Addition–cyclization reaction of nitroalkane anions with *o*-quinone derivatives *via* electron transfer in the charge-transfer complexes

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An addition–cyclization reaction of nitroalkane anions with tricyclic *o*-quinones occurs in acetonitrile to yield the corresponding 1,3-dioxole derivatives. The heat of formation of the charge-transfer complex formed between the 2-nitropropane anion and 1,7-phenanthroline-5,6-dione is of greater magnitude than the observed activation enthalpy of the addition reaction. Since such a relationship could only arise when the charge-transfer complex lies along the reaction pathway, the charge-transfer complex acts as a real intermediate rather than a bystander in the addition reaction of the 2-nitropropane anion with the *o*-quinone derivative. A comparison of the observed rate constants with those predicted for the electron transfer from nitroalkane anions to *o*-quinones indicates that the addition reaction proceeds *via* electron transfer in the charge-transfer complex formed between nitroalkane anions and the *o*-quinones, followed by C–O adduct formation and subsequent cyclization to afford the 1,3-dioxole derivatives.

Nitroalkane anions are generally believed to act as nucleophiles that undergo C–C bond formation with carbonyl compounds, which is known as the Henry reaction.[1] However, electron transfer processes involving 2-nitropropane anions play an essential role in radical chain nucleophilic substitutions ($S_{RN}1$).[2–5] Although non-chain electron transfer pathways have also been reported in thermal nucleophilic substitution reactions of strongly basic carbanions, the electron transfer mechanism has recently been questioned.[6,7] In this context, we have recently reported that the addition of 2-nitropropane anions to NAD^+ analogues proceeds *via* a polar S_N2 process rather than an electron-transfer process.[8] Such an electron-transfer as opposed to the nucleophilic alternative has been one of the central propositions in the reaction mechanism.[9] We have also reported that the addition of a sterically hindered nucleophile, β,β-dimethyl-substituted ketene silyl acetal with *p*-chloranil, proceeds *via* electron transfer from the nucleophile to the *p*-quinone to produce the carbon–oxygen adduct, but that addition of a sterically less hindered nucleophile, a non-substituted ketene silyl acetal, with *p*-fluoranil proceeds *via* an S_N2 process to yield the carbon–carbon adduct selectively.[10] In each case, charge-transfer complexes are formed between the nucleophiles and quinones.[10] The mechanistic difference between C–O and C–C bond formation has been discussed in relation to electron transfer *vs.* S_N2 processes.[11,12] However, further data are certainly required to gain a more comprehensive understanding of the electron-transfer mechanism of the nucleophiles. The actual role of charge-transfer complexes as intermediates in the reactions of nucleophiles remains to be elucidated.

This study reports the reactions of nitroalkane anions with *o*-quinones *via* electron transfer from nitroalkane anions to *o*-quinones, followed by C–O adduct formation and subsequent cyclization to yield 1,3-dioxole derivatives.[13] The reaction mechanism concerning electron-transfer *vs.* the nucleophilic alternative is revealed based on a detailed kinetic study. The formation of charge-transfer complexes and their actual role as intermediates are also reported.

Experimental

Materials

Phenanthraquinone (PQ), nitroalkanes and a methanol solution of 25% tetramethylammonium hydroxide (Me_4NOH) were obtained commercially. Benzoquinolinequinones [1-BQQ (1-azaphenanthrene-5,6-dione) and 4-BQQ (4-azaphenanthrene-5,6-dione)] and phenanthrolinequinones [1,7-PTQ (1,7-phenanthroline-5,6-dione), 1,10-PTQ (1,10-phenanthroline-5,6-dione) and 4,7-PTQ (4,7-phenanthroline-5,6-dione)] were prepared according to the reported methods.[14–16] Acetonitrile used as a solvent was obtained from Wako Pure Chemicals, and was purified and dried with CaH_2 by the standard procedure.[17]

