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REACTION OF HYDROXIDE ION WITH ELECTRON ACCEPTORS IN ACETONITRILE

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The reaction of hydroxide ion with electron acceptors gave reaction products identical to those obtained by the reaction of these electron acceptors with electron donors. The results indicate that hydroxide ion works as a reductant in acetonitrile.

Hydroxide ion is known to be oxidized at +0.75 V vs. SCE in dimethyl sulfoxide,[1] but its reducing property is so weak in aqueous solution that hydroxide ion has been little known as a reductant. Recently, immonium oxide,[2] tetrazolium ion,[3] and anthraquinone[4] were found to be reduced by hydroxide ion in methylene chloride[2] and dimethyl sulfoxide.[3,4] These observations are suggestive of the enhanced reducing property of hydroxide ion in nonaqueous aprotic solvents. In the present communication, the reaction of hydroxide ion with several electron acceptors of various reduction potentials were exemplified in order to give an evidence and a measure of the reducing ability of hydroxide ion. Acetonitrile was used as a solvent, since this solvent is widely used for the acid-base titration in analytical chemistry, while no care has been taken for the reducing property of hydroxide ion.

As the sources of hydroxide ion, tetrabutylammonium hydroxide(TBAOH, 10% in H_2O), tetraethylammonium hydroxide(TEAOH, 10% in H_2O), and potassium hydroxide (KOH, solid and 10% in H_2O) were used. Potassium t-butoxide(tBOK) and potassium hyperoxide(KO_2) were used as the electron donors. Iodine, tetracyanoquinodimethane (TCNQ), nitro blue tetrazolium chloride(NBT), 2,3,5-triphenyltetrazolium chloride (TTC), anthraquinone(AQ), and benzophenone(BP) were used as the electron acceptors. Acetonitrile(ACN) was distilled from P_2O_5. For the measurement of absorption spectra, the reaction was performed in a spectrophotometric cell equipped with a tight cap: 3ml of solution containing $(2\text{-}10)\times10^{-5}$ M(1 M = 1 mol dm^{-3}) of electron acceptor was taken in the cell, deaerated with nitrogen gas, and followed by the addition of 0.2-10 μl of hydroxide with a micro syringe. The slightly soluble electron donors were added in the cell directly.

The identification of the reaction products generated from the electron acceptors was performed by the electrochemical, spectrophotometric, and ESR measurements as summarized as follows. The results are given in Table 1.

The rate of reaction of iodine with hydroxide ion was fast enough to obtain a redox titration curve as shown in Fig. 1. The potential change at the first inflection point agreed with that obtained for the titration of iodine with KI,

indicating iodine being reduced to iodide on reaction with hydroxide ion. By taking one-electron reaction, the clear-cut disappearance of the color of iodine was found to occur at the stoichiometrically equivalent end point of the titration.

The cyclic voltammetry and controlled potential electrolysis of TCNQ showed that $TCNQ^{\cdot-}$ and $TCNQ^{2-}$ are obtained at +0.15 and -0.40 V vs. SCE, respectively. The absorption spectra of reduction products are given in Fig. 2. On reaction with hydroxides, TCNQ gave an ESR active green colored solution of $TCNQ^{\cdot-}$, which was reduced to colorless $TCNQ^{2-}$ with the further addition of an excess amount of hydroxides. The rate of reaction was very fast and the color change of the solution occurred instantaneously on mixing the reactants. $TCNQ^{2-}$ turned gradually to an unidentified substance as indicated by A in Fig. 2.

