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THE ELECTRON TRANSFER REACTION BETWEEN WURSTER'S BLUE CATION AND N,N-DIMETHYL-P-PHENYLENEDIAMINE IN AQUEOUS SOLUTION

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The electron transfer reaction between Wurster's Blue cation ($TMPD^{\ddagger}$) and N,N-dimethyl-p-phenylenediamine (DMPD) in aqueous solution is investigated by the temperature-jump method. The forward and backward rate constants of $TMPD^{\ddagger} + DMPD \rightleftharpoons TMPD + DMPD^{\ddagger}$ are determined to be $(4.2 \pm 2) \times 10^6$ and $(1.5 \pm 0.5) \times 10^8$ $M^{-1}\ s^{-1}$ at $10 \pm 2^{\circ}C$, respectively.

The organic radical systems have been of special interest since they present the simplest sort of electron transfer. Most of the reactions studied so far are the electron exchange between an ion radical and its parent molecule.1) This paper reports the temperature-jump study of the electron transfer between Wurster's Blue cation (the cation radical of N,N,N',N'-tetramethyl-p-phenylenediamine, $TMPD^{\ddagger}$) and N,N-dimethyl-p-phenylenediamine (DMPD) in aqueous solution.

$$TMPD^{\ddagger} + DMPD \rightleftharpoons TMPD + DMPD^{\ddagger} \qquad (1)$$

(1) Equilibrium Measurements. The apparent equilibrium constant defined by

$$K_{ap} = [TMPD]_t[DMPD^{\ddagger}]/[TMPD^{\ddagger}][DMPD]_t$$

is obtained by adding a known amount of DMPD·2HCl to an aqueous $TMPD^{\ddagger}ClO_4^-$ solution. Here $[TMPD]_t$ and $[DMPD]_t$ denote the total concentrations of TMPD and DMPD respectively, since a part of neutral species are present as a mono-protonated form in the investigated pH region (3 - 7).

$$TMPD + H^+ \rightleftharpoons TMPDH^+ \qquad ; \ K_T$$

$$DMPD + H^+ \rightleftharpoons DMPDH^+ \qquad ; \ K_D$$

$[TMPD^{\ddagger}]$ is calculated from the absorbance at 610 nm, using $\varepsilon_{610}(TMPD^{\ddagger}) = 1.1 \times 10^4$.2) Both $[DMPD^{\ddagger}]$ and $[TMPD]_t$ are equated to the decrease of $TMPD^{\ddagger}$. pH is adjusted by sodium acetate and hydrogen chloride.

The true equilibrium constant K of reaction (1) is expressed as

$$K = K_{ap}\,(1 + K_D[H^+])/(1 + K_T[H^+])$$

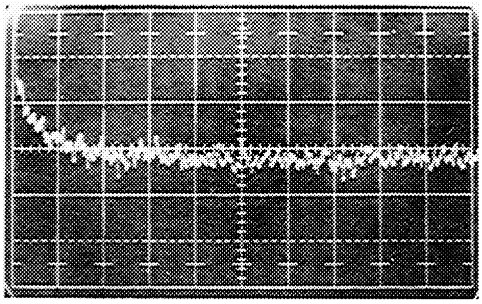

Fig. 1. The temperature-jump signal observed at 610 nm ($TMPD^{\dot{+}}$ band). $[DMPDH^+]_t$ 0.021 M, $[TMPD^{\dot{+}}]_e$ 1.0×10^{-4} M, $[TMPDH^+]_t$ 2.5×10^{-4} M, $[DMPD^{\dot{+}}]$ 2.5×10^{-4} M. $[H^+] = 6.46 \times 10^{-6}$ M. $10 \pm 2^{\circ}C$.

in which K_T and K_D are determined to be $10^{6.3 \pm 0.2}$ and $10^{6.3 \pm 0.2}$ respectively by titrating dihydrochloride salts with 0.02N NaOH. Since K_T is almost equal to K_D, the above relation is reduced to

$$K \fallingdotseq K_{ap}$$

This is confirmed by the fact that K_{ap} is independent of $[H^+]$ from pH = 3 to 7. K is determined to be 0.028 ± 0.006 at $10^{\circ}C$. Thus the free energy change of reaction (1) is equal to 2.0 kcal $mole^{-1}$.

(2) Rate Measurements. The rate measurements are performed with a Union Giken temperature-jump apparatus. The pseude first order rate constant defined by

$$d\,\Delta[TMPD^{\dot{+}}]/dt = -k_{obs}\,\Delta[TMPD^{\dot{+}}]$$

is obtained from the change of transmittance at 610 nm ($TMPD^{\dot{+}}$ band) after the temperature jump (Fig. 1). k_{obs} depends linearly on the reciprocal of $[H^+]$ as shown in Fig. 2. The observed H^+ dependence of k_{obs} is most likely to be interpreted by the assumption that the protonated forms of TMPD and DMPD are both inactive in electron transfer, so that the reaction proceeds only through the neutral form. Under this assumption k_{obs} is expressed in terms of the forward and backward rate constants of reaction (1) ($\vec{k}$ and $\overleftarrow{k}$) as below.