Product analysis

Typically, an acetonitrile solution (30 cm^3) containing 1,7-PTQ (4.76×10^{-3} mol dm^{-3}) and 2-nitropropane (47.6×10^{-3} mol dm^{-3}) in a 50 cm^3 three-necked flask was deaerated by bubbling with argon gas through a stainless steel needle for 20 min. The reaction was started by the addition of 0.30 cm^3 of a methanol solution of 25wt% Me_4NOH to the solution by means of a microsyringe. The mixture was refluxed with stirring at 333 K for 24 h under an atmospheric pressure of nitrogen. Removal of the solvents gave a brownish residue which was dissolved in 100 cm^3 of chloroform and washed with 50 cm^3 of water three times and then dried over $MgSO_4$. After removal of $MgSO_4$ by filtration, a pale green solid was obtained quantitatively by evaporation of the solvent and drying *in vacuo*. The reaction product was analysed by ^{1}H NMR spectroscopy in [$^2H_3$]acetonitrile (CD_3CN) as well as by the melting point and IR and mass spectroscopies. The spectral data of the products were in good agreement with those of the 1,3-dioxole derivatives formed in the reaction of *o*-quinones with vinylmagnesium bromide.[18] The ^{1}H NMR measurements were performed using a JEOL LNM-GSX-400 (400 MHz) NMR spectrometer. *J* Values are given in Hz. IR spectra were obtained on a HITACHI 270-30 infrared spectrophotometer. Mass spectra (MS) were obtained on a JEOL JMS-DX-303 mass spectrometer. Melting points were determined with a Yamato MP-21 apparatus and are uncorrected.

2,2-Dimethyl-1,3-dioxolo[4,5-*f*][1,7]phenanthroline (1). Mp 129–132 °C; $\delta_H(CD_3CN)$ 1.88 (6 H, s, $CH_3 \times 2$), 7.59 (1 H, dd, *J* 4.4 and 8.3), 7.66 (1 H, dd, *J* 4.4 and 8.3), 8.26 (1 H, dd, *J* 2.0 and 8.3), 8.94 (1 H, dd, *J* 1.5 and 4.4), 8.97 (1 H, dd, *J* 1.5 and 4.4), 9.48 (1 H, dd, *J* 2.0 and 8.3); ν(KBr)/cm^{-1} 1652, 1590 (C=C), 1244, 1224, 1086 (C–O); *m*/*z* (EI) 252 (M^+).

2-Methyl-1,3-dioxolo[4,5-*f*][1,7]phenanthroline (2). Mp 129–131 °C; $\delta_H(CD_3CN)$ 1.87 (3 H, d, *J* 4.9, CH_3), 6.75 (1 H, q, *J* 4.9,

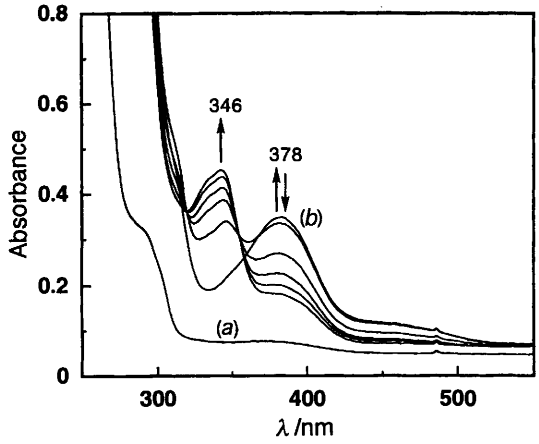


Fig. 1 UV–VIS spectra observed in the reaction of 1,7-PTQ (5.0×10^{-5} mol dm^{-3}) with the 2-nitropropane anion (3.33×10^{-3} mol dm^{-3}) in deaerated acetonitrile at 298 K; 0.8 s interval. (*a*) UV–VIS spectrum of 1,7-PTQ (5.0×10^{-5} mol dm^{-3}). (*b*) UV–VIS spectrum observed upon addition of the 2-nitropropane anion (3.33×10^{-3} mol dm^{-3}).

CH), 7.60 (1 H, dd, *J* 4.4 and 8.3), 7.67 (1 H, dd, *J* 4.4 and 7.8), 8.29 (1 H, dd, *J* 1.5 and 7.8), 8.94 (1 H, dd, *J* 1.5 and 4.4), 8.97 (1 H, dd, *J* 1.5 and 4.4), 9.48 (1 H, dd, *J* 1.5 and 8.3); ν(KBr)/cm^{-1} 1646, 1586 (C=C), 1192, 1152, 1100 (C–O); *m*/*z* (EI) 238 (M$^+$).

2,2-Dimethyl-1,3-dioxolo[4,5-*f*][4,7]phenanthroline (3). Mp 177–180 °C; δ_H(CD$_3$CN) 1.89 (6 H, s, CH$_3$ × 2), 7.59 (2 H, dd, *J* 4.4 and 8.3), 8.94 (2 H, dd, *J* 1.5 and 4.4), 9.04 (2 H, dd, *J* 1.5 and 8.3); ν(KBr)/cm^{-1} 1642, 1582 (C=C), 1200, 1128, 1088 (C–O); *m*/*z* (EI) 252 (M$^+$).

