Tetrahedron Vol 34 pp 731 to 739 Pergamon Press 1978 Printed in Great Britain

RADICAL ION REACTIVITY—I

APPLICATION OF THE DEWAR-ZIMMERMAN RULES TO CERTAIN REACTIONS OF RADICAL ANIONS AND CATIONS

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(*Received in the UK* 6 *January* 1977; *Accepted for publication* 30 *August* 1977)

Abstract—The application of the Dewar-Zimmerman rules to the interaction between radical cations, derived from 4n + 2 systems, shows that a nucleophile orbital interacting suprafacially with the ion should correspond to an antiaromatic transition state and hence to a less favored pathway relative to competing ones, e.g. electron transfer. An antarafacial interaction would on the other hand correspond to an aromatic transition state and be energetically favorable. Both types of interaction are generally possible for the same reagent, but since the suprafacial one for geometric reasons ensues and thus predominates in the early stage of the reaction, the net result should be an anomalously low reactivity of radical cations vs attack by nucleophiles.

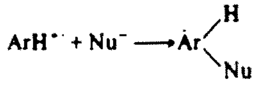
By calibration against known, qualitative reactivity data for perylene radical cation it is strongly indicated that halide ions belong to a class of reagents which do not react nucleophilically with radical cations but instead undergo electron transfer oxidation or do not react at all. This type of reaction is discussed in some detail, and several mechanisms involving radical cation/halide ion combination as a critical step can either be ruled out or considered open for reinvestigation.

The same idea can be applied to the reaction between radical anions and electrophiles. Accordingly, the protonation of radical anions derived from 4n + 2 aromatic systems is remarkably slow, as compared to that of analogous carbanions.

Radical ions are important intermediates in many redox processes.[1-4] They possess a rich and varied chemistry due to their ability to react as radicals, ions and/or electron transfer reagents, and the structural factors controlling their reactivity with respect to different pathways are largely unknown. Hence the detailed study of these species represents a major challenge to both theoretical and experimental chemists and should constitute a research area with considerable growth potential, well comparable to that of conventional carbocation and carbanion chemistry. It is indeed a puzzling problem to ponder why organic chemists have not been more active in exploring the potentialities of such a virgin field.

We and others have earlier noted that *aromatic* radical cations[5] (anions)[6,7] are not always as reactive toward nucleophiles (electrophiles) as one would expect from a comparison with even-electron species of like charge. It was also pointed out recently[8,9] that the largest single body of consistent experimental work on the reactivity of aromatic radical cations in homogeneous solution, that of Shine and coworkers,[10] presents a rather perplexing reactivity pattern toward nucleophiles with respect to the two main reaction types, electron transfer oxidation of the nucleophile (the ET reaction, eqn 1) or nucleophilic attack upon the radical cation (the N reaction, eqn 2).

$$ArH^{\cdot +} + Nu^- \longrightarrow ArH + Nu^{\cdot} \qquad (1)$$



$$ArH^{\cdot +} + Nu^- \longrightarrow \overset{\cdot}{Ar}\begin{matrix} H \\ Nu \end{matrix} \qquad (2)$$

It was suggested and to some extent substantiated that the Dewar-Zimmerman (D-Z) rules[11] might be applicable to these processes, thus providing a simple tool for at least qualitative predictions about the reactivity of aromatic radical cations toward nucleophiles with respect to competition between the ET and N reaction.

This paper is an elaboration and discussion of this idea, modified in the light of subsequent critical comments.[12,13] While the preliminary account[8] rather categorically stated that there should be a pronounced qualitative difference between halide ions and other types of nucleophiles—the reaction between halide ions and radical cations derived from 4n + 2 aromatic systems should be "forbidden"—it is now realized that a sharp qualitative distinction in terms of "forbidden" and "allowed" reactions cannot be made. On the other hand, the mere assumption that the halide ions do not interact nucleophilically with 4n + 1 radical cations brings up a host of interesting mechanistic problems that otherwise might not have surfaced. We think that a critical examination of these problems is important and hope that the discussion to follow will stimulate further experimental work in this area.

The reaction between radical cations and nucleophiles

Application of the D-Z rules. To start with a familiar example, let us look at the reaction between a carbene and a C-C double bond.[14] Here it is assumed that the carbene approaches the π system with its empty p orbital interacting suprafacially with the two π lobes, producing a two-electron Hückel transition state which is aromatic and corresponds to an allowed reaction (Fig. 1a). At the same time the filled carbene sp^2 orbital interacts antarafacially with the π system, corresponding to a four-electron Möbius system which again is aromatic. Thus *both* carbene orbitals can interact favorably with the π orbitals of the double bond. On the other

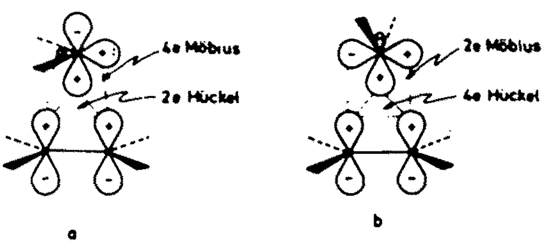


Fig. 1. Interaction between an ethylene π orbital and a carbene approaching with (a) the empty p orbital or (b) the filled sp^2 orbital.

hand, if the approach of the carbene occurs with the filled sp^2 orbital pointing toward the π system (Fig. 1b) the corresponding transition states will be of the 4e Hückel and 2e Möbius type, respectively, both antiaromatic and hence representing energetically less favorable pathways. In this case a clearcut distinction between the two possible pathways of Figs 1(a) and 1(b) can be made.

