Radical Ion Reactivity. II. A Theoretical Study of Radical Cation Reactivity *vs.* Nucleophiles, Based on Thermochemical Calculations

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It is postulated that the transition state for reaction between a radical cation ($R^{+ \cdot}$) and a nucleophile (Nu^-) is identical to that for reaction between the corresponding neutral molecule (R) and radical ($Nu^{\cdot}$). From this hypothesis it follows that the free energy of activation for $R^{+ \cdot} + Nu^-$ is equal to the sum of the standard free energy of the reaction $R^{+ \cdot} + Nu^- \rightarrow R + Nu^{\cdot}$ and the free energy of activation for $R + Nu^{\cdot}$. These latter quantities can be calculated or estimated from available thermochemical and kinetic data.

Calculations have been performed for a series of aromatic radical cations (those of perylene, 9,10-diphenylanthracene, naphthalene, and benzene) and nucleophiles (the halide ions, cyanide, hydroxide, acetate, benzoate and nitrite ion). The results show that radical cation reactivity is mainly determined by the relative oxidation potentials of R and Nu^-, respectively.
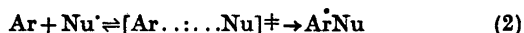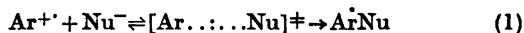
We have recently proposed that the anomalously low reactivity of certain aromatic radical ions toward certain nucleophiles/electrophiles might be explicable on the basis of the Dewar-Zimmerman rules.[1-3] In order to illuminate this problem from an entirely different angle, we now present thermochemical calculations which aim at estimating free energies of activation for radical cation/nucleophile processes. The results show that our previous picture of radical cation reactivity *vs.* nucleophiles is open for discussion, in that the standard redox potentials of the species involved turn out to be the critical variables.

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RESULTS

Starting hypothesis

We have earlier[4] briefly pointed out and commented upon the interesting analogy between the radical cation/nucleophile and the corresponding neutral molecule/neutral radical reaction (as exemplified for an aromatic molecule, Ar, in eqns. 1 and 2). It was noted that (a)

$$Ar^{+ \cdot} + Nu^- \rightleftharpoons [Ar..:...Nu]^{\ddagger} \rightarrow Ar\overset{\bullet}{N}u \qquad (1)$$

$$Ar + Nu^{\cdot} \rightleftharpoons [Ar..:...Nu]^{\ddagger} \rightarrow Ar\overset{\bullet}{N}u \qquad (2)$$

the initial states are different, (b) the final states are identical, and (c) the transition states in all likelihood must be identical, assuming identical external reaction conditions in the two cases. Assuming that the two transition states are indeed identical (see below) we can construct the hypothetical energy diagram of Fig. 1, from which it is evident that the free energy of activation of the $Ar^{+ \cdot}/Nu^-$ reaction ($\Delta G^{\ddagger}_1$) is obtained as the sum of the free energy of activation for the $Ar/Nu^{\cdot}$ reaction ($\Delta G^{\ddagger}_2$) and the standard free energy difference (ΔG°_x, assumed to be > 0 in Fig. 1) between the initial states of the two reactions (see eqns. 1 and 2). Hence we have reduced the problem of estimating values of $\Delta G^{\ddagger}_1$ (or $\Delta H^{\ddagger}_1$, if desirable) to the much simpler task of estimating ΔG°_x from thermochemical data. $\Delta G^{\ddagger}_2$ values are available from kinetic studies of aromatic free radical substitution reactions.
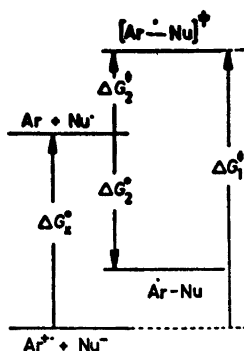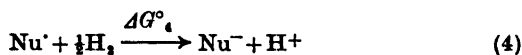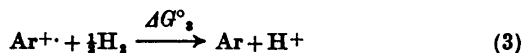
Fig. 1. Energy diagram showing the relationships between $\Delta G^\circ{}_x$, $\Delta G^{\pm}{}_1$, $\Delta G^{\pm}{}_2$ and $\Delta G^\circ{}_2$ for the case that $\Delta G^\circ{}_x \geqslant 0$.

Thermochemical calculations on the Ar+·/Nu⁻ process

General approach. In order to calculate values of $\Delta G^\circ{}_x$ we simply start from eqns. 3 and 4. The standard free energy change of eqn. 3 is

$$\text{Ar}^{+\cdot} + \tfrac{1}{2}\text{H}_2 \xrightarrow{\Delta G^\circ{}_3} \text{Ar} + \text{H}^+ \tag{3}$$

$$\text{Nu}^\cdot + \tfrac{1}{2}\text{H}_2 \xrightarrow{\Delta G^\circ{}_4} \text{Nu}^- + \text{H}^+ \tag{4}$$

seen to be directly related to the standard potential ($E^\circ{}_3$) of the Ar/Ar+· redox couple, with the normal hydrogen electrode (NHE) as reference, by the usual expression $-\Delta G^\circ{}_3 = 96.5\ E^\circ{}_3$. Likewise $\Delta G^\circ{}_4$ is related in exactly the same manner to the standard potential of the Nu⁻/Nu· redox couple. Subtraction of eqn. 4 from eqn. 3 the gives the desired quantity, $\Delta G^\circ{}_x$ (eqn. 5), as $\Delta G^\circ{}_3 - \Delta G^\circ{}_4$.

$$\text{Ar}^{+\cdot} + \text{Nu}^- \xrightarrow{\Delta G^\circ{}_x} \text{Ar} + \text{Nu}^\cdot \tag{5}$$
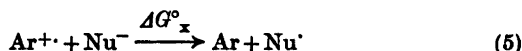
To present the results in a maximally informative way we have treated $\Delta G^\circ{}_3$ and hence the standard potential for the Ar/Ar+· redox couple, $E^\circ{}_3$, as the variable in the estimate of $\Delta G^\circ{}_x$. The results can then be shown graphically and $\Delta G^\circ{}_x$ estimated for any desired value of $E^\circ{}_3$. As solvent, we have chosen acetonitrile as the most commonly employed one for studying radical cation processes. Calculations have been carried through for the halide ions, cyanide ion, hydroxide ion, acetate ion, benzoate ion, and

nitrite ion, all species of great interest in connection with radical cation processes.