2,2-Dimethyl-1,3-dioxolo[4,5-*f*][1,10]phenanthroline (4). Mp 140–143 °C; δ_H(CD$_3$CN) 1.86 (6 H, s, CH$_3$ × 2), 7.69 (2 H, dd, *J* 4.4 and 8.3), 8.26 (2 H, dd, *J* 2.0 and 8.3), 9.01 (2 H, dd, *J* 2.0 and 4.4); ν(KBr)/cm^{-1} 1658, 1592 (C=C), 1210, 1120, 1064 (C–O); *m*/*z* (EI) 252 (M$^+$).

2,2-Dimethylbenzo[*h*]-1,3-dioxolo[4,5-*f*]quinoline (5). Mp 105–107 °C; δ_H(CD$_3$CN) 1.79 (6 H, s, CH$_3$ × 2), 7.56 (1 H, dd, *J* 4.4 and 8.3), 7.59 (1 H, ddd, *J* 1.5, 6.8 and 8.3), 7.70 (1 H, ddd, *J* 1.5, 6.8 and 8.3), 7.82 (1 H, dd, *J* 1.5 and 8.3), 8.15 (1 H, dd, *J* 2.0 and 8.3), 8.83 (1 H, dd, *J* 2.0 and 4.4), 9.18 (1 H, dd, *J* 1.5 and 8.3); ν(KBr)/cm^{-1} 1660, 1612, 1596 (C=C), 1226, 1206, 1070 (C–O); *m*/*z* (EI) 251 (M$^+$).

2,2-Dimethylbenzo[*f*]-1,3-dioxolo[4,5-*h*]quinoline (6). Mp 125–127 °C; δ_H(CD$_3$CN) 1.87 (6 H, s, CH$_3$ × 2), 7.53 (1 H, dd, *J* 4.4 and 8.3), 7.65 (1 H, ddd, *J* 1.5, 6.8 and 7.3), 7.72 (1 H, ddd, *J* 1.5, 6.8 and 8.3), 7.92 (1 H, dd, *J* 1.5 and 7.3), 8.74 (1 H, dd, *J* 1.5 and 8.3), 8.89 (1 H, dd, *J* 1.5 and 4.4), 9.06 (1 H, dd, *J* 1.5 and 8.3); ν(KBr)/cm^{-1} 1650, 1610, 1588 (C=C), 1218, 1126, 1080, 1054 (C–O); *m*/*z* (EI) 251 (M$^+$).

2,2-Dimethylphenanthro[9,10-*d*]-1,3-dioxole (7). Mp 90–92 °C; δ_H(CD$_3$CN) 1.84 (6 H, s, CH$_3$ × 2), 7.59 (2 H, ddd, *J* 1.5, 7.3 and 8.3), 7.66 (2 H, ddd, *J* 1.5, 7.3 and 7.8), 7.86 (2 H, dd, *J* 1.5 and 7.8), 8.76 (2 H, dd, *J* 1.5 and 8.3); ν(KBr)/cm^{-1} 1658, 1616 (C=C), 1220, 1120, 1060 (C–O); *m*/*z* (EI) 250 (M$^+$).

Kinetic measurements

Kinetic measurements were performed under deaerated conditions using a Hewlett Packard HP8452A diode array spectrophotometer, which was thermostatted at 298–313 K. Typically a stock solution of the Me$_4$N$^+$ salt of the 2-nitropropane anion (1.0 mol dm^{-3}) was prepared by the addition of 0.420 cm^3 of a methanol solution of 25 wt% Me$_4$NOH to 0.58 cm^3 of a deaerated acetonitrile solution containing 2-nitropropane (2.2 mol dm^{-3}). A deaerated acetonitrile solution (3.0 cm^3) of 1,7-PTQ (5.0×10^{-5} mol dm^{-3}) and a magnetic stirrer bead contained in a 10 mm quartz cuvette were placed in the cell holder of the spectrophotometer with a magnetic stirrer. The reaction was started by the addition of the 2-nitropropane anion (5×10^{-5}–2×10^{-2} mol dm^{-3}) to the acetonitrile solution of 1,7-PTQ. The rate of the reaction was followed by a decrease in absorbance due to the reaction intermediate (λ_{max} = 378 nm) and an increase in absorbance due to the final product (λ_{max} = 346 nm). The pseudo-first-order plots were linear for three or more half-lives with a correlation coefficient $\rho > 0.999$.

