some *p*-benzoquinone derivatives (Q's) in acetone was followed spectrophotometrically by means of the stopped-flow technique. The reaction was found to proceed reversibly. The rate data and the activation parameters for the forward and backward reactions were estimated. The rates were susceptible to the oxidation–reduction potentials of the Q's. The absorption spectra observed at low temperatures indicated that three kinds of intermediates were involved. Radicals formed during the reaction were detected by the ESR method. The results have been discussed in relation to those previously obtained for systems involving Leuco Crystal Violet (LCV) and Leuco Malachite Green (LMG).

Hydride-transfer reactions have been an attractive research subject together with proton-transfer reactions *in vivo* as well as *in vitro*. In hydride-transfer reactions, *N*-benzyl-1,4-dihydronicotinamide (BNAH) and related compounds have been regarded as model compounds of dihydronicotinamide coenzymes. Westheimer and co-workers^{1,2)} suggested that the oxidation–reduction reactions involved direct hydride transfers, and this idea was believed for a long time. However, Steffens and Chipman³⁾ suggested first that the so-called hydride-transfer reactions involved an intermediate with the character of a charge-transfer (CT) complex. Ohno and Kito,⁴⁾ and Fukuzumi and Tanaka⁵⁾ demonstrated that a CT complex as an intermediate is really involved in such reaction systems. The oxidations of 9,10-dihydro-10-methylacridine and its derivatives to the corresponding acridinium ions by π -acceptors were investigated by Colter and co-workers.^{6,7)} They obtained spectroscopic and kinetic evidence for CT complexing between the reactants. The involvement of quantum-mechanical tunneling in the “hydride-transfer” reaction between LCV and chloranil (CA) was advocated by Isaacs and co-workers.^{8,9)} We have observed the formation of CT complexes in the same system and in the LMG/CA system.^{10,11)} Thus, the one-step hydride-transfer mechanism is debatable. It was found in this work that the hydrogen atom on the nitrogen in BGH is abstracted in the form of a hydride ion much more easily than the hydrogen atom on the central carbon atom in LCV and LMG. We were interested in knowing how situations would change if LCV and LMG were replaced by BGH. In a preliminary study,¹²⁾ we briefly reported the reaction of BGH with tetracyanoethylene and found the reaction proceeded reversibly. The present paper reports an investigation of the reactions of BGH with a series of *p*-benzoquinones.

Experimental

Materials. Reagent-grade BGH manufactured by Dojin Chemicals Ltd. was used as received, since this compound is very difficult to purify in the usual manner; mp 119–120.5 °C.

Reagent-grade tetrachloro-*p*-benzoquinone (chloranil, CA), 2,6-dichloro-*p*-benzoquinone (2,6-DCQ), 2,5-dichloro-*p*-benzoquinone (2,5-DCQ), 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ), *p*-benzoquinone (BQ), and tetramethyl-*p*-benzoquinone (TMQ) were purchased from Tokyo Kasei Kogyo and recrystallized twice from benzene. BGH⁺ perchlorate (Würster's Blue) was prepared according to the method of Michaelis and Granick;¹³⁾ dark purple, mp 147–148 °C. Reagent-grade solvents were dried on Molecular Sieves 4A-1/16, and distilled before use.

Kinetic Measurements. When the acetone solution of BGH was mixed with that of benzoquinones, a characteristic band due to Bindschedler's Green cations (BG⁺) appeared at $\lambda_{\max}=725$ nm. All the runs were performed with excess quinone concentrations, i.e., [BGH]₀: (4–5)×10^{−5} mol dm^{−3}, and [Quinones]₀: (0.5–8)×10^{−3} mol dm^{−3}. Separately-prepared reactant solutions were deaerated by nitrogen gas bubbling and were charged in drive syringes which were thermostatically regulated within ±0.1 °C. The mixing was performed within 1 ms by means of nitrogen gas pressure. After mixing, the change in the absorbance at 725 nm was monitored by using a Unisoku USP-519 spectrophotometer. The runs were repeated 10 to 30 times and curve smoothing was performed by means of an attached computer.

Electronic Spectra at Low Temperatures. A specially designed cryostat with optical windows was set in a Union SM-401 spectrophotometer, and spectra in the visible region at various low temperatures were recorded. In order to prevent the deposition of dew on the windows, dry nitrogen gas was blown onto the windows during the measurements.

ESR Measurements. Reactant solutions of BGH and Q were introduced separately into an H-shaped tube with a side tube (i.d. 1 mm) for ESR measurements. After the solutions were degassed by freezing and thawing under vacuum, the solutions were mixed and transferred into the side tube. A JEOL JES-FE3XG spectrometer equipped with a 100 kHz field modulator and a TE 011 cavity was used for ESR measurements. The temperature in the cavity was controlled by a JEOL variable temperature regulator.