The calculations are based upon the previously[5] estimated standard potentials ($E^\circ{}_4$) of Nu·/Nu⁻ redox couples in aqueous solution (Nu⁻ being F⁻, Cl⁻, Br⁻, I⁻, CN⁻, HO⁻, AcO⁻, PhCOO⁻, NO$_2$⁻). By adding and subtracting, respectively, the free energy of transfer of Nu· and Nu⁻ ($\Delta G^\circ{}_{\text{Nu}\cdot}$ and $\Delta G^\circ{}_{\text{Nu}^-}$) from water to acetonitrile we obtain eqn. 6, which expresses

$$\Delta G^\circ{}_x = \Delta G^\circ{}_3 - \Delta G^\circ{}_4 + \Delta G^\circ{}_{\text{Nu}\cdot} - \Delta G^\circ{}_{\text{Nu}^-} =$$
$$-23.06\ (E^\circ{}_3 - E^\circ{}_4) + \Delta G^\circ{}_{\text{Nu}\cdot} - \Delta G_{\text{Nu}^-} \tag{6}$$

$\Delta G^\circ{}_x$ as a function of $E^\circ{}_3$, the standard potential of the Ar+·/Ar redox couple.

Values of $\Delta G^\circ{}_{\text{Nu}^-}$ were taken from the extensive tabulations published by Cox *et al.*,[6] whereas $\Delta G^\circ{}_{\text{Nu}\cdot}$ was put equal to zero in the absence of any data for this process. This is a reasonable approximation in view of the fact that free energies of hydration of *gaseous* Nu· are known or have been estimated to be close to zero.[5,7] The difference in solvation properties between water and acetonitrile toward neutral species would then not be expected to be significant. For fluoride ion, $\Delta G^\circ{}_{\text{Nu}^-}$ is not known but can be estimated from the reasonably good linear correlations between single ion free energies of transfer from water to acetonitrile and N,N-dimethylformamide or propylene carbonate, respectively, for a series of anions.[6] The interpolated values of $\Delta G^\circ{}_{\text{F}^-}$ are then 50 and 58 kJ mol⁻¹; the mean value of 54 kJ mol⁻¹ was used in the calculations.

$\Delta G^\circ{}_{\text{Nu}^-}$ for cyanide and nitrite ion was approximated by that of bromide ion, whereas $\Delta G^\circ{}_{\text{Nu}^-}$ for benzoate ion was assumed to be identical to $\Delta G^\circ{}_{\text{AcO}^-}$. $\Delta G^\circ{}_{\text{OH}^-}$ was taken to be identical to $\Delta G^\circ{}_{\text{F}^-}$ because of the similar characteristics of these two ions.

This treatment generates a series of straight lines, each showing the variation of $\Delta G^\circ{}_x$ for a particular nucleophile with the standard potential of the Ar+·/Ar redox couple (Fig. 2). In order to be able to discuss a few real systems in detail, $\Delta G^\circ{}_x$ values have been tabulated for $E^\circ{}_3 = 3.00$ V (Table 1, exemplifying benzene, for which radical substitution data are available to a reasonable extent), 2.08 V (Table 2, exemplifying naphthalene, an often used substrate in preparative anodic or metal ion oxidation),
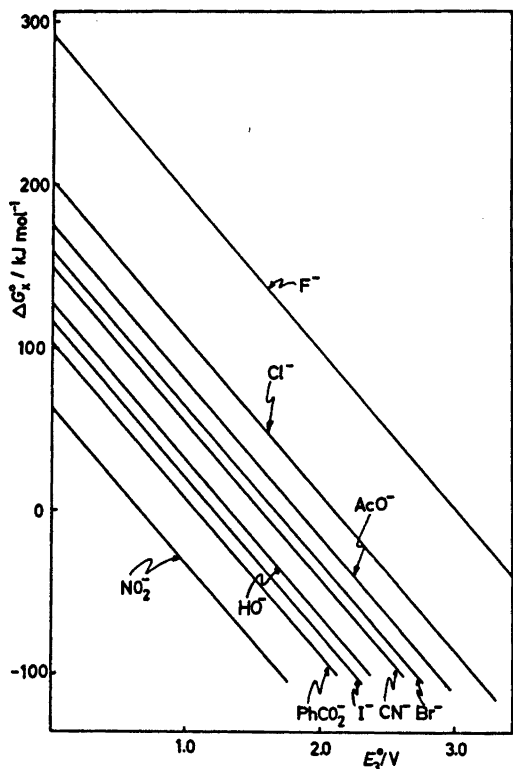
Fig. 2. Relationship between ΔG°_x and E°_3 for different nucleophiles.

Table 1. ΔG°_x, ΔG°_2, $\Delta G^{\neq}_2$ and "$\Delta G^{\neq}_1$" values for the benzene system ($E^\circ_2 = 3.00$ V [51]). All values are in kJ mol^{-1}.

Nu$^-$	ΔG°_x	$\Delta G^\circ_2{}^a$	$\Delta G^{\neq}_2$	"$\Delta G^{\neq}_1$"
F$^-$	3	-150	0	3
Cl$^-$	-85	-24	25 ^{b}	-60
Br$^-$	-128	37	37	-91
I$^-$	-173	99	99	-74
CN$^-$	-138	-192	0	-138
HO$^-$	-160	-86	0	-160
AcO$^-$	-113	12	28 ^{c}	-85 (-50^d_2)
PhCOO$^-$	-185	11	63 ^{e}	-122
NO$_2^-$	-225	94	94	-131

^{a} Gas phase values; since all participating species in eqn. 2 are neutral, no serious error is likely to be introduced by using the same values for aceto-nitrile. ^{b} See text and Fig 3. ^{c} See text. ^{d} Assuming $\Delta G^{\neq}_2$ has the same value as for PhCOO$^\cdot$ (63 kJ mol^{-1}). ^{d} Minimum value; see text.

1.44 V (Table 3, exemplifying 9,10-diphenyl-anthracene, the favorite model compound in mechanistic electroorganic chemistry), and 1.30 V (Table 4, exemplifying perylene, the radical cation of which has been extensively studied in homogeneous solution).

It turned out to be a lot more difficult than expected to extract $\Delta G^{\neq}_2$ data from the literature, either because of the fact that they do not exist at all or that available data cannot be definitely assigned to the process of interest here, radical attack on the aromatic ring (eqn. 2). Therefore, it was necessary to rely on available or estimatable data for benzene [8–11] (eqn. 2, Ar = PhH) and use these for the estimation of $\Delta G^{\neq}_2$ values for the other systems (Tables 2 – 4). The following procedure was employed, if no data were available: The standard free energy change (ΔG°_2) for eqn. 2 (Ar = PhH) was calculated according to the method given by Dorrepaal and Louw [12] (see Table 1, column 3). If ΔG°_2 was positive, it was approximated as the $\Delta G^{\neq}_2$ value for the corresponding radical attack upon benzene, whereas if it had a very large negative value (F$^-$ and CN$^-$ with -150 and -192 kJ mol^{-1}, respectively), $\Delta G^{\neq}_2$ was simply put equal to zero. Data for fluorine atom attack on benzene support this assumption.[13] For the chlorine atom, $\Delta G^{\neq}_2$ for the reaction with benzene [14] was arrived at by considering the complete energy diagram of Fig. 3. It has been shown that the chlorine atom forms a π complex with benzene (ΔG° for this reaction is -21 kJ mol^{-1}) which has a half-life of a few μs at room temperature.[15] Although it has
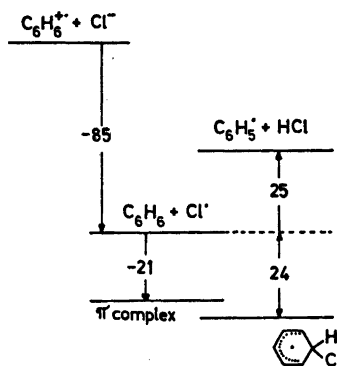
Fig. 3. Energy diagram for the (benzene)$^{+\cdot}$/Cl$^-$ system (ΔG values in kJ mol^{-1}).

