Reactions of the Cation Radicals of Aromatic Diamines with Their Parent Molecules or Aliphatic Amines

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The chemical reactions of the cation radicals of some aromatic diamines with their parent molecules, aliphatic amines or sodium hydroxide have been studied spectroscopically. In the case of the cation radical of *p*-phenylenediamine (PPD), the main products are Bandrowski's base (BB) and PPD, *p*-benzoquinone diimine being found as an intermediate. This reaction are found essentially to be a disproportionation of PPD^+ to BB and PPD in which bases added enhance the reaction rate. The thermodynamical quantities of the initial step of the reaction, proton transfer from PPD^+, are estimated and the reaction mechanism is discussed. The reaction of the cation radical of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) with triethylamine (TEA) gives the parent molecule, TMPD. This reaction is concluded to be caused by an electron transfer from TEA to $TMPD^+$ followed by a reaction of TEA with a large negative free energy change. The reaction between the cation radical of *N,N*-dimethyl-*p*-phenylenediamine and its parent molecule has also been studied.

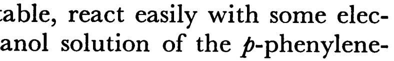
Cation radicals are expected to act as strong electron acceptors and interact with electron donating molecules. The charge resonance interaction between a cation radical and its parent molecule has been reported by several authors.[1–4] We reported the charge transfer (CT) interactions between some aromatic diamine cation radicals and aliphatic amines.[5]

The coexistence of a cation radical and an electron donating neutral molecule leads not only to the complex formation but often to chemical reaction at room temperature. For example, Würster's cations, though known to be rather stable, react easily with some electron donors. An ethanol solution of the *p*-phenylenediamine cation radical (PPD^+) changes from yellow to blue by adding *p*-phenylenediamine (PPD). Such chemical aspects of cation radicals have been relatively unexplored.

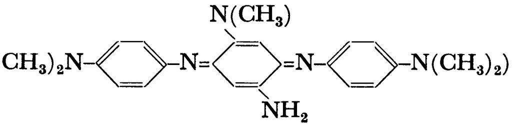
We had been interested in the physical aspects of the CT interaction between a cation radical and a neutral molecule. Recently we started work on the chemical reactions involving cation radical, because we recognized its importance for understanding the overall physical and chemical processes of these cation radicals which often play a substantial role as intermediates of various chemical reactions.

Experimental

Preparation of Material. *p*-phenylenediamine (PPD), *N,N*-dimethyl-*p*-phenylenediamine (DMPD) and *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine (TMPD) were purified according to the method described previously.[5] Their cation radical salts were synthesized according to the literature.[6] Bandrowski's base (BB,



$H_2N-C_6H_4-N=C_6H_2(NH_2)_2=N-C_6H_4-NH_2$, N^1,N^4-bis(*p*-aminophenyl)-2,5-diamino-*p*-benzoquinone diimine) was produced by oxidizing PPD with hexacyanoferrate (III) under mild alkaline conditions.[7] Found: C, 67.33; H, 5.74; N, 25.9%. Calcd for $C_{18}H_{18}N_6$: C, 67.90; H, 5.70; N, 26.40%. When DMPD was oxidized similarly, the compound corresponding to *N*-methylated Bandrowski's base



(BB′, $(CH_3)_2N-C_6H_4-N=C_6H_2(N(CH_3))(NH_2)=N-C_6H_4-N(CH_3)_2$) was obtained. Found: C, 69.60; H, 7.12; N, 20.82%. Calcd for $C_{24}H_{28}N_6$; C, 71.61; H, 7.51; N, 20.88%. Its electronic spectrum is quite similar to that of BB except for slight red shift and broadening. *p*-Benzoquinone di-imine[8] and 4,4′-bis(dimethylamino)azobenzene (AZ′)[9] were prepared according to the literature. Triethylenediamine (1,4-diazabicyclo-[2.2.2]octane) was purified by recrystallization from ether and by sublimation under vacuum. Triethylamine of the commercial GR grade was used without further treatment.

Measurement. The infrared spectra were recorded with a Hitachi EPI-G3 grating infrared spectrophotometer or a Hitachi 215 grating infrared spectrophotometer. A Shimadzu Multipurpose recording spectrophotometer MPS-50L was used for the measurements of the electronic absorption spectra.

