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KINETIC STUDIES ON FAST REACTIONS IN SOLUTION VII

The Kinetic Studies on the Reactions of *p*-Benzoquinone and Its Derivatives with Alkoxy Ions

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The fast reactions to produce semiquinone ion radicals by electron transfer from alkoxy ions (RO^-) to *p*-benzoquinone (BQ), 2-methyl-*p*-benzoquinone (MeBQ), 2-chloro-*p*-benzoquinone (ClBQ) and 2-bromo-*p*-benzoquinone (BrBQ) were kinetically studied using the stopped flow apparatus in alcoholic solutions corresponding to the alkoxy ions, by means of the spectrophotometric and ESR methods.

In the reactions of BQ and MeBQ with MeO^- , EtO^- , *n*- PrO^- and with *n*- BuO^- , the corresponding semiquinone ion radicals were first produced. And then it was found that the substitution reactions of alkoxy ion follows consecutively or concurrently, in the reaction of BQ and ClBQ with MeO^- and EtO^- . But in the case of BrBQ, the formation is presumed to be too fast to be detected. The rates of the semiquinone formation is of first order for benzoquinones and also of first order for RO^- in the cases of BQ and ClBQ, but of non-integral order for RO^- in the case of MeBQ. From these results, the reaction scheme was considered assuming a kind of the charge-transfer complex. The activation parameters were obtained, and the reaction rate was discussed in terms of electron affinities of benzoquinones and the influence of Z-value of the solvent.

Introduction

The actions of the charge-transfer complex or the σ -type complex as a reaction intermediate on the organic reaction, especially on the substitution or the addition reaction, are very interesting. The author has already reported on the reaction between a *n*-type electron donor, diethylamine, and trinitrobenzene which is a strong acceptor, and the elementary step to produce a σ -type intermediate was investigated kinetically¹⁾. Moreover, the complete electron transfer reaction was investigated in the previous paper between the halogenanils and alkali iodides in acetone solution²⁾. The formation of the C-T complex and the complete electron transfer reaction are equal in its character but the possibility that the C-T complex can exist as an intermediate in the complete electron transfer process has been considered. And it was elucidated that a kind of the C-T complex is formed as an intermediate in the reaction pathway to produce the semiquinone ion radicals and the reaction rate was discussed in terms of the electron affinity of the halogenanil or the inductive effect of the substituted halogen.

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1) J. Osugi and M. Sasaki, *This Journal*, **37**, 43 (1967)

2) M. Sasaki, *ibid.*, **39**, 27 (1969)

In relation to the previous paper, the author will report in the present paper the reaction of *p*-benzoquinone and its substituted derivatives with alkoxy ions forming the semiquinone ion radicals and alkoxy substituted ones by the electron transfer in alcoholic solutions corresponding to the used alkoxy ions. The reactions of halogenanils with alkoxy ions are too fast to be followed by the stopped flow apparatus constructed by the author. When an alkoxide is dissociated in an alcohol different from that corresponding to the alkoxide, another alkoxy ion is formed from the solvent alcohol and the accurate concentration of the desired alkoxy ion can not be determined, although it is desirable to investigate a series of reactions in the same medium in the view point of reactivity.

p-Benzoquinone are known to undergo several types of reactions including 1,4-additions³⁾, nucleophilic substitutions⁴⁾⁵⁾ and oxidation-reduction reactions⁶⁾. A thorough kinetic study of these reactions had been scarcely reported until Bishop *et al.* reported the displacement of halide from a series 2-halo-3, 5, 6-trimethyl-*p*-benzoquinones by sulfite⁹⁾.

In this work the rates were measured photometrically by means of the stopped flow method and the semiquinones were identified by UV and ESR spectra.

Experimentals

Materials

p-Benzoquinone (BQ); Commercial reagent was recrystallized from acetic acid, mp 116°.

2-Chloro-*p*-benzoquinone (ClBQ); Dry hydrogen chloride gas was passed through the chloroform solution of *p*-benzoquinone⁷⁾. The colorless 2-chlorohydroquinone was precipitated, which was then dissolved in water and oxidized with concentrated sulfuric acid and potassium dichromate⁸⁾. The yellow 2-chloro-*p*-benzoquinone was recrystallized from dilute alcoholic aqueous solution, which was identified compared with IR spectrum of a literature⁹⁾, mp 57°.

2-Bromo-*p*-benzoquinone (BrBQ)¹⁰⁾; It was prepared by oxidising 2-bromohydroquinone which was obtained by passing dry gaseous hydrogen bromide through the chloroform solution of *p*-benzoquinone. The aqueous solution of ferric chloride used as an oxidant containing BrBQ was extracted with carbon disulfide, and after complete evaporation of the solvent the reddish yellow compound was recrystallized several times from petroleum ether, mp 56°.

2-Methyl-*p*-benzoquinone (MeBQ) K & K Lab. reagent was recrystallized several times from aqueous solution, mp 69°.

Methyl and ethyl alcohols were purified by distillation using magnesium metal and iodine, other

3) T. H. James and A. Weissberger, *J. Am. Chem. Soc.*, **61**, 442 (1937); R. H. Thomson, *J. Org. Chem.*, **16**, 1081 (1951); A. Blackhall and R. H. Thomson, *J. Chem. Soc.*, **1953**, 1138; W. Ried and R. Dietrich, *Ann.*, **649**, 57 (1961)

4) H. Hopff and Y. R. Schweizer, *Helv. Chim. Acta*, **45**, 313 (1962)

5) C. A. Bishop, R. F. Porter and L. K. J. Tong, *J. Am. Chem. Soc.*, **85**, 3991 (1963)

6) J. M. Snell and A. Weissberger, *ibid.*, **61**, 450 (1939); J. E. LuValle, *ibid.*, **74**, 2970 (1952)

7) T. H. Clark, *Am. J. Chem.*, **14**, 553 (1892)

8) S. Levy and G. Schultz, *Ann. Chem.*, **210**, 133 (1881)

9) J. F. Bagli, *J. Am. Chem. Soc.*, **84**, 117 (1962)

10) E. Sarauw, *Ann. Chem.*, **209**, 93 (1881)

alcohols being distilled several times after being dried with anhydrous calcium sulfate. The water content involved in each alcohol was titrated by means of Karl-Fischer's method, which was estimated to be less than 0.02 wt% for methyl and ethyl alcohols and less than 0.07 wt% for the other alcohols.

The alkoxide solution was prepared by acting sodium metal into the corresponding alcohol, the concentration of which was determined by titrating with the standard sulfuric acid using bromthymol blue as an indicator.

Apparatus and procedure

As the rates of formation and/or disappearance of semiquinone ion radicals are rapid, the rates were measured photometrically at $443\text{ m}\mu$ using a filter, by means of the stopped flow method.^{11,12} The semiquinone ion radicals in alcohols were identified by ESR spectra in the continuous flow systems, using a glass tube of 0.2 mm inner diameter. The reaction time in the continuous flow system was calculated from the dead space between the mixing point of two reacting solutions and the observing point where the center of microwave cavity was placed. The fluid drive was operated by compressing the solution in one side and by sucking the fluid in the outlet. All measurements were performed in deaerated solutions, the dissolved oxygen being excluded by bubbling dry nitrogen gas.