In extending this type of treatment to the interaction between an aromatic radical cation and nucleophiles, we assume that the approach to the transition state for the ET and N processes, respectively (eqns 1 and 2), involves attack by the nucleophile perpendicular to the π system at the midpoint between two centers. We also assume that nucleophilic attack occurs via a transition state in which there must be a strong interaction between the reactants (since a new bond is formed). On the other hand, the transition state of the competing ET reaction need not require any such interaction if the reaction is non-adiabatic.[15] Then electron tunneling can take place with essentially no orbital coupling between the reactants. Thus, if unfavorable interactions between the orbitals involved ensue in the *early stages* of the nucleophile approach to the radical cation, the ET reaction will be favored.

To illustrate the reasoning, let us consider the benzene radical cation (1), a simple case of a radical cation derived from a 4n + 2 system. The transition state of the reaction between this species and a nucleophile interacting suprafacially or antarafacially with one of its p orbitals is shown in Figs. 2(a) and 2(b), respectively. For an odd-electron species the D-Z treatment first stipulates the addition of an electron to complete the half vacant orbital.[11] Then the transition state of Fig. 2(a) corresponds to a Hückel system containing 8 electrons, whereas that of Fig. 2(b) depicts a Möbius system containing 8 electrons. These transition states are antiaromatic and aromatic, respectively, and hence one would predict that the former case would not lead to any reaction. With the N process "forbidden", ET would seem to be the only feasible reaction to take place in the system.

The transition states depicted in Fig. 2 do however not represent real systems. If the nucleophile for example is a halide ion, say F$^-$, the pertinent basis orbitals are three p orbitals and one s orbital, all filled.[12,13] As the F$^-$ orbitals interact with (benzene)$^{\cdot+}$, as shown in Fig. 3, we find two unfavorable suprafacial interactions (the p_z orbital and the s orbital) and one favorable antarafacial one (the p_x orbital). The p_y orbital is placed orthogonal to the π system and hence does not overlap with it. This situation is then not as clearcut as in the carbene case initially discussed. Following our preliminary communication Rozhkov *et al.*[13] evaluated the overlap integrals (S_z and S_x, respectively) for the p_z and p_x orbital interactions with the carbon p orbitals as a function of the halide ion/C atom distance ($r_{C\text{-}X}$). For fluoride ion and with $r_{C\text{-}X}$ equal to 2.00 A S_z turned out to be more than twice S_x (0.118 and 0.053) whereas at shorter $r_{C\text{-}X}$ (1.49 Å) they were of comparable magnitude, yet with S_z the greater one (0.232 and 0.169). Thus, in the early stages of the approach of F$^-$ to (benzene)$^{\cdot+}$ the unfavorable p_z orbital interaction predominates and hence one would predict a low reactivity of F$^-$ in this particular reaction. It should be kept in mind that the unfavorable s orbital interaction was not included in the calculation; of course this would be noticeable at short distances only whereas our main attention is to the situation prevailing in the initial stage of the process.

Thus we preliminarily conclude that the N reaction between radical cations derived from 4n + 2 systems and certain nucleophiles might be anomalously slow and that in such cases the ET reaction should predominate (given that the nucleophile is not too difficult to oxidize in which case no reaction at all would take place). The controlling factor would be energetically unfavorable, suprafacial orbital interactions experienced by the system in the initial stages of the reaction (i.e. at large $r_{C\text{-}X}$). Before we embark on any further discussion of individual reactions, we must however find a way of discriminating between nucleophiles in the two categories. This can be done by calibration against known facts about radical cation reactivity in homogeneous solution..

The reactions undergone by the radical cations of perylene, thianthrene, phenothiazine, and dibenzodioxin with a series of nucleophiles[10] are summarized in Table 1. Starting from (perylene)$^{\cdot+}$ which is equivalent to 1 (following Dewar's procedure, one electron is added to (perylene)$^{\cdot+}$ and the two uniquely single bonds are dissolved to give two naphthalene entities, one of which is considered for interaction with the nucleophile) we find that the halide ions either do not react (F$^-$) or undergo

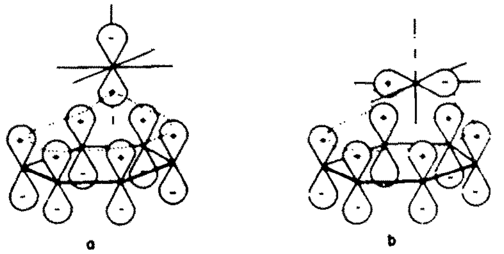


Fig. 2. Orbital representation of the transition state between benzene radical cation and a nucleophile p orbital interacting (a) suprafacially and (b) antarafacially.