Electrochemical measurements

Electrochemical measurements of *o*-quinones and nitroalkane anions were performed on a BAS 100B electrochemical analyser in deaerated acetonitrile containing 0.10 mol dm^{-3} NBu$_4$ClO$_4$ as the supporting electrolyte at 298 K. The platinum working electrode (BAS) was polished with BAS polishing alumina suspension and rinsed with acetone before use. The counter electrode was a platinum wire (BAS). The measured potentials were recorded with respect to the Ag/AgNO$_3$ (1.0×10^{-2} mol dm^{-3}) reference electrode. The one-electron reduction potentials E°_{red} (*vs.* Ag/Ag$^+$) of the quinones are converted to those *vs.* saturated calomel electrode (SCE) by adding 0.29 V.[19]

Theoretical calculations

The theoretical studies were performed using the PM3 molecular orbital method.[20,21] The calculations were performed using a COMTEC 4D RPC computer with the MOL-GRAPH program Ver. 2.8 from Daikin Industries Ltd. Final geometries and energetics were obtained by optimizing the total molecular energy with respect to all structural variables.

Results and discussion

Treatment of 1,7-phenanthroline-5,6-dione (1,7-PTQ; 4.76×10^{-3} mol dm^{-3}) with the 2-nitropropane anion (4.76×10^{-2} mol dm^{-3}) in deaerated acetonitrile at 298 K for 24 h gave 2,2-dimethyl-1,3-dioxole derivative **1** quantitatively. The structure of **1** was confirmed by spectroscopic analyses (see Experimental section). The reactions of the 2-nitropropane anion and the nitroethane anion with various tricyclic *o*-quinone derivatives also occur to yield the corresponding 1,3-dioxole derivatives selectively as shown in Table 1.

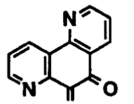
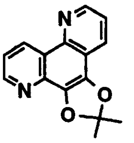
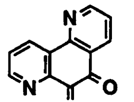
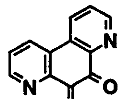
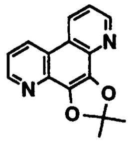
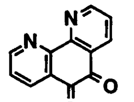
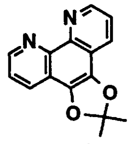
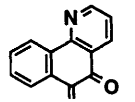
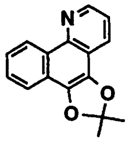
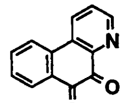
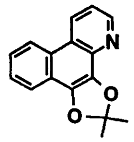
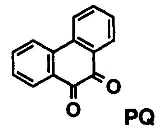
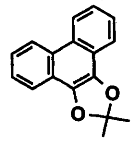
A typical spectroscopic change in the reaction of the 2-nitropropane anion with 1,7-PTQ is shown in Fig. 1, where a new absorption band at λ_{max} = 378 nm appears upon mixing the 2-nitropropane anion with 1,7-PTQ, followed by a decrease in the absorbance accompanied by an increase in absorbance at λ_{max} = 346 nm. At prolonged reaction times, the absorbance at 346 nm increases further to yield the final product **1**. The time course of initial rise and decay of the absorbance at λ_{max} = 378 nm is shown in Fig. 2. The initial change in absorbance upon mixing the 2-nitropropane anion and 1,7-PTQ, ΔA_{378}, increases with a rise in the initial concentration of the 2-nitropropane anion to reach a constant value as shown in the inset of Fig. 2. Such dependence of ΔA_{378} on the 2-nitropropane anion concentration indicates formation of a complex between the 2-nitropropane anion and 1,7-PTQ (see Scheme 1). The formation constant is determined from the plot of $\Delta A/(\Delta A - \Delta A)$ *vs.* [Me$_2$C$^-$NO$_2$] in Fig. 3 according to eqn. (1), where ΔA_∞

$$\Delta A/(\Delta A_\infty - \Delta A) = K_{CT}[\mathrm{Me_2C^-NO_2}] \qquad (1)$$

is the final difference in the absorbance between the absence and presence of a large excess of the 2-nitropropane anion, such that all quinone molecules form the 1 : 1 complex. The formation constants K_{CT} of the complexes of other *o*-quinones were also determined from the dependence of the absorption change on [Me$_2$C$^-$NO$_2$] and the K_{CT} values are listed in Table 2.