In this work the fast formation reaction of semiquinone ion radicals was only investigated and the slow reactions followed were not discussed. The rates were obtained by averaging the results of several runs for one sample.

Results

BQ-MeO⁻, EtO⁻, *n*-PrO⁻ and *n*-BuO⁻ systems

The change of the electronic spectrum of the mixture of BQ and EtO⁻ in ethyl alcohol after long (still short) time was shown in Fig. 1. The analogous behaviors have been observed with respect to MeO⁻, *n*-PrO⁻ and *n*-BuO⁻. The absorption bands appear at shorter wave length, $390\sim 430\text{ m}\mu$, than those of semiquinones of halogenanils or of *p*-benzosemiquinone ion radical which was observed by Eigen *et al.* and are between $410\sim 460\text{ m}\mu$ ¹¹. In general, the charge-transfer bands of the C-T

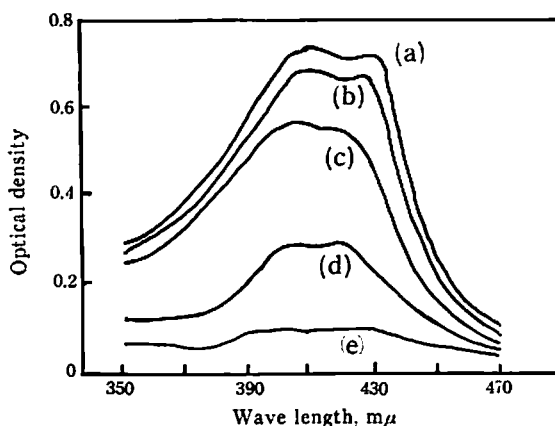


Fig. 1 The change of electronic spectra with time in BQ-EtO⁻ system [BQ]₀ = 1.0×10^{-2} (mole/l), [EtO⁻]₀ = 1.0×10^{-3} (mole/l), reaction time (sec); (a) 45 (b) 70 (c) 120 (d) 240 (e) 600

11) H. Diebler, M. Eigen and P. Matthies, *Z. Naturforsch.*, **16 b**, 629 (1961)

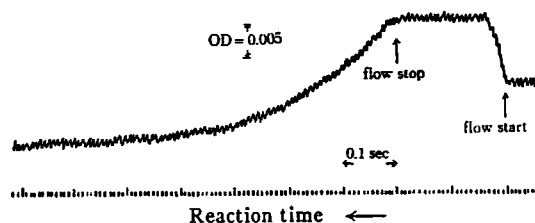


Fig. 2 The change of optical density at 443 mμ in BQ-EtO⁻ system at 20°C
 $[BQ]_0 = 5 \times 10^{-5}$ (mole/l)
 $[EtO^-]_0 = 6.8 \times 10^{-3}$ (mole/l)

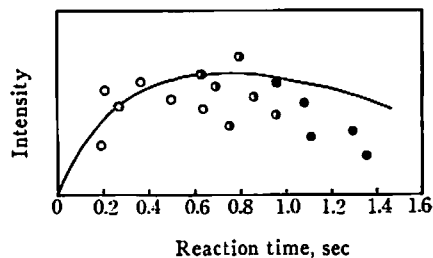


Fig. 3 The changes of optical density at 443 mμ (solid line) and ESR spectra when $[BQ]_0 = 5 \times 10^{-3}$ (mole/l) and $[EtO^-]_0 = 1.3 \times 10^{-2}$ (mole/l)
 ○: SQ⁻ (Fig. 4 I)
 ●: SQ⁻ + (EtO)₂SQ⁻ (Fig. 4 II)
 ●: (EtO)₂SQ⁻ (Fig. 4 III)

complexes are strongly influenced by the electron affinity of the acceptor and the C-T complex composed of the acceptor having weaker electron affinity or electron donative substituents gives the absorption bands at shorter wave length¹²⁾.

The examples of the changes of optical densities at 443 mμ with the reaction time were shown in Figs. 2 and 3. When the concentration of EtO⁻ is small, the change of optical density is simple, although when it is high, the slight decrease of optical density was observed after long time (solid line in Fig. 3).

The ESR spectra in the flow system were illustrated in Fig. 4 in the case of BQ-EtO⁻ in alcoholic solution where the variations of optical density and the ESR spectrum were compared each other. It was found that under the experimental condition, $[BQ]_0 = 5 \times 10^{-3}$ (mole/l) and $[EtO^-]_0 = 1.3 \times 10^{-2}$ (mole/l), the species corresponding to Fig. 4 (I) is only observed until 0.6 sec, whose intensity is varied according to the optical density. The spectrum deforms from (I) to (II) and at last to (III) with the reaction time, and the decrease of optical density after about 1 sec corresponds to the decrease of (III), although the measurement of ESR signal intensity is not so accurate as to be treated quantitatively. The species giving the ESR spectrum, Fig. 4 (I), is identified to be *p*-benzosemiquinone ion radical (SQ⁻), the quintet of which is caused by the four equivalent protons of the ring. The species, Fig. 4 (III), can be identified to be 2,5-diethoxy-*p*-benzosemiquinone ion radical ((EtO)₂SQ⁻) which gives the main quintet spectrum line due to the four equivalent methylene protons of side chains. The spectrum, Fig. 4 (II), is reasonably understood to be the superimposed of the species, SQ⁻ and (EtO)₂SQ⁻ in various ratios. And so the observed electronic spectra shown in Fig. 1 are considered to represent (EtO)₂SQ⁻ and the absorption bands at shorter wave length than that of SQ⁻ may be understood considering the weaker electron affinity due to the electron donative ethoxy substituent.

12) G. Briegleb, "Elektronen-Donator-Acceptor-Komplexe", Springer-Verlag, Berlin (1961)

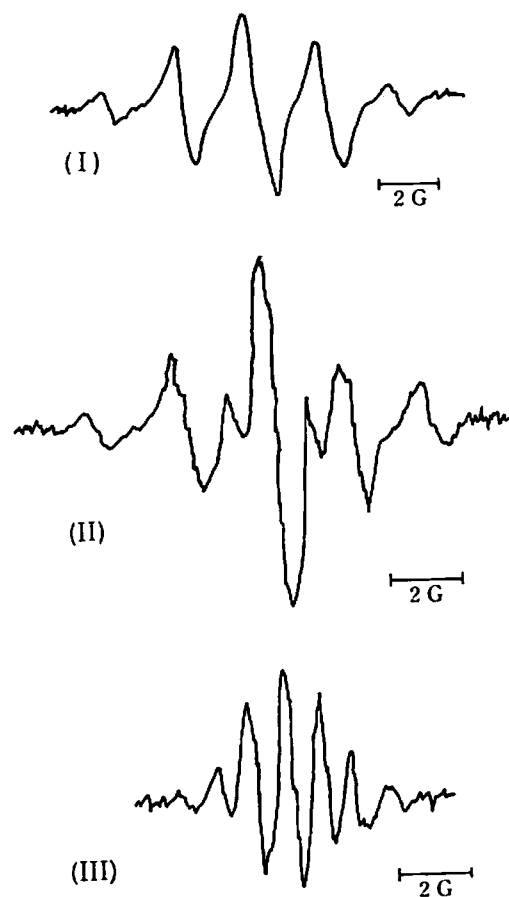


Fig. 4 The change of ESR spectra in BQ-EtO⁻ system with time [BQ]₀ = 5×10^{-3} (mole/l), [EtO⁻]₀ = 1.3×10^{-2} (mole/l) reaction time (sec); I: 0.4 II: 0.8 III: 1.4

In the case of BQ-MeO⁻ system, the analogous results were obtained, of course 2,5-dimethoxy-*p*-benzosemiquinone (MeO)₂SQ⁻ resulted in stead of (EtO)₂SQ⁻. But in the BQ-*n*-PrO⁻ and the BQ-*n*-BuO⁻ systems, only SQ⁻ was found and the species attributable to the corresponding alkoxy substituted semiquinone ion radicals could not be found.

