# HYDRIDE TRANSFER REACTIONS OF MICHLER'S HYDRIDE WITH DIFFERENT π-ACCEPTORS

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The hydride transfer reactions of 4,4'-bis(dimethylaminophenyl)methane (Michler's hydride) with p-benzoquinones were studied. The rate of formation of Michler's Hydrol Blue was followed spectrophotometrically. The second-order rate constants and the activation parameters were estimated. The formation of a charge-transfer complex was observed at low temperatures. Stable and unstable paramagnetic species formed during the reactions were assigned by ESR spectroscopy. The observed kinetic behaviour and the stoichiometry were in line with those previously obtained for the systems involving Leuco Crystal Violet, Leuco Malachite Green and Leuco Bindschedler's Green. Hence the reaction is considered to proceed according to the so-far accepted multi-step mechanism. However, when tetracyano-p-quinodimethane or tetracyanoethylene was used as a π-acceptor, a comparatively stable radical ion pair was formed as a result of a one-electron transfer, followed by the gradual formation of Michler's Hydrol Blue. The kinetic behaviour and the stoichiometry of the reaction were examined, together with the enhanced kinetic effects of added triethylamine. A modified mechanism for these systems is proposed. The role of cyanomethylenes was found to be essentially different from that of p-benzoquinones, and therefore π-acceptors are divided into two groups of cyanomethylenes and p-benzoquinones.

## INTRODUCTION

N-Benzyl-1,4-dihydronicotinamide (BNAH) and related compounds are recognized as models of important coenzymes for biological redox processes. Formerly, a mechanism of direct hydride transfer to π-acceptors in a single step was believed to occur in these systems.[1–4] Steffens and Chipman[5] were the first to cast doubt on the single-step mechanism on the basis of the kinetic isotope effects. Since then, the problem of whether the hydride transfer occurs in a single step[6–9] or stepwise electron–proton–electron (EPE) transfers[10–17] has been a subject of considerable controversy. At present it seems to be accepted that the hydride-equivalent transfer reactions of nicotinamide adenine dinucleotide (NADH) and related compounds with a variety of π-acceptors generally proceed by the EPE mechanism.

Colter and co-workers[18–21] extensively investigated the hydride transfer reactions between 9,10-dihydro-10-substituted acridine derivatives and π-acceptors including p-benzoquinones (Qs) and cyanomethylenes (CMs). Recently, Fukuzumi and co-workers[22,23] reported the energetic comparison of one-electron vs two-electron pathways for the acid-catalysed reduction of a series of p-benzoquinones by 9,10-dihydro-10-methylacridine and its dimer.

Previously, we reported the hydride-equivalent transfer reactions of Leuco Crystal Violet (LCV),[24,25] Leuco Malachite Green (LMG)[26] and Leuco Bindschedler's Green (BGH)[27] with different Qs and concluded that the reactions can be interpreted in terms of the general EPE mechanism.[17] It was found that the hydrogen atom on the nitrogen in BGH is abstracted in the form of a hydride ion much more easily than that on the central carbon atom in LCV or LMG. We were interested in knowing how the reaction would proceed if the central nitrogen atom of BGH is replaced with a carbon atom as in Michler's hydride [4,4'-bis(dimethylaminophenyl)methane, MH₂]. In a preliminary paper,[28] we presented a brief report that the reaction of MH₂ with chloranil (CA) proceeds by the general EPE mechanism via a charge-transfer (CT) complex. This work includes an extensive study for the MH₂–π-acceptor systems.

Prior to this study, we examined the hydride-transfer reaction of LCV with 7,7,8,8-tetracyano-p-quinodimethane (TCNQ) and 1,1,2,2-tetracyanoethylene (TCNE). Surprisingly, the kinetic behaviour and stoichiometry were found to be different between Qs and CMs, so far believed to act in the same manner. Hence a modified EPE mechanism for the LCV–CM system

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has been proposed.[29] It would be interesting to examine whether the modified EPE mechanism is of the general type and also valid in the present system.

## EXPERIMENTAL

*Materials.* All the chemicals were purchased commercially and were of reagent grade. $MH_2$ was recrystallized twice from methanol; m.p. 89–90 °C. Chloranil (CA), tetrabromo-*p*-benzoquinone (BA) and 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) were recrystallized twice from benzene. TCNQ was recrystallized three times from acetonitrile (MeCN) and TCNE was purified by repeated sublimations. Triethylamine (TEA) was used as received. Solvents were dried on molecular sieves 4A-1/16, distilled and then deaerated by bubbling nitrogen through just before use.

