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Structural Effects on the Mechanism of the Protonation of Anion Radicals of Aromatic Compounds. The Protonation of 1,1-Diphenylethylene Anion Radical by Methanol

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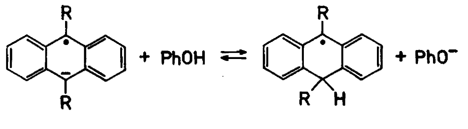
The initial proton addition to the anion radical of 1,1-diphenylethylene generates $Ph_2C^{\cdot}-CH_3$. By virtue of the fact that the proton becomes attached to an aliphatic carbon the reaction is irreversible. The kinetics of the reaction are clearly first order in anion radical and the overall reaction is of the ECE_h type. These results are in contrast to those anion radical protonations during which protons become attached to benzylic carbons reversibly giving rise to complex kinetic behaviour. The dependence of the linear sweep voltammetry peak potential on the methanol concentration during the reduction of 1,1-diphenylethylene in *N,N*-dimethylformamide indicated an apparent reaction order in methanol less than 1. The results could be explained by assuming either a dimerization equilibrium and that only monomeric methanol serves as the proton donor or association of the anion radicals with methanol resulting in a shift in E^{rev}. The latter was deemed most likely.

Recent studies on the protonation of anthracene and substituted anthracene anion radicals by phenol (1) indicate that the reactions exhibit complex kinetic behaviour.[1,2] It was observed that the reaction orders in anion radical and phenol vary between the limits of 1 and 2 and that the rate of the reaction is inhibited by phenoxide ion. These results indicate that reaction (1) is reversible and further steps along the reaction pathway contribute to controlling the rates of the reactions.



(1)

The structural features common to the initial proton adducts of the various anthracene anion radicals, as well as those of other condensed aromatic compounds, is that the proton becomes attached to a benzylic position. The objective of the present study was to show that this structural feature is responsible for the reversibility of reaction (1) and when this feature is removed by suitable structural modification then the reactions become irreversible and exhibit simple second order kinetics. The obvious structural modification is one in which the initial proton attachment occurs at an aliphatic position not conjugated with an aromatic ring. For this purpose we selected the 1,1-diphenylethylene (DPE) anion radical which was expected to react with a proton donor as in reaction (2).

$$(Ph_2C=CH_2)^{\cdot-} + ROH \longrightarrow Ph_2C^{\cdot}-CH_3 + RO^- \qquad (2)$$

RESULTS AND DISCUSSION

LSV sweep rate dependence. The dependence of the peak potential (E^p) on the voltage sweep rate (v) during linear sweep voltammetry (LSV) analysis of purely kinetic waves is given by (3).[3] The response

$$dE^p/d\log v = [\ln 10/(b+1)]RT/F \qquad (3)$$

is dependent upon the reaction order in the primary intermediate of the charge transfer reaction (4) and the temperature. The data in Table 1 are a summary

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$$A \pm e \rightleftharpoons B \tag{4}$$

of LSV experiments on solutions of DPE in DMF in the presence of methanol (25 mM). Each value of $dE^p/d \log v$ listed resulted from measurements at 100, 200, 400 and 1000 mV s^{-1} with 5 replicates at each sweep rate with standard deviations being of the order of ±0.1 mV. The last column gives the theoretical value for $b=1$ corresponding to rate determining protonation reaction (5) with methanol in excess. The mean values at the four different

$$DPE^{\cdot -} + MeOH \xrightarrow{k_5} DPE^{\cdot} - H + MeO^{-} \tag{5}$$

substrate concentrations were all reasonably close to the theoretical values. Since a reaction order of two in anion radical results in a prediction (3) of 19.7 mV/decade at 298 K, the results are only compatible with $b=1$.

LSV substrate concentration dependence. The dependence of E^p on the substrate concentration (C_A) is given by (6) where a is the reaction order

$$d \log E^p/d \log C_A =$$
$$[(a+b+i-1)/(b+1)] \ln 10\,(RT/F) \tag{6}$$

in A and i that of products formed which further participate in the process.[3] For the case where $a=0$, $b=1$, and $i=0$ which is the predicted result for rate determining reaction (5), $dE^p/d \log C_A$ is zero. The data summarized in Table 2 are values of E^p at four C_A and v measured at 23 °C. Once again each E^p is the mean of 5 replicate measurements with standard deviations of the order of ±0.1 mV. The values listed in the last column of Table 2 give the mean values of E^p averaged over all concentrations. The standard deviations found are of the order of 0.6 mV which is a clear indication that both a and i are zero and $dE^p/d \log C_A$ is zero as well.