Table 1 The proton coupling constants of *p*-benzosemiquinone ion radicals

No.		number of line	coupling constants (gauss)	
			ring proton	side chain proton
1	SQ ⁻	5	2.31 (2.33 ¹³⁾)	
2	(EtO) ₂ SQ ⁻	5		1.20 (1.17 ¹⁴⁾)
3	(MeO) ₂ SQ ⁻	7	— (0.30 ¹⁴⁾)	1.05 (1.05 ¹⁴⁾)
4	ClSQ ⁻	4	$a_3 = 2.43$ (2.453 ¹⁵⁾) $a_5 = a_6 = 2.25$ (2.208 ¹⁵⁾)	
5	MeSQ ⁻	21	$a_3 = 1.66$ (1.73 ¹³⁾) $a_5 = a_6 = 2.51$ (2.48 ¹³⁾)	2.01 (2.02 ¹³⁾)

The coupling constants of *p*-benzosemiquinones identified were listed on Table 1 together with ClSQ^- and MeSQ^- which will be described later.

As mentioned above, the change of the optical density at $443\text{ m}\mu$ does not always represent the change of SQ^- , but at the initial stage, at least, it is safely considered to represent SQ^- .

As it was too difficult to reproduce the ESR signal so as to be treated quantitatively, the rate data were obtained only from the photometric measurements at $443\text{ m}\mu$. When the initial concentration of alkoxy ion, $[\text{RO}^-]_0$ is low in the range satisfying the condition, $[\text{BQ}]_0 \ll [\text{RO}^-]_0$, the decreasing rate of optical density is sufficiently slow and the rate of semiquinone ion radical formation can be well represented by the pseudo-first order rate equation with respect to BQ, as shown in Fig. 5. When $[\text{RO}^-]_0$ is so high that a maximum appears in the curve representing the time-dependency of the optical density, Guggenheim's first order plot¹⁶⁾ was applied in the time range until the maximum appears. The calculated slopes of these plots were represented by S , whose dependency on $[\text{RO}^-]_0$

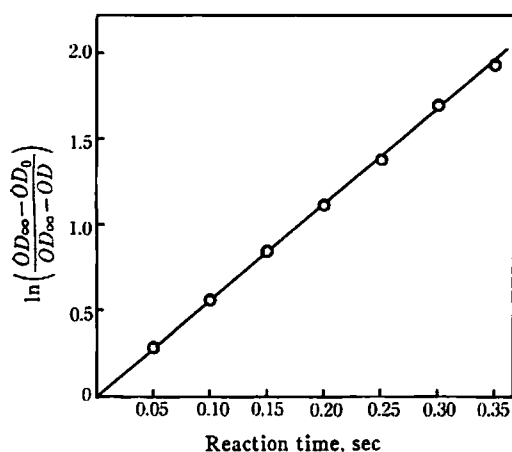


Fig. 5 Pseudo-first order plot of optical density at $443\text{ m}\mu$ in BQ-EtO $^-$ system at 20°C

$[\text{BQ}]_0 = 5 \times 10^{-5}$ (mole/l),
 $[\text{EtO}^-]_0 = 6.8 \times 10^{-3}$ (mole/l)

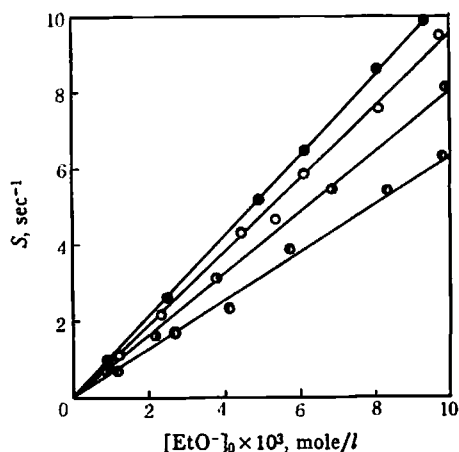


Fig. 6 The dependency of the pseudo-first order rate constant, S , on $[\text{EtO}^-]_0$ in BQ-EtO $^-$ system

○: 10°C ◐: 20°C
 ○: 30°C ●: 40°C

was illustrated in Figs. 6, 7 and 8, for the BQ-EtO $^-$, the BQ-*n*-PrO $^-$ and the BQ-*n*-BuO $^-$ systems, respectively. In every case a straight line passing through the origin was obtained, the following relation resulted.

$$S = k_2[\text{RO}^-]_0 \quad (1)$$

And so,

$$\frac{d[\text{SQ}^-]}{dt} = k_2[\text{RO}^-]_0[\text{BQ}]. \quad (2)$$

13) B. Venkataraman and G. K. Fraenkel, *J. Chem. Phys.*, **23**, 588 (1955)

14) Y. Matsunaga and C. A. McDowell, *Can. J. Chem.*, **38**, 1158 (1960)

15) B. Venkataraman, B. G. Segal and G. K. Fraenkel, *J. Chem. Phys.*, **30**, 1006 (1959)

16) E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926)

The rate is of first order for BQ and RO^- , respectively. The second order rate constants were given on Table 2 for each system at various temperatures, but for the BQ- MeO^- system, the crude value obtained only at 20°C was given because the data were inaccurate for too small displacement of the optical density.

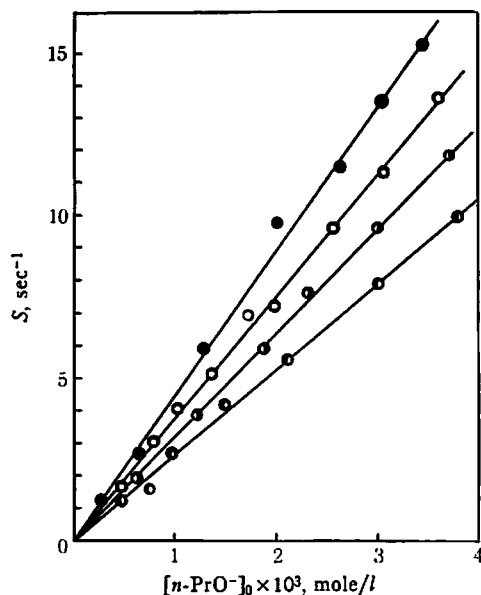


Fig. 7 The dependency of the pseudo-first order rate constant, S , on $[\text{n-PrO}^-]_0$ in BQ- n-PrO^- system