Results

A representative spectrum in the initial stage of reaction between BGH and CA is shown in Fig. 1. The absorption band at $\lambda_{\max}=725$ nm can be attributed to

Table 1. Apparent First-Order Rate Constants for the Reaction between BGH and *p*-Benzoquinones at Various Temperatures in Acetone

Temp	[CA] ₀	<i>k</i> _{obsd}	[2,6-DCQ] ₀	<i>k</i> _{obsd}	[2,5-DCQ] ₀	<i>k</i> _{obsd}
°C	mmol dm ⁻³	s ⁻¹	mmol dm ⁻³	s ⁻¹	mmol dm ⁻³	s ⁻¹
13.5	0.554	9.26				
	1.107	12.0				
	1.660	14.5				
	2.214	17.3				
18.5 ^{b)}	0.550	9.99	2.22	0.419	2.26	0.0667
	1.099	12.9	4.05	0.627	4.00	0.0739
	1.648	15.7	6.02	0.870	6.34	0.0931
	2.197	18.6	7.91	1.000	7.91	0.109
25.0	0.508	10.6	2.23	0.569	2.49	0.092
	1.107	14.0	3.95	0.815	3.93	0.103
	1.525	16.7	5.99	1.14	6.02	0.127
	2.033	19.3	8.22	1.42	8.28	0.157
32.0	0.503	11.6	2.17	0.712	2.46	0.134
	1.001	15.2	4.08	1.10	3.89	0.169
	1.509	18.0	5.99	1.42	5.96	0.196
	2.012	21.2	7.55	1.67	8.19	0.222
40.0	0.497	12.9	2.15	0.963	2.24	0.203
	0.994	16.3	4.04	1.51	3.95	0.244
	1.491	19.8	5.9	1.91	5.91	0.293
	1.988	23.2	7.46	2.25	7.90	0.346
50.0			2.10	1.21	2.19	0.267
			3.83	1.84	3.87	0.324
			5.70	2.50	5.78	0.393
			7.48	2.93	7.73	0.482

a) 17.5°C for 2,6-DCQ, and 18.0°C for 2,5-DCQ.

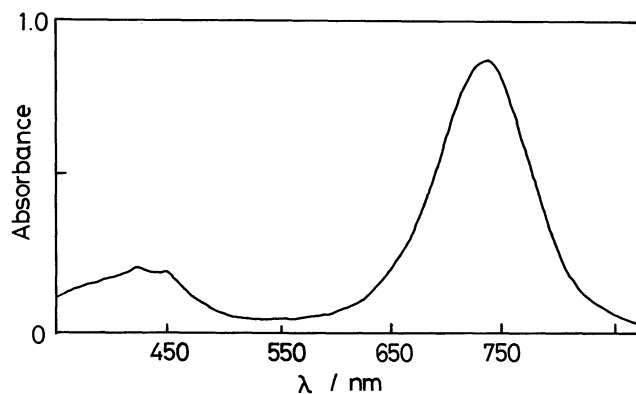
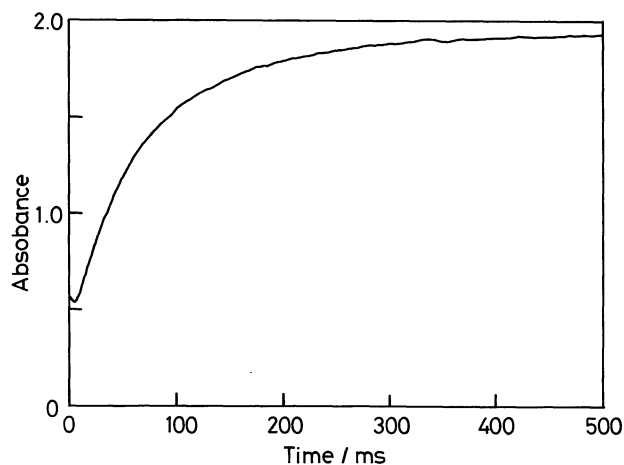


Fig. 1. Electronic spectrum of the BGH/CA system in excess of CA after the initial stage of reaction in acetone at 25°C.

BG⁺, and the peculiarly-shaped absorption band in the vicinity of 450 nm is due to semiquinone anion radicals.^{10,14)} A time-dependent curve in the initial stage of the absorbance at 725 nm after averaging the repeated runs is shown in Fig. 2. After a pseudo-equilibrium had been attained in this time scale, the absorbance at 725 nm increased gradually when the observation time scale was changed by a factor of 10³. By setting an appropriate time region in the initial stage, the curve was analyzed by the Damping Gauss–Newton method combined with the aid of an attached computer program. The estimat-

Fig. 2. Initial rise of absorbance at 725 nm as a function of time (20 cycles) in the reaction of BGH (6.92×10⁻⁵ mol dm⁻³) with CA (1.53×10⁻³ mol dm⁻³) at 25°C.

ed rate data (*k*_{obsd}) are given in Table 1.