Results

The Reaction between PPD^+Br^- and PPD. When an ethanol solution of *p*-phenylenediamine bromide (PPD^+Br^-) and that of PPD were mixed, the color of the solution changed gradually from yellow to blue. Figure 1 shows the electronic absorption spectra. The solution became acidic with the color change. On evaporating the solvent, it yielded a blue precipitate, whose infrared (IR) spectrum showed prominent bands of *p*-phenylenediamine monohydrobromide (PPD·HBr). When the reaction mixture was neutralized with NaOH, it turned from blue to red. The main products separated by the thin layer chromatography (TLC) on silica gel with a 1: 1 mixture of benzene and ether as a solvent were BB and PPD. A slight amount of 4, 4′-diaminoazobenzene (AZ) and a violet unknown substance were also separated as by-products. These were confirmed by comparison of their UV and IR spectra with those of the authentic samples.[10] In the case of AZ, the R_f values of TLC also agreed with that of the authentic sample. The yield of AZ was about 1/8 of BB in the mole ratio.

An ethanol solution of BB turns from red to blue by adding a slight amount of mineral acid. The absorption

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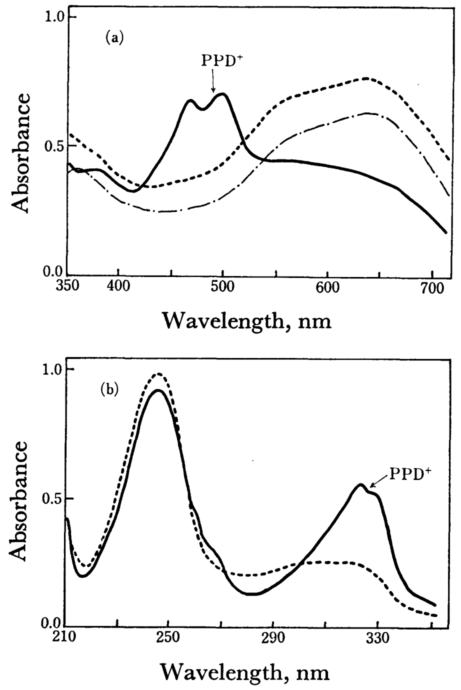


Fig. 1. The spectra of PPD^+Br^-–PPD system in ethanol at room temperature: ———; a few minutes after mixing, ------; 50 minutes after mixing.

(a) $[PPD^+Br^-]=3.51\times10^{-4}$ M, $[PPD]=3.60\times10^{-4}$ M. For reference the spectrum of the protonated Bandrowski's base in ethanol (-·-·-; [BB]/[HBr]=1) is shown in this figure.

(b) $[PPD^+Br^-]=4.80\times10^{-5}$ M, $[PPD]=5.45\times10^{-5}$ M.

of BB around 470 nm (21300 cm^{-1}) decreased by adding hydrobromic acid, while a new absorption appeared with a peak at 635 nm (15700 cm^{-1}). The intensity of the latter band showed a maximum at the molar ratio of HBr to BB of 1.17, and began to decrease by further addition of HBr as shown in Fig. 2. Therefore, the 635 nm band is assigned to the monoprotonated BB ($BB\cdot H^+$). This was also confirmed from the fact that the elemental analysis of the precipitate obtained by concentrating the solution agreed with calculated values.

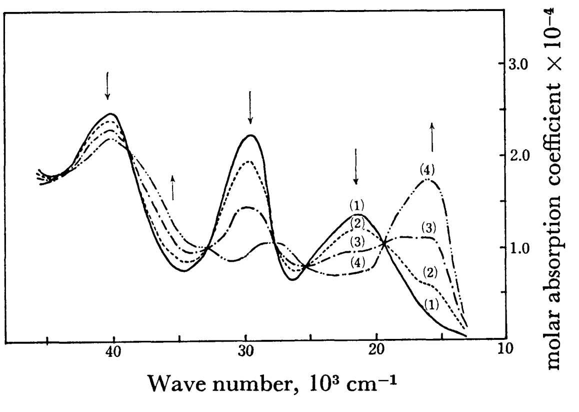


Fig. 2. The electronic absorption spectra of Bandrowski's base in ethanol with various content of HBr.

[HBr]/[BB]: (1), 0.0; (2), 0.34; (3), 0.69; (4), 1.17. The concentration of BB is constant; $[BB]=7.0\times10^{-5}$ M.