Table 2. $\Delta G^{\circ}{}_{x}$, $\Delta G^{\neq}{}_{2}$ and $\Delta G^{\neq}{}_{1}$ values for the naphthalene system ($E^{\circ}{}_{3} = 2.08$ V [51]). All values are in kJ mol^{-1}.

| Nu$^-$ | $\Delta G^{\circ}{}_{x}$ | $\Delta G^{\neq}{}_{2}$ | | $\Delta G^{\neq}{}_{1}$ | |
		Case 1 [a]	Case 2 [b]	Case 1 [a]	Case 2 [b]
F$^-$	92	0	0	92	92
Cl$^-$	3	$\leqslant 25$	15	$3 - 28$	18
Br$^-$	-40	$\leqslant 37$	27	$-(40-3)$	-13
I$^-$	-84	$\leqslant 99$	89	-84 to $+15$	5
CN$^-$	-49	0	0	-49	-49
HO$^-$	-72	0	0	-72	-72
AcO$^-$	-24	$\leqslant 28$	18	-24 to $+4$	-6 (29 [c])
PhCOO$^-$	-96	$\leqslant 63$	52	$-(96-33)$	-43
NO$_2{}^-$	-136	$\leqslant 94$	84	$-(136-42)$	-52

[a] $\Delta G^{\neq}{}_{2}$ assumed to be $\leqslant$ that for attack on benzene. [b] $\Delta G^{\neq}{}_{2}$ "scaled down" according to the method given in text. [c] Higher limit for $\Delta G^{\neq}{}_{2}$ used (*i.e.*, same as for PhCOO$^{\cdot}$).

Table 3. $\Delta G^{\circ}{}_{x}$, $\Delta G^{\neq}{}_{2}$ and $\Delta G^{\neq}{}_{1}$ values for the 9,10-diphenylanthracene system ($E^{\circ}{}_{3} = 1.44$ V). All values are in kJ mol^{-1}.

| Nu$^-$ | $\Delta G^{\circ}{}_{x}$ | $\Delta G^{\neq}{}_{2}$ | | $\Delta G^{\neq}{}_{1}$ | |
		Case 1 [a]	Case 2 [b]	Case 1 [a]	Case 2 [b]
F$^-$	154	0	0	154	154
Cl$^-$	65	$\leqslant 25$	8	$65-90$	73
Br$^-$	22	$\leqslant 37$	20	$22-59$	42
I$^-$	-23	$\leqslant 99$	82	-23 to 76	59
CN$^-$	13	0	0	13	13
HO$^-$	-10	0	0	-10	-10
AcO$^-$	38	$\leqslant 28$	11	$38-66$	49 (84 [c])
PhCOO$^-$	-34	$\leqslant 63$	46	-34 to 29	12
NO$_2{}^-$	-74	$\leqslant 94$	77	-74 to 20	3

[a] $\Delta G^{\neq}{}_{2}$ assumed to be $\leqslant$ that for attack on benzene. [b] $\Delta G^{\neq}{}_{2}$ "scaled down" according to the method given in text. [c] Higher limit for $\Delta G^{\neq}{}_{2}$ used (*i.e.*, same as for PhCOO$^{\cdot}$).

Table 4. $\Delta G^{\circ}{}_{x}$, $\Delta G^{\neq}{}_{2}$ and $\Delta^{\neq}{}_{1}$ values for the perylene system ($E^{\circ}{}_{3} = 1.30$ V [51]). All values are in kJ mol^{-1}.

| Nu$^-$ | $\Delta G^{\circ}{}_{x}$ | $\Delta G^{\neq}{}_{2}$ | | $\Delta G^{\neq}{}_{1}$ | |
		Case 1 [a]	Case 2 [b]	Case 1 [a]	Case 2 [b]
F$^-$	166	0	0	166	166
Cl$^-$	78	$\leqslant 25$	7	$78-103$	85
Br$^-$	36	$\leqslant 37$	19	$36-73$	55
I$^-$	-9	$\leqslant 99$	81	-9 to 90	72
CN$^-$	26	0	0	26	26
HO$^-$	3	0	0	3	3
AcO$^-$	51	$\leqslant 28$	10	$51-79$	61 (96 [c])
PhCOO$^-$	-21	$\leqslant 63$	45	-21 to 24	24
NO$_2{}^-$	-61	$\leqslant 94$	76	-61 to 33	15

[a] $\Delta G^{\neq}{}_{2}$ assumed to be $\leqslant$ that for attack on benzene. [b] $\Delta G^{\neq}{}_{2}$ "scaled down" according to the method given in text. [c] Higher limit for $\Delta G^{\neq}{}_{2}$ used (*i.e.*, same as for PhCOO$^{\cdot}$).

not been possible to show [15] that the disappearance of the π complex is accompanied by the appearance of the chlorocyclohexadienyl radical, we here assume that this is the actual pathway and hence can estimate $\Delta G^{\ddagger}$ for the reaction π-complex $\rightarrow$ chlorocyclohexadienyl radical to be 46 kJ mol^{-1} (assuming an A value of 10^{13} s^{-1} and $t_{1/2}$ equal to 5×10^{-6} s). Hence $\Delta G^{\ddagger}_2$ is equal to $46 - 21 = 25$ kJ mol^{-1} (see Fig. 3). A check of this estimate is available from data on the UV light catalyzed vapor phase chlorination of benzene for which hydrogen abstraction on benzene by the chlorine atom has been postulated to be the initial step. [15] This step is claimed to compete favorably with attack upon the ring (eqn. 2, Ar = PhH, Nu$^{\cdot}$ = Cl$^{\cdot}$). Assuming a late transition state for hydrogen atom abstraction, we put the free energy of activation equal to the standard free energy change of the reaction; this can be estimated at about 25 kJ mol^{-1} from known thermochemical data. Thus $\Delta G^{\ddagger}_2$, Ar = PhH, Nu$^{\cdot}$ = Cl$^{\cdot}$, must actually be somewhat greater than 25 kJ mol^{-1} but in view of the rather low selectivity for hydrogen atom abstraction vs. attack on the ring, the two estimates agree reasonably well.

