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Reaction of Hydroxide Ion with Electron Acceptors in Dimethyl Sulfoxide

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In dimethyl sulfoxide, the reaction of hydroxide ion with several electron acceptors—iodine, tetracyanoquinodimethan, Nitro Blue Tetrazolium chloride, 2,3,5-triphenyltetrazolium chloride, anthraquinone, and benzophenone—gave reaction products identical to those obtained by the reaction of these electron acceptors with electron donors. The reaction pathways of these electron acceptors were found to be composed of successive one-electron reactions similar to the electrochemical reduction of these electron acceptors. These results indicate that hydroxide ion acts as a reductant in dimethyl sulfoxide.

Hydroxide ion is known to be oxidized at +0.75 V vs. SCE in dimethyl sulfoxide,[1] but the reducing property of hydroxide ion is so weak in aqueous solution that hydroxide ion has been paid little attention as a reductant. Recently, 1-oxo-2,2,6,6-tetramethylpiperidinium salt,[2] anthraquinone,[3] and several electron acceptors[4] were found to be reduced by hydroxide ion in dichloromethane,[2] dimethyl sulfoxide,[3] and acetonitrile.[4] These observations are suggestive of the enhanced reducing power of hydroxide ion in nonaqueous aprotic solvents.

In the present paper, the reaction of hydroxide ion with several electron acceptors of various reduction potentials were studied in order to exemplify the reducing property of hydroxide ion. Dimethyl sulfoxide was used as the solvent, since this solvent is widely used as a useful nonaqueous solvent, while little has been known[3] about the reducing property of hydroxide ion in this solvent.

Experimental

As the sources of hydroxide ion, tetrabutylammonium hydroxide (0.38 M aqueous TBAOH), tetraethylammonium hydroxide (0.69 M aqueous TEAOH), and potassium hydroxide (1M aqueous KOH) were used (1 M=1 mol dm^{-3}). Potassium *t*-butoxide (tBOK, dissolved in ethanol in 0.03 M) and potassium hyperoxide (KO_2, dissolved in DMSO with 18-crown-6-ether in 0.002 M) were used as the electron donors. Iodine, tetracyanoquinodimethan (TCNQ), Nitro Blue Tetrazolium chloride (NBT), 2,3,5-triphenyltetrazolium chloride (TTC), anthraquinone (AQ), and benzophenone (BP) were used as the electron acceptors. Dimethyl sulfoxide (DMSO) was purified as described previously.[5]

The reaction of the hydroxides with the electron acceptors were carried out in a spectrophotometric cell equipped with an airtight sealing cap: a 3 ml of the DMSO solution containing (0.5—10)×10^{-5} M of an electron acceptor was taken in the cell, deaerated with nitrogen gas, and followed by the addition of the aqueous solution of 0.2—10 μl of hydroxide with a microsyringe. The concentration of the electron acceptor and the amount of the added hydroxide were chosen depending on the efficiency of each reaction. The ESR measurements were carried out by taking out an aliquot of the solution under nitrogen. The stopped-flow experiments carried out for observing the kinetic traces of the absorption spectra of the reaction intermediates were performed by using a Furue Science JP-V microfieder. The electrochemical studies were performed as described previously.[5] For the measurement of absorption spectra of electrochemically generated unstable species, the electrolysis was carried out by using an H-type cell as shown in Fig. 1, the cathode compartment of which was composed of a spectrophotometric cell. The cathode was a Pt gauze (0.5×2.0 cm) and the anode was a Pt wire. The salt bridge connected to the SCE was put in the anode compartment. Nitrogen gas was bubbled through both compartments in order to agitate the solution for an efficient electrolysis, to deaerate, and to secure the homogeneity of the solution.

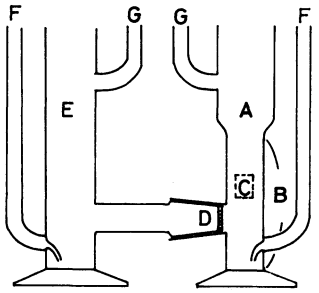


Fig. 1. Electrolysis cell. A: Cathode compartment, B: made of a spectrophotometric cell (1.0 cm×1.0 cm×5.0 cm), C: path of light beam, D: sintered glass filter, E: anode compartment, F: nitrogen inlet, G: nitrogen outlet.