*Kinetic measurements.* All the runs were performed under pseudo-first-order conditions, i.e., $[MH_2]_0 = (1-2) \times 10^{-5} \, mol \, dm^{-3}$ and $[\pi\text{-acceptors}]_0 = (1-10) \times 10^{-3} \, mol \, dm^{-3}$. When the acetone or acetonitrile solutions of $MH_2$ and *p*-benzoquinones were mixed, a characteristic band due to Michler's Hydrol Blue ($MH^+$) appeared at $\lambda_{max} = 605 \, nm$ ($\varepsilon = 147\,500 \, dm^3 \, mol^{-1} \, cm^{-1}$)[30] with characteristic peaks of *p*-benzoquinone anion radicals (e.g. $\lambda_{max} = 448 \, nm$, $\varepsilon = 9600 \, dm^3 \, mol^{-1} \, cm^{-1}$ for $CA^{-\cdot}$).[31] The change in the absorbance at 605 nm with time was monitored with a Hitachi U-3200 spectrophotometer. When necessary, the change in the absorbance at $\lambda_{max}$ of the *p*-benzoquinones was also followed. The reaction with DDQ was very fast and the stopped-flow technique was applied for this system. Detailed procedures are given elsewhere.[27] When cyanomethylenes (TCNQ or TCNE) were used as $\pi$-acceptors, a characteristic band of $TCNQ^{-\cdot}$ or $TCNE^{-\cdot}$ appeared instantaneously. The intensity of the absorption band increased gradually with the simultaneous increase in the band due to $MH^+$. The gradual formation of $MH^+$ and $TCNQ^{-\cdot}$ (or $TCNE^{-\cdot}$) was followed spectrophotometrically at the same time.

*ESR measurements.* Solutions of $MH_2$ and $\pi$-acceptors were introduced separately into an H-shaped tube with a side-tube for ESR measurements. After the solutions has been degassed by the freeze–thaw method under vacuum, the solutions were mixed and transferred to the side-tube. A JEOL JES-FE3XG X-band spectrometer equipped with a 100 KHz field modulator and a TE 011 cavity were used. The *g*-value was estimated in the usual manner by means of a frequency counter referring to the *g*-value of 1,1-diphenyl-2-picrylhydrazyl. The temperature in the cavity was controlled at 25 °C by a JEOL variable-temperature regulator.
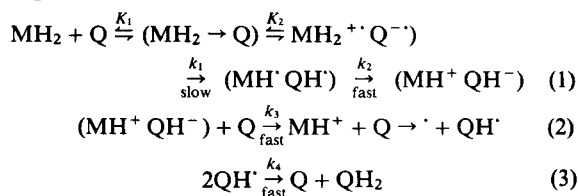
## RESULTS AND DISCUSSION

### $MH_2$–CA, DDQ systems

In excess of Qs, it was found that the formation of $MH^+$ obeys first-order kinetics. The apparent first-order rate constants ($k_{obsd}$) were estimated by using a computer program over the temperature range 25–55 °C in acetone and MeCN. In a preliminary paper,[28] the existence of a CT complex was reported. The pattern and the position of the CT band were similar to those for the LCV–CA and LMG–CA systems. Ohno and Kito[10] and Fukuzumi and Tanaka[14] also demonstrated the formation of a CT complex as an intermediate in their respective hydride-transfer systems. The oxidations of 9,10-dihydro-10-methyl-acridines to the corresponding acridinium ions by a variety of $\pi$-acceptors were investigated by Colter *et al.*[18] They also obtained spectroscopic and kinetic evidence for CT complexation between reactants.

