MECHANISM OF THE HYDRIDE TRANSFER REACTION OF LEUCO CRYSTAL VIOLET WITH CYANOMETHYLENE ACCEPTORS

NORIO NISHIMURA,* KHAN M. ZAMAN AND SHUNZO YAMAMOTO
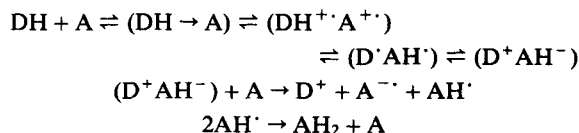
Department of Chemistry, Faculty of Science, Okayama University, Okayama 700, Japan

In the hydride transfer reaction of Leuco Crystal Violet to form the Crystal Violet cation, the role of cyanomethylene acceptors was found to be essentially different from that of p-benzoquinones, both previously believed to act as π-acceptors in the same manner.

The mechanism of hydrides transfer reactions of N-benzyl-1,4-dihydronicotinamide with various kinds of π-acceptors has attracted much interest. In the early stages of work, direct hydride transfer was believed to occur.[1-3] However, Steffens and Chipman[4] cast doubts on this and suggested the formation of a charge-transfer (CT) complex as an intermediate. Ohno and Kito[5] demonstrated by ESR that the reaction actually proceeds via a CT intermediate. During the last decade, Fukuzumi and co-workers[6-10] have investigated in detail and revealed the mechanism of hydrides transfer reactions for a variety of electron donor–acceptor systems.

Similar hydride transfer reactions of Leuco Crystal Violet (CVH)[11-14] and N-methylacridans with various kinds of π-acceptors[15-18] have also been reported. These studies seem to have established that the apparent hydride transfer reactions involve first electron transfer via a CT complex, followed by successive proton and electron transfers (Scheme 1).

Previously, we noted that in the reaction between CVH and chloranil (CA), the rate of formation of

$$DH + A \rightleftharpoons (DH \rightarrow A) \rightleftharpoons (DH^{+\cdot}A^{+\cdot})$$
$$\rightleftharpoons (D^{\cdot}AH^{\cdot}) \rightleftharpoons (D^{+}AH^{-})$$
$$(D^{+}AH^{-}) + A \rightarrow D^{+} + A^{-\cdot} + AH^{\cdot}$$
$$2AH^{\cdot} \rightarrow AH_{2} + A$$

Scheme 1. Multi-step mechanism generally accepted so far. DH denotes a hydride donor and A its acceptor. The pairs of species in parentheses are in solvent cages

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* Author for correspondence.

Crystal Violet cations (CV^{+}) agreed with that of CA$^{-\cdot}$.[13,14] Recently, similar results have been obtained for the reaction between Leuco Bindschedler's Green and CA,[19] although not stated explicitly. These findings are in harmony with the above-mentioned mechanism. However, during studies along this line we noticed the important point that the reaction proceeds in different ways, depending on the nature of the π-acceptors. In this paper we report our new findings.

When an acetone or acetonitrile solution of 7,7,8,8-tetracyano-p-quinodimethane (TCNQ) was mixed with that of CVH, a characteristic absorption band of TCNQ anion radicals, TCNQ$^{-\cdot}$ extending over the range 650–900 nm with a vibrational structure, appeared immediately (Figure 1). On cooling the solution with liquid nitrogen, the colour changed from yellowish green to light brown, but the original colour returned on warming, indicating the formation of a CT complex at low temperatures. The rate of initial rise of TCNQ$^{-\cdot}$ was so rapid at ambient temperature that we were unable to measure the rate even by means of the stopped-flow technique. Although the formation of a small amount of TCNQ was observed when TCNQ was dissolved in CH$_3$CN,[20] the absorbance of TCNQ$^{-\cdot}$ extrapolated to zero time was found to depend on both the initial concentrations of TCNQ and CVH, indicating that a rapid (pseudo) equilibrium between the reactants and the pair of radical ions (CVH$^{+\cdot}$TCNQ$^{-\cdot}$) was attained before CV^{+} began to form. From the structural point of view, the electronic spectrum due to CVH$^{+\cdot}$ may be similar to that of the cation radical of dimethylaniline. When the acetonitrile solutions of dimethylaniline and TCNQ were mixed, only the electronic spectrum of TCNQ$^{-\cdot}$ appeared in the visible region. Judging from its localized electronic
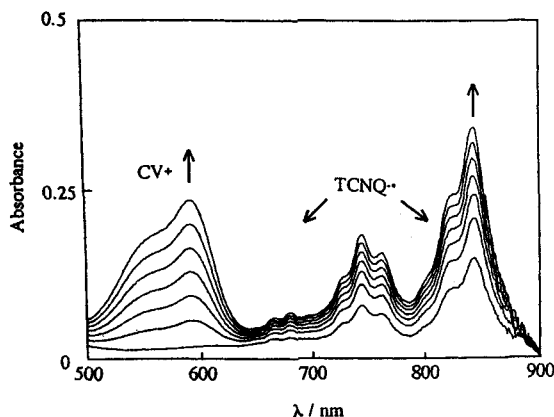
Figure 1. Spectral change as a function of time (10 min intervals) for the reaction of CVH with TCNQ in acetonitrile at $25\,^{\circ}$C. $[CVH]_0 = 2 \times 10^{-5}\,mol\,dm^{-3}$; $[TCNQ]_0 = 4 \times 10^{-3}\,mol\,dm^{-3}$