○: 20°C ◐: 30°C
○: 40°C ●: 50°C

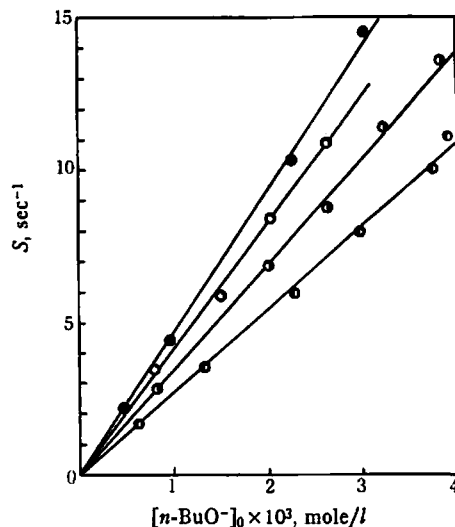


Fig. 8 The dependency of the pseudo-first order rate constant, S , on $[\text{n-BuO}^-]_0$ in BQ- n-BuO^- system

○: 20°C ◐: 30°C
○: 40°C ●: 50°C

Table 2 The second order rate constants for semiquinone ion radical formation (k_2 , $\text{l} \cdot \text{mole}^{-1} \cdot \text{sec}^{-1}$)

RO^-	Temperature (°C)				
	10	20	30	40	50
MeO^-		500			
EtO^-	680	813	980	1,770	
n-PrO^-		2,600	3,170	3,870	4,500
n-BuO^-		2,890	3,450	4,150	4,700

BQ- iso-PrO^- , iso-BuO^- and sec-BuO^- systems

In these systems SQ^- was observed, but the rate was so fast that the accurate measurement was impossible in the concentration range where the pseudo-first order treatment was allowed. When the concentration of $[\text{RO}^-]_0$ is about 2×10^{-3} (mole/l), the observed half time of the reaction is about 10 msec, which is the limit of our apparatus. The crude values at 20°C were listed on Table 5.

MeBQ-EtO⁻, *n*-PrO⁻ and *n*-BuO⁻ systems

The electronic spectra of the mixture of MeBQ and EtO⁻ in alcoholic solution were almost analogous to that in Fig. 1. The ESR spectrum of the MeBQ-EtO⁻ system in flow showed one species whose intensity was increased with time for a few seconds under suitable conditions. The change of the optical density at 443 m μ with time corresponds well to the change of intensity of ESR spectrum

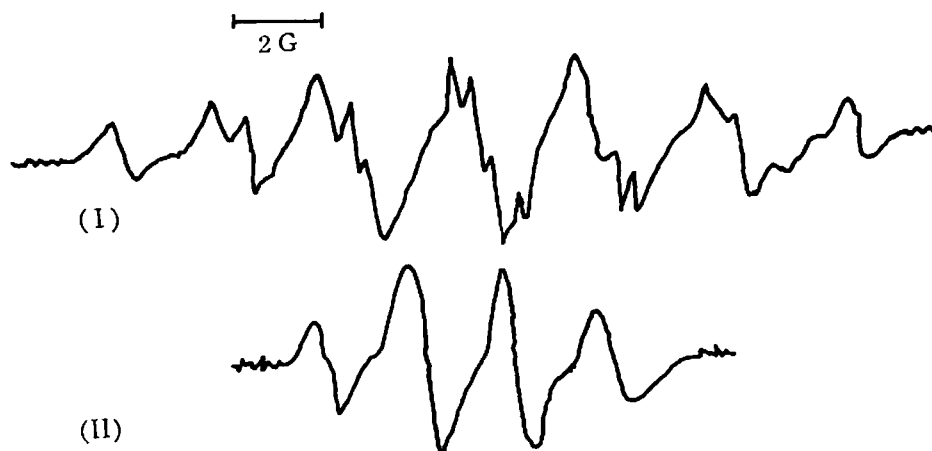


Fig. 9 ESR spectra in MeBQ-EtO⁻ and ClBQ-EtO⁻ system

I: [MeBQ]₀ = 5.0×10^{-3} (mole/l), [EtO⁻]₀ = 5.0×10^{-2} (mole/l),
1.0 sec after mixing

II: [ClBQ]₀ = 5.0×10^{-3} (mole/l), [EtO⁻]₀ = 2.0×10^{-3} (mole/l),
0.1 sec after mixing

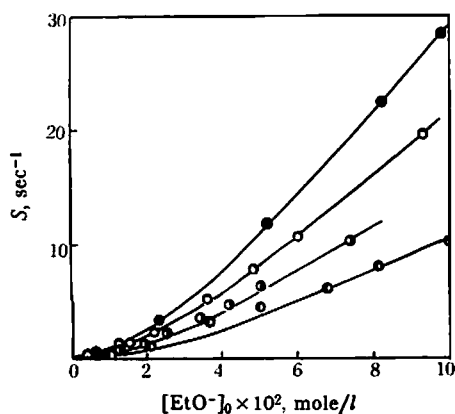


Fig. 10 The dependency of the pseudo-first order rate constant, *S*, on [EtO⁻]₀ in MeBQ-EtO⁻ system

●: 10°C ●: 20°C
○: 30°C ●: 40°C

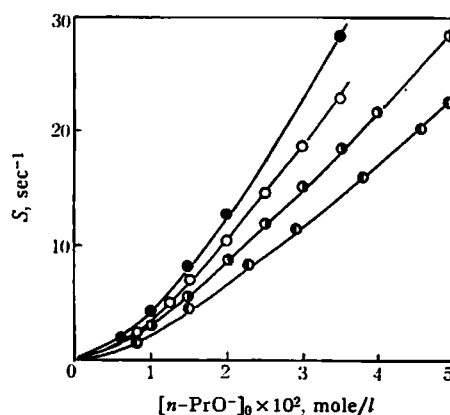


Fig. 11 The dependency of the pseudo-first order rate constant, *S*, on [n-PrO⁻]₀ in MeBQ-*n*-PrO⁻ system

●: 10°C ●: 20°C
○: 30°C ●: 40°C

(Fig. 9 (I)), which is identified to be 2-methyl-*p*-benzosemiquinone ion radical (MeSQ^-) (Table 1, No. 5). The ethoxy-substituted semiquinone ion radical was not found for a few seconds, which shows that MeSQ^- is rather stable compared with the other semiquinone ion radicals. The change of the optical density with time was found to obey the first order rate equation under the condition, $[\text{MeBQ}]_0 \ll [\text{EtO}^-]_0$. The slope of the pseudo-first order rate constant represented by S depends on $[\text{EtO}^-]_0$ as graphed in Fig. 10. In the lower concentration of $[\text{EtO}^-]_0$ the S 's are not so significantly varied but they are varied almost linearly in the higher concentration. The analogous results were obtained in the cases of $\text{MeBQ-}n\text{-PrO}^-$ and $\text{MeBQ-}n\text{-BuO}^-$ as illustrated in Figs. 11 and 12.