In order to detect paramagnetic species formed during the reaction, an ESR study was performed. The obtained ESR signals, a singlet ($g = 2 \cdot 0058$) for the $MH_2$–CA system and a quintet ($g = 2 \cdot 0053$) with intensity ratio $1 : 2 : 3 : 2 : 1$ for the $MH_2$–DDQ system, can be assigned to the corresponding anion radicals of quinones. However, no ESR signal of the counter radical cation $MH_2^{+\cdot}$ was detected. Although the reason is unclear, such cases are often encountered with other $\pi$-donor–acceptor systems in the liquid[13,16] and solid states.[32,33]

Since unstable neutral radicals can be often detected by using the spin trapping technique, 2-methyl-2-nitrosopropane (MNP) was added to the system. An ESR signal (triplet with $g = 2 \cdot 0061$ and $a^N = 15 \cdot 5 \, G$) appeared for both the $MH_2$–CA, and $MH_2$–DDQ systems. The trapped radicals were assigned to $QH^{\cdot}$ [equation (2)], since the *g* and $a^N$ values agreed with those reported recently for the BGH–CA and BGH–DDQ systems.[27] If the radical $MH^{\cdot}$ was trapped, a signal composed of a triplet or doublet should have appeared, but this was not the case. Therefore, a rapid electron transfer to produce the ion pair ($MH^+ \, QH^-$) is considered to be taking place in the solvent cage [equation (1)]. All the above findings support the multi-step EPE mechanism, which is widely accepted for the hydride-equivalent transfer reactions. Hence the reactions in the present systems could be expressed as shown in Scheme 1:
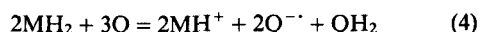
$$MH_2 + Q \underset{}{\overset{K_1}{\rightleftharpoons}} (MH_2 \rightarrow Q) \overset{K_2}{\rightleftharpoons} MH_2^{+\cdot} \, Q^{-\cdot})$$

$$\underset{slow}{\overset{k_1}{\rightarrow}} (MH^{\cdot} \, QH^{\cdot}) \underset{fast}{\overset{k_2}{\rightarrow}} (MH^+ \, QH^-) \quad (1)$$

$$(MH^+ \, QH^-) + Q \underset{fast}{\overset{k_3}{\rightarrow}} MH^+ + Q^{-\cdot} + QH^{\cdot} \quad (2)$$

$$2QH^{\cdot} \underset{fast}{\overset{k_4}{\rightarrow}} Q + QH_2 \quad (3)$$

Scheme 1

where the electronic structures of $MH_2$ and $MH^+$ are



**MH₂**



**MH⁺**
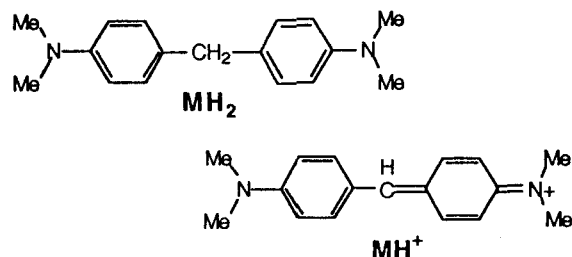
and parentheses denote solvent cages. In this mechanism the overall reaction stoichiometry should be given by

$$2MH_2 + 3Q = 2MH^+ + 2Q^{-\cdot} + QH_2 \qquad (4)$$

According to this mechanism, the reactants $MH_2$ and Q are in rapid equilibrium with the CT complex $(MH_2 \rightarrow Q)$, which is also in a rapid equilibrium with the radical ion pair $(MH_2^{+\cdot} Q^{-\cdot})$. Then proton transfer takes place from $MH_2^{-\cdot}$ to $Q^{-\cdot}$, resulting in a neutral radical pair $(MH^{\cdot} QH^{\cdot})$. This step could be regarded as the rate determining, since we have already observed remarkable isotope effects for a similar system.[24] Consequently, one-electron transfer takes place rapidly to produce an ion pair $(MH^+ QH^-)$ within the solvent cage. The net reaction is the hydride-equivalent transfer from $MH_2$ to Q. The ion pair reacts further with excess of Q to produce $MH^+$, $Q^{-\cdot}$ and $QH^{\cdot}$.

The above scheme can be justified further by the finding that the initial sudden but very small rise in the absorbance at 448 nm due to $CA^{-\cdot}$ [see equation (1)] is followed by a gradual increase. In agreement with the above stoichiometry, the ratio $[MH^+]/[CA^{-\cdot}] = 1$ was confirmed to remain constant during the reaction. This finding is the same as that already reported for the LCV–CA system.[24] According to Scheme 1, one can understand the reason why $Q^{-\cdot}$ and $QH^{\cdot}$ that escaped

from solvent cages were detected by the ESR method. In the absence of a radical trap, subsequent disproportionation of the semiquinone radical $QH^{\cdot}$ will take place. Although the dimerization of $QH^{\cdot}$ was assumed in a previous paper[27] and this possibility cannot be fully eliminated, the disproportionation reaction may be more plausible [see equation (3)].[17]

According to the above reaction mechanism, $k_{obsd}$ can be given by

$$k_{obsd} = K_1 K_2 k_1 \qquad (5)$$

The values of the second-order rate constants given by

$$k = K_1 K_2 k_1 \qquad (6)$$

were estimated and are given in Table 1. The activation parameters are listed together with relevant data in Table 2.

