Reaction of Hydroxide Ion with Electron Donors in Aprotic Solvents

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In aprotic solvents, the reaction of hydroxide ion with electron acceptors — iodine, tetracyanoquinodimethane, Nitro Blue Tetrazolium, methylviologen, 2,3,5-triphenyltetrazolium chloride, duroquinone, anthraquinone, benzil, 9-fluorenone, perylene — gave reaction products identical to those obtained by the reduction of these electron acceptors with electron donors. The paths of reaction of these electron acceptors with hydroxide ion were found to be composed of successive one-electron reactions. The efficiency of the reaction showed a good correlation with the reduction potential of the electron acceptors; the rate of the reaction decreased with increasing the reduction potential of the electron acceptors.

Hydroxide ion is oxidized at +0.75 V vs. SCE (saturated calomel electrode) in dimethyl sulfoxide,[1] and the electron donor property of hydroxide ion has been investigated in some solvents.[2—4] However, the reducing property of hydroxide ion is so weak in aqueous solution that hydroxide ion has been paid little attention as a reductant. Recently, the wide-spread use of nonaqueous solvents reveals the electron donor property of hydroxide ion. For example, 1-oxo-2,2,6,6-tetramethylpiperidinium salt,[5] anthraquinone,[6] and several electron acceptors[7—10] were found to be reduced by hydroxide ion in dichloromethane,[5] dimethyl sulfoxide,[6,9] acetonitrile,[8] and nitrobenzene.[10] The hydroxide ion on metal surface was found to act as an electron donor site in some aprotic solvents.[7] These observations suggest the enhanced reducing property of hydroxide ion in nonaqueous aprotic solvents. In the present paper, the reaction of hydroxide ion with several electron acceptors was studied in some solvents in order to exemplify how the electron donor property of hydroxide ion is enhanced in aprotic solvents of weak anion solvation and how the rate of reaction correlates with the reduction potential of the electron acceptors.

Experimental

As the source of hydroxide ion, tetrabutylammonium hydroxide (0.38 M aqueous TBAOH), tetraethylammonium hydroxide (0.71 M aqueous TEAOH), benzyltrimethylammonium hydroxide (2.0 M BTMAOH in methanol), and potassium hydroxide (1 M aqueous KOH) were used (1 M=1 mol dm^{-3}). Potassium *t*-butoxide (*t*BOK) and potassium hyperoxide (KO$_2$) were used as electron donors. Iodine, tetracyanoquinodimethane (TCNQ), Nitro Blue Tetrazolium (NBT), 2,3,5-triphenyltetrazolium chloride (TTC), methylviologen (MV), duroquinone (DQ), anthraquinone (AQ), benzil (BL), 9-fluorenone (FL), perylene (P), and benzophenone (BP) were used as electron acceptors. Dimethyl sulfoxide (DMSO), acetonitrile (ACN), dimethylformamide (DMF), propylene carbonate (PC), ethanol (EtOH), and water were purified by distillation. The spectroscopically pure grade acetone and dioxane obtained from Dojindo Laboratories were used without further purification.

For the measurement of UV-visible absorption spectra, the reaction of the hydroxides with the electron acceptors was carried out in a spectrophotometric cell: 3 ml of the solution containing (0.1—10)×10^{-5} M of an electron acceptor was taken in the cell, deaerated with nitrogen, and followed by the addition 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 measurement was carried out by taking an aliquot of solution into an ESR cell under nitrogen. The electrochemical studies were performed as described previously.[12] For the measurement of UV-visible absorption spectra of electrochemically generated unstable species, the electrolysis was carried out in a spectrophotometric cell. The cathode was a Pt gauze placed in the light path, and the anode was a Pt wire placed in a glass tube equipped with a glass-wool filter for separating the anode from the cathode. The solution was deaerated with nitrogen. The potentials were all referred to an SCE. All experiments were carried out at room temperature (20 °C).

Results and Discussion

Prior to the study of the reaction of hydroxide ion with electron acceptors, the stability of hydroxide ion in the solvents was examined potentiometrically by using a pH meter. As the response of the glass electrode in nonaqueous solvents is not specified, the measurement was carried out after mixing 10 ml of the solution with 40 ml of water. In this solvent mixture, the 0.71 M TEAOH was verified to show the same titer as in aqueous solution. Solutions of DMSO, ACN, DMF, acetone, PC, dioxane, and ethanol containing 0.071 M TEAOH were found to hold the same titer after 30 min of standing; the results indicate that hydroxide ion is stable in these solvents for the time period of ca. 10 min required for the measurement of each spectrum.