In contrast to the case of the BQ-RO^- system where the formation of SQ^- may be simple, the behavior of the MeBQ-RO^- system suggests that the formation of MeBQ^- is composed of some elementary reaction steps. As described in the later section for the cases of ClBQ and BrBQ , the order of the rates of corresponding semiquinone ion radical formation is $\text{MeBQ} < \text{BQ} < \text{ClBQ} < \text{BrBQ}$ and an intermediate, as in the case of halogenanils-alkali iodides systems, that is a kind of the C-T complex, may be produced.

ClBQ-EtO^- and BrBQ-EtO^- systems

The ESR spectrum in the case of ClBQ-EtO^- was drawn in Fig. 9 (II) after 0.1 sec, but it de-

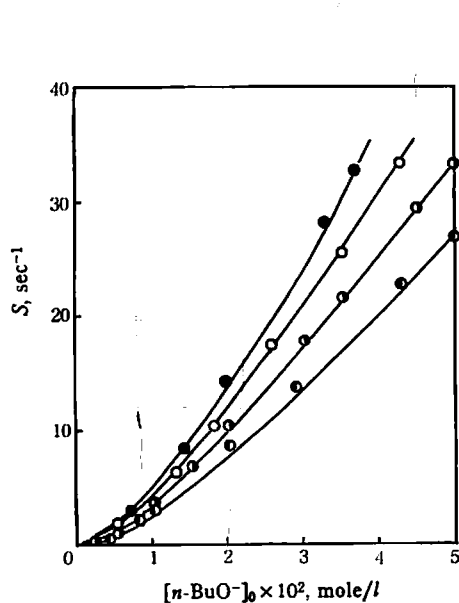


Fig. 12 The dependency of the pseudo-first order rate constant, S , on $[\text{n-BuO}^-]_0$ in $\text{MeBQ-}n\text{-BuO}^-$ system

○: 10°C ◐: 20°C
○: 30°C ●: 40°C

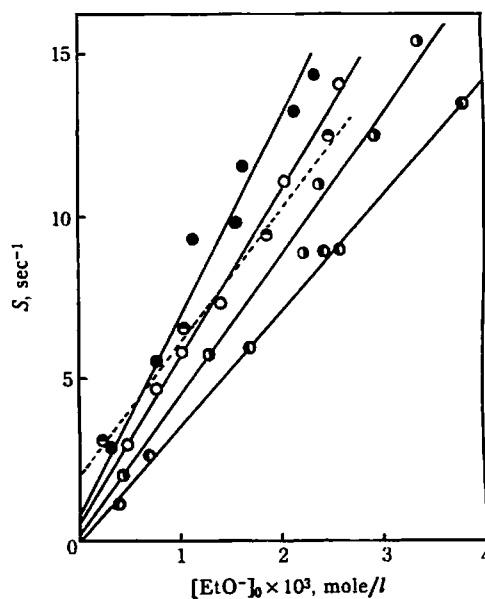


Fig. 13 The dependency of the pseudo-first order rate constant, S , on $[\text{EtO}^-]_0$ in ClBQ-EtO^- and BrBQ-EtO^- systems

ClBQ-EtO^- : —○— 10°C,
—◐— 20°C,
—○·— 30°C,
—●— 40°C
 BrBQ-EtO^- : ...◐... 20°C

forms soon into that in Fig. 4 (III). The radical corresponding to Fig. 9 (II) is identified to be 2-chloro-*p*-benzosemiquinone ion radical (CISQ⁻) as shown in Table 1.

The change of the optical density at 443 m μ is well represented by first order rate equation with respect to MeBQ. The pseudo-first order rate constant, *S*, depends on [EtO⁻]₀ in a way shown in Fig. 13, where it is seen that at lower temperature a straight line passes through the origin but at higher temperature lines do not pass through the origin. On the other hand, at each temperature in the case of BrBQ-EtO⁻, the dependency of *S* on [EtO⁻]₀ is linear, not passing through the origin (Fig. 13), though the change of the optical density well obeys first order rate equation. The ESR spectrum of the BrBQ-EtO⁻ system in flow showed only that corresponding to (EtO)₂SQ⁻ and not BrSQ⁻ in the reaction time longer than 0.03 sec. So it will be concluded that the optical density at 443 m μ represents not only CISQ⁻ and/or BrSQ⁻, but also (EtO)₂SQ⁻ and that the straight lines in Fig. 13 which do not pass through the origin is caused by the initial fast formation of CISQ⁻ or BrSQ⁻ followed by the formation of (EtO)₂SQ⁻. So it will be concluded that the slope of a plot of *S* against [EtO⁻]₀ represents the dependency of rate of (EtO)₂SQ⁻ formation on [EtO⁻]₀, especially in the case of BrBQ-EtO⁻. In the case of ClBQ-EtO⁻, the slope in Fig. 13 can be regarded approximately as the rate constant of CISQ⁻ formation.

Table 3 The second-order rate constants of semiquinone ion radical formations in ClBQ-EtO⁻ and BrBQ-EtO⁻ systems

	Temperature (°C)			
	10	20	30	40
ClBQ ^{a)}	3,570	4,300	5,100	6,000
BrBQ ^{b)}		4,100		

a) corresponding to CISQ⁻ formation reaction

b) corresponding to (EtO)₂SQ⁻ formation reaction

Discussions

At room temperature *p*-benzosemiquinone ion radicals are unstable and *p*-benzoquinones undergo many other reactions, *i.e.* addition^{9) 17)} and substitution reaction^{5) 17) 18)}, especially in acidic solutions. There exist several equilibria between *p*-benzoquinones, semiquinones, singly ionized hydroquinone ions and doubly ionized hydroquinones¹⁹⁾ and semiquinone ion radicals can be detected in alkaline aqueous solution^{20) 21)}.

Although *p*-benzoquinones undergo various reactions in solution, *p*-benzoquinone and its methyl-, chloro and bromo substituted derivatives may react with alkoxy ions in the corresponding alcohols according to the following reaction schemes, as elucidated by electronic and ESR spectra, especially

17) C. A. Bishop and L. K. J. Tong, *Tetrahedron Letters*, **41**, 3043 (1964)

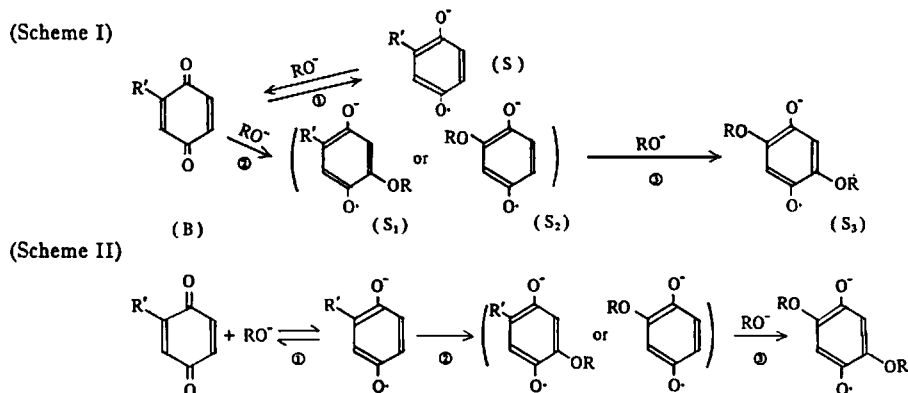
18) Y. Ogata, Y. Sawaki and S. Gotoh, *J. Am. Chem. Soc.*, **90**, 3469 (1968)

19) C. A. Bishop and L. K. J. Tong, *ibid.*, **87**, 501 (1965)

20) I. Yamazaki and L. H. Piette, *ibid.*, **87** 986 (1965)

21) B. Venkataraman and G. K. Fraenkel, *ibid.*, **77**, 2707 (1955)

when $\text{RO}^- = \text{MeO}^-$ and EtO^- .