In Fig. 3, the apparent first-order rate constants for the BGH/CA system at various temperatures are plotted as a function of initial CA concentrations. This figure shows that the rate is first-order with respect to CA at each temperature and that the reaction involves a reverse process. The same type of plots were obtained for other quinones.

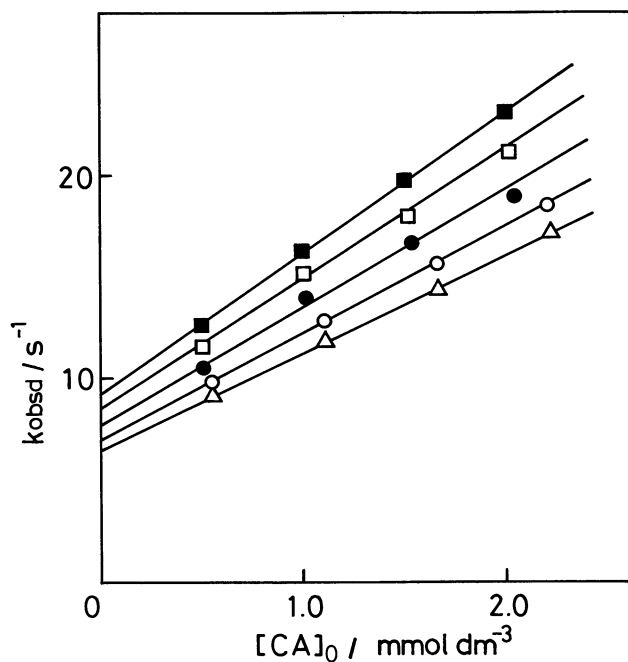


Fig. 3. Plots of k_{obsd} against the initial concentration of CA at temperatures ($^{\circ}\text{C}$): 13.5 (Δ), 18.5 ($\circ$), 25.0 ($\bullet$), 32.0 ($\square$), and 40.0 ($\blacksquare$).

In Fig. 4, the electronic spectra for the BGH/CA system in an EPA solution at various temperatures are shown. For comparison, the change in the electronic spectrum of a mixture of *N*-methyldiphenylamine (MDA) and CA in EPA is shown in Fig. 5. It is noted that the pattern of the spectrum in Fig. 4 and its temperature dependence are very different from those in Fig. 5. The pattern and the band position of the spectrum in Fig. 5 are rather similar to those of the LCV/CA and LMG/CA systems.^{10,11)}

For the BGH/CA and BGH/DDQ systems, ESR spectra assignable to the corresponding semiquinone anion radicals were observed at room temperature. For both the BGH/2,5-DCQ and BGH/2,6-DCQ systems, a very broad signal appeared at 25 $^{\circ}\text{C}$. However, when the temperature was lowered below -45°C , the signal pattern changed to an expected 1:2:1 triplet.

Discussion

Rate Equations and Reaction Mechanism. From the above results, the rate of BG^+ formation in the initial stage, under the condition $[\text{BGH}]_0 \ll [\text{Quinones}]_0$, can be given by:

$$d[\text{BG}^+]/dt = k_{\text{obsd}} ([\text{BG}^+]_e - [\text{BG}^+]) \quad (1)$$

where $[\text{BG}^+]$ and $[\text{BG}^+]_e$ denote the concentrations of BG^+ at time t and at the pseudo-equilibrium, respectively. Fukuzumi and co-workers¹⁵⁾ studied a hydride-transfer reaction between BNAH and the Q's. They found that a CT complex was first formed between BNAH and Q as evidenced by the appearance of a CT complex spectrum