For the hydroxyl radical, recent data [16,17] indicate that $\Delta G^{\ddagger}_2$ for attack on benzene is best approximated as being zero, as would indeed be expected from the substantial exothermicity of the process.

The acetoxy radical would seem to be a fairly reactive species from its rather low $\Delta G^{\ddagger}_2$ value, but it should be noted that this is a minimum value (as is of course also the case for the bromine atom reaction). Since the acetoxy radical decarboxylates so rapidly [18] (k ca. 10^9 s^{-1} at 60 °C, E_a ca. 28 kJ mol^{-1}) it has never been possible to acetoxylate benzene or any other aromatic substrate via acetoxy radical attack,[19] and one can therefore only know with certainty that $\Delta G^{\ddagger}_2$ is greater than 28 kJ mol^{-1}. For the much more stable benzoyloxy radical, $\Delta G^{\ddagger}_2$ is known [20,21] to be between 63 and 84 kJ mol^{-1}, and it is reasonable to assume that the acetoxy radical has a similar $\Delta G^{\ddagger}_2$ for attack on benzene. Results for both cases are given in Tables 1 – 4.

Since benzene is least reactive toward radical attack of the compounds under discussion, two ways are open for estimating $\Delta G^{\ddagger}_2$ and hence

$\Delta G^{\ddagger}_1$ for naphthalene, 9,10-diphenylanthracene (DPA), and perylene. Firstly, one can simply assume that $\Delta G^{\ddagger}_2$ values are equal to or less than those of benzene which in some cases gives $\Delta G^{\ddagger}_1$ values within rather wide limits. Secondly, one can try to "scale down" benzene $\Delta G^{\ddagger}_2$ values by some equation which relates $\Delta G^{\ddagger}_2$ with E°_2. Such an equation was derived from the methyl affinity values for aromatic hydrocarbons,[9] in particular those of benzene, naphthalene and anthracene ($E^{\circ}_2 = 1.31$ V), by calculating $\Delta G^{\ddagger}_2$ values from known rate constants (51, 1140, and 4.2 10^4 M^{-1} s^{-1}, respectively, giving $\Delta G^{\ddagger}_2$ 72, 63 and 53 kJ mol^{-1}). A plot of $\Delta G^{\ddagger}_2$ vs. E°_2 gave a straight line with a slope of 10.9 kJ mol^{-1} V^{-1}; this value was then used for scaling down benzene $\Delta G^{\ddagger}_2$ values to those pertaining to naphthalene, DPA, and perylene. In this way we arrived at the second set of $\Delta G^{\ddagger}_1$ values of Tables 2 – 4.

DISCUSSION

General considerations

Fig. 1 depicts one extreme situation with respect to the value of ΔG°_x, in that the equilibrium position of eqn. 5 is assumed to be strongly on the left-hand side ($\Delta G^{\circ}_x \gg 0$). Another extreme case, shown in Fig. 4, exists for $\Delta G^{\circ}_x \ll 0$ when the equilibrium position is strongly on the right-hand side and consequently reaction 5 is strongly exothermic. These extremes correspond to radical cations of low and high energy, respectively, and it therefore seems appropriate to conduct the discussion of the data of Tables 1 – 4 along the lines of a

Table 5. Reactions possibly involving benzene radical cation, formed via anodic oxidation.

Nu$^-$/solvent	Reaction product [a] (%)	Ref.
H$_2$F$_4^-$/MeCN	PhF (36)	28
CN$^-$/MeOH	PhCN (0.1)	29
MeO$^-$/MeOH	No reaction	30
MeCOO$^-$/HOAc	PhOAc (2.4)	31
CF$_3$COO$^-$/HOAc	PhOCOCF$_3$ (27;25)	32a,b

[a] Only monosubstitution product included.

Table 6. Reactions involving the perylene radical cation.

Nu⁻/solvent	Reaction product or rate constant ($M^{-1} s^{-1}$ at 298 K)	Ref.
F⁻/MeCN	No reaction	26
F⁻/MeCN	Fluoroperylene (low yield)	39
Cl⁻/MeCN	Cl_2	26
Cl⁻/MeCN	(1) Cl_2 (2) Chloroperylenes or possibly direct nucleophilic reaction [a]	39
Br⁻/MeCN	Br_2	26
Br⁻/MeCN	(1) Br_2 (2) Bromoperylenes [a]	39
I⁻/MeCN	I_2	26
CN⁻/MeCN	Cyanoperylene *and* product(s) from electron transfer	40
MeCOO⁻/MeCN	Acetoxyperylene	26
PhCOO⁻/MeCN	Benzoyloxyperylene	26
NO₂⁻/MeCN	Nitroperylene	41
NO₂⁻/MeCN	(1) $NO_2(N_2O_4)$. (2) Nitroperylene [a]	39
Cl⁻/MeCN	6.3×10^5	25
Br⁻/MeCN	1.0×10^6	25
I⁻/MeCN	2.1×10^{10}	25
Cl⁻/MeOH	6.9×10^4	25
Br⁻/MeOH	9.1×10^4	25
I⁻/MeOH	4.7×10^9	25
CN⁻/MeOH	4.6×10^5	25
MeCOO⁻/MeOH	7.5×10^4	25

[a] The numbering indicates the order of consecutive reactions.

Table 7. Reactions involving DPA radical cation.

Nu⁻/solvent q	Reaction product (%)	Ref.
H₂F₃⁻/MeCN [a]	9,10-F_2-DPA (43)	42
H₂F₄⁻/MeCN [b]	9,10-F_2-DPA (75)	43
Cl⁻/MeCN [c]	9,10-Cl_2-DPA (85)	45
Br⁻/MeCN [c]	Br_2	44
I⁻/MeCN [c]	I_2	44
HO⁻/MeCN [c]	Not known; electron transfer may occur partially	44
MeO⁻/MeCN [c]	Not known; electron transfer may occur partially	44
MeCOO⁻ [c]	Probably 9,10-$(AcO)_2$DPA	44

[a] This reaction was run anodically at a potential high enough for dication formation to occur. [b] Run anodically at the potential for formation of DPA⁺·. [c] Homogeneous solution process.

matrix arrangement, in which we first consider the reactivity of typical extreme cases [(benzene)⁺· and (perylene)⁺·/DPA⁺·, Tables 5 — 7],

then of an intermediate case [(naphthalene)⁺·, Table 8], and finally the reactivity of individual nucleophiles *vs.* different radical cations. Only attack upon the aromatic ring will be considered in this context, although the same type of treatment can equally well be applied to deal with proton loss from the radical cation. This reaction type will be considered in a coming paper of this series, as will also the behaviour of radical anions *vs.* electrophiles.

Before starting the discussion of individual species we first must deal in somewhat more detail with the case shown in Fig. 4, *i.e.* where reaction 5 has $\Delta G°_x < 0$. It is well documented [22-24] that the rate of most electron transfer reactions is encounter-limited whenever the electron transfer is exothermic, *i.e.* $\Delta H°_x < 0$. Since we can be sure that $\Delta S°_x$ is positive — eqn. 5 represents a cation-anion annihilation process — a value of $\Delta H°_x < 0$ necessarily means that also $\Delta G°_x < 0$.