The electronic spectrum due to the complex in Fig. 1(*b*) has two absorption maxima which are determined as λ_{max} = 373 and 453 nm from the spectral resolution using Gaussian

Table 1 Reaction of *o*-quinones and nitroalkane anions ($R^1R^2C^-NO_2$)[a]

Quinone	E°_{red}/V[b]	R^1	R^2	*t*/h	Product	Yield (%)
 **1,7-PTQ**	−0.50	Me	H	24	 **1**	100
 **1,7-PTQ**	−0.50	Me	Me	24	 **2**	100
 **4,7-PTQ**	−0.50	Me	Me	24	 **3**	100
 **1,10-PTQ**	−0.50	Me	Me	24	 **4**	67
 **1-BQQ**	−0.60	Me	Me	24	 **5**	93
 **4-BQQ**	−0.58	Me	Me	24	 **6**	68
 **PQ**	−0.67	Me	Me	72	 **7**	94

[a] In refluxing acetonitrile under N_2. [b] *vs.* SCE; one-electron reduction potential determined by cyclic voltammetry in acetonitrile containing 0.1 mol dm^{-3} tetrabutylammonium perchlorate.

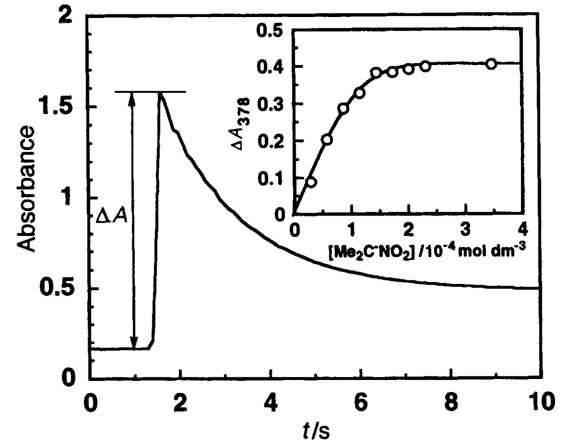


Fig. 2 Change of absorbance at λ = 378 nm in the reaction of 1,7-PTQ (5.0×10^{-5} mol dm^{-3}) and the 2-nitropropane anion (1×10^{-2} mol dm^{-3}) in deaerated acetonitrile at 298 K. Inset: Plot of ΔA at λ = 378 nm due to the formation of the complex between 1,7-PTQ (5.0×10^{-5} mol dm^{-3}) and the 2-nitropropane anion *vs.* $[Me_2C^-NO_2]$.

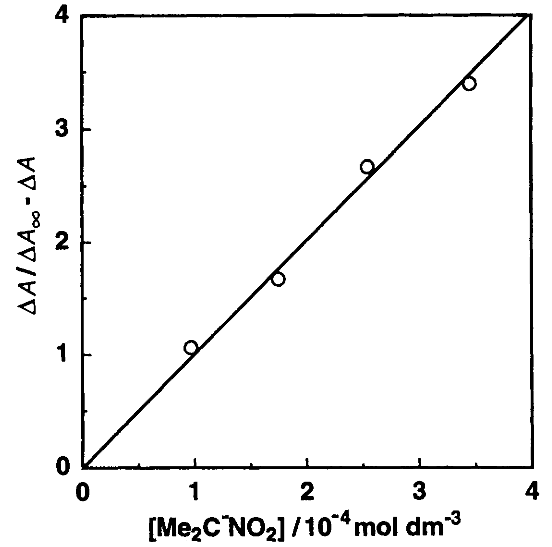


Fig. 3 Plot of $\Delta A/(\Delta A_{\infty} - \Delta A)$ at λ = 378 nm due to the formation of the complex between 1,7-PTQ (5.0×10^{-5} mol dm^{-3}) and the 2-nitropropane anion *vs.* $[Me_2C^-NO_2]$

