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Reaction kinetics of electrogenerated 9,10-bis(4-substituted-phenyl)anthracene cation radicals with methanol: A change in mechanism brought about by remote substituents

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The reactions of 9,10-bis(4-nitrophenyl)- and 9,10-bis(4-methoxyphenyl)anthracene cation radicals ($\mathrm{DNA}^{\cdot+}$ and $\mathrm{DAA}^{\cdot+}$) with methanol (MeOH) in acetonitrile were analyzed using a pulse electrolysis stopped-flow method. The reaction of $\mathrm{DNA}^{\cdot+}$ was found to proceed *via* the same rate law as the 9,10-diphenylanthracene cation radical ($\mathrm{DPA}^{\cdot+}$), *i.e.* $-\mathrm{d}[\mathrm{DNA}^{\cdot+}]/\mathrm{d}t = k[\mathrm{DNA}^{\cdot+}][\mathrm{MeOH}]^2$, with a reaction rate 6 times faster. In contrast, the rate law governing the reaction of $\mathrm{DAA}^{\cdot+}$ with MeOH was different from that of $\mathrm{DPA}^{\cdot+}$, and was found to be $-d[\mathrm{DAA}^{\cdot+}]/\mathrm{d}t = k[\mathrm{DAA}^{\cdot+}]^2[\mathrm{MeOH}]$. Reflecting this difference in the rate laws, an acceleration of the reaction was observed in the decay of $\mathrm{DAA}^{\cdot+}$ relative to $\mathrm{DPA}^{\cdot+}$, though methoxy groups usually stabilize aromatic cation radicals. This unusual remote substituent effect, which involves a change in the reaction mechanism, is discussed in terms of stabilization of intermediates in the proposed reaction mechanisms.

Introduction

The kinetics and mechanism of the reaction of aromatic cation radicals with nucleophiles have been studied extensively over the past four decades.[1–4] Studies in this area are still ongoing; mechanistic issues to be addressed are well summarized by Parker.[5]

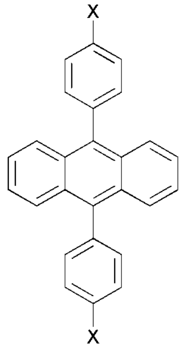
The cation radical of 9,10-diphenylanthracene (DPA, **1a**) is one of compounds most thoroughly studied because of its high stability in aprotic solvents, such as acetonitrile (AN), which is due to the blocking effect of its phenyl groups and the charge delocalization effect. If one phenyl group is substituted the kinetics and mechanism of the reaction of the cation radical with nucleophiles is affected significantly, as has been proved previously for reactions of 9-substituted-10-phenylanthracene cation radicals.[6] In this case, the substituents on the 9-position dramatically altered the reaction rates in reactions with water and methanol.[6]

In addition to such direct substituent effects, observation of remote substituent effects also helps elucidate further the reaction kinetics and mechanism. Such studies were recently carried out by Parker *et al.*[7]

Thus, in the present work, we have analyzed the reaction kinetics of electrogenerated 9,10-bis(4-substituted-phenyl)-anthracene (DXA) cation radicals with methanol (MeOH) in AN. DPA derivatives with electron donating methoxy groups (**1b**; DAA) and electron withdrawing nitro groups (**1c**; DNA) were also studied to examine how the kinetics and mechanism are changed by the electronic properties of the remote substituents.

The electrochemical response of DAA has been studied by Parker and co-workers.[8–10] They showed that electrooxidized states were stabilized by the remote methoxy substituents, but the effects of this substituent on the reaction kinetics and mechanism remain unknown. So, kinetic analysis should elucidate further the reactivity and stability of the cation radicals.