LSV methanol concentration dependence. For a pseudo first order reaction of intermediate B (eqn. 1) with a reactant in excess (X), the dependence of the peak potential on C_X is given by eqn. (7) where x

$$dE^p/d \log C_X = (x \ln 10)/(b+1)\, RT/F \tag{7}$$

is the reaction order in X.[3] For rate determining reaction (5), x (X = MeOH) is expected to be 1 and $dE^p/d \log C_X$ to equal (1/2) RT/F. The data summarized in Table 3 show that this relationship is not followed. At all four sweep rates, $dE^p/d \log C_X$, which result from measurements at four different concentrations, are markedly dependent upon temperature. The theoretical slopes for $x=1$ are those

Table 1. LSV sweep rate dependence during the reduction of DPE in DMF containing methanol.[a]

	$dE^p/d \log v$ (mV/decade) at C_{DPE}					
T/°C	0.3 mM	0.5 mM	0.7 mM	1.0 mM	Mean (s.d.)[b]	Theory[c]
−7	27.5	27.9	28.8	30.1	28.6(1.2)	26.4
11	27.0	27.8	28.1	29.2	28.0(0.9)	28.2
23	28.0	28.6	28.7	29.5	28.7(0.6)	29.4
39	29.5	29.7	30.2	29.1	29.6(0.5)	31.0

[a] Measurements at a mercury electrode in solvent containing Bu_4NBF_4 (0.1 M) and methanol (25 mM). [b] The mean and standard deviation at all substrate concentrations. [c] The theoretical value for a reaction first order in anion radical.

Table 2. The variation of the peak potential with changes in the substrate concentration.[a]

	$-E^p$ (mV)[b] at C_{DPE}(mM)				
v/mV s^{-1}	0.3	0.5	0.7	1.0	Mean (s.d.)
100	689.8	689.7	690.2	690.7	690.1(0.5)
200	697.2	697.2	697.7	678.5	697.7(0.6)
400	705.7	706.2	706.4	707.3	706.4(0.7)
1000	717.6	718.2	718.7	(720.1)[c]	718.2(0.6)

[a] For conditions see Table 1, T= 23 °C. [b] The LSV peak potential *vs.* a potentiostat bias potential of −2.100 V *vs.* Ag/Ag^+. [c] Not included in the averaging.

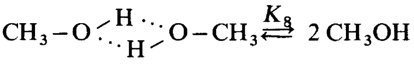
Table 3. The dependence of the peak potential on the methanol concentration during the reduction of DPE in DMF.[a]

v/V s^{-1}	T/°C	dE^p/d log C_{MeOH}[b]
100	−7	−20.3
100	11	−24.8
100	23	−27.6
200	−7	−19.8
200	11	−24.7
200	23	−27.5
400	−7	−18.9
400	11	−24.3
400	23	−27.8
1000	−7	−18.6
1000	11	−23.7
1000	23	−26.7

[a] Conditions as in Table 1, C_{DPE} = 1.0 mM. [b] Methanol concentrations of 25, 50 and 100 mM.

given in the last column of Table 1. The deviations from the theoretical values are temperature dependent and are greatest at the lower temperature. The data indicate that the apparent reaction order in methanol is less than unity and is variable.

A possible dimer-monomer equilibrium. The data in Table 3 suggested that methanol may possibly be involved in a concentration dependent equilibrium which reduces the effective concentration of the proton donor. An obvious possibility is the dimerization equilibrium (8) which suggests that



$$CH_3{-}O\overset{H\cdots}{\underset{\cdots H}{}}O{-}CH_3 \overset{K_8}{\rightleftharpoons} 2\,CH_3OH \qquad (8)$$

the hydrogen bonded cyclic dimer could be a poorer proton donor than monomeric methanol. The data in Table 4 are based on the experimental data in Table 3. At each temperature the apparent reaction order in methanol was obtained by applying eqn. (7) to estimate the effective methanol concentration. Assuming equilibrium (8), the total methanol concentration, $|MeOH|_{tot}$, is given by (9) and the effective concentration, $|MeOH|_{eff}$, is related to the equilibrium constant K_8 by (10). Equilibrium

$$|MeOH|_{tot} = |MeOH|_{eff} + 2|(MeOH)_2| \qquad (9)$$

$$|MeOH|_{eff} = ((K_8{}^2 + 8\,K_8|MeOH|_{tot})^{\frac{1}{2}} - K_8)/4 \qquad (10)$$

constants were estimated at each temperature and $|MeOH|_{eff}$ obtained from (10) were then used to calculate dE^p/d log C_{MeOH}. The mean values, standard deviations, and theoretical values are summarized in Table 4. As a further test to determine whether or not eqn. (10) gives consistent values of K_8, the data were treated according to eqn. (11). If the K_8 values are consistent, a linear relationship