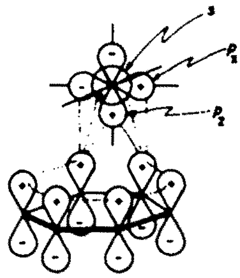


Fig. 3. Possible orbital interactions between a halide ion and benzene radical cation (p_y orbital not shown).

Table 1. Reactivity patterns of radical cations *vs.* nucleophiles in homogeneous solution[10]

Nucleophile	Reaction type[a]			
	(Perylene)$^{+\cdot}$	(Thianthrene)$^{+\cdot}$	(Phenothiazine)$^{+\cdot}$	(Dibenzodioxin)$^{+\cdot}$
Fluoride ion	No reaction	-	No reaction[b]	-
Chloride ion	ET	N	N	-
Bromide ion	ET	-	N	-
Iodide ion	ET	ET	ET	ET
Nitrite ion	N	-	N	N
Cyanide ion	N	ET	ET	ET
Acetate ion	N	-	-	-
Benzoate ion	N	-	-	-
Water	N	N	[b]	N
Pyridine	N	N	[b]	N
Ammonia, amines	-	N	-	ET

[a] ET, electron transfer; N, nucleophilic reaction; -, not known.

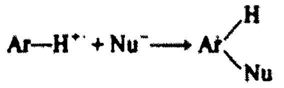
[b] Fluoride ion acts as a base toward (phenothiazine)$^{+\cdot}$, ultimately giving 3,10'-biphenothiazine. The same reaction occurs with water and partly with pyridine.

ET, whereas the remaining nucleophiles undergo the N reaction. If we assume that the halide ion reactions of (perylene)$^{+\cdot}$ indeed correspond to the situation depicted in Fig. 2(a) and the remaining ones to the situation in Fig. 2(b), we have obtained the desired discriminatory tool and can proceed one step further and look at the heterocyclic radical cations listed in Table 1. When one electron is added, the isoconjugate species of these ions is anthracene dianion, a 4n system. Here the middle ring is a 4n species, for which the situation in Fig. 2(a) does not suffer any restriction. Thus a radical cation derived from such a system should undergo nucleophilic attack by any kind of nucleophile, including halide ions, as is indeed indicated by the reactivity of, e.g. (phenothiazine)$^{+\cdot}$ toward bromide and chloride ion. We also note that ET, for which no restrictions are predicted, may be the predominant reaction mode for nucleophiles of low oxidation potential (i.e. iodide and cyanide ion).

Apart from the experimentally consistent set of reactions of Table 1, a large number of radical cation-nucleophile combination reactions have been postulated in the literature.[1] Many of these relate to anodic oxidation processes involving aromatic or heterocyclic compounds,[16-18] whereas others involve conventional one-electron oxidants of different types.[19,20] In these cases we are dealing with electrochemical or homogeneous varieties of the so-called ECE mechanism (E = electron transfer step, C = chemical step), shown in eqns (3–5). We now proceed to examine some representative cases of such reactions in order to see if application of the ideas above might lead to any mechanistic revisions or better understanding of the more equivocal cases. Naturally, those halogenation reactions which are assumed to take place via radical cation-halide ion combination will be in the focus of interest. According to the reasoning above, many of them might actually proceed via conventional halogenation mechanisms or other mechanisms not requiring the C step of eqn (4).

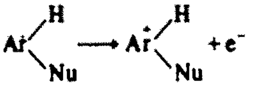
E: $$\mathrm{Ar{-}H} \longrightarrow \mathrm{Ar{-}H}^{+\cdot} + e^- \quad (3)$$

C:



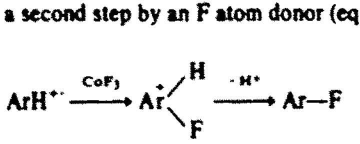
$$\mathrm{Ar{-}H}^{+\cdot} + \mathrm{Nu}^- \longrightarrow \mathrm{Ar}^{\cdot}(\mathrm{H})(\mathrm{Nu}) \quad (4)$$

E:



$$\mathrm{Ar}^{\cdot}(\mathrm{H})(\mathrm{Nu}) \longrightarrow \mathrm{Ar}^{+}(\mathrm{H})(\mathrm{Nu}) + e^- \quad (5)$$