The reaction products generated from the electron acceptors in the reaction with hydroxide were identified from the ESR and UV-visible absorption spectra. Although the details of the reaction of the individual

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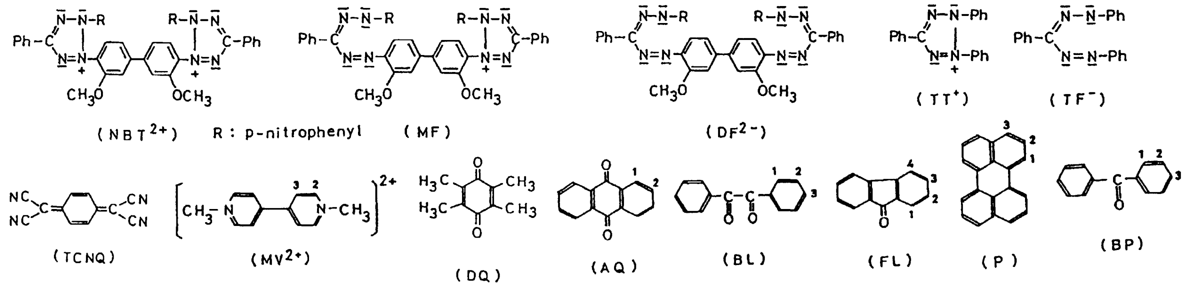
Table 1. Reaction Products Identified in the Reaction of Electron Acceptors with Hydroxides and Electron Donors in DMF

Electron acceptor	Hyroxide				Electron donor			Reduction potential / V vs. SCE
	BTMAOH	TBAOH	TEAOH	KOH	tBOK	K_2O	Electrochemical reduction	
I_2	I_3^- I^-	I_3^- I^-	I_3^- I^-	I_3^- I^-	I_3^- I^-	I_3^- I^-	I_3^- I^-	+0.62 +0.27
TCNQ	$TCNQ^{-\bullet}$ $TCNQ^{2-}$	$TCNQ^{-\bullet}$ $TCNQ^{2-}$	$TCNQ^{-\bullet}$ $TCNQ^{2-}$	$TCNQ^{-\bullet}$ $TCNQ^{2-}$	$TCNQ^{-\bullet}$ $TCNQ^{2-}$	$TCNQ^{-\bullet}$ $TCNQ^{2-}$	$TCNQ^{-\bullet}$ $TCNQ^{2-}$	+0.27 −0.32
NBT^{2+}	$NBT^{+\bullet}$ MF, DF^{2-}	$NBT^{+\bullet}$ MF, DF^{2-}	$NBT^{+\bullet}$ MF, DF^{2-}	$NBT^{+\bullet}$ MF, DF^{2-}	$NBT^{+\bullet}$ MF, DF^{2-}	$NBT^{+\bullet}$ MF, DF^{2-}	$NBT^{+\bullet}$, MF DF^{2-}	−0.21
MV^{2+}	$MV^{+\bullet}$ A	$MV^{+\bullet}$ A	$MV^{+\bullet}$ A	$MV^{+\bullet}$ A	$MV^{+\bullet}$ A	$MV^{+\bullet}$ A	$MV^{+\bullet}$ A	−0.42
TT^+	$TT^\bullet$,TF^-	$TT^\bullet$,TF^-	$TT^\bullet$,TF^-	$TT^\bullet$,TF^-	$TT^\bullet$,TF^-	$TT^\bullet$,TF^-	$TT^\bullet$,TF^-	−0.49
DQ	$DQ^{-\bullet}$	$DQ^{-\bullet}$	$DQ^{-\bullet}$	$DQ^{-\bullet}$	$DQ^{-\bullet}$	$DQ^{-\bullet}$	$DQ^{-\bullet}$	−0.78
AQ	$AQ^{-\bullet}$	$AQ^{-\bullet}$	$AQ^{-\bullet}$	$AQ^{-\bullet}$	$AQ^{-\bullet}$	$AQ^{-\bullet}$	$AQ^{-\bullet}$, AQ^{2-}	−0.84
BL	$BL^{-\bullet}$	$BL^{-\bullet}$	$BL^{-\bullet}$	$BL^{-\bullet}$	—	—	$BL^{-\bullet}$	−1.09
FL	$FL^{-\bullet}$	$FL^{-\bullet}$	$FL^{-\bullet}$	$FL^{-\bullet}$	—	—	$FL^{-\bullet}$	−1.25
P	$P^{-\bullet}$ a)	—	—	—	—	—	$P^{-\bullet}$	−1.65
BP	—	—	—	—	—	—	$BP^{-\bullet}$	−1.74

a) Trace amount of radical was detected by ESR method. (—); No reaction was observed