In the present work, MeOH was chosen as a nucleophile. This is because, as we have discussed in our earlier report on the reaction kinetics and mechanism of $\mathrm{DPA}^{\cdot+}$ with water and alcohols in AN,[11] reaction with MeOH can be regarded as a prototype reaction for that with water and alcohols, and tends to obey some standard rate laws.[11] The reason for this behavior can be explained by the state of MeOH in AN. Because MeOH–nitrile interactions are stronger than MeOH–MeOH interactions in AN, it has been reported that MeOH remains as a monomer in concentrations up to 4.0 M from IR data.[12]



1a: $X = H$
1b: $X = CH_3O$
1c: $X = NO_2$

For the kinetic analysis, a pulse electrolysis stopped-flow method[6,11,13] was used. By comparing the results with those obtained in the reaction analysis of $\mathrm{DPA}^{\cdot+}$,[11] the remote substituent effect is discussed.

Experimental

Apparatus and procedures for kinetic analysis

The details of obtaining spectroscopic measurements using the pulse electrolysis stopped-flow method have been described previously.[6,13] Because the required cation radicals are stable in AN, the measurements were carried out using a non-mixing mode,[13] that is the AN solution containing both DPA derivatives and MeOH with 0.10 M tetraethylammonium perchlorate (TEAP) was held in one reservoir. Then, synchronized with the pulse electrolysis for 100 ms, the electrolyzed solution was sent to an optical flow-cell (light path, 2.0 mm) by the piston drive. In the cell, the changes in absorption spectra with time or the decay curves of absorbance at a fixed wavelength over time were observed. The temperature was controlled at 25 °C by circulating water outside the cell.[13] Electrolysis was performed with a PAR Model 173 Potentiostat.

Electrochemical analysis

Cyclic voltammograms (CVs) were measured using a PAR 174 analyzer. A Pt disk electrode of 1.6 mm diameter was used as the working electrode. The reference electrode used was the Pt|(I_3^-, I^-) in AN. All CV experiments were performed in an H-shaped cell at *ca.* 25 °C.

Product analysis was carried out using a batchwise controlled-potential electrolysis for suspensions of 5.0 mM DPA derivative in AN (due to the low solubility of the substrate) with 0.1 M TEAP and 3 M MeOH. Using a platinum mesh working electrode, the stirred solution was electrooxidized at the potential to form the cation radical until the electrolytic current decreased to almost zero. After this the solution was evaporated and extracted with benzene, and the products were then purified on a silica-gel column with benzene as an eluent. The products were identified by NMR and MS.

Reagents

Acetonitrile (AN, Nacalai Tesque, GR grade) was twice-distilled over P_2O_5. The supporting electrolyte, tetraethylammonium perchlorate (TEAP), was made from sodium perchlorate and tetraethylammonium bromide, and purified by recrystallization five times from water. Methanol (Wako Co. Ltd., infinity pure grade) was used as received. 9,10-Bis(4-methoxyphenyl)anthracene (9,10-dianysilanthracene, DAA, Aldrich Co. Ltd.) was used as received. 9,10-Bis(4-nitrophenyl)anthracene (9,10-dinitrophenylanthracene, DNA) was synthesized from anthracene and nitrophenyl diazonium salt following the method of Dickerman *et al.*[14]

Results and discussion

Electrochemical and spectroscopic properties of $DXA^{\bullet+}$

The cyclic voltammograms in the oxidation processes of DAA and DNA were measured by the conventional method. Similar voltammograms to that of DPA were obtained; *i.e.* one electron oxidation process is reversible and the second is irreversible. The formal redox potentials to form the cation radicals of DAA, DPA and DNA were 0.98, 1.02 and 1.22 V (*vs.* I_3^-, I^-), respectively. The tendency of the potential to shift depending on the substituents is similar to that of 9-substituted-10-phenylanthracenes[6] and 9-substituted-anthracenes;[15] *i.e.* a positive shift was observed for electron withdrawing groups and a negative one for electron donating groups. However, the degree of shift was found to be small for the remote substituents studied here. The oxidation peak potentials to form the dications of DAA, DPA and DNA were 1.19, 1.47 and 1.52 V, respectively. These values were obtained for acetonitrile solutions of saturated DXA (less than 1 mM) at a scan rate of 100 mV s^{-1}.