Found: C, 54.62; H, 4.78; N, 20.82%. Calcd for $C_{18}H_{19}N_6Br$: C, 54.14; H, 4.80; N, 21.05%. When a solution of BB and HBr at the mole ratio of 1: 1 was neutralized by adding an ethanol solution of NaOH, it returned from blue to red, showing the spectrum of BB. Thus, the reaction is a reversible acid-base reaction.

$$\mathrm{BB} \xrightleftharpoons[\mathrm{NaOH}]{\mathrm{HBr}} \mathrm{BB\cdot H^+}$$

As seen in Fig. 1, the absorption spectrum of the reaction mixture in the longer wavelength region is quite similar to that of $BB\cdot H^+$ with regard to both the absorption shape and peak positions, showing that the blue color comes from $BB\cdot H^+$.

The absorption at 245 nm (in Fig. 1b) is attributable mainly to PPD and BB. This absorption increases a little with the progress of the reaction. The IR spectrum of the reaction products shows that PPD exists as a monoprotonated species (PPD·HBr).

The formation of BB was investigated spectroscopically varying the concentration of PPD and keeping the initial concentration of PPD^+ constant. The amount of $BB\cdot H^+$ formed was found to be independent of the added PPD ranging from 0.28 to 7.46 molar equivalent to the PPD, though the rate of reaction increased with the concentration of PPD. The BB formed was about 1/6.5 of PPD^+ in molar quantity.

Based on the above results, the following stoichiometric equation is set up.

$$6PPD^+Br^- \longrightarrow BB + 3PPD + 6HBr \qquad (1)$$

Since, this reaction is accelerated by added PPD, we add rather randomly 2 PPD, to both sides of Eq. 1. Then, we have

$$6PPD^+Br^- + 2PPD \longrightarrow BB + 5PPD + 6HBr \qquad (2)$$

We mixed PPD^+Br^- and PPD at the molar ratio of 6: 2, and, after the reaction was completed, compared the spectrum of the reaction mixture with that of a solution containing BB, PPD and HBr at the concentrations as given by Eq. 2. The absorption spectra of the two solutions agreed very well with each other both in shape and in intensity (Fig. 3). This confirms that the stoichiometry of the reaction is like that of Eq. 1 or 2. As Eq. 1 shows, this reaction is considered essentially to be a disproportionation of PPD^+ to BB and PPD in which

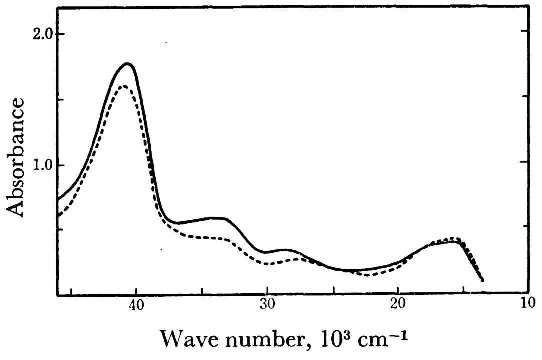


Fig. 3. The absorption spectrum of the reaction mixture of PPD^+Br^- (1.46×10^{-4} M) and PPD (0.51×10^{-4} M) (———), and that of BB (0.24×10^{-4} M), PPD (1.23×10^{-4} M), and HBr (1.48×10^{-4} M) (------).

bases added enhances the rate of reaction.

When PPD was oxidized in ethanol with bromine, a blue solution was obtained. The blue precipitate formed from this solution showed the electronic and IR spectra quite similar to those of the products of the above reaction, indicating the formation of the same products as the reaction between PPD$^+$ and PPD.

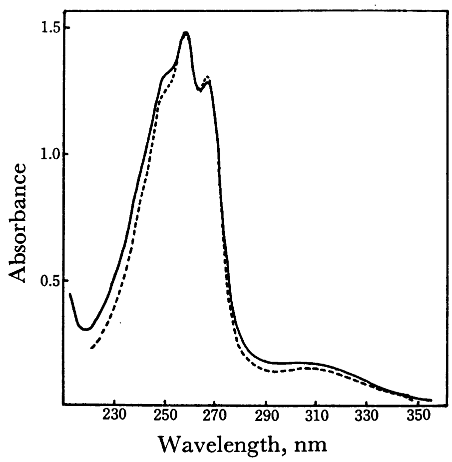
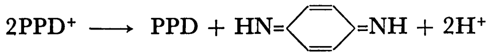


Fig. 4. The absorption spectrum of the reaction mixture of PPD$^+$Br$^-$ (0.866×10^{-4} M) and NaOH (1.99×10^{-4} M) (——), and the theoretically calculated one (------) based on Eq. 3 and the spectral data of Fig. 5.