On the cyclic voltammogram of NBT^{2+}, two predominant reduction waves were observed at -0.25 and -1.15 V vs. SCE. At the early stage of the constant potential electrolysis at the first wave, a blue colored solution of monoformazan (MF, λ_{max}= 650 nm) was generated at the surface of the electrode, which turned to monoformazan ion(MF^+, λ_{max}= 520 nm) upon diffusing into the bulk of the solution or by the addition of acids. Upon completion of the electrolysis, precipitate of diformazan(DF) was obtained with the consumption of overall four electrons for each molecule of NBT^{2+}. The electrolysis at the second wave gave a sky blue solution of diformazan anion(DF^{2-}, λ_{max}= 700 nm), which turned to DF on addition of acids. The reaction scheme of NBT^{2+} is given as follows: $NBT^{2+} \xrightarrow{e} NBT^{+\cdot} \xrightarrow{e} MF \xrightarrow{H^+} MF^+ \xrightarrow{2e} DF^{2-} \xrightarrow{2H^+} DF$. The characteristic absorption bands of these species are given in Fig. 3. NBT^{2+} reacted with hydroxides very fast; in a few seconds after mixing the reactants, a blue colored solution containing MF and MF^+ was obtained. The solution also gave an ESR spectrum identified to the tetrazolinyl radical($NBT^{+\cdot}$). The tetrazolinyl radical and MF thus generated were converted to MF^+ on addition of acids.

The electrochemical study of TTC[5] showed that TT^+ is reduced to tetrazolinyl radical($TT^{\cdot}$, λ_{max}= 345 nm) at -0.45 V vs. SCE and that 1,3,5-triphenylformazan anion(TF^-, λ_{max}= 530 nm) is generated by the disproportionation reaction of $TT^{\cdot}$ or by the reduction of TT^+ at -0.75 V vs. SCE. The reaction scheme of TT^+ is given as follows: $TT^+ \xrightarrow{e} TT^{\cdot} \xrightarrow{e} TF^- \xrightarrow{H^+} TF$. The characteristic absorption bands of these species are given in Fig. 4. On reaction with hydroxides, TT^+ generated $TT^{\cdot}$ and TF^-. The solution also gave an ESR spectrum identified to $TT^{\cdot}$. The rate of reaction was not so fast as in the reactions of iodine, TCNQ, and NBT; the intensities of the absorption bands of $TT^{\cdot}$ and TF^- were observed to increase gradually after mixing the reactants. $TT^{\cdot}$ and TF^- thus generated were converted to TF with addition of acids.

The cyclic voltammetry of AQ showed that AQ is reduced to $AQ^{\cdot-}$ and AQ^{2-} at -0.96 and -1.45 V vs. SCE, respectively. The constant potential electrolysis at the first wave gave a red colored solution of $AQ^{\cdot-}$(λ_{max}= 535 nm) as shown in Fig. 5. $AQ^{\cdot-}$ turned to a yellow colored species(absorption band indicated by B in Fig. 5) on standing. The yellow colored species did not give any ESR signal and has not been identified yet. AQ reacted with hydroxides to give B, but the rate of reaction was too slow to afford the accumulation of detectable amount of $AQ^{\cdot-}$. No reaction was observed for KOH because of the poor solubility of KOH in ACN.

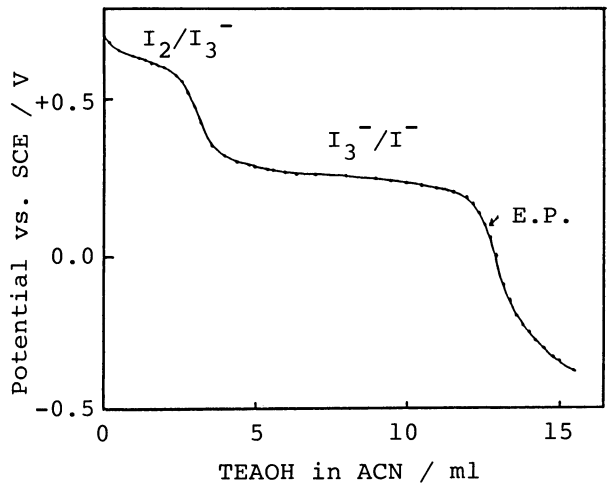


Fig. 1. Titration curve of iodine with TEAOH. Iodine: 20 ml of 3.73 mM(as I) in ACN. TEAOH: 5.9 mM in ACN. End point(E.P.): 12.6 ml of TEAOH.

