Charge-Transfer Complexes Acting as Real Intermediates in Hydride Transfer from Michler's Hydride to 2,3-Dichloro-5,6-dicyano-p-benzoquinone via Electron Transfer

Khan M. Zaman, Shunzo Yamamoto, and Norio Nishimura

*Department of Chemistry
Faculty of Science, Okayama University
3-1-1 Tsushima-naka, Okayama 700, Japan*

Junichi Maruta and Shunichi Fukuzumi*

*Department of Applied Chemistry
Faculty of Engineering, Osaka University
Suita, Osaka 565, Japan*

Received July 25, 1994

Charge-transfer complexes formed between electron donors and acceptors have been studied extensively since the early development of the Mulliken charge-transfer (CT) theory.[1] The CT complexes have been implicated as intermediates in a variety of reactions of electron donors (D) and acceptors (A), eq 1.[2]

$$D + A \overset{K_{CT}}{\rightleftharpoons} (DA) \xrightarrow{k_1} \text{products} \qquad (1)$$

However, the mechanistic involvement of CT complexes has always been questioned by an alternative mechanism in which the CT complex is merely an innocent bystander in an otherwise dead-end equilibrium, as shown in eq 2.[3] The difference lies

$$(D\ A) \overset{K_{CT}^{-1}}{\rightleftharpoons} D + A \xrightarrow{k_2} \text{products} \qquad (2)$$

in whether the overall second-order rate constant is a product of the rate constant for the passage of the CT complex to the transition state and the formation constant of the CT complex, $k_{obs} = k_1K_{CT}$ in eq 1, or a simple bimolecular rate constant, $k_{obs} = k_2$ in eq 2, although the two processes in eqs 1 and 2 are kinetically indistinguishable.[3,4] Kiselev and Miller[5] have reported the observation of negative activation enthalpy for the second-order rate constant of the Diels–Alder reaction of tetracyanoethylene with 9,10-dimethylanthracene, taken as experimental proof that the Diels–Alder reaction passes through formation of the CT complex. Such a negative activation enthalpy ($\Delta H^{\ddagger}_{obs} < 0$) could be obtained only if the second-order rate constant is a product, $k_{obs} = k_1K_{CT}$, and the CT complex is so strong that the heat of formation of the CT complex ($\Delta H_{CT} < 0$) is of greater magnitude than the activation enthalpy for the passage of the CT complex to the transition state ($\Delta H^{\ddagger}_1 > 0$), *i.e.*, $\Delta H^{\ddagger}_{obs} = \Delta H_{CT} + \Delta H^{\ddagger}_1$. It seems extremely difficult to find an appropriate electron donor–acceptor system which is suitable to detailed kinetic analysis, since strong electron donor–acceptor systems prerequisite to observe negative $\Delta H^{\ddagger}_{obs}$ values are usually too fast to follow the reactions. Thus, no independent determination of ΔH_{CT} and $\Delta H^{\ddagger}_1$ has so far been reported to confirm the relation, $\Delta H^{\ddagger}_{obs}$ $(< 0) = \Delta H_{CT} + \Delta H^{\ddagger}_1$.[6]

We report herein that bis(4-(dimethylamino)phenyl)methane (MH_2, Michler's hydride) and 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) form sufficiently strong CT complexes that the $\Delta H^{\ddagger}_{obs}$ value of hydride transfer from MH_2 to DDQ is negative, being equal to the sum of ΔH_{CT} and $\Delta H^{\ddagger}_1$, both of which have been determined successfully.