The Reaction of PPD$^+$Br$^-$ with NaOH and Aliphatic Amines in Ethanol. Figure 4 shows the absorption spectrum of the reaction mixture of an ethanol solution of PPD$^+$Br$^-$ (0.866×10^{-4} M) and NaOH (1.99×10^{-4} M). The dotted line shows the spectrum drawn by assuming the following dispropotionation reaction being completed.


(3)

The spectrum was drawn using the absorption spectra of PPD and *p*-benzoquinone diimine (Fig. 5). As seen in Fig. 4, the spectrum obtained experimentally agrees fairly well with the theoretically expected one, indicating that the reaction proceeds mainly as defined by Eq. 3.

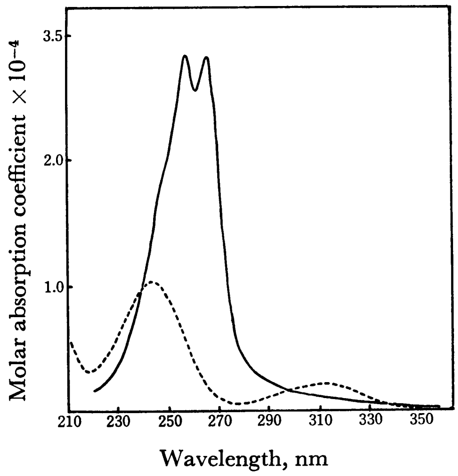


Fig. 5. The absorption spectra of *p*-phenylenediamine (------) and *p*-benzoquinone diimine (——).

The formation of the diimine was also observed when triethylamine was used instead of NaOH. The quantity in this case was about 80% of the expected one. In the case where triethylenediamine was used, the quantity of the diimine formed was still less. In both cases of amines, the diimine was unstable and changed into Bandrowski's base having the absorption peak at 470 nm, while it was fairly stable in the case of NaOH. When the amount of triethylamine was decreased to about 1/10 to 1/20 molar equivalent of PPD$^+$Br$^-$, the diimine was observed weakly, only as an absorption shoulder at 267 nm at the early stage of the reaction. Then the absorption spectra changed rapidly, showing the formation of BB·H$^+$ with a peak at 635 nm. The spectrum in both the ultraviolet and visible regions agreed fairly well with that expected from Eq. 1, suggesting that the reaction mechanism in this case is essentially the same as in the case of the reaction between PPD$^+$ and PPD.

The Reaction between DMPD$^+$ClO$_4^-$ and DMPD. When an ethanol solution of *N,N*-dimethyl-*p*-phenylenediamine perchlorate (DMPD$^+$ClO$_4^-$) and that of DMPD were mixed, the color changed gradually from red (the color of the cation) to blue. Figure 6 shows the absorption spectra. After 4 days, the reaction mixture was neutralized with NaOH and was separated by TLC with the 3: 1 mixture of benzene and ethanol. The main products separated were 4,4'-bis(dimethylamino)-azobenzene(AZ'), *N,N*-dimethylated Bandrowski's base (BB'), DMPD and an unknown substance ($\lambda_{max}=590$ nm, 650 nm). The latter two substances were produced more than BB' and AZ'. The amount of BB' formed was nearly equal to that of AZ'. The absorption at 660 nm which appeared in the course of the reaction (Fig. 6) might be attributable to the protonated species of BB' or AZ'. However it is not clear which contribution of the

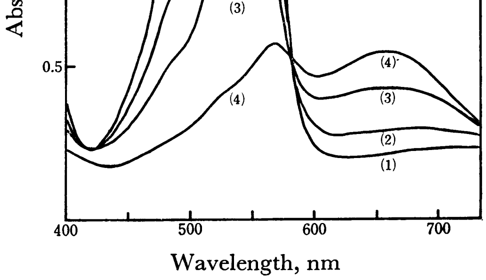


Fig. 6. Spectroscopic course of the reaction in DMPD$^+$ClO$_4^-$–DMPD system in ethanol.
[DMPD$^+$ClO$_4^-$]$=2.22\times10^{-4}$ M, [DMPD]$=2.20\times10^{-4}$ M.
(1) 4 min, (2) 14 min, (3) 44 min, (4) 170 min after mixing.

two is larger, because both of the protonated species have their absorption peaks at the same wavelength, 660 nm. The absorption at 660 nm decreased again with time and new absorptions appear at 590 nm and 650 nm, suggesting that BB′·H+ or AZ′·H+ reacts further. The similar phenomenon was observed, when DMPD was oxidized in ethanol with bromine.