The activation energy is greater in MeCN than in acetone for the $MH_2$–CA system, whereas the activation entropy is greater in MeCN than in acetone, owing to which the rate constants are greater in MeCN than in acetone. Since the apparent activation energy values involve the $\Delta H$ terms for the rapid equilibration processes, it is difficult to discuss the activation parameters in the true rate-determining step.

Kinetic substituent effects are remarkable. The $k_{obsd}$ values for DDQ are much greater than those for CA and BA. Recently, we reported that the rate in the logarithmic scale is closely correlated to the redox potential $E^{\circ}(Q/Q^{-\cdot})$ of $p$-benzoquinones for the BGH–Q systems.[27] The present rate data show a similar trend and, therefore, an extraordinarily large value of $k_{obsd}$ for DDQ is not surprising.

The rate for the $MH_2$–CA system was found to be 2–100 times faster than those for the LCV–CA and LMG–CA systems. One of the reasons may be a less severe steric hindrance for $MH_2$, although electronic problems might also be involved. However, the rate is much slower and the activion energy is greater than those for the BGH–CA system. The reason in this case

Table 1  Rate data for the reactions betweeen $MH_2$ and $p$-benzoquinones in acetone and MeCN

| $T/^{\circ}C$ | $10^2 k_{obsd}/dm^3 mol^{-1} s^{-1}$ | | | | | |
| --- | --- | --- | --- | --- | --- | --- |
| | 25 | 30 | 35 | 40 | 45 | 55 |
| CA in acetone | 4·34 | 4·87 | 5·29 | 5·70 | 6·53 | |
| BA in acetone | | | | | 26·7 | |
| CA in MeCN | 4·73 | | 8·42 | | 11·7 | 16·2 |
| BA in MeCN | | | | | 16·1 | |
| DDQ in acetone | $7·1 \times 10^5$ | $8·1 \times 10^{5 a}$ | | $9·6 \times 10^5$ | $10·2 \times 10^5$ | $10·5 \times 10^{5 b}$ |
| DDQ in MeCN | $5·0 \times 10^6$ | | $5·2 \times 10^6$ | | $5·5 \times 10^6$ | $5·8 \times 10^6$ |

[a] $32^{\circ}C$
[b] $50^{\circ}C$

Table 2  Activation parameters for the reactions betweeen MH$_2$ and p-benzoquinones

| System | Solvent | $E_a$/kJ mol$^{-1}$ | $\Delta S^{\neq}_{298\ K}$/J K$^{-1}$ mol$^{-1}$ |
|---|---|---|---|
| MH$_2$–CA | Acetone | 15·4 ± 1 | −228 ± 4 |
| | MeCN | 32·7 ± 2 | −168 ± 6 |
| MH$_2$–DDQ | Acetone | 14·9 ± 1 | −135 ± 2 |
| | MeCN | 3·9 ± 0·1 | −150 ± 1 |
| LCV–CA[a] | CHCl$_3$ | 30·0 | −148 |
| | MeCN | 43·1 | −135 |
| LMG–CA[b] | MeCN | 83·6 | −55 |
| BGH–CA[c] | Acetone | 10·2 | −147 |

[a] Data from Ref. 24.
[b] Data from Ref. 26.
[c] Data from Ref. 27.

may be the large difference in the electronegativity between the central nitrogen and carbon atoms. Heterolytic fission of the N—H bond is expected to be easier than that of the C—H bond in the proton-transfer step.

*DH$_2$–TCNQ system.* In this system a characteristic absorption band of TCNQ$^{-\cdot}$ with vibrational structures extending over the range 650–850 nm ($\varepsilon = 43\,300$ dm$^3$ mol$^{-1}$ cm$^{-1}$ at $\lambda_{max} = 843$ nm)[34] appeared immediately, followed by a gradual increase with a simultaneous increase in the absorbance at $\lambda_{max} = 605$ nm due to MH$^+$ (Figure 1). The same was the case in the LCV–TCNQ system.[29] This indicates that a pre-equilibration between reactants and their radical ion pair took place before the formation of MH$^+$.