A recent kinetic study [25] (rate constants, see Table 6) of the reaction between (perylene)⁺· and Nu⁻ allows us to calibrate our $\Delta G°_x$ values with respect to rate constants. Fig. 5 shows

Table 8. Reactions, possibly involving naphthalene (NpH) radical cation, formed *via* anodic oxidation or Ag(II) oxidation (last entry).

Nu⁻/solvent	Reaction product (% yield)	Ref.
F⁻/MeCN	1,4-DifluoroNpH (70)	52
H₃F₄⁻/MeCN	NpF (27 %), 1-isomer	52
Cl⁻/H₂O	1-NpCl	53
Br⁻/MeCN	1-NpBr (38)	54
MeO⁻/MeOH	1-NpOMe and higher methoxylation products	55
CN⁻/MeOH	NpCN (17), 1-/2- 90/10	56
CN⁻/CH₂Cl₂	NpCN (30 − 70), 1-/2- 86/14	57
MeCOO⁻/MeCOOH	NpOAc (25), 1-/2- 96/4	58
PhCOO⁻/MeCN	NpOCOPh (25)	59
NO₂⁻/MeCN	1-NpNO₂ (8)	47
MeCOO⁻/MeCOOH	1-NpOAc (190 [a]) 1-/2- 95/5	60

[a] Reaction is catalytic in Ag(II).

a plot of log k for this reaction in methanol *vs.* $E°_3$ (assumed to be equal to the values calculated for aqueous solution [5]). In principle this is a Marcus plot,[23] of the form shown in eqn. 7 and with a calculated slope of − 8.5 V⁻¹ at

$$\log k = \text{Const.} - \frac{0.5 \times 23.06}{2.303\,RT} E°_3 \qquad (7)$$

298 K. If we assume that iodide, cyanide, and bromide ion react with electron transfer to (perylene)+·, the slope of a straight line through these points is − 7.9 V⁻¹, in good agreement with the calculated value. It is unfortunate that

rate constants in acetonitrile were not given for all systems; a Marcus type treatment of log k values for iodide and bromide ion in acetonitrile *vs.* $\Delta G°_x$ (Tables 4 and 6) gives a slope of − 0.103 mol kJ⁻¹, in fair agreement with the calculated value, − 0.088 mol kJ⁻¹.

Thus we can safely conclude that the rate of electron transfer between Ar+· and Nu⁻ is diffusion controlled whenever $\Delta G°_x < 0$. For the (perylene)+·/I⁻ reaction, our principal calibration mark, $\Delta G°_x$ is equal to − 9 kJ mol⁻¹ (Table 4), and the process has been shown[26] to be 100 % electron transfer (100 % yield of elemental iodine obtained).
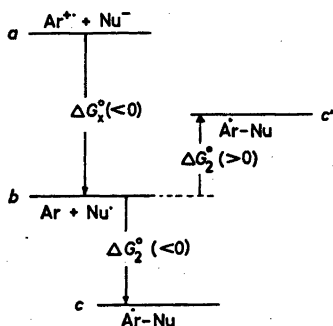

Fig. 4. Energy diagram showing the relationships between $\Delta G°_x$ and $\Delta G°_2$ for the cases that $\Delta G°_x$ and $\Delta G°_2 < 0$ (*a*, *b* and *c*) or $\Delta G°_x < 0$ and $\Delta G°_2 > 0$ (*a*, *b* and *c'*).
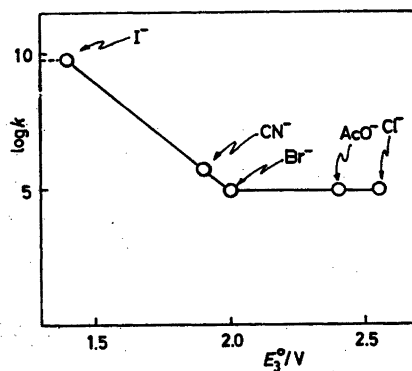

Fig. 5. Plot of log k for the reaction between (perylene)+· and nucleophiles in methanol (298 K) *vs.* $E°_3$ for X⁻/X· in water.

Consideration of individual radical cations

Benzene radical cation. This species is extremely reactive and undergoes very fast follow-up reactions when generated anodically in non-nucleophilic media, presumably *via* coupling-polymerization reactions. [27] Table 5 lists anodic reactions of benzene which may involve or have been claimed to involve formation of (benzene)+· followed by its nucleophilic reaction with an anion present in the electrolyte. Inspection of Table 1 shows that ΔG°_{x} is strongly negative for all anions considered here, except fluoride ion (to be discussed separately below), indicating that electron transfer between (benzene)+· and these ions in acetonitrile* is strongly exothermic. Is it then correct to assume that diffusion controlled electron transfer must be the initial step in all cases?

This is not as simple a problem as it looks. Electron transfer takes place *via* transition states in which the two components are very loosely coupled [38] (overlap energies < 5 kJ mol⁻¹) and need seemingly not be as close to each other as in a bond-forming process. We do, however, deal with anion-cation combination reactions for which has been postulated [34] a translation state with the ions separated by one solvent molecule "in the process of being eliminated". Whether these two types of transition states differ, and, if so, by which features, is not possible to say at the present stage of knowledge. We can therefore only state with any degree of certainty that cases in which a large negative ΔG°_{x} is combined with a negative ΔG°_{2} (*i.e.*, $a \rightarrow b \rightarrow c$ in Fig. 4) may involve initial electron transfer, followed by a very fast attack by Nu· (or Nu-Nu, if this species has time to form) on the aromatic ring.

This behaviour would then be expected for Nu = Cl⁻, CN⁻ and HO⁻ whereas for Br⁻, I⁻, AcO⁻, PhCOO⁻ and NO₂⁻ which in addition have available a direct bond-forming pathway ($a \rightarrow c'$), we cannot easily tell which mechanism will be the preferred one. For Cl⁻, Br⁻, I⁻, and

NO₂⁻ the problem is a rather academic one, since (benzene)+· can only be generated anodically at very high potentials which are very difficult to reach with so easily oxidizable ions present. The anodic chlorination [35] and bromination [36] of benzene has been reported, but in all probability proceeds *via* anodically formed chlorinating or brominating agents (*e.g.* $Cl_2^{-·}$ or Br_2).

The fluoride ion reaction, with $\Delta G^{\circ}_{x} = 3$ and $\Delta G^{\circ}_{2} = -150$ kJ mol⁻¹ ought to be a nucleophilic process in view of the extreme exothermicity of the process $a \rightarrow c$ of Fig. 4. Experimentally,* this reaction has been performed anodically with $H_2F_4^-$ instead of F⁻ as the nucleophile. [20] Since hydrogen bonding of three hydrogen fluoride molecules to F⁻ should produce an ion with a considerably more diffuse charge [37] and consequently less strongly solvated than F⁻ itself, $\Delta G^{\circ}_{H_3F_4^-}$ (eqn. 6) should be less than $\Delta G^{\circ}_{F^-}$ and hence $\Delta G^{\circ}_{x} > 0$. In this situation initial electron transfer is even less likely.