The Reaction between TMPD+ClO4− and Triethylamine (TEA) in Ethanol. When TEA was added to an ethanol solution of $TMPD^+ClO_4^-$, the blue color characteristic of $TMPD^+$ disappeared and the solution became colorless. The absorption spectrum after the reaction showed a strong band at 263 nm which agreed very well with that of TMPD both in shape and position. An ether extract from the reaction mixture gave a colorless crystalline solid whose IR spectrum agreed with that of TMPD. Moreover, when bromine was added to the reaction mixture, it turned blue, giving the absorption spectrum of $TMPD^+$. From the absorption intensity the amount of $TMPD^+$ recovered was determined to about 80% of $TMPD^+$ before the reaction. This suggests that 80% of $TMPD^+$, at least, changes into TMPD by adding TEA. Figure 7 shows the spectrum of the reaction mixture together with the one which was obtained by assuming 100% conversion of $TMPD^+$, into TMPD.

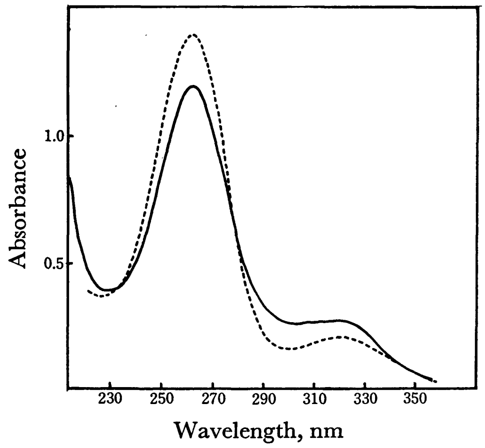


Fig. 7. The absorption spectrum of the reaction mixture of TMPD (0.885×10^{-4} M) and TEA (2.01×10^{-4} M) at 3 h after mixing (——), and the spectrum of TMPD (0.885×10^{-4} M) in EtOH (------).

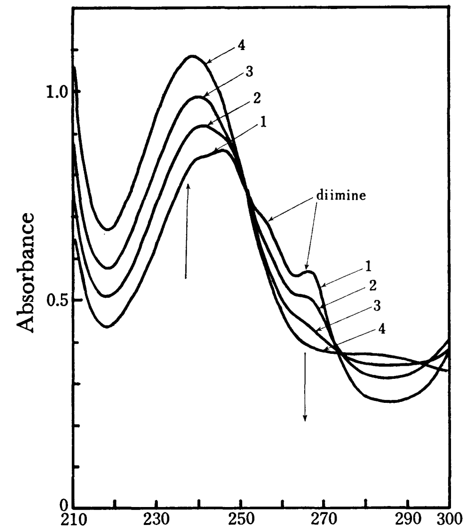
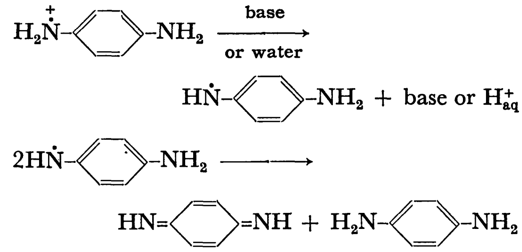


Fig. 8. Spectroscopic changes during the decomposition of PPD^+Br^- in a 1 : 2 (volume ratio) mixture of water and ethanol at room temperature. (1) 4 min, (2) 9 min, (3) 13 min, (4) 31 min after mixing.