Fluorination. Aromatic compounds can be fluorinated directly by (a) xenon difluoride,[21] (b) high valency transition metal fluorides[22] (HVMFs, e.g. CoF_3) or (c) via anodic oxidation.[12,23] Recently a *common* mechanism was invoked for these reactions, in that Burdon *et al.*[22] suggested that all three proceed via an initial oxidation of the substrate (eqn 6) to give a radical cation which is trapped in a second step by an F atom donor (eqn 6). The latter can be a species like XeF or CoF_3 in reactions (a) and (b), respectively, and high-valency nickel fluoride formed at the Ni anode in the electrochemical process (c), taking place in liquid hydrogen fluoride electrolytes. This trapping reaction would not be subject to restrictions imposed by the D–Z treatment and hence is a feasible elementary step. A later, very thoughtful and detailed study[24] of the consequences of the radical cation fluorination theory provided additional arguments that the sequence in eqn (6) is a reasonable mechanism even though the simplicity inherent in eqn (6) is deceptive. The crucial trapping step, which determines the product distribution, is not simply dependent upon the spin density of the radical cation but instead appears to be governed by Wheland intermediate stability. Hence such a step is best formulated as a ligand transfer oxidation step with the transition state closely resembling the Wheland intermediate.



$$\mathrm{ArH}^{+\cdot} \xrightarrow{\mathrm{CoF_3}} \mathrm{Ar}^{+}(\mathrm{H})(\mathrm{F}) \xrightarrow{-\mathrm{H}^+} \mathrm{Ar{-}F} \quad (6)$$

Table 2. Isomer distribution of XeF_2[21a] and anodic fluorination,[12] compared to anodic acetoxylation[28] (trifluoroacetoxylation[29]) of aromatic compounds

Compound	Fluorination by XeF_2			Anodic fluorination			Anodic acetoxylation$^{\underline{a}}$		
	o	m	p	o(2)	m(3)	p	o(2)	m(5)	p
Toluene	50	8	42	43	-	57	$43^{\underline{c}}$	$11^{\underline{c}}$	$46^{\underline{c}}$
Isopropylbenzene				$49^{\underline{b}}$	-	$51^{\underline{b}}$	$44^{\underline{c}}$	$17^{\underline{c}}$	$39^{\underline{c}}$
t-Butylbenzene				$20^{\underline{b}}$	-	$80^{\underline{b}}$	35	22	43
Anisole	47	4	49	$44^{\underline{b}}$	-	$56^{\underline{b}}$	67	4	29
Fluorobenzene	25	6	69	-	-	99	34	8	58
Chlorobenzene	24	5	71	$29^{\underline{b}}$	-	$71^{\underline{b}}$	37	5	58
Bromobenzene		*		$26^{\underline{b}}$	-	$74^{\underline{b}}$	30	3	67
Naphthalene				100	-		96	4	
Methyl benzoate				46	34	20	51	34	15
Acetophenone				51	29	20	54	32	14
Benzonitrile				56	29	15	45	30	25
Benzotrifluoride	-	95	5	-	100	-	35	47	18
Nitrobenzene	23	63	14	50	50	-	22	59	19

$^{\underline{a}}$ The last five entries refer to trifluoroacetoxylation. $^{\underline{b}}$ Normalized after correction for the percentage of *ipso* substitution. $^{\underline{c}}$ Normalized after correction for the percentage of side-chain substitution

It is, however, the proposed ECE mechanism of a fourth type of fluorination reaction, anodic oxidation of aromatic compounds at platinum in acetonitrile/$Et_4NH_3F_4$[12,25] or $Me_4NH_2F_3$,[26] that directly conflicts with predictions based on the D-Z rules. Here the ECE mechanism (eqns 3–5, $Nu^- = F^-$) contains a step that is forbidden for radical cations derived from $4n+2$ aromatic systems, and yet a fair number of such fluorinations, seemingly displaying the characteristics of anodic radical cation mediated processes, have been reported.[12,25,26] For the two homogeneous cases given in Table 1 it is seen that $(\text{perylene})^{+\cdot}$ indeed does not react with fluoride ion in agreement with predictions, whereas $(\text{phenothiazine})^{+\cdot}$, for which nucleophilic attack by fluoride ion is feasible, actually loses a proton with eventual formation of a dehydrodimer, 3,10′-biphenothiazine. This is not surprising in view of the acidic nature of $(\text{phenothiazine})^{+\cdot}$ and the strongly basic properties of fluoride ion in acetonitrile.

Table 2 compares isomer distributions of the anodic fluorination process with those of another anodic substitution reaction, acyloxylation, known to proceed via the ECE mechanism.[16,27] For comparison, available data for fluorination by XeF_2 are also included. The data for the anodic fluorination process, based on largely synthetic experiments, are probably not entirely comparable with those for the acyloxylation reaction, but are the only ones available.† Excluding the case of bromobenzene, where the result is further complicated by the fact that 1,4-bromofluorobenzene is partly converted to 1,4-difluorobenzene under the conditions employed, fluorination appears to be more selective than acetoxylation, as would indeed be expected if a radical cation is trapped by fluoride ion, a weaker and hence more selective nucleophile than acetate ion.