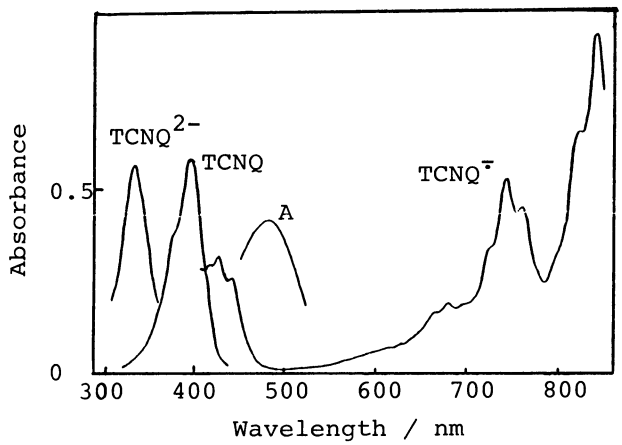


Fig. 2. Absorption spectra of reaction products of TCNQ.

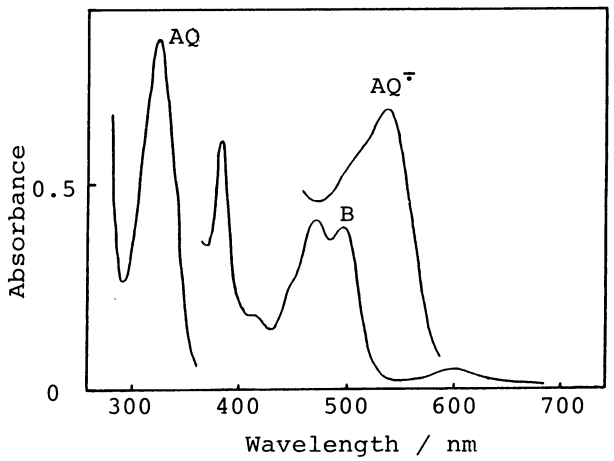


Fig. 5. Absorption spectra of reaction products of AQ.

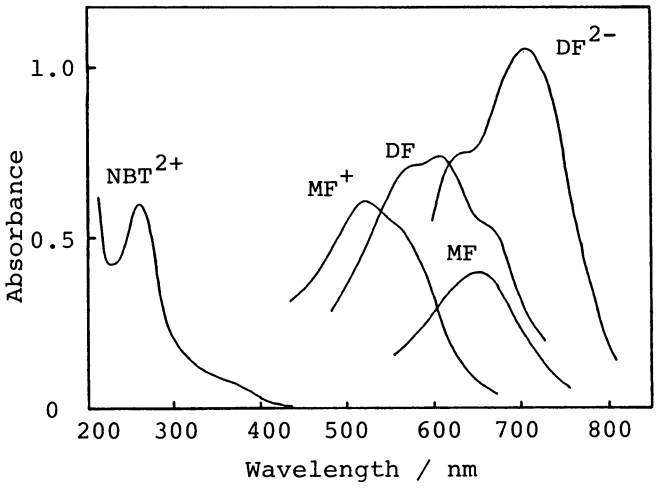
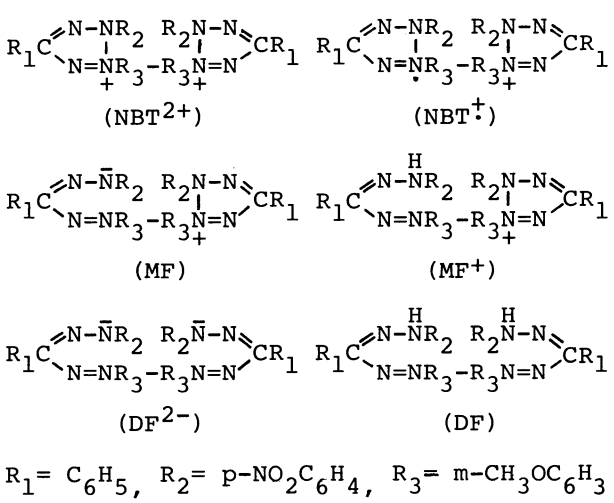


Fig. 3. Absorption spectra of reaction products of NBT.