Discussion

The Reaction of PPD+Br− with PPD, NaOH and Aliphatic Amines. When two molar equivalents of NaOH, triethylamine or triethylenediamine was added to an ethanol solution of PPD^+Br^-, the formation of *p*-benzoquinone diimine was observed clearly as shown in Fig. 4. In the case of the reaction of PPD^+ with triethylamine, the absorption intensity of the diimine in the region of 256—265 nm became weak with decreasing amount of triethylamine. When it was decreased to 1/10 molar equivalents of PPD^+, only a weak shoulder of the diimine was observed at about 270 nm. PPD^+Br^- decomposes easily in water showing the absorption of the diimine, though it is fairly stable in ethanol. Figure 8 shows the spectra of the solution in a water–ethanol mixture, ethanol being added to decrease the rate of decomposition. In the reaction between PPD^+ and PPD, a shoulder at 267 nm was observed immediately after the mixing and disappeared in a while, as shown in Fig. 1. From these results, this absorption is attributable to *p*-benzoquinone diimine, which may be formed by a process shown below



(4)

(5)

Let us estimate the Gibbs's free energy change $\Delta G_4°$ for the Reaction 4 in the case without a base. It can be estimated by using the following Born-Haber cycle.

$$\begin{tikzcd}
\cdot RH^+_{solv} \arrow[r] \arrow[d, "G_4°"] & \cdot RH^+_{gas} \arrow[r, "e"] & RH_{gas} \arrow[d] \\
\cdot R_{solv} + H^+_{solv} & & \cdot R_{gas} + \cdot H_{gas} \arrow[ll, "-e"']
\end{tikzcd}$$

Here the cation radical of PPD is denoted as $\cdot RH^+$. $\Delta G_4°$ is expressed approximately by the equation

$$\Delta_4°G^0_4 = -E^a_A(PPD^+) + S(PPD^+) + D(N\text{–}H) + I^a_P(H\cdot) - S(H^+) - S(R\cdot) \qquad (6)$$

where $E_A{}^a$, S, D, and $I_P{}^a$ represent adiabatic electron affinity, solvation energy, bond energy and adiabatic ionization energy, respectively.

The following values are obtained from the literatures.

$E^a_A(PPD^+) = I^a_P(PPD) = 6.8$ eV.[11]

$I^a_P(H\cdot) = 13.6$ eV, $D(N\text{–}H) = 4.0$ eV.[12]

$$S(\mathrm{H^+\ in\ water}) \cong 11.5\ \mathrm{eV}.^{[13,14]}$$

S(PPD^+ in water) is evaluated to be 2.2 eV using Born's equation with the dielectric constant of water at 25 °C, 78.5, and the effective radius of PPD^+, 3.24 Å.[15] Though the value of S (R·) is not certain, it can be taken to be the order of 0.1 eV. When these values are substituted in Eq. 6, $\Delta G_4°$ (in water) of 1.2 eV is obtained.

Since the solvation energy of a proton is smaller in ethanol than in water, $\Delta G_4°$ is calculated to be larger in ethanol than in water. This explains the fact that PPD^+-Br^- is fairly stable in ethanol though it is unstable in water.

It is important that the values of $\Delta G_4°$, though derived approximately, are positive and fairly large both in water and ethanol. It indicates that the equilibrium of Eq. 4 is inclined to the left and the concentration of the semiquinone R· is small. Nevertheless, the experimental fact that the diimine is formed easily from PPD^+ in water or water–ethanol mixture indicates that the free energy change of the reaction of Eq. 3 is nagative. Since $\Delta G_4°$ is positive, $\Delta G_5°$, the free energy for the formation of diimine from the semiquinone, must be a fairly large negative value to make up for $\Delta G_4°$.

In the presence of bases (B), one must take account of the reaction,

$$\mathrm{B + H^+ \rightleftarrows B{\cdot}H^+} \qquad (7)$$

the standard free energy change for this reaction in water, $\Delta G_7°$, at 25 °C are obtained as follows:[16]

$$\Delta G_7°(\mathrm{PPD}) = -0.36\ \mathrm{eV},\ \Delta G_7°(\mathrm{TEA}) = -0.60\ \mathrm{eV}$$

$$\Delta G_7°(\mathrm{OH^-}) = -0.83\ \mathrm{eV}$$

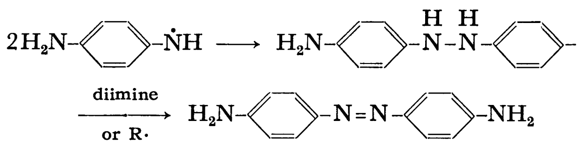
The standard free energy change of Eq. 4, $\Delta G_4°$, in the presence of a base, is reduced from that in water estimated above by these amounts.