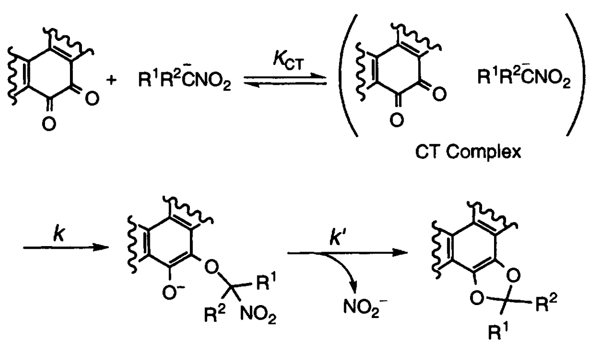
functions.[22] The broad new absorption bands of the complex in Fig. 1(*b*) are characteristic of charge-transfer (CT) absorption bands of intermolecular complexes formed by the nucleophile–electrophile interactions.[23,24] The appearance of the twin CT bands can be readily explained in terms of the two unoccupied molecular orbital levels of 1,7-PTQ which are located close together. The energy difference $\Delta h\nu_{CT}$ between the first and second CT bands (0.59 eV) corresponds to the calculated energy difference between the lowest and second lowest unoccupied

Table 2 Observed complex formation constants, $K_{\rm CT}$, and the first-order rate constants, k and k', in the reaction of the *o*-quinones and the 2-nitropropane anion in acetonitrile at 298 K

Quinone	$K_{\rm CT}$/mol^{-1} dm^3	k/s^{-1}	k'/s^{-1}
1,7-PTQ	1.0×10^4	0.46	6.5×10^{-4}
1,10-PTQ	8.8×10^3	0.69	3.6×10^{-4}
4,7-PTQ	1.2×10^4	0.72	4.8×10^{-4}
4-BQQ	8.0×10^2	0.64	2.5×10^{-4}

molecular orbital levels of 1,7-PTQ (0.77 eV), calculated by the PM3 method (see Experimental section).

The decay of the CT band is accompanied by a rise of a new absorption band at $\lambda_{\rm max}$ = 346 nm [Fig. 1(*a*)], which may be ascribed to the formation of an intermediate adduct as shown in Scheme 1. The intermediate adduct may then cyclize to yield the final product, *i.e.*, the 1,3-dioxole derivative. The rate of decay of the CT absorbance obeyed first-order kinetics. The observed first-order rate constant may correspond to that of the addition of the 2-nitropropane anion to 1,7-PTQ in the CT complex (k). The k values were independent of the 2-nitropropane anion concentration, since it is an intramolecular process. The subsequent slow reaction at a prolonged reaction time may correspond to the intramolecular cyclization process (k') in Scheme 1. The k' values were also independent of the 2-nitropropane concentration.



Scheme 1

The mechanistic involvement of the CT complexes formed between electron donors (D) and acceptors (A) as an intermediate, [reaction (2)], has always been questioned by an

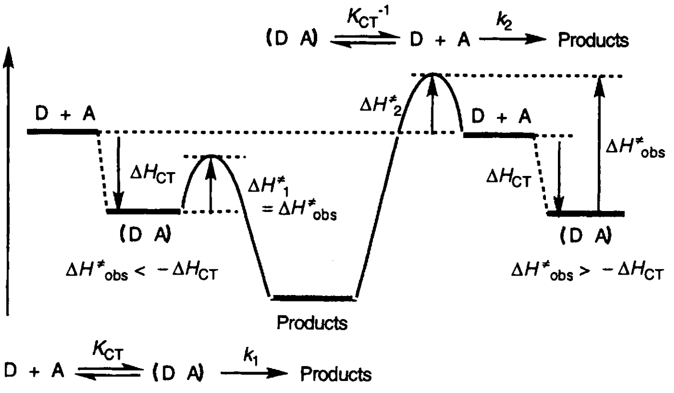
$$\mathrm{D} + \mathrm{A} \underset{}{\overset{K_{\rm CT}}{\rightleftharpoons}} (\mathrm{DA}) \xrightarrow{k_1} \text{Products} \qquad (2)$$

alternative mechanism in which the CT complex is merely an innocent bystander in an otherwise dead-end equilibrium, as shown in reaction (3). The difference lies in whether the

$$(\mathrm{DA}) \overset{K_{\rm CT}^{-1}}{\rightleftharpoons} \mathrm{D} + \mathrm{A} \xrightarrow{k_2} \text{Products} \qquad (3)$$

observed first-order rate constant for the decay of the CT complex is a rate constant (k_1) for the passage of the CT complex to the transition state, $k = k_1$ in reaction (2), or the rate constant is divided by the formation constant, $k = k_2/K_{\rm CT}$ in reaction (3), when only an uncomplexed 2-nitropropane anion (the ratio corresponds to $1/K_{\rm CT}$) reacts with 1,7-PTQ. Although these two processes are kinetically indistinguishable, they can be distinguished on the basis of the temperature dependence of the observed rate constant (*vide infra*).