When the temperature was lowered below −50 °C, the colour of the solution changed from green to brown, turning back to green at room temperature, indicating the reversible formation of a CT complex. Unfortunately, we have been unsuccessful in obtaining the exact CT band owing to some experimental limitations. A small amount of TCNQ$^{-\cdot}$ formation was observed when TCNQ alone was dissolved in MeCN, probably due to some contamination. However, this was found to be negligible and did not affect the following procedures. In the initial stage of reaction, the following (pseudo) equilibrium can be assumed:

$$MH_2 + TCNQ \overset{K_3}{\rightleftharpoons} (MH_2^{+\cdot}\,TCNQ^{-\cdot}) \tag{7}$$
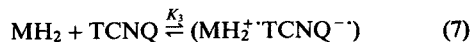
The equilibrium constant ($K_3 = K_1 K_2$), under the condition [MH$_2$]$_0 \ll$ [TCNQ]$_0$, is given by

$$K_3 = X/[TCNQ]_0 ([MH_2]_0 - X) \tag{8}$$

where X is the concentration of the ion pair and it was equated to the measured concentration of [TCNQ$^-$] extrapolated to $t = 0$. The average $K_3$ value of 30·3 ± 0·2 dm$^3$ mol$^{-1}$(25 °C in MeCN) was obtained under various initial concentrations of MH$_2$ and TCNQ. In a trial, the equilibrium constant was calculated on the free-ion assumption, and the $K_3$-values obtained were found to be considerably scattered. In a subsidiary experiment, N,N-dimethylaniline was chosen as a dummy of MH$_2$ for which a similar electron-transfer reaction is expected but not the subsequent reactions. The average K-value obtained of 19·4 dm$^3$ mol$^{-1}$ is of a comparable order of magnitude
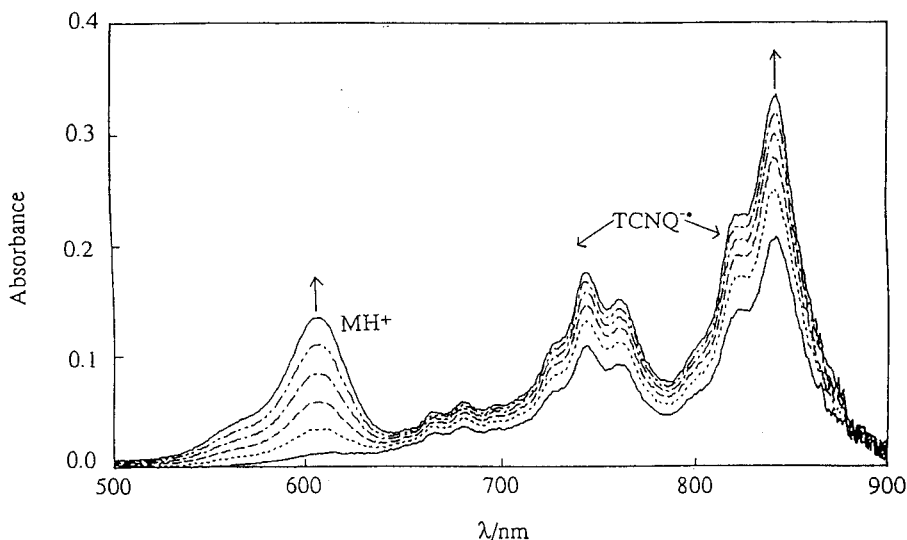