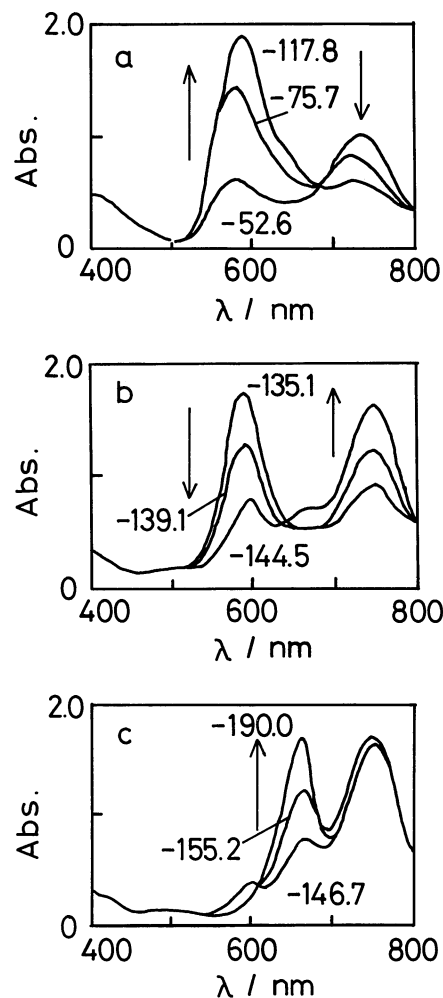


Fig. 4a—c. Spectral change as a function of temperature for the BGH/CA system in EPA. Arrows show the direction of decreasing temperature, and numerical values in the figure denote measurement temperatures in $^{\circ}\text{C}$; $[\text{BGH}]_0, [\text{CA}]_0 \approx 10^{-5} \text{ mol dm}^{-3}$.

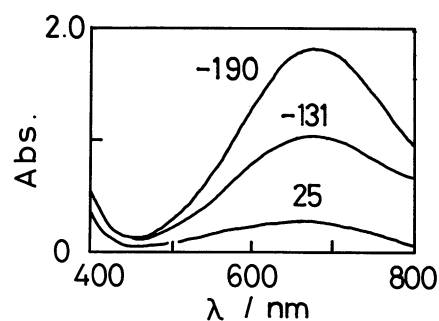
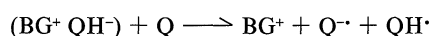
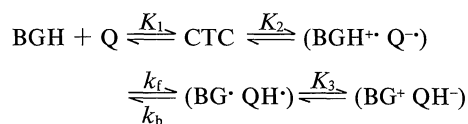


Fig. 5. Temperature dependence of a CT band that appeared in the CA/MDA system. Numerical values in the figure denote measurement temperatures in $^{\circ}\text{C}$.

in the visible region at room temperature. They proposed that, the CT complex was in rapid equilibrium with the radical ion pair (BNAH^+Q^-). Thereafter, irreversible proton transfer takes place to form the radical pair

(BNA[•] QH[•]). Subsequently, electron transfer yielding BNA⁺ and QH[•] takes place.

If we accept their proposed mechanism as a whole and take into account the reverse reaction and the gradual increase in BG⁺ after the pseudo-equilibrium is reached, a plausible reaction mechanism in harmony with the above empirical equation may be as follows:



where Q denotes benzoquinones, and parentheses denote cages. Hydride-transfer reactions usually show large kinetic isotope effects (k_H/k_D).^{3,6,8,10} Therefore, if the rate-determining step involves a proton transfer and the other steps are in rapid equilibrium in the initial stage, k_{obsd} can be given by:

$$k_{\text{obsd}} = k_b/K_3 + K_1K_2k_f[\text{Q}]_0 \quad (2)$$

From the plots of k_{obsd} against the initial concentration of quinones (Fig. 3), the values of $K_1K_2k_f$ and k_b/K_3 were estimated and are given in Table 2. The activation parameters are given in Table 3. The overall pseudo-equilibrium constant K is given by:

$$K = K_1K_2(k_f/k_b)K_3 \quad (3)$$

By utilizing the kinetic data, K can be calculated. For example, K at 25 °C for the BGH/CA system is 713 dm³ mol⁻¹. Under the condition $[\text{BGH}]_0 \ll [\text{CA}]_0$, K is given by:

$$K = [\text{BG}^+ \text{QH}^-]_e / [\text{BGH}]_e [\text{CA}]_0$$

$$= \frac{A_e/\varepsilon}{([\text{BGH}]_0 - A_e/\varepsilon)[\text{CA}]_0} \quad (4)$$

where A_e denotes the absorbance at 725 nm after the pseudo-equilibrium has been attained, and ε the molar absorptivity at this wavelength. Unfortunately, the ε -value is not known. However, if we assume ε as

Table 2. Rate Data for the Forward and Backward Reactions between BGH and *p*-Benzoquinones in Acetone (probable errors in parentheses)

$T/^\circ\text{C}$	$K_1K_2k_f$ dm ³ mol ⁻¹ s ⁻¹					
	13.5	18.5 ^{a)}	25.0	32.0	40.0	50.0
CA	4810(50)	5210(20)	5670(180)	6280(140)	6920(20)	
2,6-DCQ		105(6)	143(4)	177(5)	240(9)	324(14)
2,5-DCQ		7.56(0.56)	11.4(0.6)	14.9(1.2)	25.3(0.3)	38.8(1.3)
DDQ			1.46(0.20)×10 ⁶			
	k_b/K_3 s ⁻¹					
	13.5	18.5 ^{a)}	25.0	32.0	40.0	50.0
CA	6.61(0.07)	7.14(0.03)	7.95(0.25)	8.60(0.20)	9.45(0.03)	
2,6-DCQ		0.200 (0.031)	0.257 (0.018)	0.350 (0.027)	0.484 (0.044)	0.574 (0.071)
2,5-DCQ		0.0469 (0.0030)	0.0605 (0.0031)	0.104 (0.007)	0.145 (0.002)	0.177 (0.007)
DDQ			284(13)			

a) 17.5 °C for 2,6-DCQ, 18.0 °C for 2,5-DCQ.