Results and Discussion

Hydroxide ion is known to be gradually decomposed in DMSO, but 0.069 M TEAOH and 0.038 M TBAOH in DMSO were found to remain the same titers after 30 min of standing, indicating that hydroxide ion is stable in DMSO for the time period of ca. 30 min required for the measurement of each spectrum.

The identification of the reaction products and the reaction intermediates generated from the electron acceptors was performed by electrochemical, spectrophotometric, and ESR measurements as summarized as follows.

Iodine. Iodine reacts with the hydroxides and the electron donors very fast and the color of iodine disappeared instantaneously on addition of an excess amount of the hydroxides and the electron donors examined. The generation of iodate in the reactions

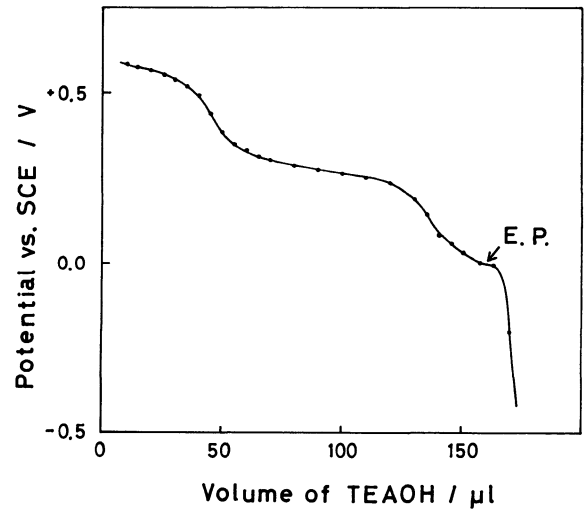


Fig. 2. Titration of iodine with TEAOH in DMSO. Iodine: 20 ml of 5.36 mM (as I) in DMSO. TEAOH: 0.69 M aqueous solution. End point (E.P.): 160 μl of TEAOH. Indicator electrode: Pt.

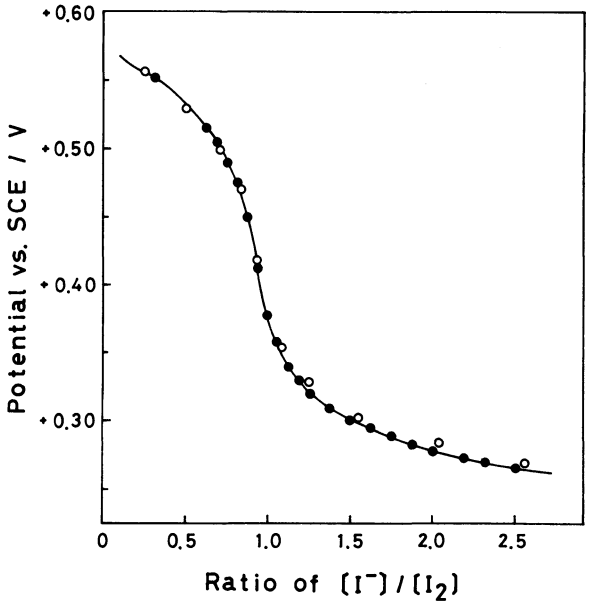


Fig. 3. The equiliblium potential change of I_2/I_3^- system in DMSO.
●: Titration of 20 ml of 3.6 mM iodine (as I_2) with 43.7 mM potassium iodide in DMSO.
○: Titration of iodine with TEAOH. The ratio of $[I^-]/[I_2]$ was calculated from the first inflection point of the titration curve shown in Fig. 2. Indicator electrode: Pt.

was ruled out since iodate is sparingly soluble in DMSO, while no precipitate was found in the solutions. The reaction of iodine with the hydroxides gave a redox titration curve as shown in Fig. 2. The potential change at the first inflection point agreed well with that obtained for the titration of iodine with KI as shown in Fig. 3, indicating iodine being reduced to iodide ion on reaction with hydroxide ion. By taking one-electron reaction, the clear-cut disappearance of