If $\text{R}' = \text{Me}$, the semiquinone (S) was only found and if $\text{R}' = \text{H}$ or Cl , (S) and diethoxy-substituted semiquinone ion radical (S_3) was also found. The intermediate (S_1) or (S_2) was not found in either case, but it will be reasoned by the assumption that ② is slow and ③ is fast. When $\text{RO}^- = n\text{-PrO}^-$ or $n\text{-BuO}^-$, the semiquinones (S_1), (S_2) and (S_3) were not found but only (S) was found.

BQ-MeO⁻, EtO⁻, n-PrO⁻ and n-BuO⁻ systems

The rate of SQ^- formation is of first order for both BQ and RO^- . Though the alkyl peroxides (ROOR) can not be detected, the reaction may take place according to the one electron transfer from RO^- to BQ²²⁾.

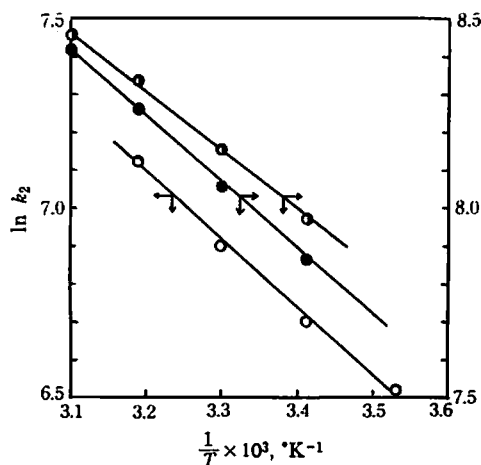


Fig. 14 The Arrhenius plots of k_2 in BQ- RO^- systems

- : BQ-EtO⁻
●: BQ-n-PrO⁻
◐: BQ-n-BuO⁻

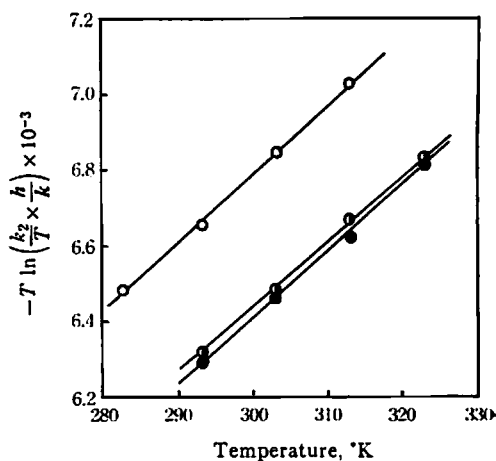


Fig. 15 The plots according to equation (6) in BQ- RO^- systems

- : BQ-EtO⁻
◐: BQ-n-PrO⁻
●: BQ-n-BuO⁻

22) R. W. Brandon and E. A. C. Lucken, *J. Chem. Soc.*, 1961, 4273



The second-order rate constant, k_2 , was given on Table 2 and the energies of activation and the entropies of activation were calculated according to equations (5) and (6) as shown in Figs. 14 and 15, and the numerical values were given on Table 5.

$$\frac{d \ln k_2}{dT} = \frac{\Delta E^\ddagger}{RT^2} \quad (5)$$

$$T \ln \left(\frac{k_2}{T} \times \frac{h}{k} \right) = \frac{\Delta S^\ddagger}{R} T - \frac{\Delta H^\ddagger}{R} \quad (6)$$

MeBQ-EtO⁻, *n*-PrO⁻ and *n*-BuO⁻ system

The rate of MeSQ⁻ formation is of first order with respect to MeBQ, but is of non-integral order with respect to RO⁻ in contrast to the case of the BQ-RO⁻ system. In this case also the analogous reaction scheme to the semiquinone ion radical formation of halogenanils may be considered, that is,

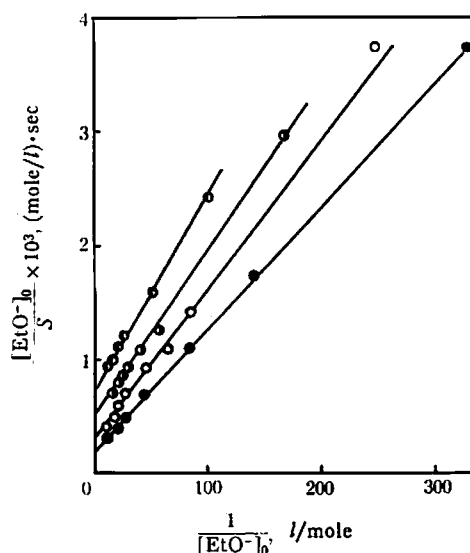
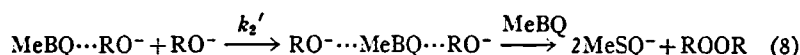


Fig. 16 The dependency of the pseudo-first order rate constant, S , on $[\text{EtO}^-]_0$ according to equation (12) in MeBQ-EtO⁻ system

● : 10°C ◐ : 20°C
○ : 30°C ● : 40°C

where MeBQ \cdots RO⁻ or RO⁻ \cdots MeBQ \cdots RO⁻ represents a kind of the C-T complex as an intermediate. If reaction (7) is fast and the step assigned to k_2' is rate determining, the following equations can be deduced.

$$\frac{d[\text{MeSQ}^-]}{dt} = \frac{k_2' K [\text{RO}^-]_0^2}{1 + K [\text{RO}^-]_0} ([\text{MeSQ}^-]_\infty - [\text{MeSQ}^-]) \quad (9)$$

$$-\ln \left(\frac{[\text{MeSQ}^-]_\infty - [\text{MeSQ}^-]}{[\text{MeSQ}^-]_\infty - [\text{MeSQ}^-]_0} \right) = \frac{k_2' K [\text{RO}^-]_0^2}{1 + K [\text{RO}^-]_0} t \quad (10)$$

So the pseudo-first order rate constant, S , in Figs. 10, 11 and 12 can be expressed by equations (11) and (12).