Figure 1. Time dependence of the spectrum in the reaction between MH$_2$ and TCNQ in MeCN at 25 °C. [MH$_2$]$_0 = 2 \times 10^{-5}$ mol dm$^{-3}$; [TCNQ] $= 4 \times 10^{-3}$ mol dm$^{-3}$; cycle time = 10 min
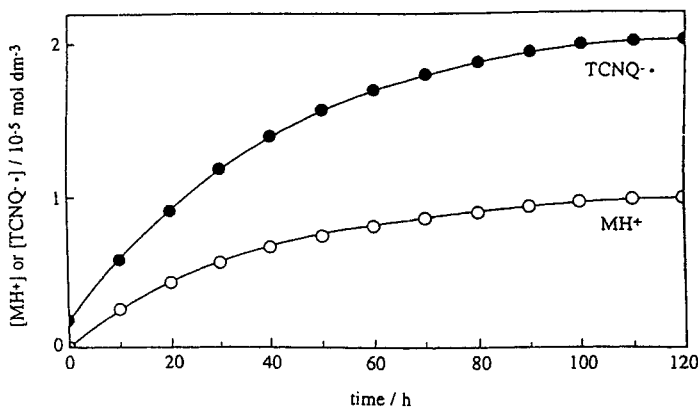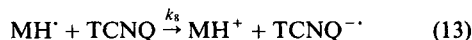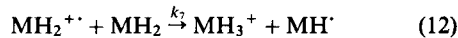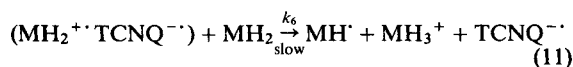
Figure 2. Change in the concentrations of ($\bigcirc$) $MH^+$ and ($\bullet$) $TCNQ^{+\cdot}$ as a function of time at $25\,^\circ C$ MeCN. $[MH_2]_0 = 2 \times 10^{-5}\,mol\,dm^{-3}$; $[TCNQ]_0 = 4 \times 10^{-3}\,mol\,dm^{-3}$

to the above value. This confirms the reliability of the $K_3$ value for the $MH_2$–TCNQ system.

The ratio of the concentrations of $MH^+$ and $TCNQ^{-\cdot}$ asymptotically approached $1:2$ with time, and this ratio was kept constant (Figure 2). Finally, the concentration of $MH^+$ became almost half of the initial concentration of $MH_2$. The above findings cannot be explained in terms of the general EPE mechanism as could be applied to the $MH_2$–Qs systems ($1:1$ stoichiometry for $MH^+/Q^{-\cdot}$). A modified mechanism which is in harmony with the above findings is shown in Scheme 2:

$$MH_2 + TCNQ \overset{k_4}{\underset{}{\rightleftharpoons}} {}^{(MH}{}_2 \rightarrow TCNQ) \overset{K_5}{\rightleftharpoons} (MH_2^{+\cdot}\,TCNQ^{-\cdot}) \quad (9)$$

$$(MH_2^{+\cdot}\,TCNQ^{-\cdot}) \overset{k_5}{\underset{slow}{\rightarrow}} MH_2^{+\cdot} + TCNQ^{-\cdot} \quad (10)$$

$$(MH_2^{+\cdot}\,TCNQ^{-\cdot}) + MH_2 \overset{k_6}{\underset{slow}{\rightarrow}} MH^\cdot + MH_3^+ + TCNQ^{-\cdot} \quad (11)$$

$$MH_2^{+\cdot} + MH_2 \overset{k_7}{\rightarrow} MH_3^+ + MH^\cdot \quad (12)$$

$$MH^\cdot + TCNQ \overset{k_8}{\rightarrow} MH^+ + TCNQ^{-\cdot} \quad (13)$$
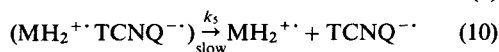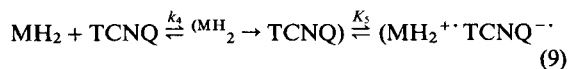
Scheme 2

The stoichiometry for this scheme can be given by

$$2MH_2 + 2TCNQ = 2TCNQ^{-\cdot} + MH^+ + MH_3^+ \quad (14)$$

If reactions (10) and (11) are rate determining, then the initial sudden rise in the spectrum due to $TCNQ^{-\cdot}$ (see Figure 1), followed by the gradual appearance of $MH^+$, can be explained according to this scheme [equation (13)]. On the steady-state assumption for $MH_2^{+\cdot}$ and $MH^\cdot$, the rate of formation of $MH^+$ in the initial state is given by

$$R = K_6[TCNQ]_e\ [MH_2]_e\ \{k_5 + k_6[MH_2]_e\} \quad (15)$$

where $K_6$ denotes $K_4K_5$. Judging from the $K_3$ value, about $3\%$ of $MH_2$ was found to be converted into $MH_2^{+\cdot}$ at the initial pseudo-equilibrium state. Hence equation (15) can be approximated to