Unfortunately, we cannot estimate thermochemical data for the trifluoroacetate reaction with (benzene)+·, but qualitatively this ion would be expected to behave as the two other carboxylates, albeit with a less negative ΔG°_{x} than acetate ion (trifluoroacetate is more difficult to oxidize than acetate [38]).

Perylene and DPA radical cations. At the other extreme we encounter the rather unreactive (perylene)+· and DPA+·, with E°_{2} values for formation from the parent hydrocarbon of 1.30 and 1.44 V, respectively. Since this potential difference corresponds to a small energy difference only, *ca* 12 kJ mol⁻¹ (Tables 3 and 4) we can consider the reactivity of these ions (see Tables 6 and 7) together and in fact treat them as if they were of equal energy without introducing any qualitatively significant errors.

For both (perylene)+· and DPA+· a general situation is that $\Delta G^{\circ}_{x} > 0$ (F⁻, Cl⁻, Br⁻, CN⁻ and AcO⁻) and that $\Delta G^{\ddagger}_{2}$ is ≥ 0. Here one would expect the rate of electron transfer to be slower, the larger ΔG°_{x} is, and consequently that bond formation between Ar+· and Nu⁻ would take place directly without any preceding

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* The preparative experiments in Table 5 have not been run in acetonitrile, except for $H_3F_4^-$, but it is unlikely that $\Delta G^{\circ}_{Nu^-}$ values (see eqn. 6) in methanol and acetic acid would be so drastically different from those pertaining to acetonitrile that our conclusions would have to be modified.

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* Our own unsuccessful efforts to fluorinate aromatics *via* this anodic reaction have been commented upon in Ref. 3.

electron transfer (unless symmetry restrictions operate).[1-3] For reaction between (perylene)+· or DPA+· and fluoride ion the $\Delta G°_x = \Delta G\!\neq_1$ values would seem to be so high so as to preclude anything but an extremely slow reaction. This agrees with the observation that (perylene)+· does not react with fluoride ion [36] — or reacts very slowly [39] — but is contradicted by the claim that anodically generated DPA+· reacts fast with $H_3F_4^-$ to give 9,10-DPA-F_2.[43] This ion would, as discussed above, be expected to be even less reactive than fluoride ion in view of its hydrogen-bonded structure.

Chloride ion has been suggested to react with (perylene)+· with initial electron transfer [36] or direct bond formation [39] and with DPA+· to give a π (?) complex which is oxidized by a second DPA+· to give an ordinary carbocation.[45] In the latter case, C−Cl bond formation would take place in the oxidation step: DPA+····Cl⁻+ DPA+·→DPA+−Cl+DPA. This mechanism is attractive since it is analogous to that suggested [46] for anisylation of (thianthrene)+· and circumvents the need for postulating a possibly symmetry-forbidden step.[1-3]

Bromide ion is predicted to react both with (perylene)+· and DPA+· with electron transfer which seems reasonable on the basis of $\Delta G°_x$ being 36(22) kJ mol⁻¹ and $\Delta G\!\neq_1$ 55(42) kJ mol⁻¹. Cyanide ion, with a low positive value of $\Delta G°_x = \Delta G\!\neq_1$, is expected to be a borderline case, with both electron transfer and direct bond formation possible, as is indeed indicated by its reported behaviour [40] toward (perylene)+·.

Acetate ion, again with $\Delta G°_x$ equal to $\Delta G\!\neq_1$ but with a rather high positive $\Delta G°_x$ value (see above; for reaction with (perylene)+· $\Delta G\!\neq_1$ can be 51−79 kJ mol⁻¹ and for DPA+· 38−66 kJ mol⁻¹; from the rate constant one can calculate a $\Delta G\!\neq_1$ value for the perylene reaction equal to ≈35 kJ mol⁻¹, assuming an A value of 10¹¹ M⁻¹ s⁻¹) is predicted to react with direct bond formation in both cases. On the other hand, $\Delta G°_x$ for reaction with benzoate ion is -21 and -34 kJ mol⁻¹, respectively, so that here one should have reason to look for a mechanism involving an initial electron transfer step, followed by benzoyloxy radical attack upon the parent compound.[8] Since this reaction hardly can be 100 % effective, one should be able to detect products from the usual side-reactions in this type of reaction, such as decarboxyla-

tion of PhCOO·, reactions of phenyl radicals, etc. Both iodide and nitrite ion, with negative $\Delta G°_x$ values, are expected to react with electron transfer to (perylene)+· and DPA+·. For iodide ion experimental evidence [36] is in agreement with this prediction, whereas the reaction between nitrite ion and (perylene)+· has been claimed [41] to involve direct bond formation, as was also postulated [47] in the mechanism for anodic nitration of aromatic substrates in acetonitrile/silver nitrite. In view of the calculations presented here this mechanism should be reconsidered.*

Naphthalene radical cation. With $E°_3 = 2.08$ V,[51] this ion represents an intermediate case for which very little, if any, solid mechanistic information is available, mainly because of its high reactivity which makes kinetic studies difficult (see Table 8). Therefore hypotheses about the mechanism of the reaction between (naphthalene)+·=Naph+· and different Nu⁻ are rather tentative at present, based as they are on constant potential electrolysis experiments at best. As has been correctly concluded such experiments do not permit unambiguous choices among different possible mechanisms.[61,62]

Table 2 shows that most of the Naph+·/Nu⁻ combinations exhibit large negative $\Delta G°_x$ (Br⁻, I⁻, CN⁻, HO⁻, PhCOO⁻, NO$_2^-$) and hence mechanistic discussions are vulnerable to ambiguities in the same way as for (benzene)+·, only that we here do not have access to $\Delta G°_2$ values due to the deplorable lack of thermochemical data on naphthalene derivatives. Qualitatively, one might suspect that the behaviour of Naph+· would follow that of (benzene)+·, since the relative positions of the different energy levels would not be appreciably effected by the difference in resonance energy — per ring — between the two systems. Therefore, Naph+· would be predicted to react with CN⁻ and HO⁻ via a pathway analogous to a→b→c in Fig. 4, whereas for the reaction with Br⁻, I⁻, PhCOO⁻ and NO$_2^-$ routes analogous to both the mentioned one and a→c' in principle are possible.