And yet we wish to propose that trapping of a $4n+1$ radical cation by fluoride ion is an energetically unfavorable process in order to have a consistent view of all types of oxidative aromatic halogenations. The anodic fluorination reaction would then have to proceed via a different reaction sequence. We have earlier[9,31] argued in favor of an EEC mechanism, involving trapping of a dication by F^- (eqn 7), but in view of the fact that most preparative electrolyses have been carried out at potentials close to that required for radical cation formation (Table 3), this route seems less likely.

$$ArH \xrightarrow{e^-} ArH^{+\cdot} \xrightarrow{e} ArH^{2+} \xrightarrow{F} \overset{+}{Ar}\begin{smallmatrix}H\\F\end{smallmatrix} \qquad (7)$$

Looking for other possible mechanisms we can also dismiss the one involving fluorination via electrochemically generated fluorine species. The electrochemical characteristics of the anodic fluorination process in acetonitrile/$Et_4NH_3F_4$ or $Me_4NH_2F_3$‡ show that the solvent-supporting electrolyte is very difficult to oxidize; only at potentials above *ca* 2.8 V vs sce does oxidation take place.[25] Hence fluorination via anodically generated fluorine atoms or elemental fluorine can be excluded in

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†Isomer distributions for anodic acyloxylation have been obtained at low conversion in order to avoid further oxidation of the monosubstitution products with concomitant uncertainty in the isomer distributions.[28,29] Experiments to determine more accurate isomer distributions for the anodic fluorination reaction, attempted in this Laboratory during an extended period of time, have consistently failed;[30] no fluorination whatsoever has been observed for a number of substrates. The same was reported for the attempted naphthalene fluorination in acetonitrile /$Me_4NH_2F_3$.[26a]

‡The nature of the salt employed in these fluorinations, $Et_4NH_3F_4$ or $Me_4NH_2F_3$, is a matter of considerable uncertainty, as can be seen from the methods of preparation. The tetraethylammonium salt is prepared by pumping on a solution of tetraethylammonium chloride in liquid HF, followed by heating the salt at 160° for 6 hr.[16a] On the other hand, the tetramethylammonium salt is prepared by carefully controlled pumping on a solution of tetramethylammonium chloride in liquid HF, a process that cannot be allowed to proceed too long without risk of loosing HF to give the (largely insoluble) hydrogen difluoride salt.[16b] We can confirm that the tetraethylammonium system behaves in the same way as the tetramethylammonium system; after prolonged pumping the salt analyzes for Et_4NF, 1.1 HF.[25]

Table 3. Anode potentials employed in the preparative anodic fluorination of aromatic compounds in acetonitrile/fluoride in relation to $E_{1/2}$[25,26]

Compound	Potential in preparative run/V[a]	$E_{1/2}$/V[a]
Benzene	2.4	2.34
Toluene	2.4	2.26
Isopropylbenzene	2.1	2.18
_t_-Butylbenzene	2.0	2.17
Anisole	1.6	1.70
Fluorobenzene	2.4	2.45
Chlorobenzene	2.4	2.37
Bromobenzene	2.4	2.28
Naphthalene	1.8	1.64
Methyl benzoate	2.7	-
Acetophenone	2.7	2.51[b]
Benzonitrile	3.0	2.90[b]
Benzotrifluoride	3.2	2.86[b]
Nitrobenzene	3.5	3.09[b]
4-_t_-Butyltoluene	2.0	2.02
4-Fluorotoluene	2.3	2.1
4-Fluorobiphenyl	1.8	1.95
4-Fluoroanisole	1.7	1.77
9-Phenylanthracene	1.35	1.28
9,10-Diphenylanthracene	1.65	1.27

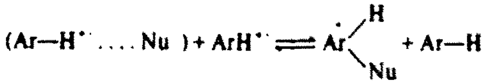
[a] _Vs_. sce. [b] Estimated from the correlation between $E_{1/2}$ and ionization potential given by Miller _et al_.[32]

those cases which have been performed at considerably lower potentials. Only for deactivated benzene derivatives (see Table 3) do preparative anode potentials fall above 2.7 V vs sce. The selectivity for monofluorination speaks however strongly against the involvement of fluorine atoms or elemental fluorine.

A mechanism equivalent to that depicted by the sequence in eqn (6) is also possible for the anodic fluorination carried out at Pt electrodes. It has been shown[33] that in liquid HF/F⁻ electrolytes platinum becomes covered by a layer of platinum difluoride already at around 1.0 V vs the hydrogen electrode which at higher potentials (_ca_ 2 V) is transformed to platinum tetrafluoride. This layer is probably several hundred angstroms thick. In acetonitrile containing anions of the type $H_nF_{n+1}^-$ conditions exist for the formation of such a layer, which can act as an F atom donor to a radical cation (analogously to eqn 6). This trapping reaction would serve to bring in all types of oxidative fluorinations under a common mechanism, so the feasibility of this pathway should be explored.