$$R = K_6[TCNQ]_0\ [MH_2]_0\ \{k_5 + k_6[MH_2]_0\} \quad (16)$$

In Figures 3 and 4, the initial rates of formation of $MH^+$ are plotted as functions of $[MH_2]_0$ and $[TCNQ]_0$, respectively, keeping the other constant. It is seen that the plots in Figure 3 are curved slightly upwards whereas those in Figure 4 are linear, as could be expected from equation (16). Equation (16) can be rearranged as follows:

$$R/K_6[TCNQ]_0\ [MH_2]_0 = k_5 + k_6[MH_2]_0 \quad (17)$$
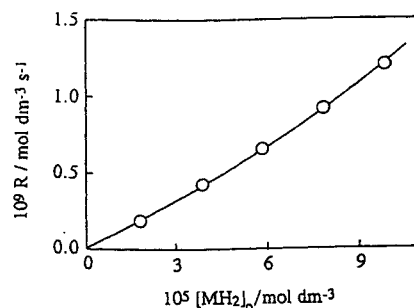
It was found that the plot of the left-hand-side term



Figure 3. Initial rate of $MH^+$ formation as a function of the initial concentrations of $MH_2$ in MeCN at $25\,^\circ C$. $[TCNQ]_0 = 4 \times 10^{-3}\,mol\,dm^{-3}$
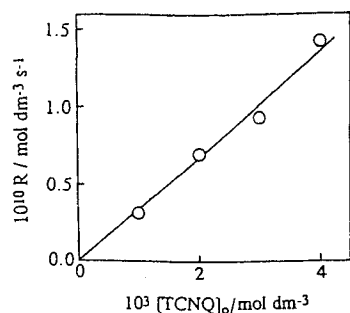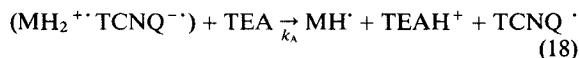
Figure 4. Initial rate of $MH^+$ formation as a function of the initial concentrations of TCNQ in MeCN at $25°C$. $[MH_2]_0 = 1 \times 10^{-5}\,mol\,dm^{-3}$



Figure 5. Effect of TEA on the initial rate of reaction between $MH_2$ and TCNQ in MeCN at $25\,°C$. $10^{-5}[TEA]_0$: (1) 0; (2) 1; (3) 5; (4) 10; (5) 20 $mol\,dm^{-3}$ $[MH_2]_0 = 1 \times 10^{-5}\,mol\,dm^{-3}$; $[TCNQ]_0 = 4 \times 10^{-3}\,mol\,dm^{-3}$

against $[MH_2]_0$ gave straight line and from the intercept and slope, $k_5$ and $k_6$ were estimated to be $8.35 \times 10^{-5}\,s^{-1}$ and $0·184\,dm^3\,mol^{-1}\,s^{-1}$, respectively. In the present system, $MH_2$ is behaving as a base in the sense that it accepts a proton. In order to ascertain the presence of $MH_3^+$, the wavelength scan is expanded down to the UV region. A new peak observed at $\lambda_{max} = 221$ nm could be ascribed to $MH_3^+$, since a similar peak appeared at the expense of the band at 266 nm due to $MH_2$ when a small amount of hydrochloric acid was added to the solution of $MH_2$.

Fukuzumi et al.[17] reported that the addition of pyridine accelerates the rate of the hydride-transfer reaction between BNAH and TCNE. In order to examine the effect of added amine on the rate, excess of triethylamine (TEA) over $MH_2$ was added to the system. Figure 5 shows the effect of TEA on the initial rate of $MH^+$ formation. In this case, the following reaction should be added to Scheme 2:

$$(MH_2^{+\cdot}TCNQ^{-\cdot}) + TEA \xrightarrow{k_A} MH^\cdot + TEAH^+ + TCNQ^{-\cdot} \tag{18}$$

Then, the rate equation can be modified to

$$R_A/R_0 = 1 + k_A[TEA]_0/(k_5 + k_6[MH_2]_0) \tag{19}$$

where $R_A$ and $R_0$ denote the initial rate of formation of $MH^+$ in the presence and absence of TEA, respectively. Figure 6 shows that the relationship actually holds. From the slope, $k_A$ for TEA was evaluated to be $1·24\,dm^3\,mol^{-1}\,s^{-1}$, about seven times greater than $k_6$. Indeed with the addition of TEA, the concentration of $TCNQ^{-\cdot}$ increased immediately owing to the electron-transfer reaction between TCNQ and TEA [equation(9)].