(NBT^{2+}) R : p-nitrophenyl (MF) (DF^{2-}) (TT$^+$) (TF$^-$)

(TCNQ) (MV^{2+}) (DQ) (AQ) (BL) (FL) (P) (BP)

Table 2. Reaction Products Identified in the Reaction of Hydroxide Ion with Electron Acceptors in Various Solvents

Electron acceptor	Solvent							
	DMF	DMSO	ACN	Acetone	PC	Dioxane	EtOH	H_2O
TCNQ	$TCNQ^{-\bullet}$ a) $TCNQ^{2-}$	$TCNQ^{-\bullet}$ $TCNQ^{2-}$	$TCNQ^{-\bullet}$ $TCNQ^{2-}$	$TCNQ^{-\bullet}$ $TCNQ^{2-}$	$TCNQ^{-\bullet}$ $TCNQ^{2-}$	$TCNQ^{-\bullet}$ $TCNQ^{2-}$	$TCNQ^{-\bullet}$ $TCNQ^{2-}$	×
NBT^{2+}	$NBT^{+\bullet}$ MF, DF^{2-}	$NBT^{+\bullet}$ MF	$NBT^{+\bullet}$ MF	$NBT^{+\bullet}$ MF	MF	$NBT^{+\bullet}$ MF	MF b)	—
MV^{2+}	$MV^{+\bullet}$ A	$MV^{+\bullet}$ A	$MV^{+\bullet}$ A	$MV^{+\bullet}$ A	$MV^{+\bullet}$ A	A	$MV^{+\bullet}$	—
TT^+	$TT^\bullet$ TF^-	$TT^\bullet$ TF^-	$TT^\bullet$ TF^-	$TT^\bullet$ TF^-	TF^-	$TT^\bullet$ TF^-	TF b)	—
DQ	$DQ^{-\bullet}$	$DQ^{-\bullet}$	$DQ^{-\bullet}$	$DQ^{-\bullet}$	$DQ^{-\bullet}$	$DQ^{-\bullet}$ b)	$DQ^{-\bullet}$ b)	—
AQ	$AQ^{-\bullet}$	$AQ^{-\bullet}$	$AQ^{-\bullet}$	$AQ^{-\bullet}$ b)	$AQ^{-\bullet}$ b)	$AQ^{-\bullet}$ b)	—	—
BL	$BL^{-\bullet}$	$BL^{-\bullet}$	$BL^{-\bullet}$	—	—	—	—	—
FL	$FL^{-\bullet}$	$FL^{-\bullet}$	—	—	—	—	—	—
P	$P^{-\bullet}$ b)	$P^{-\bullet}$ b)	—	—	—	—	—	×
BP	—	—	—	—	—	—	—	—

a) TCNQ was partially reduced by DMF. b) Trace amount of the product was detected. (×); Insoluble. (—); No reaction observed.

electron acceptors were slightly different in different solvents depending on the stability and the efficiency of the reaction in each solvent, its reaction path was similar for all solvents. The results obtained in the reaction in DMF are given in Table 1 as a typical example. The molecular structures of the electron acceptors are shown at the footnote of Table 1. The structures of the radicals unspecified in the footnote are the same as the starting molecules. The unpaired electron of the radicals was found to be delocalized in the molecule as evidenced by the hyperfine structure observed in the ESR spectrum. Analogous results obtained in other solvents is given in Table 2. The general feature of each reaction was summarized as follows by taking examples in the reaction in DMF.

TCNQ is a typical electron acceptor and is known to be reduced to $TCNQ^{-\cdot}$ and $TCNQ^{2-}$ by successive one electron reactions in aprotic solvents; their absorption and ESR spectra are well-established:[9] $TCNQ^{-\cdot}$; λ_{max}=680, 750, 820 nm, a_H=0.139 mT, a_N=0.094 mT: $TCNQ^{2-}$; λ_{max}=320 nm. By reaction with the hydroxides and the electron donors, TCNQ gave green colored $TCNQ^{-\cdot}$ 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, $TCNQ^{-\cdot}$ was reduced to colorless $TCNQ^{2-}$. From these observations, the reaction of TCNQ with hydroxide ion is considered to be composed of following sebsequent electron transfer reactions.