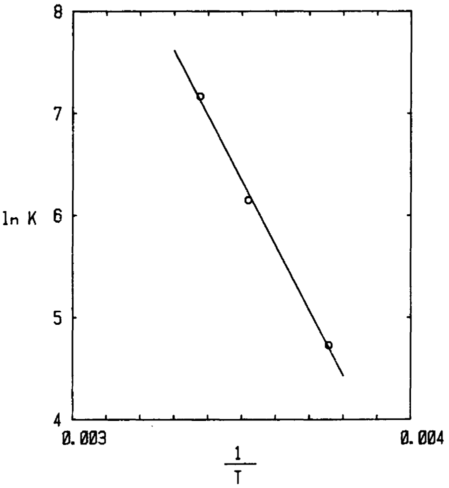


Fig. 1. The temperature dependence of the equilibrium constants calculated assuming a dimerization equilibrium of methanol in DMF.

Table 4. Correction of the peak potential dependence on the methanol concentration assuming a methanol dimerization equilibrium.[a]

T/K	296	284	266
K_8/M	1.300	0.470	0.113
(−dE^p/d log C_X)$_{corrected}$	29.3(0.5)	28.2(0.6)	26.4(1.1)
(−dE^p/d log C_X)$_{theory}$	29.4	28.2	26.4

[a] Data from Table 3 treated as described in the text for a reaction first order in anion radical and methanol.

Table 5. Correction of the peak potential dependence on the methanol concentration assuming association of the anion radical and methanol.[a]

T/K	296	284	266
K_{13}/M^{-1}	0.60	1.30	2.90
$\Delta E^{\mathrm{rev}}(C_X=25\ \mathrm{mM})/\mathrm{mV}$	0.38	0.78	1.60
$\Delta E^{\mathrm{rev}}(C_X=50\ \mathrm{mM})/\mathrm{mV}$	0.75	1.54	3.10
$\Delta E^{\mathrm{rev}}(C_X=100\ \mathrm{mM})/\mathrm{mV}$	1.49	2.99	5.84
$(-\mathrm{d}E^{\mathrm{p}}/\mathrm{d}\log C_X)_{\mathrm{corrected}}$[b]	29.3(0.4)	28.0(0.5)	26.4(0.8)
$(-\mathrm{d}E^{\mathrm{p}}/\mathrm{d}\log C_X)_{\mathrm{theory}}$[c]	29.4	28.2	26.4

[a] Data from Table 3 corrected as described in the text assuming eqn. (13). [b] In mV/decade corrected for the appropriate change in E^{rev}. [c] In mV/decade assuming rate determining reaction (14).

$$\ln K_8 = -\Delta H_8/RT + c \qquad (11)$$

is expected. The data plotted in Fig. 1 resulted in $\Delta H_8 = 12.7$ kcal/mol with a correlation coefficient of 0.999.

Possible anion radical–methanol association equilibrium. Another plausible explanation for the low and variable values of $\mathrm{d}E^{\mathrm{p}}/\mathrm{d}\log C_X$ is that the anion radicals are reversibly associated with methanol and the overall electrode process is described by eqns. (12)–(14). The reversible potential for

$$\mathrm{DPE} + e^- \rightleftarrows \mathrm{DPE}^{\cdot -} \qquad (12)$$

$$\mathrm{DPE}^{\cdot -} + \mathrm{MeOH} \overset{K_{13}}{\rightleftarrows} \mathrm{DPE}^{\cdot -}/\mathrm{MeOH} \qquad (13)$$

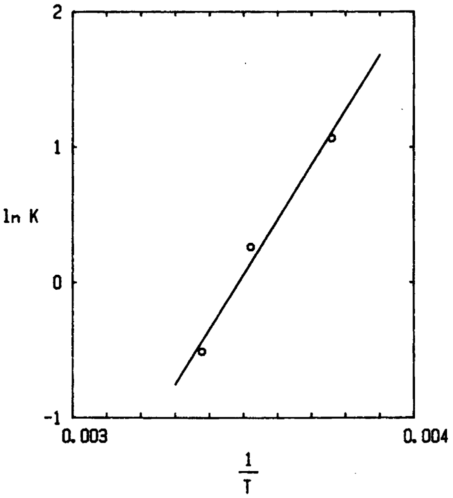


Fig. 2. The temperature dependence of the equilibrium constants calculated assuming association of diphenylethylene anion radical with methanol.

$$\mathrm{DPE}^{\cdot -}/\mathrm{MeOH} \xrightarrow{k_{14}} \mathrm{DPE}^{\cdot}-\mathrm{H} + \mathrm{MeO}^- \qquad (14)$$

reactions (12)–(13) is described by eqn. (15) and the difference in E^{rev} measured in the presence and absence of methanol (ΔE^{rev}) by (16).