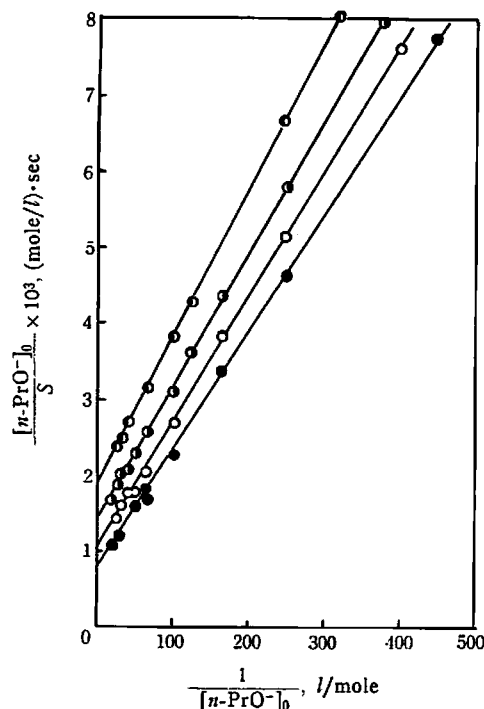


Fig. 17 The dependency of the pseudo-first order rate constant, S , on $[n\text{-PrO}^-]_0$ according to equation (12) in MeBQ- $n\text{-PrO}^-$ system

●: 10°C ◐: 20°C
○: 30°C ●: 40°C

$$S = \frac{k_2' K [\text{RO}^-]_0^2}{1 + K [\text{RO}^-]_0} \quad (11)$$

$$\frac{[\text{RO}^-]_0}{S} = \frac{1}{k_2'} + \frac{1}{k_2' K} \times \frac{1}{[\text{RO}^-]_0} \quad (12)$$

The results shown in Figs. 10~12 can be expressed by equation (12) over a wide range of $1/[\text{RO}^-]_0$ as illustrated in Figs. 16, 17 and 18. The numerical values of k_2' and K could be obtained from the intercepts and the slopes in these figures and were put on Table 4.

From the dependence of the rate constant, k_2' , on temperature as shown in Figs. 19 and 20, the activation quantities were calculated according to equations (5) and (6). The enthalpy and entropy changes accompanying pre-equilibrium (7) were calculated according to equation (13), as shown in Fig. 21, and the numerical values were put together on Table 5.

$$\ln K = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad (13)$$

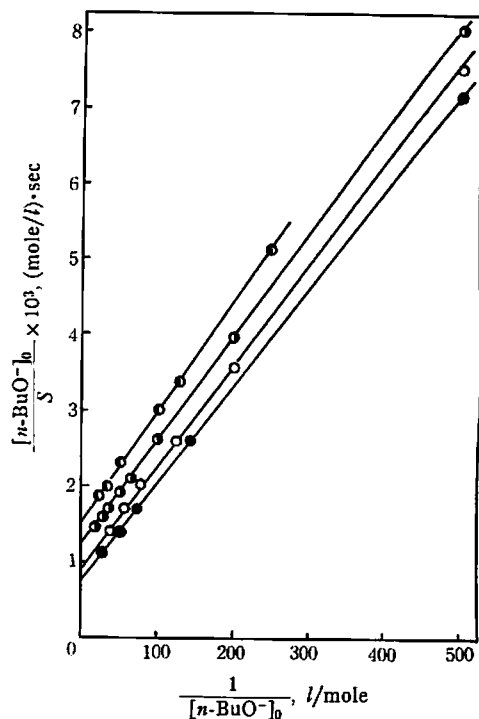
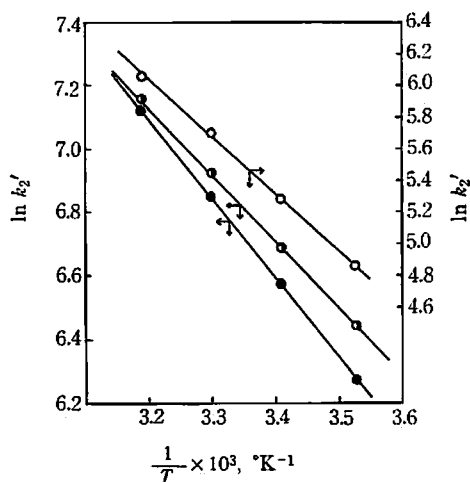


Fig. 18 The dependency of the pseudo-first order rate constant, S , on $[n\text{-BuO}^-]_0$ according to equation (12) in MeBQ- $n\text{-BuO}^-$ system

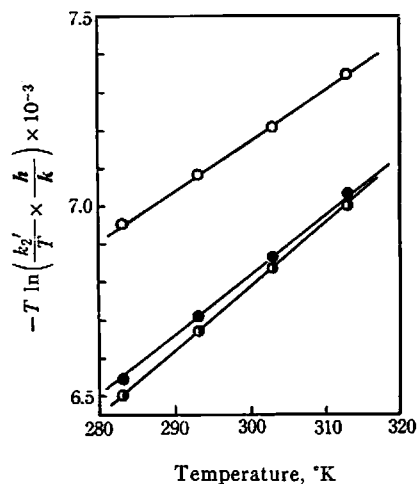
●: 10°C ◐: 20°C
○: 30°C ●: 40°C

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Fig. 19 The Arrhenius plots of k_2' in MeBQ-RO⁻ system

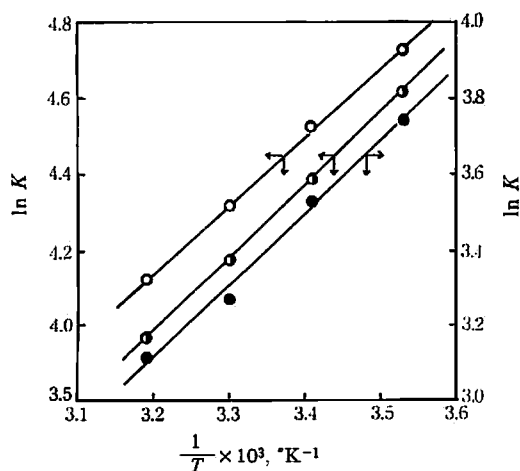
○ : MeBQ-EtO⁻
 ● : MeBQ-*n*-PrO⁻
 ◐ : MeBQ-*n*-BuO⁻

Fig. 20 The plots according to equation (6) in MeBQ-RO⁻ system

○ : MeBQ-EtO⁻
 ● : MeBQ-*n*-PrO⁻
 ◐ : MeBQ-*n*-BuO⁻

Table 4 The second order rate constants, k_2' , and the pre-equilibrium constants, K , for MeSQ⁻ formation reactions in MeBQ-RO⁻ systems

RO ⁻	Temp. (°C)	k_2' (l·mole ⁻¹ ·sec ⁻¹)				K (l·mole ⁻¹)			
		10	20	30	40	10	20	30	40
EtO ⁻		129	195	295	419	42.7	34.9	26.0	22.7
<i>n</i> -PrO ⁻		530	715	942	1,240	100	80.0	64.8	52.7
<i>n</i> -BuO ⁻		626	805	1,010	1,270	112	91.0	75.1	61.9

Fig. 21 The dependency of the pre-equilibrium constant, K , on temperature in MeBQ-RO⁻ systems

● : MeBQ-EtO⁻
 ◐ : MeBQ-*n*-PrO⁻
 ○ : MeBQ-*n*-BuO⁻

If the reaction scheme like (7) and (8) is applied to the BQ-RO⁻ system, the pseudo-first order rate constant, S , is represented by equation (14) under the condition, $K[\text{RO}^-]_0 \gg 1$.

$$S = k_2'[\text{RO}^-]_0 \quad (14)$$

So k_2 in equation (1) is considered to be equivalent to k_2' and it can be reasonably concluded that the reaction mechanism in the BQ-RO⁻ system is not different from that in the MeBQ-RO⁻ system, but the case where the condition, $K[\text{RO}^-]_0 \gg 1$, is allowed in the general mechanism as expressed in (7) and (8). The condition mentioned above may be allowed in BQ-RO⁻, because the electron affinity of BQ is higher than that of MeBQ and pre-equilibrium (7) may shift greatly to the right hand side.