The visible absorption spectra of $DXA^{\bullet+}$ were measured by using the pulse electrolysis stopped-flow method. Similar spectra to that of $DPA^{\bullet+}$ were also obtained. A slight shift to longer wavelength was observed for $DNA^{\bullet+}$ and to shorter wavelength for $DAA^{\bullet+}$, which is also similar to the 9-substituted-10-phenylanthracenes[6] and is known to be a general tendency.

Product analysis in the reaction between $DXA^{\bullet+}$ and MeOH

In advance of the kinetic analysis, the products of the reactions with MeOH were determined. From the results of the batchwise electrolysis, the only product formed was identified as 9,10-dimethoxy-9,10-bis(4-substituted-phenyl)-9,10-dihydroanthracene ($DXA(MeO)_2$, **2**).

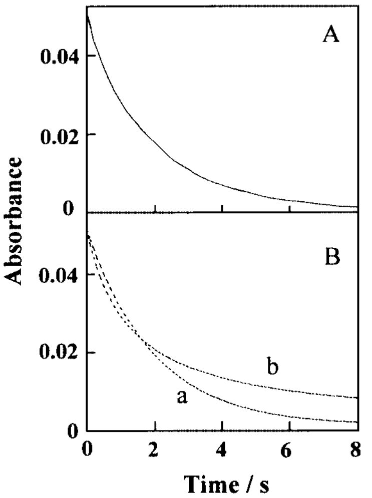
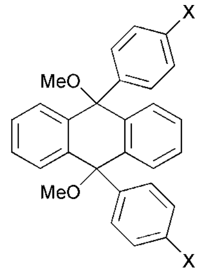


Fig. 1 (A) Time decay curve of $DNA^{\bullet+}$ recorded for its reaction with 1.0 M MeOH. Measured wavelength: 720 nm. (B) Time decay curves obtained by simulations assuming (a) first-order decay and (b) second-order decay for $[DNA^{\bullet+}]$.



2a: X = H
2b: X = CH_3O
2c: X = NO_2

Because the reaction products (**2b** and **2c**) were similar to that obtained in the reaction of $DPA^{\bullet+}$ and MeOH, it is likely that the reaction processes of $DAA^{\bullet+}$ and $DNA^{\bullet+}$ with MeOH are expressed by eqn. (1) or eqn. (1′).

$$2\,DXA^{\bullet+} + 2\,MeOH \longrightarrow DXA(MeO)_2 + DXA + 2\,H^+ \quad (1)$$

$$2\,DXA^{\bullet+} + 4\,MeOH \longrightarrow DXA(MeO)_2 + DXA + 2\,MeOH_2^+ \quad (1')$$

This is, of course, the case in homogeneous solution. In batchwise electrolysis, the DXA on the right is totally consumed to form the product, **2**.

Kinetic analysis of the reaction of $DNA^{\bullet+}$ with MeOH

By following the change in absorbance of one of the absorption maxima of $DNA^{\bullet+}$ at 720 nm in the optical cell, the kinetic process in the reaction of $DNA^{\bullet+}$ with MeOH was observed. Fig. 1A shows the decay in absorbance, *i.e.* the concentration, of $DNA^{\bullet+}$ in its reaction with 1.0 M MeOH. This curve coincides with the simulated curve for first-order decay of $[DNA^{\bullet+}]$, shown in Fig. 1B(a). The reaction was therefore found to be first order in $[DNA^{\bullet+}]$ as expressed by eqn. (2), and

$$-d[DNA^{\bullet+}]/dt = k_{1app}[DNA^{\bullet+}] \quad (2)$$

the pseudo-first order rate constant, k_{1app}, was determined to be 0.48 s^{-1} in the reaction with 1.0 M MeOH.