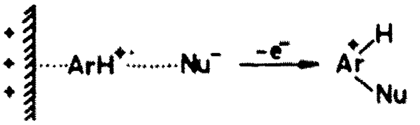
A fourth mechanism for anodic fluorination is equivalent to that proposed for the arylation of radical cations in homogeneous solution.[34] Kinetic evidence here favors a mechanism in which initially a complex between the radical cation and the nucleophile is formed (eqn (8), $Nu^- = Ar'{-}H$), followed by one-electron oxidation of the complex by a second radical cation (eqn (9).

$$Ar{-}H^{+\cdot} + Nu \rightleftharpoons (ArH^{+\cdot} \ldots\ldots Nu\ ) \qquad (8)$$



$$(Ar{-}H^{+\cdot} \ldots\ldots Nu\ ) + ArH^{+\cdot} \rightleftharpoons \dot{A}r\langle^{H}_{Nu} + Ar{-}H \qquad (9)$$

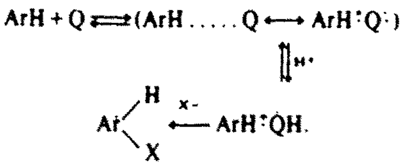
$Nu^- = Ar'{-}H$). At the electrode, this mechanism would translate into a sequence involving formation of an adsorbed radical cation which has to form an electrode complex with the nucleophile before the second electron transfer can occur (eqn 10, $Nu^- = F^-$). Conceptually, this mechanism is identical to the nucleophile assisted ("concerted") two-electron transfer proposed earlier for anodic acetoxylation and cyanation.[27,28,35]



(10)

Chlorination. The perylene radical cation is reduced to the parent compound by chloride ion with formation of chlorine (Table 1), in agreement with the predictions based on the D–Z rules. Likewise obeying these rules, the 4n-1 species, thianthrene and phenothiazine radical cation, enter into nucleophilic reaction with chloride ion with formation of thianthrene oxide† and 3-chlorophenothiazine, respectively. In the thianthrene case, electron transfer also occurs as a side-reaction (_ca_ 10%). Kinetic studies are however necessary to establish the direct nucleophilic interaction in the last-mentioned case, before the mechanism can be established with certainty.

The charge-transfer (CT) complexes between tetrachloro-_o_-benzoquinone (Q) and polycyclic aromatic hydrocarbons (PAH) have been shown[36] to react with hydrogen chloride to give monochloro derivatives of the PAH. It was suggested that protonation of one of the quinone carbonyls would result in one-electron transfer within the CT complex, followed by reaction between the radical cation and chloride ion (eqn 11, X = Cl).



$$ArH + Q \rightleftharpoons (ArH \ldots\ldots Q \longleftrightarrow ArH^{+}Q^{-}) \xrightarrow{H^+} ArH^{+}\dot{Q}H \xrightarrow{X^-} Ar\langle^{H}_{X} \qquad (11)$$

Since the latter reaction is a "forbidden" process, we have sought an alternative mechanism based upon the strongly oxidizing nature of tetrachloro-_o_-benzoquinone (E° in ethanolic hydrogen chloride being 0.88 V) toward chloride ion. The Cl⁻/Cl₂ redox couple has an E° of 1.35 V in water but this value is known to be lower in nonaqueous solvents.[37]

Indeed, treatment of tetrachloro-_p_-benzoquinone with hydrogen chloride under the conditions employed for the chlorination of PAH's, liberates chlorine[38] in spite of the fact that the oxidizing power of the _para_ compound is lower than that of the _ortho_ (E° = 0.70 vs 0.88 V). It was also shown a long time ago[39] that tetrachloro-_p_-ben-

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†The formation of this compound is entirely reasonable on the basis of an attack of Cl⁻ upon sulfur in the radical cation, the middle ring being the 4n-1 part of the ion and thus the sulfur atom the logical point of attack. The resulting radical would then undergo a one-electron oxidation by a second (thianthrene)⁺˙ whereafter water, the presence of which was not ruled out under the experimental conditions employed,[10c] completes the sequence by attacking the positive sulfur atom ($=\dot{S}{-}Cl \xrightarrow{-e} =\overset{+}{S}{-}Cl \xrightarrow{H_2O} =\overset{+}{S}(OH_2)Cl \xrightarrow{-H^+} =S(OH)Cl \xrightarrow{HCl} =S{-}O$).

zoquinone is reduced to the hydroquinone by boiling concentrated hydrochloric acid, presumably with formation of chlorine, since there is not other reductant present but chloride ion under these conditions. The *ortho* quinone would certainly be a stronger oxidant toward hydrogen chloride and thus there is no need to invoke the radical cation mechanism of eqn (11).

A third type of reaction, chlorination of aromatic hydrocarbons in aqueous acetonitrile by the $Cl^-/S_2O_8^{2-}/CuCl_2$ system, initially suggested[40] to proceed via radical cation-chloride ion combination has conclusively been shown to be a conventional chlorination process.[41,42] Chlorine is formed by peroxodisulfate oxidation of chloride ion, and the cupric chloride presumably acts as a weak catalyst for the chlorination reaction.

Most anodic chlorination processes appear to be of the indirect variety,[18] e.g. anodically formed chlorine (or perhaps $Cl_2^{-\cdot}$) is the attacking species. A kinetic study of the reaction between $DPA^{+\cdot}$ and chloride ion showed it to be second order in $[DPA^{+\cdot}]$ and first order in $[Cl^-]$, with no dependence upon [DPA]. A mechanism analogous to that proposed for the arylation of radical cations (eqns (8) and (9), $Nu^- = Cl^-$) fits well with this rate equation and was indeed proposed.[43]

Bromination. The reaction between bromide ion and perylene and phenothiazine radical cation follows the pattern predicted by the D–Z rules (Table 1), although again kinetic studies are required in order to check the mechanism proposed for the latter reaction.