CIBQ-EtO⁻ and BrBQ-EtO⁻ systems

It has been mentioned that the formation of ClSQ⁻, especially of BrSQ⁻, is very fast and that the plot of S against $[\text{RO}^-]_0$ does not pass through the origin. And it has been suggested that SQ⁻ and XSQ⁻ (X=Cl, Br) may be formed according to either scheme (I) or (II) and that the distinguishment between them is impossible in the cases of BQ and MeBQ. If the plot in Fig. 13 is represented for (EtO)₂SQ⁻ formation in the case of BrBQ, the rate is obviously of first order with respect to EtO⁻ and scheme (I) may be favored rather than scheme (II) because second order dependency is expected when the reaction takes place according to scheme (II).

Bishop *et al.* have thoroughly investigated the displacement reaction of halide from 2-halo-3, 5, 6-trimethyl-*p*-benzoquinones by sulfite and found the order of displacement rate is I⁻ > Br⁻ > Cl⁻ in acidic solution²³. Considering these facts, the alkoxy-substituted semiquinone ion radicals are not always formed consecutively but may be produced concurrently, though in any case the semiquinone ion radicals corresponding to the parent benzoquinones are much faster formed. In the case of CIBQ, the plot in Fig. 13 representing for ClSQ⁻ formation, the activation quantities were calculated and listed on Table 5.

The electron affinities of *p*-benzoquinones²³ are given at the bottom in Table 5. The dielectric constants and the Z -values as a measure of polarity signifying the solvent-solute specific interaction²⁴ are also given.

With respect to the effect of alkoxy ions, the order of rate of semiquinone ion radical formation is *iso*-PrO⁻ > *iso*-BuO⁻ \approx *sec*-BuO⁻ > *n*-BuO⁻ > *n*-PrO⁻ > EtO⁻ > MeO⁻. The order of dielectric constants is MeOH > EtOH > *n*-PrOH > *iso*-PrOH > *iso*-BuOH > *n*-BuOH > *sec*-BuOH and the reaction rate is faster with decreasing dielectric constant only for normal chain alcohols but not for side-chain alcohols. On the other hand, the Z -value is in the order, MeOH > EtOH > *n*-PrOH > *n*-BuOH > *iso*-PrOH > *iso*-BuOH and the reaction rate is well represented in terms of the Z -value. The rate is faster with decreasing Z -value, which is related to the extent to which the transition state in the electron transfer process is stabilized by the rearrangement of solvent^{25, 26}. Larger is the Z -value, the specific sol-

23) K. M. C. Davis, P. R. Hammond and M. E. Poever, *Trans. Faraday Soc.*, **61**, 1516 (1965)

24) E. M. Kosower, *J. Am. Chem. Soc.*, **80**, 3253 (1958)

25) E. M. Kosower, *J. Chim. Phys.*, **61**, 230 (1964)

26) E. M. Kosower, "Progress in Physical Organic Chemistry, vol 3", p. 81, Interscience Pub. Inc., New York, London and Sydney (1965)

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Table 5 Kinetic and thermodynamic quantities accompanying the semiquinone ion radical formation reactions

RO ⁻	ϵ^a	Z ^a		MeBQ	BQ	CIBQ	BrBQ
MeO ⁻	32.6	83.6	k_2 (l·mole ⁻¹ ·sec ⁻¹) ^b		500		
EtO ⁻	24.3	79.6	k_2	195	813	4,300	4,100 ^c
			ΔE^\ddagger (kcal·mole ⁻¹)	7.2	3.8	3.1	
			ΔS^\ddagger (e.u.)	-27	-35	-34	
			K (l·mole ⁻¹)	34.9			
			ΔH° (kcal·mole ⁻¹)	-3.8			
			ΔS° (e.u.)	-6.0			
n-PrO ⁻	20.1	78.3	k_2	715	2,600		
			ΔE^\ddagger	5.1	3.6		
			ΔS^\ddagger	-29	-33		
			K	80.0			
			ΔH°	-4.0			
			ΔS°	-4.2			
n-BuO ⁻	17.1	77.7	k_2	805	2,890		
			ΔE^\ddagger	4.2	3.0		
			ΔS^\ddagger	-33	-35		
			K	91.0			
			ΔH°	-3.5			
			ΔS°	-2.9			
iso-PrO ⁻	18.3	76.3	k_2	$\approx 5 \times 10^4$			
iso-BuO ⁻	17.7	?	k_2	$\approx 10^4$			
sec-BuO ⁻	15.8	?	k_2				
electron affinity (eV)				1.36	1.40	1.58	1.59

a) dielectric constant (ϵ) and Z-value of the alcohol corresponding to the alkoxy ion (RO⁻)b) This corresponds to k_2 in BQ-RO⁻ system and to k_2' in MeBQ-RO⁻ system.c) the slope in Fig. 13 which corresponds to (EtO)₂ SQ⁻ formation

vent-solute interaction in the initial state is stronger. It can be explained on the account that the rearrangement of the solvent dipole does not immediately accompany the electron transfer from RO⁻ to BQ, so that the transition state is more unstable, that is, the free energy of activation is higher, to make the reaction slow. Moreover, this suggests that the electron transferred to benzoquinone is localized on carbonyl oxygen rather than is delocalized among π -molecular orbital, so as to cause the change of the direction of dipole moment upon the transition of an electron. This seems to be supported by the fact that the entropy of activation, ΔS^\ddagger is greatly negative for each system. As seen from Table 5, the reaction rate is influenced by both K and k_2 (or k_2') and it can be considered that the sequence of rate with respect to alkoxy ion is mostly due to the difference of the energy of activation. These can be explained not only by the solvent effect mentioned above but also by the electro-donative tendencies of alkoxy ion, whose order is considered to be *sec*-BuO⁻ > *iso*-BuO⁻ > *iso*-PrO⁻ > *n*-BuO⁻.

$>n\text{-PrO}^- > \text{EtO}^- > \text{MeO}^-$. It is impossible to distinguish from only the present result which is an important effect, the property of the solvent or the electronic property of the alkoxy ion.

With respect to the effect of benzoquinones, the order of reaction rates producing parent semiquinone ion radicals is $\text{MeBQ} < \text{BQ} < \text{ClBQ} < \text{BrBQ}$. This order and the tendency of energy of activation are qualitatively parallel with the electron affinity (E.A.) of benzoquinones, as seen on Table 5. The electron affinity is important both on pre-equilibrium (7) and on the step of rate determining. The facts that ΔE^\ddagger is low and that $-\Delta S^\ddagger$ is fairly large deduce the condition, $\Delta E^\ddagger < -T\Delta S^\ddagger$, at room temperature and suggest that ΔS^\ddagger is predominant on the reaction rate and the orientation of reacting species is effectively accompanied by the activation.

Moreover, the effects of substituents other than E.A.'s of benzoquinones must be considered to explain the order of ΔS^\ddagger , $\text{ClBQ} \approx \text{BQ} < \text{MeBQ}$.

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