From measurements at various concentrations of MeOH, the k_{1app}s at several concentrations of MeOH could be obtained from well-fitted first order plots for $[DNA^{\bullet+}]$. Fig. 2 shows the plot of log k_{1app} *vs.* log [MeOH], whose slope is the reaction order in MeOH. The reaction was found to be second order in MeOH (Fig. 2), so the rate law of the reaction between $DNA^{\bullet+}$ and MeOH is expressed by eqn. (3), which is identical to that

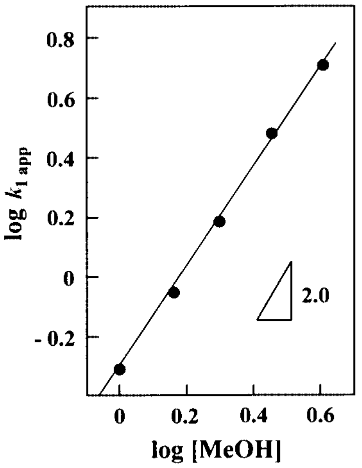


Fig. 2 Reaction order analysis for the reaction of $DNA^{\bullet +}$ with MeOH. Log k_{1app} was plotted *versus* log [MeOH].

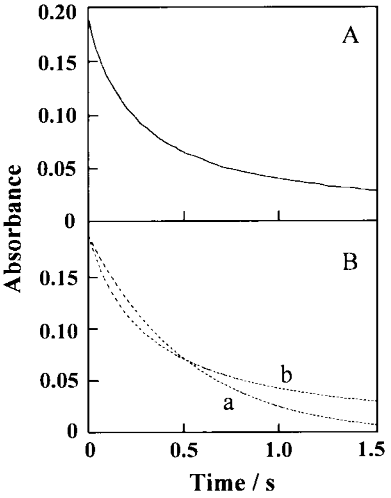


Fig. 3 (A) Time decay curve of $DAA^{\bullet +}$ recorded for its reaction with 1.0 M MeOH. Measured wavelength: 672 nm. (B) Time decay curves obtained by simulations assuming (a) first-order decay and (b) second-order decay for $[DAA^{\bullet +}]$.

$$-d[DNA^{\bullet +}]/dt = k[DNA^{\bullet +}][MeOH]^2 \qquad (3)$$

for $DPA^{\bullet +}$ and MeOH.[11] Similarly good linearity of log k_{1app} *vs.* log [MeOH] is also observed in the reaction of $DPA^{\bullet +}$ and MeOH.[11]

Kinetic analysis of the reaction of $DAA^{\bullet +}$ with MeOH

Next, the reaction of $DAA^{\bullet +}$ with MeOH was analyzed in a similar manner. Generally speaking, the reaction of $DAA^{\bullet +}$ with MeOH tended to be faster than that of $DPA^{\bullet +}$, though methoxy substituents usually stabilize the oxidation state of aromatic cation radicals.[6–10,16] Here, our studies revealed that the rate law is different for both reactions.

Fig. 3A shows the decay curve of $DAA^{\bullet +}$ in its reaction with 1.0 M MeOH, in which absorbance of one of the absorption maxima of $DAA^{\bullet +}$ at 672 nm was followed. This decay curve does not fit the first order decay profile, but fits well to the second order decay curve shown in Fig. 3B(b). The value of absorbance can be related to $[DAA^{\bullet +}]$ by the value of its absorption coefficient (ε; 1.5×10^4 M^{-1} cm^{-1}) reported previously.[10] From our analysis, the reaction of $DAA^{\bullet +}$ with MeOH is second order in $[DAA^{\bullet +}]$ as expressed by eqn. (4).

$$-d[DAA^{\bullet +}]/dt = k_{2app}[DAA^{\bullet +}]^2 \qquad (4)$$

The apparent second order rate constant was determined to be 3.0×10^4 M^{-1} s^{-1} in the reaction with 1.0 M MeOH.

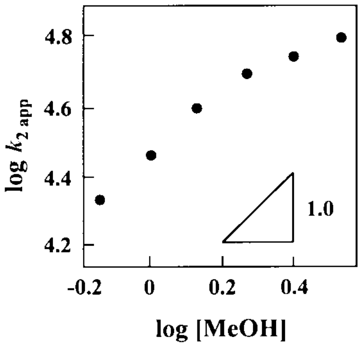


Fig. 4 Reaction order analysis for the reaction of $DAA^{\bullet +}$ with MeOH. The log k_{2app} values were plotted *versus* log [MeOH].