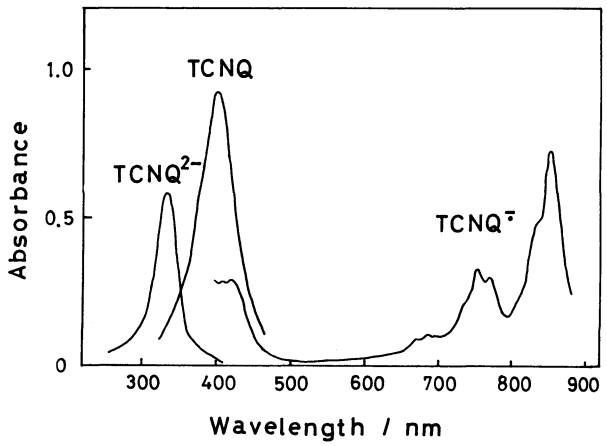
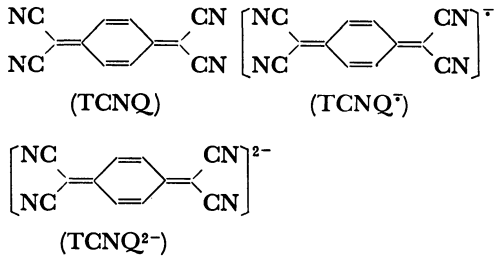


Fig. 4. Absorption spectra of reduction products of TCNQ obtained from 3.7×10^{-5} M of TCNQ in DMSO.



the color of iodine was found to occur at the stoichiometrically equivalent end point of the titration; a ratio of $[I]/[OH^-]=1:1.03$ was found experimentally.

TCNQ. The cyclic voltammogram of TCNQ showed two reversible one-electron redox waves with reduction potential of +0.25 and −0.30 V vs. SCE, respectively. By the controlled potential electrolysis at the first reduction wave, an ESR active green colored solution of $TCNQ^-$ was obtained. By the constant potential electrolysis at the second reduction wave, $TCNQ^-$ was reduced to the colorless $TCNQ^{2-}$. Upon addition of TCNQ to the solution containing $TCNQ^{2-}$ alone, $TCNQ^-$ was found to be generated. By taking these results, the redox reaction scheme of TCNQ is given as follows.

$$TCNQ \overset{e}{\rightleftharpoons} TCNQ^- \overset{e}{\rightleftharpoons} TCNQ^{2-} \quad (1)$$

$$TCNQ^{2-} + TCNQ \longrightarrow 2\,TCNQ^- \quad (2)$$

The absorption spectra of these reduction products are given in Fig. 4.

On reaction with the hydroxides and the electron donors examined, TCNQ gave $TCNQ^-$ when the concentration of the hydroxides or the electron donors is less than the equivalent amount of TCNQ and with the addition of an excess amount of the hydroxides or the electron donors, $TCNQ^-$ was reduced to $TCNQ^{2-}$. The rate of reaction of TCNQ with the hydroxides and the electron donors was so fast that the color change of the solution occurred instantaneously upon mixing the reactants. From the observations of the stepped

generation of $TCNQ^{\cdot-}$ and $TCNQ^{2-}$ from TCNQ, TCNQ is considered to be reduced by hydroxide ion by successive one-electron reactions as shown as follows.

$$TCNQ + OH^- \longrightarrow TCNQ^{\cdot-} + OH \quad (3)$$

$$TCNQ^{\cdot-} + OH^- \longrightarrow TCNQ^{2-} + OH \quad (4)$$

The hydroxy radical is known to be unstable to give oxygen and water[1] or hydrogen peroxide[2] according to the following reactions.

