Rate of the Electron-transfer Reaction between Tetracyanoquinodimethane and *NNN'N'*-Tetramethyl-*p*-phenylenediamine in Acetonitrile

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Summary Forward (k_1) and backward (k_{-1}) rate constants for the one-electron transfer between tetracyanoquinodimethane and *NNN'N'*-tetramethyl-*p*-phenylenediamine were determined in acetonitrile solvent: $k_1 = (4 \pm 2) \times 10^8$ and $k_{-1} = (6 \pm 2) \times 10^9$ l mol^{-1} s^{-1} at 23 ± 2 °C.

WE have previously reported temperature-jump studies of the electron-transfer reaction between an organic ion-radical and a different neutral molecule.[1,2] Most electron-transfer reactions so far studied proceed nearly at an encounter-controlled rate, when the free-energy change of the reaction is negative. We now report the electron-transfer reaction between tetracyanoquinodimethane (TCNQ) and *NNN'N'*-tetramethyl-*p*-phenylenediamine (TMPD) in acetonitrile. This reaction was chosen in order to examine the effect of charge-transfer (CT) interactions between these reactants on the electron-transfer rate.†

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† Although there have been a number of studies concerning the ionization between electron donor–acceptor (EDA) pairs, either or both of which are electronically excited, this report is the first determination of reversible electron transfer between an EDA pair with both components in the ground state.

$$\mathrm{TCNQ} + \mathrm{TMPD} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{TCNQ}^- + \mathrm{TMPD}^+ \qquad (1)$$

The equilibrium constant, K, and the thermodynamic parameters of reaction (1) were obtained spectrophotometrically by mixing a solution of the tetraethylammonium salt of TCNQ with a solution of the perchlorate salt of TMPD, both in acetonitrile. At 25 °C, $K = (7 \pm 2) \times 10^{-2}$, $\Delta H = -(4 \pm 1)$ kcal mol^{-1}, and $\Delta S = -(17 \pm 5)$ cal K^{-1} mol^{-1}. The large negative ΔS value indicates that ordering of solvent molecules around TCNQ$^-$ and TMPD$^+$ takes place on ionization of TCNQ and TMPD. No CT complex was detected in acetonitrile, but the CT complex TCNQ–TMPD was found to be formed in chloroform with a formation constant, K_{CT} of $(3 \pm 0{\cdot}5) \times 10^2$ l mol^{-1} and an extinction coefficient, ϵ, of $(1{\cdot}4 \pm 0{\cdot}4) \times 10^4$ at 530 nm and 25 °C.[3] Using this ϵ value and the absorbance observed at 530 nm when acetonitrile was used, the upper limit of K_{CT} in acetonitrile was estimated to be 1 l mol^{-1}. The rate of reaction (1) was obtained using a temperature-jump apparatus in the presence of 0·02 M Et_4NClO_4 as supporting electrolyte.[4] At this concentration of Et_4NClO_4, the ion radicals are not ion-paired with counter-ions.[2] The forward, k_1, and backward, k_{-1}, rate constants were determined to be $(4 \pm 2) \times 10^8$ and $(6 \pm 2) \times 10^9$ l mol^{-1} s^{-1}, respectively at 23 ± 2 °C. k_{-1}, corresponding to a negative free energy change for the reaction, is nearly an encounter-controlled rate constant in spite of the fact that the reaction in this direction is accompanied by an increase in enthalpy. Calculating k from simple collision theory with an activation energy of 4 kcal mol^{-1} gives a k_{-1} value of *ca.* 10^8 l mol^{-1} s^{-1}, which is *ca.* 60 times smaller than the observed value.‡ This implies that the activation entropy is positive, probably arising from desolvation processes of the solvent molecules caused by neutralization of the reactant ions. The present result, that k_{-1} is almost encounter-controlled, means that we cannot detect any evidence for CT interaction playing a role in the present reaction. However the steric requirements for the occurrence of electron-transfer must be small, because the activation entropy is positive. It may be concluded that if the electron-transfer does take place *via* a CT complex, that complex cannot have a definite geometrical configuration like the complexes observed in the crystalline state.[5]

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‡ The activation enthalpy must be larger than the enthalpy change of this reaction, which is 4 kcal mol^{-1}.

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