Table 3. Activation Parameters for Reactions between BGH and *p*-Benzoquinones

System	Solvent	Forward		Backward	
		E_a	$\Delta S_{298\text{K}}^\ddagger$	E_a	$\Delta S_{298\text{K}}^\ddagger$
		kJ mol ⁻¹	J K ⁻¹ mol ⁻¹	kJ mol ⁻¹	J K ⁻¹ mol ⁻¹
BGH/CA	Acetone	10.2±0.1	-147±1	10.1±0.2	-202±1
BGH/2,6-DCQ	Acetone	27.1±0.4	-121±1	26.6±1.3	-175±4
BGH/2,5-DCQ	Acetone	40.2±1.1	-99±4	34.6±2.6	-160±8
LCV/CA ^{a)}	CHCl ₃	30.1±0.8	-148±3		
	CH ₃ CN	43.1	-135		
LMG/CA ^{b)}	CH ₃ CN	86.0±0.8	-55±3		

a) Data cited from Ref. 10. b) Data cited from Ref. 11.

74000 dm³ mol⁻¹ cm⁻¹, and use the A_e -values obtained for various initial CA concentrations, the average K -value was found to agree well with the one obtained from the kinetic data.

When we compare the kinetic data for the BGH/CA system with those for the LCV/CA and LMG/CA systems, we can notice two distinctive points: the rate is faster in the order of 10³–10⁵ and the activation energy is remarkably smaller (Table 3) than those for the LCV/CA and LMG/CA systems. Secondly, the reaction involves a reversible process in the rate-determining step. Moreover, the electronic spectra which appeared in the visible region are remarkably different from those observed in the LCV/CA and LMG/CA systems.

Substituent Effects. The values of $K_1K_2k_f$ as well as k_b/k_3 decrease in the order DDQ>>CA>2,6-DCQ>2,5-DCQ>>BQ, TMQ (Table 2). In the hydride-transfer reaction of BNAH with the Q's, Fukuzumi et al.¹⁵⁾ found that the rate varies significantly with the redox potentials $E^\circ(Q/Q^{\cdot-})$. In our case, if one-electron transfer takes place prior to the hydrogen transfer (or successive proton and electron transfer), the rate of the forward reaction will also be correlated to $E^\circ(Q/Q^{\cdot-})$. In Fig. 6, the $K_1K_2k_f$ values in logarithmic scale are plotted as a function of E° . Since there are no available data for E° in acetone, we used the values of E° in acetonitrile.¹⁶⁾ It can be seen that the plot of $\log K_1K_2k_f$ vs. E° is approximately parallel to that of the BNAH/Q system. This fact suggests that the mechanisms for both systems are similar. It was found that the linear free energy relationship holds well for both the forward and backward reactions, suggesting that these reactions proceed by the single interaction mechanism.¹⁷⁾ However, it is hard to explain the remarkably large negative values of $\Delta S^\ddagger$ for the backward process. We propose the following reason: according to the absolute

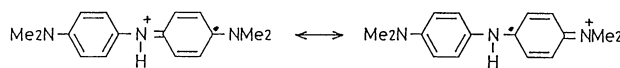
rate theory, the rate constant is given by:

$$k = (e \kappa k_B T / h) e^{\Delta S^\ddagger / R} e^{-E_a / RT} \quad (5)$$

where κ denotes the transmission coefficient. We usually calculate $\Delta S^\ddagger$ on the assumption of $\kappa=1$. However, if the formation of (BG $\cdot$ QH $\cdot$) takes place via a triplet transition state, the value of κ must be much smaller than unity due to intersystem crossing. In this case, the assumption of $\kappa=1$ gives rise to an apparent small $\Delta S^\ddagger$ value. The activation energies for the forward and backward processes are similar (Table 3). This means that the heat of reaction is nearly equal to zero. As ion-pair formation reactions from neutral species are generally exothermic, this is another curious point. At present, the cause is not obvious.