$$\mathrm{TCNQ} + \mathrm{OH}^- \rightarrow \mathrm{TCNQ}^{-\cdot} + \mathrm{OH} \qquad (1)$$

$$\mathrm{TCNQ}^{-\cdot} + \mathrm{OH}^- \rightarrow \mathrm{TCNQ}^{2-} + \mathrm{OH} \qquad (2)$$

The rate of the reaction was very fast in all solvents, and the color change of the solution occurred instantaneously upon mixing the reactants. The consumption of stoichiometric amount of hydroxide ion was confirmed potentiometrically by using PH meter. In DMF, TCNQ is not stable and is gradually reduced by DMF. However, the generation of $TCNQ^{-\cdot}$ by the addition of hydroxides was clearly observed as in other aprotic solvents. As the hydroxyl radical generated by the oxidation of hydroxide ion is already known to give oxygen and water[1] or hydrogen peroxide,[13] the reaction of hydroxyl radical was not further examined in the present work.

Iodine is an efficient electron acceptor with a very low oxidation potential. Iodine reacts with the hydroxides and the electron donors very fast in all solvents examined. The color of iodine disappeared instantaneously by addition of an excess amount of the hydroxides. Both the cyclic voltammogram and absorption spectrum indicated that I_2 is reduced to I^- (λ_{max}=250 nm) via I_3^- (λ_{max}=290, 360 nm) on reaction with hydroxide ion. From these observations, the reaction of iodine with hydroxide ion is considered as follows

$$1/2\ \mathrm{I}_2 + \mathrm{OH}^- \rightarrow \mathrm{I}^- + \mathrm{OH} \qquad (3)$$

$$\mathrm{I}_2 + \mathrm{I}^- \rightarrow \mathrm{I}_3^- \qquad (4)$$

The potentiometric titration of iodine with hydroxide gave a titration curve which exhibited two inflection points. The first inflection point appeared at the consumption of 1/3 of iodine according to Eq. 3, namely, at the stoichiometry of $[I_2]:[I^-]=1:1$. The potential change at the first inflection point was confirmed to coincide with that corresponding to the equilibrium of I_2/I_3^- observed in the titration of I_2 with I^-. The second one appeared at the consumption of I_2 with a stoichiometric amount of hydroxide ion ($[I_2]:[OH^-]=1:2$)

NBT^{2+} is an electron acceptor widely used for monitoring the activity of electron donors, and its reduction scheme is well-established:[12,14] NBT^{2+} is reduced to tetrazolinyl radical ($NBT^{+\cdot}$, a_N=0.52 mT) by one electron reduction, and subsequently to blue colored monoformazan (MF, λ_{max}=680 nm) by successive one more electron reduction, and finally to sky blue colored bisformazan anion (DF^{2-}, λ_{max}=720 nm) by total four electron reduction. By reaction with the hydroxides, NBT^{2+} immediately gave $NBT^{+\cdot}$ and MF in all aprotic solvents by one and two electron reductions. In DMF, further addition of hydroxide gave DF^{2-}. The reducing property of hydroxide ion is considered to be most pronounced in DMF among the solvents examined.

TTC is another well-characterized electron acceptor used for monitoring the activity of electon donors. TT^+ is first reduced to tetrazolinyl radical ($TT^\cdot$, a_N=0.52 mT, λ_{max}=340 nm) and subsequently to 1,3,5-triphenylformazan anion (TF^-, λ_{max}=520 nm) by successive one more electron reduction.[8,9] By reaction with hydroxide, TT^+ gave a red colored solution of TF^-. The solution simultaneously gave an ESR spectrum identified to $TT^\cdot$. The kinetic traces of the absorption bands showed that the rate of increase of TF^- is correlated with the rate of decrease of $TT^\cdot$, indicating that $TT^\cdot$ is a precursor of TF^- in the reaction sequence.

Analogous reactions were observed with electron acceptors bearing more negative reduction potential, such

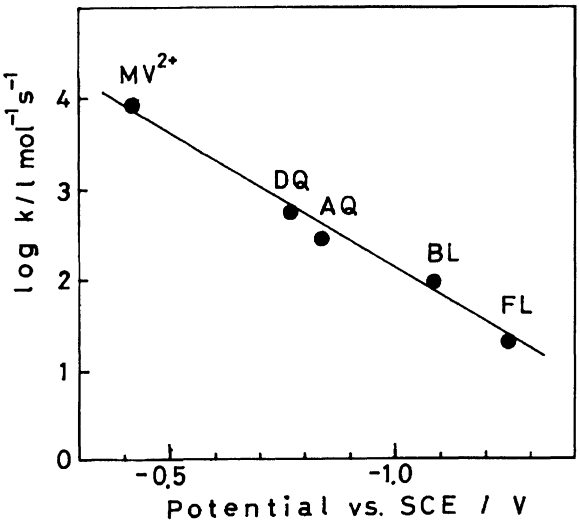


Fig. 1. The relation between the reduction potential and the rate of the reaction of electron acceptors with hydroxide ion in DMF.