Since the solvation energy of a proton is smaller in ethanol than in water, the equilibrium will shift to the right so that $\Delta G_7°$ becomes smaller in ethanol. Fairly large negative values of $\Delta G_7°$ are thought to be the reason why the reaction is enhanced by the addition of bases. Experimentally, the rates of decrease of the visible absorption band of PPD^+ at about 460 nm with various bases lie in the order OH^-, TEA and PPD, in agreement with that of their basicities.

In the actual reaction course, the interactions through the hydrogen bond are considered to be important. Since PPD^+ is thought to be a strong proton donor, a hydrogen bond complex between PPD^+ and PPD or aliphatic amines is formed. A proton will transfer easily through this hydrogen bond. The CT interaction between PPD^+ and TEA was reported previously.[5] Though we tried to find the dimer cation formed between PPD^+ and PPD in ethanol, we could not find it spectroscopically in the temperature range from room temperature to about −50 °C. Therefore the dimer cation may not play an important role.

With the addition of 2 molar equivalents of bases to an ethanol solution of PPD^+Br^-, the diimine produced reached about 100% of the theoretically expected quantity in the case of NaOH, while in the case of TEA it was about 80% and in the case of PPD a trace amount was detected as a shoulder of the absorption spectrum (Fig. 1). The diimine formed was stable in the case of NaOH, though in the case of both TEA and PPD it decomposed easily into Bandrowski's base. These observations can be explained as follows: Due to the relation, $\Delta G_7°(\mathrm{PPD}) > \Delta G_7°(\mathrm{TEA}) > \Delta G_7°(\mathrm{OH^-})$, the rate of the formation of the diimine is in the order of OH^-, TEA and PPD. Corbett studied the reaction of *p*-benzoquinone diimine with PPD in water and discussed the mechanism of the formation of Bandrowski's base.[17] According to his result, the rate of the reaction of the diimine with PPD increases greatly with lowering pH in the region of pH>6.[17] Since the basicity becomes lower in the order of PPD, TEA, and NaOH, the diimine formed is expected to be unstable in this order. The result is consistent with these expectations.

The result of TLC shows that 4,4′-diaminoazobenzene (AZ) is formed at the molar ratio of about 1/8 of BB. The following reaction is suggested for this.



(8)

As is seen from the comparison of the molecular structures of AZ and BB, thus, AZ is formed by the bonding between the N atoms of the amino groups, while BB is formed by the bonding between the C atom of the benzene ring and the N atom of the amino group. The fact that BB is formed more than AZ indicates that the C atom of the benzene ring is attacked more easily by the aminonitrogen, in the above reactions.

$TMPD^+ClO_4^-$+triethylamine (TEA). In this case, the first step of the reaction is considered to be an electron transfer.

$$\mathrm{TMPD^+ + TEA \rightleftarrows TMPD + TEA^+} \qquad (9)$$

The cation radical of TEA (TEA^+) produced is considered to be quite unstable and undergo further reaction, causing the shift in the equilibrium of Eq. 9 to produce TMPD.

The free energy change for the electron transfer reaction of Eq. 9 can be expressed approximately by

$$\Delta G_9° = I_\mathrm{P}^\mathrm{a}(\mathrm{TEA}) - E_\mathrm{A}^\mathrm{a}(\mathrm{TMPD^+}) + \mathit{\Delta} P \qquad (10)$$

The following values are obtained from the literature.

$$I_\mathrm{P}^\mathrm{a}(\mathrm{TEA}) = 7.5\ \mathrm{eV},^{[18]}$$

$$E_\mathrm{A}^\mathrm{a}(\mathrm{TMPD^+}) = I_\mathrm{P}^\mathrm{a}(\mathrm{TMPD}) = 6.20\ \mathrm{eV}^{[19]}$$

ΔP represents the difference of the polarization energy before and after the reaction and it is expressed as

$$\Delta P = P(\mathrm{TEA^+}) - P(\mathrm{TMPD^+})$$

The value is estimated to be −0.4 eV by using Born's equation, assuming 4.3 Å and 3.5 Å as the effective radii of $TMPD^+$ and TEA^+, respectively. When these valuie are substituted in Eq. 10, $\Delta G_9°$=0.9 eV is obtained. Since it is a large positive value, it seems improbable that the electron transfer reaction proceeds to the right without the second step of TEA^+ decomposition.

$DMPD^+ClO_4^-$+DMPD. In this case, a large amount of AZ′ was produced. The formation of AZ′ and BB′ would be explained by taking into consideration the similar reactions with those for PPD^+. However the reaction proceeds further to form an unknown product in this case.

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