R_1= C_6H_5, R_2= p-$NO_2C_6H_4$, R_3= m-$CH_3OC_6H_3$

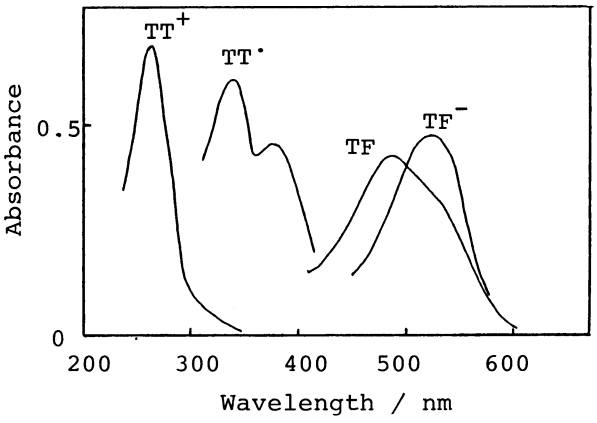
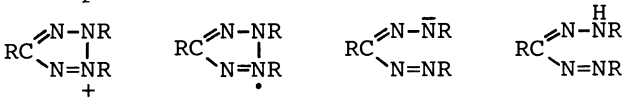


Fig. 4. Absorption spectra of reaction products of TTC.



R= C_6H_5

The electrochemical study of BP showed that BP is reduced to blue colored $BP^{\cdot-}$ at -1.75 V vs. SCE. However, BP did not react with hydroxides and electron donors examined.

Table 1. Reaction products identified in the reaction of electron acceptors with hydroxides and electron donors in acetonitrile

Electron acceptor	Hydroxide			Electron donor			Reduction potential vs. SCE / V
	TBAOH	TEAOH	KOH	tBOK	KO_2	Electrochemical reduction	
I	I^-	I^-	I^-	I^-	I^-	I^-	+0.56 (I_2/I_3^-) +0.25 (I_3^-/I^-)
TCNQ	$TCNQ^{\cdot-}$ $TCNQ^{2-}$	$TCNQ^{\cdot-}$ $TCNQ^{2-}$	$TCNQ^{\cdot-}$ $TCNQ^{2-}$	$TCNQ^{\cdot-}$ $TCNQ^{2-}$	$TCNQ^{\cdot-}$ $TCNQ^{2-}$	$TCNQ^{\cdot-}$ $TCNQ^{2-}$	+0.15 -0.40
NBT	$NBT^{+\cdot}$, MF, MF^+	$NBT^{+\cdot}$, MF, MF^+	$NBT^{+\cdot}$, MF, MF^+	$NBT^{+\cdot}$, MF, MF^+	$NBT^{+\cdot}$, MF, DF^{2-}, DF	MF, MF^+, DF^{2-}, DF	-0.25
TTC	$TT^{\cdot}$, TF^-	$TT^{\cdot}$, TF^-	$TT^{\cdot}$, TF^-	$TT^{\cdot}$, TF^-	$TT^{\cdot}$, TF^-, TF	TF^-, TF	-0.45
AQ	B	B	-	$AQ^{\cdot-}$	$AQ^{\cdot-}$, B	$AQ^{\cdot-}$, AQ^{2-}, B	-0.96
BP	-	-	-	-	-	$BP^{\cdot-}$	-1.75

As shown in Table 1, the reaction of electron acceptors with hydroxides gave reaction products or intermediates identical to those obtained by the reaction of these electron acceptors with electron donors. The rate of reaction was found to show a qualitative correlation with the reduction potentials of the electron acceptors; the less negative the reduction potential, the faster the reaction proceeds. These observations would lead us to suppose that hydroxide ion acts as an electron donor in the reactions examined. In order to establish the reducing property of hydroxide ion, examinations in various solvents are under working.

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