As shown in Scheme 2, the activation enthalpy of the reaction of the CT complex in reaction (2) is directly determined from the observed activation enthalpy, *i.e.* $\Delta H^{\ddagger}_{\rm obs} = \Delta H^{\ddagger}_1$. On the other hand, the observed activation enthalpy in reaction (3) is



Scheme 2

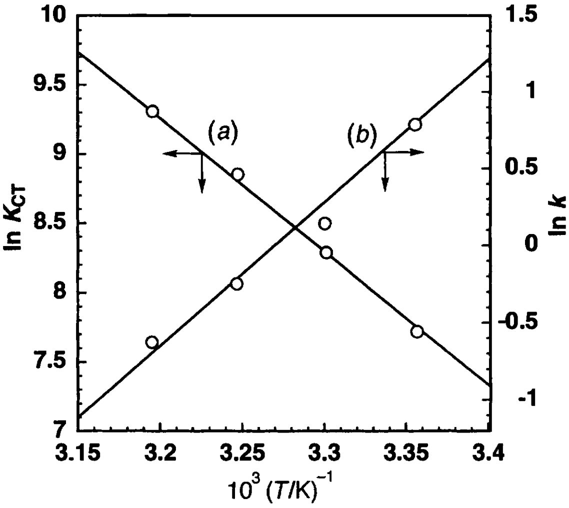


Fig. 4 Temperature dependence of (*a*) the complex formation constants (ln $K_{\rm CT}$) and (*b*) the observed first-order rate constants (ln k) for the reaction of 1,7-PTQ (5.0×10^{-5} mol dm^{-3}) and the 2-nitropropane anion in deaerated acetonitrile

the result of the subtraction of the heat of formation of the CT complex ($\Delta H_{\rm CT}$) from $\Delta H^{\ddagger}_1$, *i.e.* $\Delta H^{\ddagger}_{\rm obs} = \Delta H^{\ddagger}_2 - \Delta H_{\rm CT}$ (Scheme 2). In this case, the observed activation enthalpy $\Delta H^{\ddagger}_{\rm obs}$ should be larger than $-\Delta H_{\rm CT}$, since the $\Delta H^{\ddagger}_2$ and $\Delta H_{\rm CT}$ values are positive and negative, respectively. In contrast, the $\Delta H^{\ddagger}_{\rm obs}$ value in reaction (2) can be smaller than $-\Delta H_{\rm CT}$ as shown in Scheme 2. In order to determine the $\Delta H_{\rm CT}$ and $\Delta H^{\ddagger}_{\rm obs}$ values, we have examined the temperature dependence of the formation constant of the CT complex ($K_{\rm CT}$) as well as that of the rate constant (k) of decay of the CT complex. The plots of ln $K_{\rm CT}$ and ln k *vs.* T^{-1} are shown in Fig. 4(*a*) and (*b*), respectively. The $\Delta H_{\rm CT}$ and $\Delta H^{\ddagger}_{\rm obs}$ values are determined to be −4.8 kcal mol^{-1} and 4.5 kcal mol^{-1}, respectively.† The smaller value of $\Delta H^{\ddagger}_{\rm obs}$ than the $-\Delta H_{\rm CT}$ value, indicates clearly that the CT complex acts as a real intermediate [reaction (2)] rather than a bystander [reaction (3)] in the reaction of the 2-nitropropane anion with 1,7-PTQ as shown in Scheme 1.

The k value of the reaction of the nitroethane anion with 1,7-PTQ was determined as 3.1×10^{-4} s^{-1}, which is much smaller than that of the 2-nitropropane anion (0.46 s^{-1}). Such a decrease in the rate constant of the nitroethane anion as compared to that of the 2-nitropropane anion may be ascribed to the more positive one-electron oxidation potential ($E^{\circ}_{\rm ox}$ *vs.* SCE) of the nitroethane anion (0.21 V) than that of the 2-nitropropane anion (0.02 V). The $E^{\circ}_{\rm ox}$ values were determined using second harmonic ac voltammetry as reported previously.[8] If the addition of the nitroalkane anion with 1,7-PTQ proceeds *via* electron transfer from the nitroalkane anion to 1,7-PTQ in the

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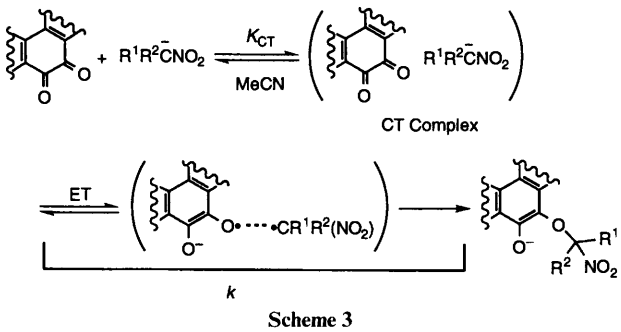
† 1 cal = 4.184 J.