From measurements at various concentrations of MeOH, the k_{2app}s at several [MeOH] could be obtained from well-fitted second order plots for $[DAA^{\bullet +}]$. Fig. 4 shows the plot of log k_{2app} *vs.* log [MeOH]. Although the concentration range of MeOH was sufficiently low for it to exist as the monomer in AN, a good linear relationship was not obtained, and a little curvature was observed. This is slightly different from the results for the reactions of $DPA^{\bullet +}$ and $DNA^{\bullet +}$ with MeOH. However, on the whole, it was found that the reaction could be regarded as first order in MeOH at lower concentrations. Thus, the rate law for the reaction of $DAA^{\bullet +}$ and MeOH is expressed by eqn. (5).

$$-d[DAA^{\bullet +}]/dt = k[DAA^{\bullet +}]^2[MeOH] \qquad (5)$$

Mechanistic discussion of the reactions of $DXA^{\bullet +}$ with MeOH

On the basis of the rate laws obtained above for both of the reactions, the reaction mechanisms given in Scheme 1 and Scheme 2, could be postulated for the reactions of $DNA^{\bullet +}$ and $DAA^{\bullet +}$, respectively.

$$DNA^{\bullet +} + MeOH \overset{K}{\rightleftharpoons} DNA(MeOH)^{\bullet +} \qquad (6)$$

$$DNA(MeOH)^{\bullet +} + MeOH \xrightarrow[\text{rds}]{k} DNA(MeO)\cdot + MeOH_2^+ \qquad (7)$$

$$DNA(MeO)\cdot + DNA^{\bullet +} \longrightarrow DNA(MeO)^+ + DNA \qquad (8)$$

$$DNA(MeO)^+ + 2MeOH \longrightarrow DNA(MeO)_2 + MeOH_2^+ \qquad (9)$$

Scheme 1

$$DAA^{\bullet +} + MeOH \overset{K}{\rightleftharpoons} DAA(MeOH)^{\bullet +} \qquad (10)$$

$$DAA(MeOH)^{\bullet +} + DAA^{\bullet +} \xrightarrow[\text{rds}]{k} DAA(MeOH)^{2+} + DAA \qquad (11)$$

$$DAA(MeOH)^{2+} + MeOH \longrightarrow DAA(MeO)^+ + MeOH_2^+ \qquad (12)$$

$$DAA(MeO)^+ + 2MeOH \longrightarrow DAA(MeO)_2 + MeOH_2^+ \qquad (13)$$

Scheme 2

For the reaction of $DNA^{\bullet +}$ with MeOH, on the basis of its similarity with that of $DPA^{\bullet +}$, Scheme 1 is proposed. The first encounter between $DNA^{\bullet +}$ and MeOH is in equilibrium [eqn. (6)], and H^+ abstraction by another MeOH is the rate determining step (rds) [(eqn. (7)], as has been shown for $DPA^{\bullet +}$.[11] Compared with the reaction of $DPA^{\bullet +}$, the overall rate constant of the reaction of $DNA^{\bullet +}$ with MeOH was *ca.* 6 times greater. It is likely that introduction of electron withdrawing nitro-substituents promotes the release of H^+ in eqn. (7) as well as the reactivity of $DNA^{\bullet +}$ in eqn. (6).

On the other hand, for the reaction of $DAA^{\bullet +}$ with MeOH, the second order dependence on $[DAA^{\bullet +}]$ strongly suggests that the mechanism should follow Scheme 2 because disproportionation of two $DAA^{\bullet +}$s can usually be ruled out for nucleophilic reactions of cation radicals.[1–5] In Scheme 2, before abstracting H^+, it is likely that electron transfer occurs by interacting with another $DAA^{\cdot+}$ as the rds [eqn. (11)].