On the basis of product studies at different anode potentials Millington[44] has proposed that the anodic bromination of anthracene and naphthalene in acetonitrile/tetraethylammonium bromide should occur via formation of the radical cation which would react with bromide ion. Additional studies[45] on the anodic bromination of toluene and *p*-xylene in acetic acid/sodium perchlorate–sodium bromide have, however, shown the reaction to be of considerable complexity. With a ratio of $[substrate]/[Br^-]$ of about 300 (Millington used a ratio of 0.0015) two voltammetric waves were observed, the first one at $E_{1/2} = 0.78$ V corresponding to the usual bromide ion oxidation step and the second one at 1.15 and 1.25 V for *p*-xylene and toluene, respectively. Neither of these can be due to the oxidation of the substrates alone, known to have $E_{1/2}$ values in the region of 1.9–2.1 V.

Cpe at a potential on the plateau of the first wave established that bromine is formed and subsequently reacts with the substrate or the solvent, but only when the system is illuminated. Preparative cpe at a potential above that of the second wave gave nuclear and *α* bromination products, more of the latter being formed under illumination than in the dark. It is difficult to suggest a consistent mechanism for anodic aromatic bromination at high potential, but clearly the process is considerably more complex than the simple radical cation-bromide ion combination suggested by Millington.[44]

The CT complexes between tetrachloro-*o*-benzoquinone and PAHs upon treatment with hydrogen bromide in benzene solution give brominated derivatives of PAH.[36] Analogously to the reaction with hydrogen chloride, the *para* quinone liberates bromine upon treatment with hydrogen bromide in benzene.[38] Boiling it with concentrated hydrobromic acid has earlier been shown to produce bromine and the corresponding hydroquinone.[39] In view of these findings there is no need to discuss the radical cation mechanism (eqn 11) until the proper kinetic studies have been made.

The reaction between anion radicals and proton donors

The interaction between a proton donor and a radical anion derived from a pericyclic $4n+2$ system involves suprafacial use of the proton 1s orbital and leads to a situation analogous to that depicted in Fig. 1(a). Therefore it is predicted[8] that protonation of a $4n+3$ radical anion should correspond to an unfavorable pathway and either be unexpectedly slow compared to, e.g. protonation of ordinary carbanions, or proceed via indirect mechanisms, as for example disproportionation and protonation of the dianion formed. It is, however, to be noted that also the corresponding dianions are predicted to obey the same rule and hence should undergo proton attack at a relatively slow rate.

Radical anion chemistry is presently under very active study[2–4] and many problems are not resolved yet. Nevertheless, a reasonably clear picture of the protonation process has emerged in recent years, and one fairly general conclusion is that the protonation of anion radicals is indeed unusually slow. Before we proceed to consider the facts, it is of interest to quote the opinion on radical anion basicity of some of the most experienced investigators in the area. Bank and Bockrath in a study[46] of the protonation of $(naphthalene)^{\cdot-}$ commented that "the radical anion is an enormously weak base" and later in a study[6] of $(anthracene)^{\cdot-}$ stated: "The striking conclusion of this study is the low absolute magnitude for the rate constant of sodium anthracenide. This kinetic basicity is surprisingly low for a conjugate carbon base, and has implications for both the study of reaction mechanisms of radical anions and for synthetic exploitation". At the same time, Szwarc *et al.*[7] found that the protonation of $(perylene)^{-\cdot}$ $(Pe^{-\cdot})$ proceeds via a dianion mechanism (disproportionation of two radical anions) and raised the same problem: "The question arises why the final products are not formed directly, e.g. through the sequence†

$$Pe^{-\cdot}, Na^+ + ROH \longrightarrow PeH\cdot + RO^-Na^+ \tag{12}$$

$$PeH\cdot + Pe^{-\cdot}, Na^+ \longrightarrow PeH^-, Na^+ + Pe \tag{13}$$

$$PeH^-, Na^+ + ROH \longrightarrow PeH_2 + RO^-, Na^+. \tag{14}$$

The protonation of a radical anion, a relatively weak base, by a *weak* acid seems to require a prohibitively high activation energy while the protonation of a dianion, a powerful base, is relatively facile."

The experimental background is summarized in Table 4. Reported second order rate constants for the protonation of a number of radical anions and two dianions in a number of solvents are listed, together with the enthalpy of activation, when known. It is immediately seen that the solvent— and the counterion in a complex interplay with the solvent—plays an important role in determining the rate of protonation. In going from THF (list of abbreviations, see Table 4) via DME to DMF, the rate of protonation by water decreases more than million-fold for $(naphthalene)^{-\cdot}$ and $(anthracene)^{-\cdot}$, as the state of aggregation changes from a contact ion pair in THF, via a solvent-separated ("loose") ion pair in DME, and the

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†This sequence is analogous to the ECE mechanism of eqns (3)–(5).