When MH_2 and *p*-chloranil (CA) are mixed in EPA (ether–pentane–alcohol) at low temperatures (*e.g.*, 123 K), a new absorption band with $\lambda_{max} = 660$ nm is immediately observed, and the absorbance increases with a decrease in the temperature. The broad absorption band is characteristic of an intermolecular CT complex.[1,2,7] The CT complex becomes unstable at higher temperatures, and hydride transfer from MH_2 to CA occurs to yield the Michler's hydride cation (MH^+), which has the absorption maximum at $\lambda_{max} = 605$ nm ($\epsilon_{max} = 147\,500$ M^{-1} cm^{-1}).[8,9] The second-order rate constant (k_{obs}) for the formation of MH^+ is determined as 4.7×10^{-2} M^{-1} s^{-1} in acetonitrile at 298 K. The $\Delta H^{\ddagger}_{obs}$ value is also determined as 33 ± 3 kJ mol^{-1} from the temperature dependence at 298–323 K.

When *p*-chloranil was replaced by a stronger one-electron oxidant (DDQ), the rates of formation of MH^+ became much faster, and they were determined by using a stopped-flow spectrophotometer. The rates of formation of MH^+ in the presence of a large excess of DDQ obeyed pseudo-first-order kinetics.[10] The pseudo-first-order rate constant (k_{exp}) increases linearly with an increase in [DDQ] at low concentrations ($<1.0 \times 10^{-4}$ M) but exhibits deviation from the linear correlation at higher concentrations (*e.g.*, 5.0×10^{-4} M). Such curvature demonstrates the presence of a CT complex formed between MH_2 and DDQ during the reaction.[11] According to eqs 1 and 2, k_{exp} is expressed as a function of [DDQ] as shown in eqs 3 and 4, respectively. In each case, the plot of k_{exp}^{-1} and $[DDQ]^{-1}$

$$k_{exp} = k_1K_{CT}[DDQ]/(1 + K_{CT}[DDQ]) \qquad (3)$$

$$k_{exp} = k_2[DDQ]/(1 + K_{CT}[DDQ]) \qquad (4)$$

is expected to give a straight line, and from the ratio of intercept/slope is obtained the K_{CT} value. From the intercept is obtained the limiting rate constant k_{max}, which corresponds to k_1 and k_2/K_{CT} in eqs 3 and 4, respectively. In fact, the linear correlation is obtained between k_{exp}^{-1} and $[DDQ]^{-1}$ for the hydride transfer reaction from MH_2 to DDQ in trichloroethane at various

(1) (a) Mulliken, R. S.; Person, W. B. *Molecular Complexes, a Lecture and Reprint Volume*; Wiley-Interscience: New York, 1969. (b) Mataga, N.; Kubota, T. *Molecular Interactions and Electronic Spectra*; Marcel Dekker: New York, 1970.

(2) (a) Foster, R. *Organic Charge Transfer Complexes*; Academic Press: New York, 1969. (b) Chanon, M.; Tobe, M. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 1. (c) Kochi, J. K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1227. (d) Jones, G. II. In *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; Part A, p 245. (e) Kochi, J. K. *Acc. Chem. Res.* **1992**, *25*, 39. (f) Fukuzumi, S. In *Advances in Electron Transfer Chemistry*; Mariano, P. S., Ed.; JAI Press: Greenwich, CT, 1992; pp 67–175.

(3) Sustmann, R.; Korth, H.-G.; Nüchter, U.; Siangouri-Feulner, I.; Sicking, W. *Chem. Ber.* **1991**, *124*, 2811.

(4) (a) Fukuzumi, S.; Mochida, K.; Kochi, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 5961. (b) Fukuzumi, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 2141. (c) Sustmann, R.; Dern, M.; Kasten, R.; Sicking, W. *Chem. Ber.* **1987**, *120*, 1315.

(5) Kiselev, V. D.; Miller, J. G. *J. Am. Chem. Soc.* **1975**, *97*, 4036.

(6) Anomalous reactivities of donor–acceptor molecules with a strong collective donor–acceptor interaction in the solid and liquid phase at extremely low temperatures have previously been recognized: Lishnevskii, V. A. *Russ. J. Phys. Chem.* **1978**, *52*, 1.