$$2\,OH \longrightarrow H_2O_2 \quad (5)$$

$$H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2 \quad (6)$$

The consumption of hydroxide ion in the reaction was detected by using a pH meter. As the response of the glass electrode in pure DMSO is not specified, the measurement was carried out after dissolving 10 ml of DMSO into 30 ml of water. In this solvent mixture, the 0.69 M TEAOH showed the same titer as in aqueous solution. The indicator of the pH meter was calibrated by adding a known amount of hydroxide in 10 ml of DMSO before mixing with 30 ml of water. When no hydroxide was added, the meter indicated at pH 5.0 (880 mV), and when 15 μl of 0.69 M TEAOH was added in 10 ml of DMSO (1.0×10^{-3} M), the meter indicated at pH 10.8 (530 mV). When 15 μl of 0.69 M TEAOH was added into 10 ml of DMSO containing 1.37×10^{-3} M TCNQ, the pH meter showed pH 5.3 (860 mV), indicating almost no hydroxide ion being left in the solution after the reaction with TCNQ proceeded. No oxygen was detected as the reaction product as evidenced by the observation of no oxygen wave at −0.8 V vs. SCE on the cyclic voltammogram taken after the reaction of hydroxide ion with TCNQ completed. The detection of hydrogen peroxide was unsuccessful because of the reactivity of DMSO on the permanganate method and of the color interference of TCNQ on the titanium chloride method. The hydroxy radical is known to react with some solvents,[6] but the reaction product of OH and DMSO was not confirmed or excluded in the present work.

NBT. On the cyclic voltammogram of NBT^{2+}, three predominant reduction waves were observed at −0.28, −1.28, and −1.66 V vs. SCE. The first wave which has a slight shoulder was attributed to the reduction of the tetrazolium ring as shown below. The second and the third waves are considered to correspond to the reduction of the nitro group of NBT^{2+}, since these potentials are close to those of para-substituted nitrobenzene derivatives. At the early stage of the constant potential electrolysis at −0.55 V vs. SCE, corresponding to the first reduction wave, a blue colored solution of monoformazan (MF, λ_{max}=680 nm) was obtained. The solution also gave an ESR spectrum identified to that of bitetrazole cation radical ($NBT^{\cdot+}$). The monoformazan thus generated turned to

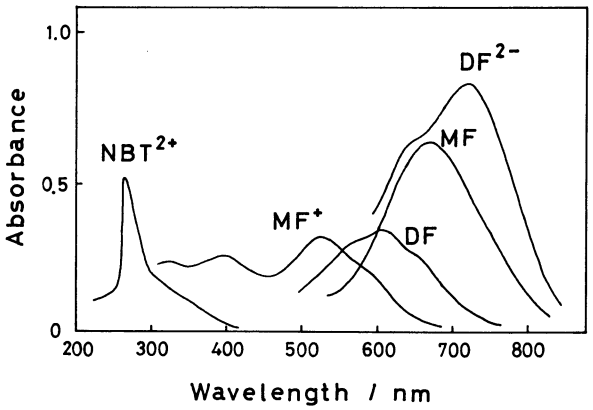
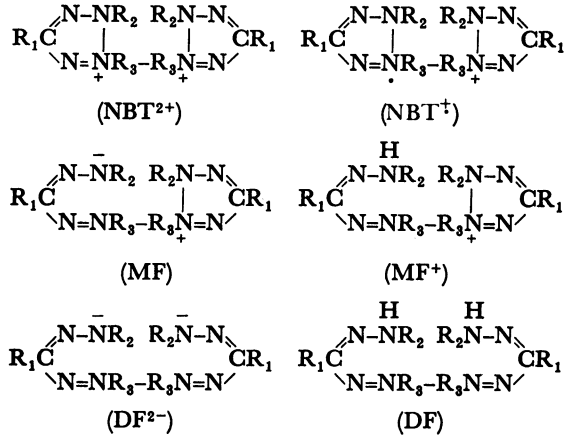


Fig. 5. Absorption spectra of reduction products of NBT obtained from 8.2×10^{-6} M of NBT in DMSO.