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* Nitrogen dioxide — or dinitrogen tetroxide — is known to be a nitrating agent in itself.[48] Preliminary experiments [49] have shown that both anisole and naphthalene are nitrated in acetonitrile solution by this reagent in a reasonably fast process;[50] perylene would be expected to react even faster.
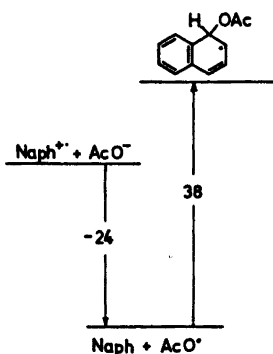
Fig. 6. Energy diagram (kJ mol^{-1}) for formation of acetoxybenzocyclohexadienyl radical.

The reaction between Naph$+\cdot$ and F^{-} has $\Delta G^{\circ}{}_{x} = \Delta G^{\ddagger}{}_{1} = 92$ kJ mol^{-1}, indicating the possibility of a measurably fast reaction ($k \approx 10^{-5}$ M^{-1} s^{-1}, assuming $A = 10^{11}$ M^{-1} s^{-1}).

For Cl^{-}, with $\Delta G^{\circ}{}_{x}$ very close to zero and $\Delta G^{\ddagger}{}_{1}$ 18 kJ mol^{-1}, electron transfer would seem to be the favored process.

An attempt was made to calculate $\Delta G^{\circ}{}_{3}$ for the acetoxy radical/naphthalene reaction. Although thermochemical data [63] are not entirely suited for the estimation of $\Delta G^{\circ}{}_{f}$ of acetoxybenzocyclohexadienyl radical, a reasonable value of $\Delta G^{\circ}{}_{3}$ was calculated to be 38 kJ mol^{-1} (see Fig. 6), which gives then a lower limit of $\Delta G^{\ddagger}{}_{3}$ of 38 kJ mol^{-1}. Thus competition between direct bond formation and electron transfer, followed by decarboxylation of acetoxy radical ($E_{a} \approx 28$ kJ mol^{-1}), is a likely situation in this particular case, whereas acetoxy radical attack on naphthalene after initial electron transfer does not seem to be feasible. It should be remembered, though, that estimates for cases such as this, where only small energy differences are involved, are fairly sensitive to errors in the thermochemical data used.

Consideration of different reactions

General. In viewing oxidative aromatic substitution from the standpoint of competition between electron transfer and direct bond formation, it is obvious from Fig. 2 that a single mechanism need not be valid over the whole spectrum of radical cation reactivity for different reactions or even for one and the same reaction, however desirable this may be from an epistemological point of view. For each nucleophile it is possible to define an $E^{\circ}{}_{3}$ value, above which $\Delta G^{\circ}{}_{x}$ is negative (see Table 9), *i.e.*, electron transfer is exothermal and hence in principle can take place at diffusion controlled rate. In such a case, it is if the cyclohexadienyl radical intermediate has an energy between 0 and $\Delta G^{\circ}{}_{x}$ that direct bond formation also will be possible. For $\Delta G^{\circ}{}_{x} > 0$ electron transfer will become increasingly less probable with increasing $\Delta G^{\circ}{}_{x}$ and above a certain value (presumably different in different cases) direct bond formation will take place exclusively.

Oxidative halogenation. In the first paper [s] of this series the reaction between aromatic radical cations and halide ions was discussed as a possible case of symmetry-restricted processes, and at that time available data seemed to support this idea. In the light of the thermochemical calculations performed here, a more balanced picture has emerged, in that the oxidizing power of Ar$+\cdot$ and the reducing power of Nu^{-} and the interplay between these two variables − in summary, $\Delta G^{\circ}{}_{x}$ (eqns. 3−5) − has been identified as the major factor in deciding between electron transfer or direct bond formation. We therefore have reason to ask if there are still any cases for which the Dewar-Zimmerman rules would seem to restrict the direct bond formation pathway or whether the thermochemical treatment has at least qualitatively settled the problems. And immediately we can answer that the question cannot be answered at present but will require a lot of further experimentation, both of qualitative and quantitative nature. It is, however, evident that fluoride ion is inherently unreactive toward radical cations, especially low-reactivity ones like (perylene)$+\cdot$ and DPA$+\cdot$ (estimated $\Delta G^{\ddagger}{}_{1}$ 166 and 154 kJ mol^{-1}, corresponding to second-order rate constants of the order of 10^{-16} and 10^{-14} M^{-1} s^{-1}, respectively). Chloride ion is more reactive *vs.* (perylene)$+\cdot$ than predicted ($\Delta G^{\ddagger}{}_{1} \approx 40$ kJ mol^{-1} *vs.* the estimated value, 85 kJ mol^{-1}, for direct bond formation and 78 kJ mol^{-1} for electron transfer), whereas the value for bromide ion comes out reasonably well, found 38 kJ mol^{-1} *vs.* estimated 55 kJ mol^{-1} for direct bond formation and ≤ 36 kJ mol^{-1} for electron transfer. It should be added

Table 9. Standard potentials $(E°_s)$ above which $\Delta G°_x$ is below 0.

Nu⁻	$E°_s$/V	Nu⁻	$E°_s$/V
F⁻	3.0	HO⁻	1.3
Cl⁻	2.1	I⁻	1.2
AcO⁻	1.8	PhCOO⁻	1.1
Br⁻	1.7	NO₂⁻	0.7
CN⁻	1.6		

that ordinary carbonium ions react extremely fast with halide ions.[64] *e.g.*, triphenylmethyl cation with Cl⁻, Br⁻ and I⁻ at $k \approx 5 \times 10^{10}$ M⁻¹ s⁻¹ in 1,2-dichloroethane (297 K).

Oxidative cyanation. Radical cations with $E°_s$ above 1.6 V (Table 9) should oxidize cyanide ion in a diffusion-controlled reaction to cyano radical, a very reactive species that subsequently should attack the closely positioned parent molecule in a very fast process, again possibly diffusion-controlled. Thus we would expect a nonselective substitution pattern in the anodic cyanation of monofunctional benzenes, contrary to what is actually observed. Anodic cyanation of aromatics is highly selective, whereas other homogeneous reactions proceeding *via* cyano radical indeed are nonselective [65] (Table 10).