(7) Single-component CT spectra observed in this case indicate that no different conformational arrangements of donor and acceptor molecules are involved in the CT complex. For multicomponent CT spectra with different conformational arrangements, see: Solaro, R.; Chiellini, E.; Ledwith, A. *J. Chem. Soc., Chem. Commun.* **1980**, 583.

(8) Gorden, P. F.; Gregory, P. *Organic Chemistry in Colour*; Springer-Verlag: Berlin, 1987; p 248.

(9) The initial reduced product of DDQ is $DDQH^-$ which undergoes a comproportionation reaction with DDQ to yield $DDQ^{\bullet-}$ and the corresponding hydroquinone ($DDQH_2$). The formation of $DDQ^{\bullet-}$ has been confirmed by the ESR spectrum ($g = 2.0053$); see: (a) Fukuzumi, S.; Nishizawa, N.; Tanaka, T. *J. Org. Chem.* **1984**, *49*, 3571. (b) Zaman, K. M.; Nishimura, N.; Yamamoto, S. *J. Phys. Org. Chem.* **1994**, *7*, 309.

(10) The clean pseudo-first-order kinetics may preclude the participation of a radical chain reaction.

(11) Although the CT spectrum of the stable MH_2–CA complex is readily detected, the large concentrations of reactants required to observe the CT spectrum of the MH_2–DDQ complex have precluded the clear-cut detection because of the limited solubility of reactants in trichloroethane. The observation of transient CT spectra in similar systems has been reported previously.[9a]

0002-7863/94/1516-12099$04.50/0

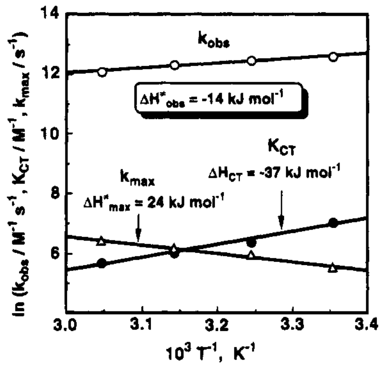

Figure 1. Arrhenius plots of K_{CT} and k_{max} as well as the observed overall second-order rate constant (k_{obs}) for the hydride-transfer reaction from MH_2 (1.0×10^{-5} M) to DDQ (5.0×10^{-5}–5.0×10^{-4} M) in trichloroethane.

temperatures. Figure 1 shows the Arrhenius plots of K_{CT} and k_{max} as well as the observed second-order rate constant (k_{obs}) at low concentrations, which corresponds to k_1K_{CT} and k_2 in eqs 3 and 4, respectively. It is clearly shown that the heat of formation of the CT complex ($\Delta H_{CT} = -37 \pm 3$ kJ mol^{-1}) is of greater magnitude than the activation enthalpy of k_{max} ($\Delta H^{\neq}_{max} = 24 \pm 3$ kJ mol^{-1}). Moreover, the observed *negative* $\Delta H^{\ddagger}_{obs}$ value (-14 ± 2 kJ mol^{-1}) agrees well with the sum of the negative ΔH_{CT} value (-37 kJ mol^{-1}) and the positive $\Delta H^{\ddagger}_{max}$ value (14 kJ mol^{-1}).[12] Such a *negative* $\Delta H^{\ddagger}_{obs}$ value, being equal to $\Delta H_{CT} + \Delta H^{\neq}_{max}$, could only arise when the CT complex lies along the reaction pathway (eq 1).