According to Scheme 2, $MH^\cdot$ radicals are expected to be trapped by MNP. However, no ESR signal appeared, probably owing to steric hindrance at the central carbon. However, when 1,1-diphenyl-2-
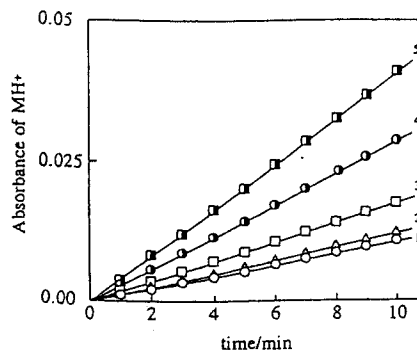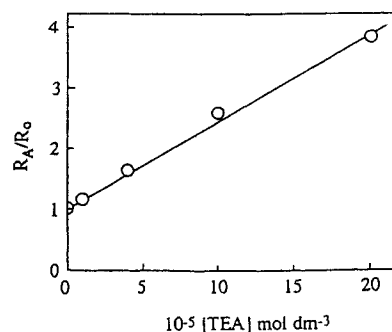


Figure 6. Relative rate of formation of $MH^+$ as a function of $[TEA]_0$

picrylhydrazyl (DPPH) or Verdazyl, both well known radical scavengers, was added to the system, their respective colours faded gradually, showing that unstable neutral radicals are formed during the reaction. It is worth noting that both $MH_2$ and TCNQ were unreactive to both Verdazyl and DPPH. These findings could be regarded indirect evidence for the existence of $MH^\cdot$ the present system.

When TCNE was used in place of TCNQ, a band extending over 350–460 nm with vibrational structures assignable to $TCNE^{-\cdot}$ appeared immediately. The thermodynamic and kinetic behaviour and the stoichiometry were virtually identical with those of TCNQ. Unfortunately, the molar absorptivity of the band is much smaller than that of $TCNQ^{-\cdot}(\varepsilon = 5670\,dm^3\,mol^{-1}\,cm^{-1}$ at 457 nm),[35] and therefore no further quantitative work was carried out.

## Comparison of Schemes 1 and 2

It has been revealed that the hydride-equivalent transfer reactions between $MH_2$ and $\pi$-acceptors such as CA

and TCNQ start through the initial formation of a CT complex, followed by one-electron transfer to form the corresponding radical ion pairs in a cage. Thereafter, these ion pairs behave differently depending on the nature of the $\pi$-acceptors. Benzoquinones can successively accept an electron and a proton from $MH_2$ within solvent cages, whereas cyanomethylenes can accept an electron but not a proton. Melby et al.[34] and Yamagishi and Sakamoto[36] examined the effects of strong mineral acids on the stability of $TCNQ^{-\cdot}$. They found that $TCNQ^{-\cdot}$ reacts with $H^+$ to produce p-phenylene-dimalononitrile ($TCNQH_2$) and TCNQ with 1:1 stoichiometry via the intermeditate $TCNQH^\cdot$ as follows:

$$2TCNQ^{-\cdot} + 2H^+ \rightarrow 2TCNQH^\cdot \rightarrow TCNQ + TCNQH_2 \quad (20)$$
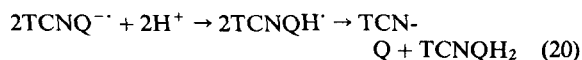
In the light of such situations, $TCNQ^{-\cdot}$ will be able to accept a proton only under extreme conditions. Although species such as $TCNQH^-$ ($TCNEH^-$) and $TCNQH^\cdot$ ($TCNEH^\cdot$) have been assumed[15,18-21,35-37] in the hydride-transfer reactions to explain the kinetic behaviour of $TCNQ^{-\cdot}$ ($TCNE^{-\cdot}$) and the stoichiometry, we have succeeded in explaining the kinetic behaviour in terms of Scheme 2 without such assumptions. In this work, we could follow the time dependence of the two products simultaneously, and this clarifies the difference in the role between p-benzoquinones and cyanomethylenes in the hydride-transfer reactions. From the foregoing discussion it is concluded that the behaviour of cyanomethylenes is essentially different from that of p-benzoquinones and, therefore, $\pi$-acceptors can be divided into two groups of cyanomethylenes and p-benzoquinones.

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