$R_1 = C_6H_5$, $R_2 = p\text{-}NO_2C_6H_4$, $R_3 = m\text{-}CH_3OC_6H_3$

the monoformazan ion (MF^+, λ_{max}=530 nm) on addition of acids. Upon completion of the controlled potential electrolysis at −0.55 V vs. SCE, a sky blue solution of biformazan dianion (DF^{2-}, λ_{max}=724 nm) was obtained with the consumption of overall four electrons for each molecule of NBT^{2+}. The biformazan dianion was turned to biformazan (DF) on addition of acids. The reaction scheme of NBT^{2+} was given as follows.[7]

$$NBT^{2+} \xrightarrow{e} NBT^{\cdot+} \xrightarrow{e} MF \xrightarrow{H^+} MF^+ \quad (7)$$

$$MF \xrightarrow{2e} DF^{2-} \xrightarrow{2H^+} DF \quad (8)$$

The characteristic absorption bands of these species are given in Fig. 5. The formation of MF according to the following disproportionation reaction of $NBT^{\cdot+}$ is also probable,[7]

$$2\,NBT^{\cdot+} \rightleftharpoons NBT^{2+} + MF \quad (9)$$

but it was not confirmed whether MF is formed by the electronation or the disproportionation of $NBT^{\cdot+}$. It is most reasonable to consider that both reactions are operative in the reduction process of NBT^{2+}.

On reaction with the hydroxides, NBT^{2+} immediately gave a blue-colored solution of MF. The solution

also gave an ESR spectrum identified to $NBT^{\ddagger}$. The MF and $NBT^{\ddagger}$ thus generated were converted to MF^+ on addition of acids. The reaction scheme of NBT^{2+} with hydroxide ion is considered to be as follows.

$$NBT^{2+} + OH^- \longrightarrow NBT^{\ddagger} + OH \quad (10)$$

$$NBT^{\ddagger} + OH^- \longrightarrow MF + OH \quad (11)$$

and/or

$$2\,NBT^{\ddagger} \rightleftharpoons NBT^{2+} + MF \quad (9)$$

The consumption of hydroxide ion in this reaction was confirmed by using a pH meter as in the case of TCNQ. The reaction of the hydroxides with NBT^{2+} was fast but not so effective as in the reactions of iodine and TCNQ. For example, by the reaction of 8.2×10^{-6} M NBT^{2+} with 1.64×10^{-5} M TEAOH required from the stoichiometry of the reactions shown by Eqs. 10, 11, or 9, only half amount of NBT^{2+} was reduced. As the reduction potential of NBT^{2+} is more negative than those of iodine and TCNQ, the electron donating property of hydroxide ion is considered to be less effective for NBT^{2+} than for iodine and TCNQ.

TTC. The electrochemical study of TTC showed that 2,3,5-triphenyltetrazolium ion (TT^+) is reduced to a tetrazolyl radical ($TT^{\cdot}$) and to 1,3,5-triphenylformazan anion (TF^-, λ_{max}=536 nm) at −0.49 and −0.74 V vs. SCE, respectively. TF^- was also generated by the disproportionation reaction of $TT^{\cdot}$ generated by the constant potential electrolysis at −0.55 V vs. SCE.[5] The reaction scheme of TT^+ is given as follows.[5]

$$TT^+ \xrightarrow{e} TT^{\cdot} \xrightarrow{e} TF^- \xrightarrow{H^+} TF \quad (12)$$

$$2\,TT^{\cdot} \rightleftharpoons TT^+ + TF^- \quad (13)$$

The characteristic absorption bands of these species are given in Fig. 6.

Upon reaction with the hydroxides, TT^+ gave a highly red colored solution of TF^-. The solution also gave an ESR spectrum identified to $TT^{\cdot}$. On addition of acids, the ESR spectrum disappeared and the solution gave an absorption spectrum characteristic to 1,3,5-triphenylformazan (TF, λ_{max}=485 nm). The reaction of TTC with hydroxide ion is given as follows.