The CT complexes have so far been implicated as prerequisite intermediates for efficient electron transfer from electron donors to acceptors.[2,13] In fact an electron transfer pathway followed by proton and electron transfer has been well established for hydride transfer reactions from typical biological hydride donors (nicotinamide adenine dinucleotide, dihydroflavins and analogues) to a strong electron acceptor such as DDQ.[14,15] In order to determine the energetics of electron transfer from MH_2 to DDQ, the one-electron oxidation potential (E°_{ox}) of MH_2 must be determined, since the one-electron reduction potential of DDQ is known as 0.51 V (vs SCE) in acetonitrile. Although the E°_{ox} value cannot be determined by the conventional cyclic voltammetry (CV) because of the instability of the resulting radical cation ($MH_2^{\bullet+}$), the irreversible anodic wave in acetonitrile becomes reversible by raising the scan rate to 200 V s^{-1} using a platinum microelectrode. The E°_{ox} value in acetonitrile at 298 K, determined as the average of the anodic and cathodic current maxima, is 0.75 V vs SCE. Thus, the free energy change of electron transfer (ΔG°_{et}) from MH_2 to DDQ in acetonitrile at 298 K is determined as 23 kJ mol^{-1} using the relation $\Delta G^\circ_{et} = F(E^\circ_{ox} - E^\circ_{red})$, where F is the Faraday constant. Although the unknown value of the reorganization energy of electron transfer in the present system has precluded direct comparison between the calculated value of the rate constant of electron transfer from MH_2 to DDQ based on the Marcus theory[16] with the observed value, the ΔG°_{et} value (23 kJ mol^{-1}) being comparable with the $\Delta H^{\ddagger}_{max}$ value (24 kJ mol^{-1}) suggests that the hydride transfer from MH_2 to DDQ occurs via electron transfer in the CT complex formed between MH_2 and DDQ.[17,18]

Acknowledgment. This work was partially supported by a Grant-in-Aid from the Ministry of Education, Science, and Culture, Japan.

(12) The appropriate choice of solvents is essential to observe the negative $\Delta H^{\ddagger}_{obs}$ value. The change of solvent from trichloroethane to acetonitrile resulted in an increase in the $\Delta H^{\ddagger}_{obs}$ value, which was 0 ± 2 kJ mol^{-1}.

(13) The Diels–Alder reaction of anthracene derivatives with electron acceptors such as tetracyanoethylene and *p*-benzoquinone derivatives has been reported to proceed *via* electron transfer: (a) Fukuzumi, S.; Kochi, J. K. *Tetrahedron* **1982**, *38*, 1035. (b) Fukuzumi, S.; Okamoto, T. *J. Am. Chem. Soc.* **1993**, *115*, 11600.

(14) (a) Carlson, B. W.; Miller, L. L.; Neta, P.; Grodkowski, J. *J. Am. Chem. Soc.* **1984**, *106*, 7233. (b) Fukuzumi, S.; Koumitsu, K.; Hironaka, K.; Tanaka, T. *J. Am. Chem. Soc.* **1987**, *109*, 305.

(15) (a) Eberlein, G.; Bruice, T. C. *J. Am. Chem. Soc.* **1983**, *105*, 6685. (b) Fukuzumi, S. Kitano, T.; Ishikawa, M.; Matsuda, Y. *Chem. Phys.* **1993**, *176*, 337.

(16) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

(17) In an endergonic region, the activation free energy for electron transfer in the CT complex may be approximately equal to the free energy change of electron transfer in the CT complex ($\Delta G'_{et}$), which is given by $\Delta G'_{et} = \Delta G^\circ_{et} + w_p - w_r$, where ΔG°_{et} corresponds to the standard free energy change of the electron-transfer process: $D + A \rightarrow D^{\bullet+} + A^{\bullet-}$ and the work terms w_p and w_r represent the energy required to bring together the products and reactants, respectively.[16] Thus, the agreement between the ΔG°_{et} and $\Delta H^{\ddagger}_{max}$ values suggests the cancellation of the w_r and w_p terms as well as the entropy term, which can be usually neglected for electron-transfer processes.

(18) The electron transfer in the CT complex may be followed by proton and electron transfer to complete the net hydride transfer as in the case of hydride transfer reactions from coenzyme analogues to strong electron acceptors such as DDQ.[14,15]