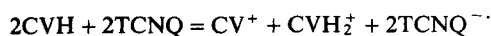Figure 2. Time dependences of $[CV^+]$ and $[TCNQ^{-\cdot}]$

structure, it is not unexpected that no spectrum due to $CVH^{+\cdot}$ appeared in the visible region.

Under the conditions $[TCNQ]_0 \gg [CVH]_0$, the equilibrium constant was calculated using the following equation:

$$K = x/[TCNQ]_0([CVH]_0 - x) \qquad (1)$$

where x denotes the concentration of $TCNQ^{-\cdot}$ coexisting with $CVH^{+\cdot}$ in a solvent cage, and it was estimated from the absorbance at $\lambda_{max} = 843$ nm ($\varepsilon = 43\,300\,dm^3\,mol^{-1}\,cm^{-1}$) due to $TCNQ^{-\cdot}$. With variations of $[TCNQ]_0$ and $[CVH]_0$, the average value of K obtained at $25\,^{\circ}$C was $37\cdot9 \pm 0\cdot9\,dm^3\,mol^{-1}$. After the pre-equilibration, the absorbance increased gradually, and simultaneously the intensity of the band at $\lambda_{max} = 589$ nm due to CV^+ ($\varepsilon = 117\,000\,dm^3\,mol^{-1}\,cm^{-1}$) also increased (Figure 1). With an excess of TCNQ over CVH, it was found that the rate of formation of CV^+ followed first-order kinetics with respect to $[CVH]$ and that the rate was also proportional to $[TCNQ]_0$. On the basis of Figure 1, the time dependences of $[TCNQ^{-\cdot}]$ and $[CV^+]$ were plotted as shown in Figure 2. It can be seen that the rate of formation of $TCNQ^{-\cdot}$ is nearly twice as great as that of CV^+. The rate ratio continued for a long time, indicating that the reaction proceeds with 2:1 stoichiometry. A plausible reaction scheme which accommodates the above findings may be as shown in Scheme 2.

The overall stoichiometry is given by

$$2CVH + 2TCNQ = CV^+ + CVH_2^+ + 2TCNQ^{-\cdot}$$

where CVH_2^+ denotes protonated CVH. Assuming a steady state for $[CVH^{+\cdot}]$ and $[CV^\cdot]$, the initial rate of formation of CV^+ after the pre-equilibration could be
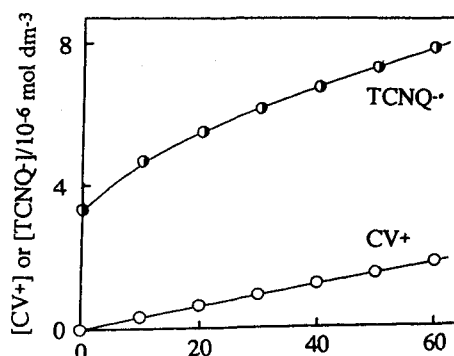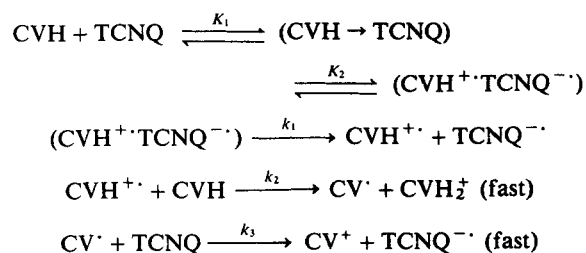
given by

$$R = Kk_1[TCNQ]_e[CVH]_e \qquad (2)$$

where $K = K_1K_2$. Since at the pre-equilibrium about 3% of CVH was found to be converted into $CVH^{+\cdot}$, this expression could be approximated as follows:

$$R = Kk_1[TCNQ]_0[CVH]_0 \qquad (3)$$

This expression is consistent with the observation stated above. The Kk_1 value at $25\,^{\circ}$C is estimated to be $7\cdot20 \times 10^{-3}\,dm^3\,mol^{-1}\,s^{-1}$, which leads to $k_1 = 1\cdot9 \times 10^{-4}\,s^{-1}$. This extraordinarily small value means that the pair of radical ions are stabilized by the coulombic force. Therefore, the diffusive process to form $CVH^{+\cdot}$ and $TCNQ^{-\cdot}$ from the ion pair is inferred to be extremely slow.