$$E^{\mathrm{rev}} = E^{\circ} + RT/F \ln (K|\mathrm{MeOH}| + 1) \qquad (15)$$

$$\Delta E^{\mathrm{rev}} = RT/F \ln (K|\mathrm{MeOH}| + 1) \qquad (16)$$

In order to test the applicability of eqn. (16) to explain the LSV data, the value of ΔE^{rev}, at each methanol concentration and temperature, was estimated from the observed values of $\mathrm{d}E^{\mathrm{p}}/\mathrm{d}\log C_X$ and $(\ln 10)\ RT/2F$, the expected value for mechanism (12)–(14). The ΔE^{rev} values were then used in (16) to estimate K_{13}. The results are summarized in Table 5. Correlation of $\ln K_{13}$ *vs.* 1/T (Fig. 2) resulted in ΔH_{13} of -8.1 kcal/mol with a correlation coefficient of 0.98.

CONCLUSIONS

The point of crusial importance in terms of the overall mechanism of the protonation of $\mathrm{DPE}^{\cdot -}$ by methanol is which of the alternatives for the dependence of the LSV peak potential on the methanol concentration is correct. Unfortunately, it was not possible to measure the reversible potential, to the degree of precision required, by phase sensitive second harmonic *a.c.* voltammetry because of interference by the kinetics of the follow-up reaction. If it had been possible to measure E^{rev} in the absence and presence of methanol, the question would have been resolved. However, the very small ΔE^{rev} values required by the second alternative, that of association of $\mathrm{DPE}^{\cdot -}$ with methanol, as shown in

Table 5 are less than the error in the reversible potential measurements.

Methanol dimer has recently been shown to be significant in non-polar solvents.[6] A theoretical study[7] predicts that the most stable form of the dimer in isolation is a *trans* near-linear form in which only one of the hydrogens is involved in hydrogen bonding. It does not seem likely that such a dimer would be ineffective as a proton donor. However, it is possible that in DMF the dimer is cyclic as in eqn. (8) and this form would be expected to donate protons less effectively than monomeric methanol. We have been unable to find literature data for the dimerization of methanol in DMF. On the other hand infrared spectral evidence has been reported which indicates that methanol is monomeric in acetonitrile at concentrations as great as 4 M.[8] The methanol–nitrile interactions are apparently greater than those between solute molecules. DMF would be expected to be a better hydrogen bonding solvent than acetonitrile which makes methanol dimerization appear highly unlikely.

We are then left with eqns. (12)–(14) as the most likely initial steps in the mechanism. These are then followed by solution electron transfer (17) and rapid protonation of the resulting carbanion (18). This

$$\mathrm{DPE^{\cdot}-H + DPE^{\cdot -} \rightleftharpoons DPE^{-}-H + DPE} \quad (17)$$

$$\mathrm{DPE^{-}-H + MeOH \longrightarrow DPE(H_2) + MeO^{-}} \quad (18)$$

mechanism is similar to that earlier suggested to be the general reaction pathway for the protonation of aromatic hydrocarbon anion radicals.[5] But even in this relatively simple case, a pre-equilibrium is highly probable and the rate law for the reaction is (19). Rate data are not related to a simple microscopic step but the LSV analysis provides values for

$$\mathrm{Rate} = k_{14}K_{13}|\mathrm{DPE^{\cdot -}}||\mathrm{MeOH}| \quad (19)$$

K_{13}. Under the conditions of our measurements the apparent first order rate constant for the reaction was greater than about 10^4 and out of range of measurement by cyclic voltammetry at voltage sweep rates less than about 1000 V/s.

EXPERIMENTAL

Reagent grade 1,1-diphenylethylene was reagent grade and used as received. The procedure for solvent and electrolyte purification as well as data handling was similar to that described for related work from this laboratory.[9] The practical details of the LSV analysis have recently been summarized.[10]

REFERENCES

1. Parker, V. D. *Acta Chem. Scand. B 35* (1981) 349.
2. Parker, V. D. *Acta Chem. Scand. B 35* (1981) 583.
3. Parker, V. D. *Acta Chem. Scand. B 35* (1981) 259.
4. Ahlberg, E. and Parker, V. D. *Acta Chem. Scand. B 35* (1981) 117.
5. Fry, A. J. and Schuettenberg, A. *J. Org. Chem. 39* (1974) 2452.
6. Brink, G. and Glasser, L. *J. Phys. Chem. 82* (1978) 1000.
7. Brink, G. and Glasser, L. *J. Comput. Chem. 2* (1981) 14.
8. Mitra, S. S. *J. Chem. Phys. 36* (1962) 3286.
9. Ahlberg, E. and Parker, V. D. *Acta Chem. Scand. B 34* (1980) 97.
10. Parker, V. D. *Acta Chem. Scand. B 35* (1981) 373.

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