This difference is reasonable taking into account the substituent effect of the electron donating methoxy group on the intermediates, $DAA(MeOH)^{\cdot+}$ and $DAA(MeOH)^{2+}$, and the putative intermediate, $DAA(MeO)^{\cdot}$. Because the reactive positive charge is expected to be diminished by the effect of the methoxy substituents, $DAA(MeOH)^{\cdot+}$ and $DAA(MeOH)^{2+}$ should be stabilized much more than $DAA(MeO)^{\cdot}$. For this reason, it is likely that eqn. (11) to form $DAA(MeOH)^{2+}$ precedes the abstraction of H^+ from $DAA(MeOH)^{\cdot+}$. If the reaction to form $DAA(MeO)^{\cdot}$ were the rds, the appreciable decay rate of $DAA^{\cdot+}$ in the reaction with MeOH would be slower than that of $DPA^{\cdot+}$. Thus, the unusual apparent fast reaction of $DAA^{\cdot+}$ can be attributed to a change in mechanism of the reactions.

Conclusion

Remote substituent effects on the nucleophilic reaction of DPA derivatives toward MeOH were analyzed using the pulse electrolysis stopped-flow method. In the reaction of the nitro-substituted cation radical, $DNA^{\cdot+}$, it was found that the reaction proceeds following the same rate law as that of $DPA^{\cdot+}$ with an increased reaction rate. This agrees with the general tendency of the substituent effect of an electron-withdrawing group on the reactivity of cation radicals, *e.g.* as in ref. 6.

In contrast, in the reaction of the methoxy-substituted cation radical, $DAA^{\cdot+}$, an apparent acceleration of the reaction was found in comparison with the reaction of $DPA^{\cdot+}$. This does not agree with the general tendency of the substituent effect of an electron-donating methoxy group.[6–10,16] Detailed kinetic analysis showed that the introduction of the methoxy substituent alters the reaction mechanism, even though the substituents are in a remote position.

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References

1 V. D. Parker, in *Advances in Physical Organic Chemistry*, ed. V. Gold and D. Bethell, Academic Press, London, 1983, vol. 19, p. 131.
2 K. Yoshida, *Electrooxidation in Organic Chemistry*, John Wiley & Sons, Inc., New York, 1984.
3 O. Hammerich and V. D. Parker, in *Advances in Physical Organic Chemistry*, ed. V. Gold and D. Bethell, Academic Press, London, 1984, vol. 20, p. 55.
4 V. D. Parker, *Acc. Chem. Res.*, 1984, **17**, 243.
5 V. D. Parker, *Acta Chem. Scand.*, 1998, **52**, 145.
6 M. Oyama, K. Nozaki and S. Okazaki, *J. Electroanal. Chem.*, 1991, **304**, 61.
7 V. D. Parker, M. Pedersen and B. Reitstoen, *Acta Chem. Scand.*, 1993, **47**, 560.
8 O. Hammerich and V. D. Parker, *Electrochim. Acta*, 1973, **18**, 537.
9 O. Hammerich and V. D. Parker, *J. Am. Chem. Soc.*, 1974, **96**, 4289.
10 U. Svanholm and V. D. Parker, *J. Am. Chem. Soc.*, 1976, **98**, 997.
11 M. Oyama, K. Nozaki, T. Nagaoka and S. Okazaki, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 33.
12 S. S. Mitra, *J. Chem. Phys.*, 1962, **36**, 3286.
13 M. Oyama, K. Nozaki and S. Okazaki, *Anal. Chem.*, 1991, **63**, 1387.
14 S. C. Dickerman, A. M. Felix and L. B. Levy, *J. Org. Chem.*, 1964, **29**, 26.
15 S. Okazaki, M. Oyama and S. Nomura, *Electroanalysis*, 1997, **9**, 1242.
16 M. Oyama, T. Sasaki and S. Okazaki, *J. Electroanal. Chem.*, 1997, **420**, 1.