Electronic Spectra at Low Temperatures. The electronic spectra of a mixture of BGH and CA in EPA solution were taken at low temperatures (Fig. 4a–c). In the figure, the band due to the semiquinone radical (Fig. 1) is obscure. This was found to be caused by an instrumental problem, not by the absence of the radical. It is notable that these spectral changes, as shown in Fig. 4, have not been reported so far for similar hydride-transfer systems. Due to experimental limitations, we were forced to start the spectral measurements after the pseudo-equilibrium had been attained. At –52.6 °C, we can see two distinct bands at $\lambda_{\max}=730$ nm (referred to as band A) and at $\lambda_{\max}=590$ nm (band B). Since $\lambda_{\max}$ for BG⁺ is known to be 725 nm at room temperature, it is obvious that BG⁺ is responsible for the band A. A small red shift upon cooling may be due to solvent effects. As the temperature was lowered, the intensity of the band B increased at the expense of the band A (Fig. 4a). This provides direct evidence of the reverse process. At lower temperatures, new bands appeared at $\lambda_{\max}=750$ nm (band C) and $\lambda_{\max}=660$ nm (band D) (Fig. 4b, c).

It is very difficult to assign these spectra unambiguously. From the viewpoint of the canonical electronic structures of BG⁺, it would not be responsible for any of the bands in Fig. 4. On the other hand, the electronic structures of the moiety BGH⁺ can be described as follows:



Therefore, it is likely that one of these bands may be assigned to BGH⁺. Foster and Thomson¹⁸⁾ observed the electronic spectrum of the cation radicals of *N,N,N',N'*-tetramethyl-*p*-phenylenediamine (TMPD) in the vicinity of 600 nm. Nakayama and Suzuki¹⁹⁾ examined the temperature dependence of the spectra of Würster's cation radicals including TMPD⁺, and found that at lower temperatures the absorption band of their dimers appears on the longer wavelength side. If these situations are taken into account, the band B could be assigned to BGH⁺ and the band D to its dimer.

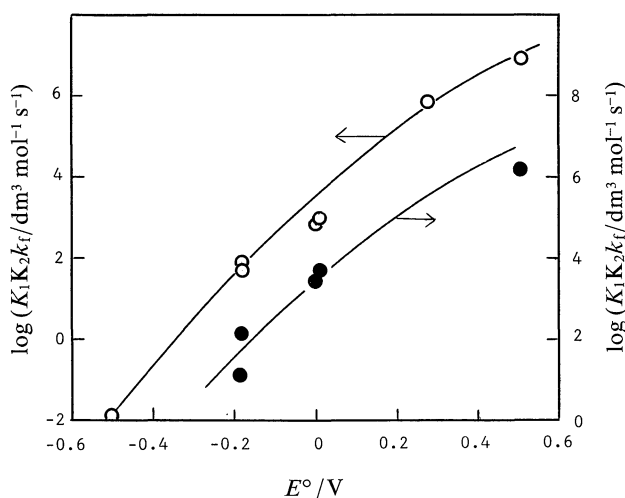


Fig. 6. Correlation between $\log(K_1K_2k_f)$ and the redox potential of *p*-benzoquinones E° ; ●: this work, ○: data cited from Ref. 15.

In order to confirm this, $\text{BGH}^+\text{ClO}_4^-$ was prepared and dissolved in ethanol-rich EPA. The solution was cooled rapidly to -188.5°C . We observed two distinct bands (λ_{max} at 660 and 750 nm). As the temperature was increased (-155°C), the intensity of the band at $\lambda_{\text{max}}=660$ nm decreased, and at the same time, a shoulder appeared in the vicinity of 600 nm. Above -100°C , the band at 660 nm and the shoulder disappeared and only the band on the longer wavelength side assignable to BG^+ survived; the process of BG^+ formation from BGH^+ is not

clear. It is noted that in this system the formation of a CT complex is impossible. Accordingly, the band D observed in the BGH/CA system could be assigned to the dimer of BGH^+ , and the shoulder to BGH^+ . Temperature dependence of the intensity of the band B relative to D, and the band positions are somewhat different from those for the BGH/CA system in usual EPA. This is probably due to solvent effects.

It is recognized that the absorption band due to outer CT complexes between CA and aromatic amines appears in the range of 500–800 nm. For example, the λ_{max} -values are 616 nm for *N,N*-dimethylaniline, 660 nm for MDA (Fig. 5), 680 nm for LCV,¹⁰⁾ 670 nm for LMG,¹¹⁾ and 800 nm for TMPD.¹⁸⁾ In the light of these situations, we can expect the formation of an outer CT complex in the present system, too. Judging from the temperature dependence of the band C, this band could be assigned to an outer CT complex if the assignments of the bands, A, B, and D are correct.