CT complex, the reactivity of the nitroethane anion would be decreased by a factor of 1.6×10^3 compared with that of the 2-nitropropane anion judging from the difference in the one-electron oxidation potentials (0.19 V); $F\Delta E^{\circ}_{ox}/2.3RT = 1.6 \times 10^3$ at 298 K. The calculated difference in the electron transfer rate agrees well with the observed difference in the k values (the rate ratio of the 2-nitropropane anion to nitroethane is 1.5×10^3). Such a good agreement indicates that addition of the nitroalkane anion to 1,7-PTQ proceeds *via* electron transfer from the nitropropane anion to 1,7-PTQ in the CT complex, followed by the radical coupling of the 2-nitropropane radical to oxygen of 1,7-PTQ radical anion, as shown in Scheme 3.



Scheme 3

The Gibbs energy change of electron transfer from the nitroalkane anion to 1,7-PTQ in the CT complex is obtained from the one-electron oxidation potential of the nitroalkane anion (E°_{ox}) and the one-electron reduction potential of 1,7-PTQ (E°_{red}) using eqn. (4), where F is the Faraday constant and

$$\Delta G^{\circ}_{et} = F(E^{\circ}_{ox} - E^{\circ}_{red}) + w_p \qquad (4)$$

w_p is the work term required to bring the products to the distance of the transition state.[23] Since electron transfer from the nitroalkane anion to 1,7-PTQ involves no net change of total charge, the w_p term may be neglected in the estimation of ΔG°_{et} in eqn. (4). The one-electron reduction potential of 1,7-PTQ in acetonitrile has been determined to be 0.50 V (Table 1). Thus, the ΔG°_{et} values of electron transfer from the 2-nitropropane anion and the nitroethane anion to 1,7-PTQ are determined from eqn. (4) as 12.0 and 16.4 kcal mol^{-1}, respectively. The rate constant of the intracomplex electron-transfer in the CT complex may be evaluated on the basis of the Gibbs energy relationship for the electron-transfer processes shown in eqn. (5),[24,25] where $\Delta G^{\ddagger}_0$ is the intrinsic barrier to the

$$\Delta G^{\ddagger}_{et} = (\Delta G^{\circ}_{et}/2) + [(\Delta G^{\ddagger}_0)^2 + (\Delta G^{\circ}_{et}/2)^2]^{\frac{1}{2}} \qquad (5)$$

electron-transfer reactions. The $\Delta G^{\ddagger}_0$ value of the 2-nitropropane anion has previously been determined as 2.1 kcal mol^{-1}.[8] By using these values the $\Delta G^{\ddagger}_{et}$ values of electron transfer from the 2-nitropropane anion and the nitroethane anion can be evaluated as 12.4 and 16.7 kcal mol^{-1}, respectively. The $\Delta G^{\ddagger}_{et}$ values are converted to the corresponding values of rate constant of intracomplex electron transfer (k_{et}) using eqn. (6),

$$k_{et} = (kT/h)\exp(-\Delta G^{\ddagger}_{et}/RT) \qquad (6)$$

where k is the Boltzmann constant. The k_{et} values thus evaluated are 5.0×10^3 and 5.8 s^{-1}, respectively. The observed k values are 10^3 times smaller than the estimated k_{et} values, indicating that the radical coupling process between the nitroalkane radical and the 1,7-PTQ radical anion following electron transfer is slower than the back electron transfer from the 1.7-PTQ radical anion to the nitroalkane radical in Scheme 3. Application of Marcus theory[26] to predict the rate constants of electron transfer leads to the same conclusion, although the estimated k_{et} values are much smaller than those from eqns. (5) and (6). Direct nucleophilic attack of the nitropropane anion on carbon of 1,7-PTQ may be inhibited by the large steric hindrance of the phenanthrene moiety, when it is energetically feasible for electron transfer in the CT complex to become the dominant process in the reactions of nitroalkane anions with 1,7-PTQ.

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