$$k_{obs} = (\vec{k}/[H^+]K_D)([TMPD^{\dot{+}}]_e + [DMPDH^+]_e) + (\overleftarrow{k}/[H^+]K_T)([TMPDH^+]_e + [DMPD^{\dot{+}}]_e),$$

where $[\ ]_e$ denotes the equilibrium concentration of each species after the temperature rise. In derviving the above equation, it is assumed that $[TMPDH^+]_e$ and $[DMPDH^+]_e$ are present in large excess over $[TMPD]_e$ and $[DMPD]_e$, respectively. Again, setting $K_D = K_T$, this equation is reduced to

$$k_{obs} = (\overleftarrow{k}/[H^+]K_T)\{K([TMPD^{\dot{+}}]_e + [DMPDH^+]_e) + [TMPDH^+]_e + [DMPD^{\dot{+}}]_e\},$$

where $K = \vec{k}/\overleftarrow{k}$ is introduced. This expression agrees with the linear dependence of k_{obs} on $1/[H^+]$ as exhibited in Fig. 2. Figure 3 shows that $k_{obs}[H^+]$ increases linearly with the quantity, $K([TMPD^{\dot{+}}]_e + [DMPDH^+]_e) + [TMPDH^+]_e + [DMPD^{\dot{+}}]$. From the slope of the straight line, $\vec{k}$ and $\overleftarrow{k}$ are determined to be

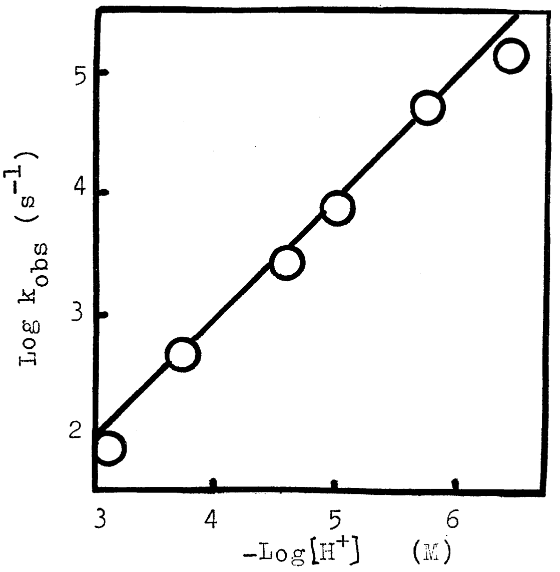

Fig. 2. The dependence of k_{obs} on [H^+]. [$DMPDH^+$]$_e$ 0.019 M, [$TMPD^{\dot{+}}$]$_e$ 6.5 x 10^{-5}M, [$TMPDH^+$]$_e$ 1.7 x 10^{-4}M, and [$DMPD^{\dot{+}}$]$_e$ 1.7 x 10^{-4}M. 10 ± 2°C.

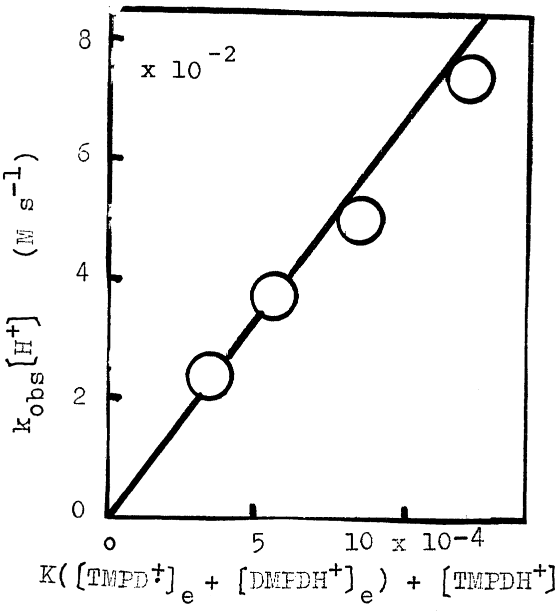

Fig. 3. The dependence of $k_{obs}\cdot$[H^+] on the quantity, K([$TMPD^{\dot{+}}$]$_e$ + [$DMPDH^+$]$_e$) + [$TMPDH^+$]$_e$ + [$DMPD^{\dot{+}}$]$_e$. pH 4.49 - 4.57. 10 ± 2°C.

$$\vec{k} = (4.2 \pm 2) \times 10^6\ M^{-1}\ s^{-1}$$

$$\overleftarrow{k} = (1.5 \pm 0.5) \times 10^8\ M^{-1}\ s^{-1} \qquad \text{at } 10 \pm 2^{\circ}C.$$

k_{obs} is independent of the concentration of sodium acetate from 0.033 M to 0.33 M. This excludes the possibility that the overall rate is determined by the proton transfer of either TMPD or DMPD.

It should be noted that $\overleftarrow{k}$ which corresponds to the negative free energy change of the reaction is more than one order below the diffusion controlled limit, ca. 10^{10} M^{-1} s^{-1}. The electron exchange reactions (2) and (3) were previously studied by the ESR method.[3-5]

$$TMPD^{\dot{+}} + TMPD^{*} \rightleftharpoons TMPD + TMPD^{*\dot{+}} \quad ;\ k_2 \qquad (2)$$

$$DMPD^{\dot{+}} + DMPD^{*} \rightleftharpoons DMPD + DMPD^{*\dot{+}} \quad ;\ k_3 \qquad (3)$$

k_2 is reported to be (2.1 ± 0.8) x 10^8 M^{-1} s^{-1} in water 3) and (2.0 ± 1.0) x 10^8 or (1.0 ± 0.2) x 10^9 M^{-1} s^{-1} in acetonitrile.4,5) k_3 is (7.5 ± 0.8) x 10^8 M^{-1} s^{-1} in acetonitrile.5) Comparing the present result to these values, it is concluded that in the electron transfer of the substituted p-phenylenediamine cation system, there exists a certain activating process which makes the rate constant smaller than a diffusion controlled one. This circumstance is different from the reactions between the anion radical of tetracyanoquinodimethane and substituted p-benzoquinones.6) In the latter case, the rate constant corresponding to the negative free energy change of the reaction is always close to a diffusion controlled one. The effect of solvents and molecular structures on the electron transfer rate will make clear the nature of the activating process in the present system. The results of further studies will be reported soon.

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