$$TT^+ + OH^- \longrightarrow TT^{\cdot} + OH \quad (14)$$

$$TT^{\cdot} + OH^- \longrightarrow TF^- + OH \quad (15)$$

and/or

$$2\,TT^{\cdot} \rightleftharpoons TT^+ + TF^- \quad (13)$$

The reaction of TTC with hydroxide ion was less effective than the reactions of iodine, TCNQ, and NBT^{2+} as predicted from the reduction potential of TTC which is more negative than the reduction potentials of iodine, TCNQ, and NBT^{2+}. For example,

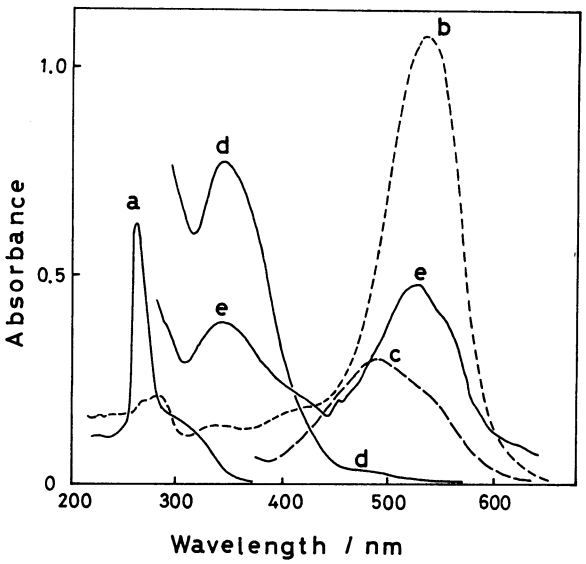
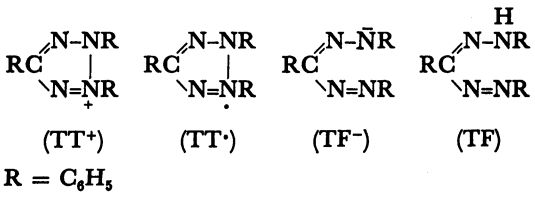


Fig. 6. Absorption spectra of (a): 3.5×10^{-5} M TTC, (b): TF^- generated from (a) by the reaction with TBAOH, (c): TF generated from (b) with the addition of benzoic acid, (d): $TT^{\cdot}$ generated by the reaction of TF^- with TT^+ in DMSO-benzene mixture (DMSO:benzene=20:80 in volume), (e): $TT^{\cdot}$ and TF^- obtained 2 s after mixing of 1.0×10^{-4} M TTC and 1.0×10^{-2} M TBAOH by flowing the solutions.



when 3.5×10^{-5} M TTC was reacted with 7.0×10^{-5} M TEAOH, only one third of the amount of TTC was reduced.

Although $TT^{\cdot}$ was detected by the ESR method in the reaction of TTC with an equimolar amount of hydroxide, any absorption band attributable to $TT^{\cdot}$ was not observed in pure DMSO. However, when benzene was added into the solution of TF^- with an excess amount of TTC, the color of the solution turned from red to yellow and a new absorption band appeared at 345 nm with the consumption of the absorption band of TF^- as shown in Fig. 6d. In a typical experiment, 1 ml of DMSO solution of TF^- generated by the reaction of 3.5×10^{-5} M TTC with 5×10^{-4} M TBAOH was added into 8 ml of pure benzene. The solution showed an absorption spectrum of TF^- alone. To this solution 1 ml of DMSO solution containing 3×10^{-3} M TTC was added. The color of the solution turned from red to yellow. The yellow colored solution gave an intense ESR spectrum identical to that of $TT^{\cdot}$ as shown in Fig. 7. Thus, the absorption band at 345 nm was identified to that of $TT^{\cdot}$. This band was gradually substituted by that of TF^- with the successive increase of the content of DMSO in the DMSO-benzene mixture. These observa-

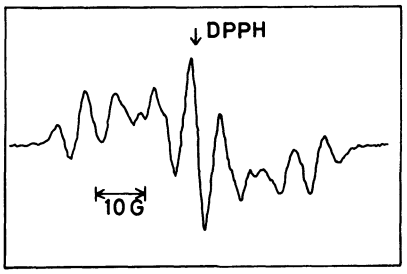


Fig. 7. ESR spectrum of TT·, generated by the reaction of TTC with TBAOH in DMSO.