Temperature dependence of the intensities of the above bands is shown in Fig. 7. It was confirmed that the spectral change with temperature took place reversibly. Similar absorption bands and the temperature dependence of their intensities were observed for the $\text{BGH}/2,5\text{-DCQ}$ system, too. Using the data in Fig. 7, together with the Arrhenius parameters (Table 2), and assuming dimer formation, we constructed an approximate energy diagram as shown in Fig. 8. The heat of formation of the dimer agrees with those reported for similar systems (ca. 35 kJ mol^{-1}).¹⁹⁾ The energy levels of usual outer CT complexes are known to be at most 20 kJ mol^{-1} lower than that of the reactants, while the energy level of the proposed CT complex in this study is too low. Therefore, a different character of CT complex seems to be formed in our system. Indeed, the band C is well-characterized (Fig. 4), while the outer CT band is generally very broad (Fig. 5). Recently, we

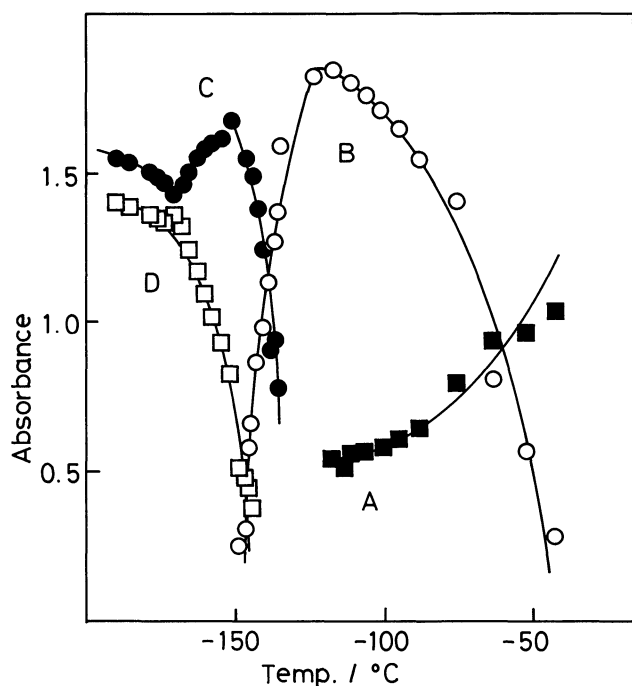


Fig. 7. The change in absorbances at λ_{max} /nm: 730 (band A), 590 (band B), 750 (band C), and 660 (band D) as a function of temperature.

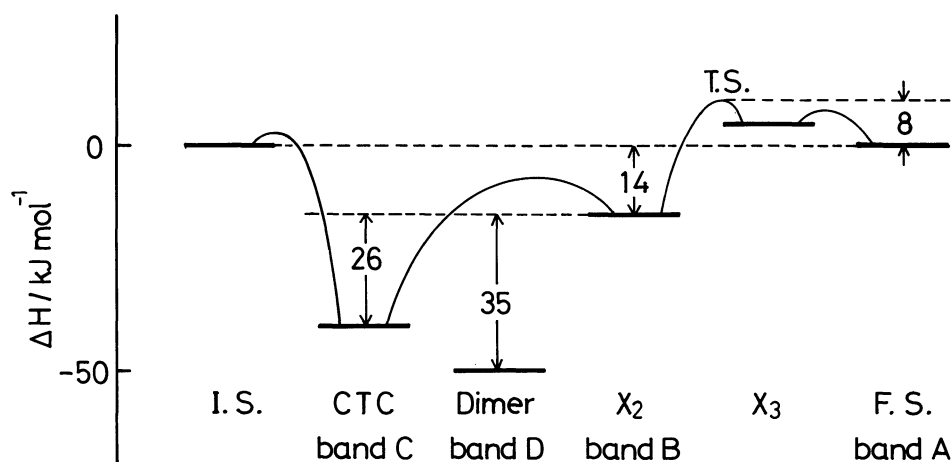


Fig. 8. Approximate energy diagram for the reaction between BGH and CA. X_2 denotes $(\text{BGH}^+ \text{Q}^-)$ and X_3 denotes $(\text{BG}^+ \text{QH}^-)$.

reported that a CT complex was formed between TBPE* and aliphatic amines through hydrogen bonding.²⁰⁾ This CT complex exhibited a well-characterized absorption at ca. $\lambda_{\text{max}}=550$ nm. It has been accepted that hydrogen bonding involves a CT character.^{21,22)} Because of the large electronegative nature of nitrogen atom, the formation of such a type of CT complex is likely. In this CT complex, electron transfer will take place easily through hydrogen bonding followed by the forward and backward H-atom (or proton + electron) oscillations. The heat of hydrogen bond formation may be ca. 20 kJ mol⁻¹. If this value is taken into account for the formation of the above type of CT complex, the energy diagram in Fig. 8 may not be so surprising. The well-characterized structure of band C suggests that this CT complex is "tight".