as methylviologen, duroquinone, anthraquinone, benzil, 9-fluorenone, and perylene. By reaction with hydroxide ion, these compounds yielded individual radicals by one electron reduction of each molecule. The hyperfine coupling constants and the absorption maxima characterizing the radicals are as follows. $MV^{+\bullet}$: $a_N=0.42$ mT, $a_H(CH_3)=0.40$ mT, $a_{H(2)}=0.13$ mT, $a_{H(3)}=0.16$ mT; $\lambda_{max}=400$, 610 nm. $DQ^{-\bullet}$: $a_H=0.18$ mT; $\lambda_{max}=$ 320, 450 nm. $AQ^{-\bullet}$: $a_{H(1)}=0.10$ mT, $a_{H(2)}=0.029$ mT; $\lambda_{max}=395$, 405, 550 nm. $BL^{-\bullet}$: $a_{H(1)}=0.103$ mT, $a_{H(2)}=0.035$ mT, $a_{H(3)}=0.113$ mT; $\lambda_{max}=690$ nm. $FL^{-\bullet}$: $a_{H(1)}=0.191$ mT, $a_{H(2)}=0.068$ mT, $a_{H(3)}=0.113$ mT; $\lambda_{max}=540$ nm. $P^{-\bullet}$: $a_{H(1)}=0.308$ mT, $a_{H(2)}=0.041$ mT, $a_{H(3)}=0.347$ mT; $\lambda_{max}=580$ nm. The monocation radical of methylviologen gradually changed to an unidentified substance ($\lambda_{max}=405$ nm) which was tentatively presented by A in Table 1. The other radicals were stable in aprotic solvents and no side reaction was observed if free from oxygen and proton donors.

If the reaction of hydroxide ion with these electron acceptors is electron-transfer reaction, the rate constant of the reaction will correlate with the reduction potential of the electron acceptors. The kinetic study of the reaction was performed by analyzing the transient increase of the intensity of the absorption spectra of the generated radicals according to the conventional pseudo-first order rate analysis or the second order rate analysis. Among the electron acceptors, the kinetic study was limited to methylviologen, duroquinone, anthraquinone, benzil, and 9-fluorenone, since the rate of reaction of hydroxide with TCNQ and iodine was too fast and the reaction of hydroxide with NBT and TTC was not simple but complicated by successive electron transfer reactions.

The rate constants of the reactions are summarized in Fig. 1. It is seen that the rate constants of the reaction is quantitatively correlated with the reduction potentials of the electron acceptors according to a kinetic relation characterizing an electron-transfer reaction. The efficiency of the reaction was observed to be suppressed as the reduction potential of the electron acceptors becomes more negative. Perylene gave only ESR detectable trace amount of anion radical and benzophenone did not react with the hydroxides. The reduction potential of benzophenone is too negative to be reduced by hydroxide ion.

The results summarized in Table 2 show the solvent effect of the reactions. By surveying the results, it is noticed that the reducing property of hydroxide ion is enhanced in solvents of poor anion solvation. As the electron affinity of hydroxide ion (2.6 eV in gas phase) is less than that of iodide ion (3.2 eV), hydroxide ion may exhibit stronger reducing property in dry state. Accordingly, in poorly solvating aprotic solvents, the reducing property of hydroxide ion may be stronger than in solvating protic solvents. In mixed solvents, containing water or ethanol, the reducing property of hydroxide ion was observed to be suppressed. Water was more effective than ethanol. Perylene reacted only with methanolic solution of BTMAOH but did not react with aqueous hydroxides. The effect of the added protic solvents was less effective in DMF and DMSO than in ACN, dioxane, acetone, and PC. DMSO and DMF are more effective solvents for the reducing property of hydroxide ion, since the activity of trace amount of water (less than 0.1%) usually contained as impurity is suppressed by strong structure making association with these solvent molecules.[11]

The reducing property of hydroxide ion is of interest since this property may play an essential role in some base-catalyzed reactions in hydrophobic environment.

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