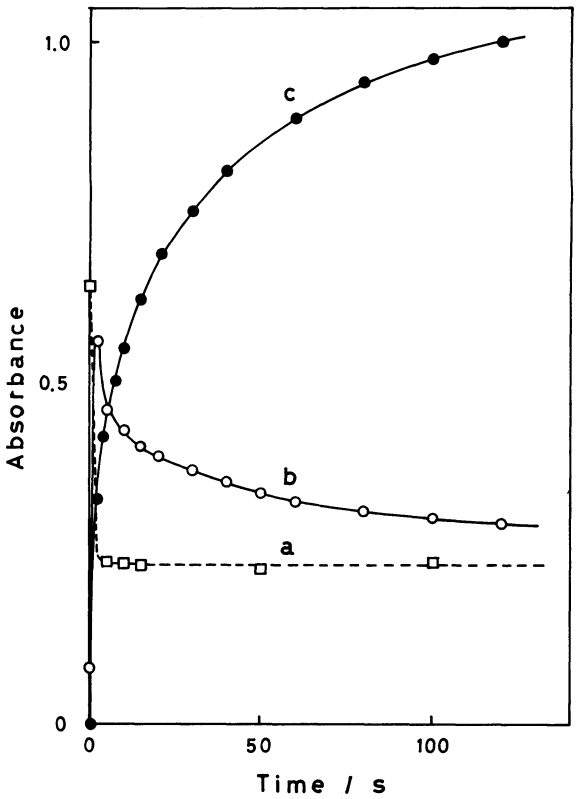


Fig. 8. Stopped-flow kinetic traces of absorption bands observed in the reaction of 7.0×10^{-5} M TTC with 7.6×10^{-3} M TBAOH in DMSO.
(a): TT^+ at 258 nm, (b) TT· at 345 nm (the range of absorbance: ×2), and (c): TF^- at 536 nm.

tions indicate that in pure DMSO the equilibrium constant of the disproportionation reaction (Eq. 13) is so large that the concentration of TT· is kept too low to be detected by the spectrophotometric method at the equilibrium state. However, if the reaction of TTC with hydroxide ion is induced by the electron transfer from hydroxide ion to TT^+, the transient accumulation of TT· should be observed at the early stage of the reaction. In order to verify the probable accumulation of TT·, the reaction was studied by a flow method. The reactants were introduced into a spectrophotometric flow-cell by using a double-channeled microfeeder. On the absorption spectrum taken immediately after mixing the reactants, absorption bands of both TT· and TF^- were observed as shown

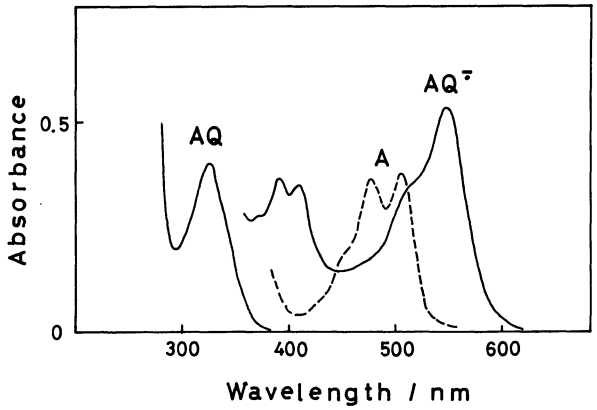
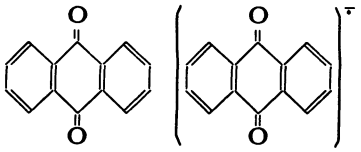


Fig. 9. Absorption spectra of reaction products of anthraquinone (AQ) in DMSO.
AQ: 8.0×10^{-5} M. AQ^- and A: generated from 2.3×10^{-3} M of AQ by the reaction with TEAOH.



in Fig. 6e. The stopped-flow kinetic traces of absorption bands of TT^+, TT·, and TF^- are given in Fig. 8. Although the time courses of these kinetic traces are not so simple as to allow a rigorous kinetic analysis; the rate of increase of TF^- is seen to be well intercorrelated with the rate of decrease of TT·, indicating that TT· is working as a precursor of TF^- in the reaction sequence.