When an acetone or acetonitrile solution of tetracyanoethylene (TCNE) was mixed with that of CVH, an absorption band extending over the range 350–460 nm with a vibrational structure appeared immediately, followed by slow formation of CV^+. Therefore, the role of TCNE in the hydride-equivalent transfer is considered to be the same as that of TCNQ. Unfortunately, the molar absorptivity of this band assigned to $TCNE^{-\cdot}$[21] is much smaller than that of $TCNQ^{-\cdot}$, which made its kinetic measurement difficult. Hence no

$$CVH + TCNQ \; \overset{K_1}{\rightleftharpoons} \; (CVH \rightarrow TCNQ)$$

$$\overset{K_2}{\rightleftharpoons} \; (CVH^{+\cdot}TCNQ^{-\cdot})$$

$$(CVH^{+\cdot}TCNQ^{-\cdot}) \; \overset{k_1}{\longrightarrow} \; CVH^{+\cdot} + TCNQ^{-\cdot}$$

$$CVH^{+\cdot} + CVH \; \overset{k_2}{\longrightarrow} \; CV^\cdot + CVH_2^+ \; (fast)$$

$$CV^\cdot + TCNQ \; \overset{k_3}{\longrightarrow} \; CV^+ + TCNQ^{-\cdot} \; (fast)$$

Scheme 2. Proposed multi-step mechanism for CVH–TCNQ system

further quantitative measurements were done for TCNE.

It is worth noting that in this mechanism, TCNQ acts as an electron acceptor, but not as a hydride acceptor or a hydrogen acceptor, although species such as $TCNQH^-$ ($TCNEH^-$) and $TCNQH^{\cdot}$ ($TCNEH^{\cdot}$) have been assumed.[7,15-18] On the other hand, it is well known that the oxidation–reduction reaction between quinones and the corresponding hydroquinones involves multi-step processes. Therefore, it is reasonable that p-benzoquinones such as CA can accept an electron followed successively by a proton and an electron from a π-donor (Scheme 1). In this case, the proton transfer step is rate determining, as evidenced by the remarkable kinetic isotope effects.[4,11,13] The species $TCNQH^{\cdot}$ might be formed by the reaction

$$CVH^{+\cdot} + TCNQ \rightarrow CV^+ + TCNQH^{\cdot}$$
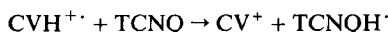
The neutral radical $TCNQH^{\cdot}$ is known to be formed as an intermediate of the reaction of $TCNQ^{-\cdot}$ with strong mineral acids and it disproportionates to form TCNQ and p-phenylenedimalononitrile.[20,22] However, the rate equation derived on this assumption leads to the same rate of formation of CV^+ as that of $TCNQ^{-\cdot}$ and hence to 1 : 1 stoichiometry, which is inconsistent with our observation. Meanwhile, CVH not only behaves as a successive electron–proton–electron donor to give net CV^+, but also acts as a base to accept protons. In fact, during the reaction, a new peak appeared at $\lambda_{max} = 222$ nm. This band can be assigned to CVH_2^+, since the same band appeared on adding a small amount of HCl to the acetonitrile solution of CVH.

Fukuzumi et al.[7] found that added pyridine accelerates the rate of a hydride transfer reaction. Indeed, the rate of formation of CV^+ increased proportionately to the added triethylamine (TEA). If their view is taken into account, the rate of formation of CV^+ may be aided by the reaction

$$(CVH^{+\cdot}TCNQ^{-\cdot}) + TEA \rightarrow CV^{\cdot} + TEAH^+ + TCNQ$$
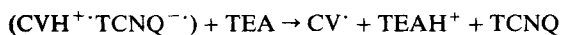
Under the conditions of excess of CVH over TCNQ, second-order kinetics such that

$$(CVH^{+\cdot}TCNQ^{-\cdot}) + CVH \rightarrow CV^{\cdot} + CVH_2^+ + TCNQ^{-\cdot}$$
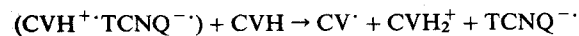
cannot be neglected. Although no contribution of this term was found under our experimental conditions, we have found recently in another system that such a term plays a considerable role.

In conclusion, it has been clarified that in the hydride transfer reaction of CVH, the behaviour of cyanomethylene acceptors is essentially different from that of p-benzoquinones. The difference arises from the reasonable assumption that p-benzoquinones can accept both electrons and protons, whereas cyanomethylenes can accept only electrons. Previously, only one of the species formed during the hydride transfer

reactions has been followed spectrophotometrically,[6-10,15-18] and no distinction has been made between p-benzoquinones and cyanomethylenes. Hence some speculations were required to infer the mechanism. In this study, we followed the formation of two products at the same time, and this made the mechanism clearer. Details of the difference in the roles of p-benzoquinones and cyanomethylenes in the hydride transfer reactions will be discussed elsewhere.

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