ESR Spectra. For the BGH/CA system, a singlet ESR spectrum with $g=2.0058$ was obtained in acetone at 25 °C. This can be assigned to the corresponding semiquinone anion radical (Q^{-•}).¹⁰⁾ This radical is comparatively stable, but it decays according to the strict first-order kinetics with $k_{\text{decay}}=1.29 \times 10^{-4} \text{ s}^{-1}$ (25 °C). For the BGH/DDQ system, a quintet ESR spectrum with intensity ratios of 1:2:3:2:1 was obtained. The signal is assignable to the corresponding semiquinone anion radicals.²³⁾ Spin trapping is known to be a powerful method for detecting unstable neutral radicals. 2-Methyl-2-nitrosopropane (MNP) is known as a radical trap. In order to obtain further information for radicals occurring in our systems, we added MNP to the BGH/DDQ system. Figure 9a is the resulting ESR signal. We can easily see that the signal is composed of three kinds of radical species. A quintet near the center is obviously due to the semi-quinone. A triplet with a hyperfine coupling constant (hfcc) of 1.56 mT and $g=2.0057$ can be ascribed to a spin adduct.

Lai and Colter²³⁾ reported that *N*-methyl-acridanyl radical was trapped by MNP in the oxidation reaction of *N*-methylacridan by 2,3-dicyano-1,4-benzoquinone. Since our system is similar to theirs, the trapped radical may be BG[•] rather than QH[•].

The remaining wavy signal spreading over a wide range of the magnetic field (>3 mT) is very weak, but shows a remarkably small hfcc. The g -value was estimated to be about 2.003. The authentic ESR signal of BGH^{•+} obtained by dissolving BGH^{•+} perchlorate in acetone at 25 °C is shown in Fig. 9b. The g -value was calculated to be 2.0030. If these situations and the proposed mechanism are taken into account, the wavy weak signal could be attributed to BGH^{•+}. Kolodny and Bowers²⁴⁾ reported that when acetonitrile solutions of *p*-phenylenediamine (PPD) and DDQ were mixed in a flow system, superimposed ESR signals attributable to PPD^{•+} and DDQ^{-•} were obtained. They found that the

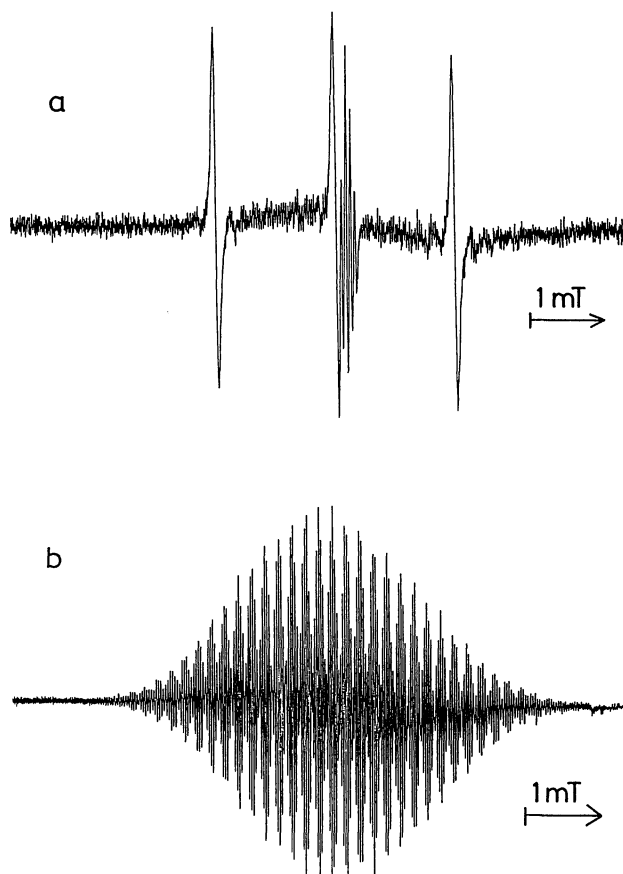


Fig. 9. (a) ESR spectra for the BGH/DDQ system in the presence of MNP in acetonitrile, $[\text{BGH}]_0=1.08$, $[\text{DDQ}]_0=0.27$, $[\text{MNP}]_0=12.9 \text{ mmol dm}^{-3}$. (b) ESR signal of BGH^{•+}.

intensity of the PPD^{•+} signal was much weaker and decayed rapidly. Although the reason is not clear, the weak signal in our case is in line with their observation.

The above findings, together with the spectrophotometric observations, provide direct evidence for the existence of the intermediates, assumed to be formed during the stepwise pathway for the present reaction systems.

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* 2,6-Dibromo-4-[3,5-dibromo-4-hydroxyphenyl](2-ethoxy-carbonylphenyl)methylene]-2,5-cyclohexadien-1-one.

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