Anthraquinone. The cyclic voltammetry of AQ showed that AQ is reversibly reduced to AQ^- and AQ^{2-} at −0.83 and −1.53 V vs. SCE, respectively. The constant potential electrolysis at the first reduction wave gave a red colored solution of AQ^- (λ_{max}=550 nm) as shown in Fig. 9.

On reaction with the hydroxides, AQ gave a red-colored solution of AQ^-. The solution showed an ESR signal. The reaction of AQ with the hydroxides was not so effective as in the reactions of iodine, TCNQ, NBT, and TTC as predicted from the reduction potential of AQ which is the most negative among these electron acceptors. In order to obtain an absorption spectrum of AQ^-, higher concentration of AQ was required as compared with the other electron acceptors examined. AQ^- turned gradually to a yellow colored species (shown by A in Fig. 9) on standing, which did not give any ESR signal and has not been identified yet.

Benzophenone. The electrochemical study of BP showed that BP is reduced to blue colored BP^- at −1.77 V vs. SCE. However, BP did not react with the hydroxides and the electron donors examined. The reduction potential of BP is too negative to be reduced by the hydroxides and the electron donors examined.

Conclusion. The reaction products and intermediates identified in the reactions of the electron

Table 1. Reaction Products Identified in the Reaction of Electron Acceptors with Hydroxides and Electron Donors in DMSO

Electron acceptor	Hydroxides			Electron donors			Reduction potential vs. SCE/V
	TBAOH	TEAOH	KOH	tBOK	KO_2	Electrochemical reduction	
I_2	I^-	I^-	I^-	I^-	I^-	I^-	+0.53 (I_2/I_3^-) +0.28 (I_3^-/I^-)
TCNQ	$TCNQ^{\cdot-}$ $TCNQ^{2-}$	$TCNQ^{\cdot-}$ $TCNQ^{2-}$	$TCNQ^{\cdot-}$ $TCNQ^{2-}$	$TCNQ^{\cdot-}$ $TCNQ^{2-}$	$TCNQ^{\cdot-}$ $TCNQ^{2-}$	$TCNQ^{\cdot-}$ $TCNQ^{2-}$	+0.25 −0.30
NBT	NBT^{+}, MF	NBT^{+}, MF	NBT^{+}, MF	NBT^{+}, MF, DF^{2-}	NBT^{+}, DF^{2-}	NBT^{+}, MF, DF^{2-}	−0.28
TTC	$TT^{\cdot}$, TF^-	$TT^{\cdot}$, TF^-	$TT^{\cdot}$, TF^-	$TT^{\cdot}$, TF^-	$TT^{\cdot}$, TF^-	$TT^{\cdot}$, TF^-	−0.49
AQ	$AQ^{\cdot-}$	$AQ^{\cdot-}$	$AQ^{\cdot-}$	$AQ^{\cdot-}$	$AQ^{\cdot-}$	$AQ^{\cdot-}$, AQ^{2-}	−0.83
BP	—	—	—	—	—	$BP^{\cdot-}$	−1.77

acceptors with the hydroxides and the electron donors in DMSO are summarized in Table 1. As shown in Table 1, the reaction of the electron acceptors with the hydroxides gave reaction products or intermediates identical to those obtained by the reaction of these electron acceptors with the electron donors. The efficiency of the reactions was shown to have a qualitative correlation with the reduction potentials of the electron acceptors: the less negative the reduction potential, the more efficiently the reaction proceeded. These observations would lead us to suppose that hydroxide ion acts as an electron donor in the reactions examined.

The reducing property of hydroxide ion is of interest, since this property may possibly play an essential role in some, not all, of the so-called base-catalyzed reactions. Further studies to clarify the role of hydroxide ion are also required in analytical chemistry, since the reducing property of hydroxide ion has been paid little attention in the acid-base reactions in nonaqueous solvents.

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