The recent suggestion [50] that nitration of reactive aromatics *via* nitronium ion proceeds *via* an initial electron transfer within the π complex followed by spin density controlled coupling within the radical pair opens a way for explaining the high selectivity of anodic cyanation of aromatics. An analogous mecha-

nism in the anodic cyanation case would then be radical coupling between ArH⁺· and cyano radical, simultaneously generated at the electrode by anodic oxidation of Ar-H and cyanide ion in a suitable solvent. The collapse of an ArH⁺·/CN· radical pair would, similarly to the ArH⁺·/NO₂ radical pair, occur with high selectivity due to the non-uniform spin density in ArH⁺·. This mechanism also explains the current-potential characteristics of the cyanation reaction, *i.e.*, that addition of the aromatic substrate sometimes moves the current-potential curve of solvent/CN⁻ toward more anodic potentials and that discharge of the substrate is a prerequisite for the reaction to occur.[55b,66]

This type of mechanism has recently been advocated also for anodic acetoxylation [61,62] and methoxylation [67] (see below).
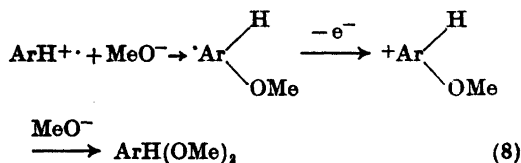
Oxidative hydroxylation (methoxylation). Somewhat surprisingly, and certainly against the intuition of the organic chemist, hydroxide ion should be oxidized in a very fast reaction by any radical cation with an $E°_s \geq 1.3$ V, *i.e.* hydroxide is only a shade more difficult to oxidize than iodide ion (Table 9). With the extremely high reactivity of the hydroxyl radical in mind [16,17] one would again expect attack upon the parent molecule to be very fast and correspondingly non-selective. Unfortunately, there are no pertinent data for oxidative hydroxylation available — almost all anodic hydroxylations have been run under acidic conditions [30] — and hence it is not possible to check this prediction immediately. The situation is only marginally better [30] for anodic methoxylation in MeOH/MeO⁻; this would

Table 10. Isomer distribution (*o:m:p* or α:β) in aromatic cyanation by different methods.[65]

Compound	Cyanation method								
	Anodic [a]			*Via* CN· in homogeneous medium					
				A [b]			B [c]		
Anisole	53	0.1	47	58	14	28	44	13	43
Chlorobenzene	50	0.5	50	27	27	46	41	9	50
Biphenyl	24	0.4	76	44	28	28	54	29	17
Toluene	40	8	52	48	31	21	50	27	23
Naphthalene	90	10		61	39		60	40	

[a] In methanol/sodium cyanide at a Pt anode. [b] Generated by photolysis of iodine cyanide. [c] Generated by diazotation of cyanamide.

otherwise be a good model reaction for hydroxylation in view of the negligible difference between hydroxide and methoxide ion with respect to ΔG°_4 (eqn. 4). In fact, if we limit ourselves to anodic aromatic substitution, only one substrate, anisole, has been studied [30] and shown to give an *o:m:p* ratio of approximately 39:3:58. The reason for the lack of data on isomer distributions is the strong tendency for methoxide ion to add onto the intermediate methoxycyclohexadienyl cation instead of abstracting a proton (eqn. 8).

$$ArH^{+\cdot} + MeO^- \rightarrow \cdot Ar\begin{array}{c}H\\\backslash\\OMe\end{array} \xrightarrow{-e^-} +Ar\begin{array}{c}H\\\backslash\\OMe\end{array}$$

$$\xrightarrow{MeO^-} ArH(OMe)_2 \qquad (8)$$

Judging from the anisole methoxylation substitution pattern, the anodic methoxylation reaction, like cyanation, is a selective process in contrast to hydroxylation *via* hydroxyl radical.[68] Similarly to cyanation, a reasonable mechanism for anodic methoxylation would seem to involve coupling between simultaneously formed methoxy radical and radical cation, as has recently been suggested.[67]

Oxidative acetoxylation. Anodic acetoxylation was the first reaction for which a radical cation/nucleophile interaction mechanism was substantiated by controlled potential [69,70] and anodic gassing [31,71] experiments. It has later been suggested [61,62] that an electrocatalytic mechanism (see also below), *i.e.*, oxidation of acetate ion by an initially formed radical cation followed by acetoxy radical attack upon the parent molecule, or a mechanism involving coupling between the acetoxy radical and a radical cation might be feasible. We have recently [19] analyzed in detail the situation with respect to possible homolytic substitution reactions of the acetoxy radical and concluded that its extremely high rate of decarboxylation, $k \approx 1.6 \times 10^9$ s^{-1} at 333 K with E_a equal to 28 kJ mol^{-1}, would seem to preclude the former suggestion. Of course the latter one cannot be easily dismissed since most coupling reactions are extremely fast processes [9] with essentially zero activation energy. Isomer distributions for anodic aromatic substitution reactions,[68]

being fairly selective, would not seem to militate against this mechanism either.

It is, however, rather implausible that the oxidative acetoxylation process promoted by Ag(II) in homogeneous acetic acid solution with acetate ion present [60] would take place *via* bimolecular coupling between concurrently formed acetoxy radical and radical cation. This reaction gives good yields of acetoxy derivatives of aromatic compounds which almost certainly excludes the possibility of the acetoxy radical playing an important role in the mechanism. Moreover, the Ag(II) process gives results almost identical with those obtained for anodic acetoxylation. Looking at the energetics of the acetoxylation reaction (Tables 1–4) no serious objections against direct bond formation between acetate ion and radical cation can be raised from this point of view; this elementary step still maintains its position as the most plausible one in oxidative acetoxylation.

In this context it is of considerable interest to note that anodically generated radical cations of the triarylaminium type, *e.g.* $(4\text{-}BrC_6H_4)_3N^{+\cdot}$ with $E^\circ_3 = 1.3$ V in acetonitrile, oxidize carboxylates, $CH_3(CH_2)_nCOO^-$ to give $CH_3(CH_2)_nH$ and $CH_3(CH_2)_nCH_2CN$ among other products.[72] A radical pathway nicely rationalizes these findings (eqns. 9–11, R = $CH_3(CH_2)_n$, Ar = $4\text{-}BrC_6H_4$). For eqn. 9, ΔG°_x can be estimated to be 33 kJ mol^{-1}, using the E° value earlier

$$RCOO^- + Ar_3N^{+\cdot} \rightarrow RCOO^\cdot + Ar_3N \qquad (9)$$

$$RCOO^\cdot \rightarrow R^\cdot + CO_2 \qquad (10)$$

$$R^\cdot + CH_3CN \rightarrow RH + \cdot CH_2CN \xrightarrow{R^\cdot} RCH_2CN \qquad (11)$$

calculated [5b] for propionate and butyrate ion in water, 2.23 V, and otherwise the same data as for acetate and benzoate. This is not unreasonable for the fast electron transfer process actually observed (fast discoloration of the radical cation as it diffuses away from the anode surface).

Oxidative nitration. The reaction taking place between nitrite ion and a radical cation is of the type that allows for either an initial, diffusion controlled electron transfer, followed by nitration *via* nitrogen dioxide or direct bond formation (see Tables 1–4 and Fig. 4). In view of the fact that aromatic nitration *via* nitrogen dioxide is a rather slow process for

moderately activated substrates,[49] such as anisole and naphthalene, it should be comparatively easy to decide between these possibilities by kinetic studies. In the anodic nitration process [47] (*i.e.*, in NO_2^-/CH_3CN) the possibility that nitrogen dioxide is oxidized further to NO_2^+ ($E_{1/2}$ for the oxidation of NO_2 is 1.82 V vs. Ag/0.01 M Ag$^+$ in acetonitrile [50]) cannot be dismissed unless controlled potential experiments are performed.

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