Table 4. Rate constants (k_p) for protonation of radical anions and one dianion in different solvents[6,7,46-50]

Compound		Solvent[a]	Proton donor	Temperature/°C	k_p/$M^{-1}s^{-1}$	ΔH^{*}/kcal/mol
(Naphthalene)$^{\cdot -}$	Na^+	THF	H_2O	20.0	$1.01\cdot10^4$	10
	Na^+	THF/DME	H_2O	20.0	$0.79\cdot10^4$	14
	Na^+	DME	H_2O	20.0	$0.31\cdot10^4$	13
	Na^+	THF/tetraglym	H_2O	20.0	$2.3\cdot10^2$	17
	Et_4N^+	DMF	H_2O	20.0	$4.6\cdot10^{-3}$	
	b	i-PrOH	i-PrOH	25.0	$4.4\cdot10^4$	
(Anthracene)$^{\cdot -}$	Na^+	THF	H_2O	20.0	$6.6\cdot10^2$	12
	Na^+	THF/DME	H_2O	20.0	13	18
	Na^+	DME	H_2O	20.0	17	17
	Na^+	DME	H_2O	25.0	18[c]	
	Na^+	THF/tetraglym	H_2O	20.0	5.6	16
	Et_4N^+	DMF	H_2O	20.0	$2.0\cdot10^{-4}$	
	Na^+	DME	MeOH	25.0	196[c]	
	b	MeOH	MeOH	25.0	$8.1\cdot10^4$	2.1
	Na^+	DME	EtOH	25.0	75[c]	
	b	EtOH	EtOH	25.0	$2.3\cdot10^4$	2.4
	Na^+	DME	i-PrOH	25.0	11[c]	
	b	i-PrOH	i-PrOH	25.0	$3.6\cdot10^3$	6.7
	Na^+	DME	t-BuOH	25.0	1.2[c]	
(Biphenyl)$^{\cdot -}$	Et_4N^+	DMF	H_2O	20.0	$1.8\cdot10^{-2}$	
	b	MeOH	MeOH	25.0	$6.9\cdot10^4$	2.7
	b	EtOH	EtOH	25.0	$2.6\cdot10^4$	3.1
	b	i-PrOH	i-PrOH	25.0	$5.5\cdot10^3$	5.8
(Perylene)$^{\cdot -}$	Na^+	THF	H_2O	25.0	> 0.01	
(Anthracene)$^{2-}$	$2Bu_4N^+$	THF	MeOH	10.0	$1.5\cdot10^7$	
(Perylene)$^{2-}$	$2Na^+$	THF	H_2O	25.0	$8.4\cdot10^4$	
		THF	MeOH	25.0	$1.2\cdot10^6$	
		THF	MeOH	10.0	$7.5\cdot10^4$	
		THF	EtOH	25.0	$0.8\cdot10^6$	
		THF	i-PrOH	25.0	$0.52\cdot10^6$	
	THF	THF	t-BuOH	25.0	$1.1\cdot10^5$	

[a] THF = tetrahydrofuran, DME = 1,2-dimethoxyethane, DMF = N,N-dimethylformamide. [b] Pulse radiolysis experiment. [c] Calculated for $[H_2O]$ = 0.1 M.

essentially free ion in DMF (a medium of high dielectric constant and good solvating properties). In the present context we are primarily interested in the chemical properties of the free radical anions, and conclude that protonation rates for a few representatives of such species fall in the region 10^{-3}–10^{-2} $M^{-1}s^{-1}$ in DMF.† In THF/tetraglym, where the counter-ion is tetraglymated, rates are approximately 10^4 times greater, and there are yet two powers of ten before the rate of protonation of the contact ion pair is approached. In THF/tetraglym the enthalpy of activation for the protonation of (naphthalene)$^{\cdot -}$ by water is 17 kcal mol^{-1}.

The protonation rates in pure alcohols, as determined by the pulse radiolysis method,[49] are higher than expected when one compares with the other solvents. At least in methanol and ethanol would the rates be expected to pertain to the reactivity of free radical anions, and hence be relatively slow. Nevertheless, rate constants in the region 10^3–10^5 are reported, and found to correspond to very low enthalpies of activation.

In order to be able to compare with protonation rates of ordinary carbanions, Table 5 lists a number of such data. Relatively few rate constants have been determined for this type of reaction, but the results in Table 5 nevertheless show that similar relationships as for radical anions hold, e.g. ion pairs react faster than free anions and the dependence upon proton donor acidity shows the same order.

It is not altogether obvious how the data should be treated. We have chosen to compare the benzyl anion with (naphthalene)$^{\cdot -}$, noting that triphenylmethanide is protonated only three orders of magnitude slower, thus indicating that the less pronounced negative charge dispersal in the benzyl anion than in (naphthalene)$^{\cdot -}$ is not

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†It should be noted that water might be unusually weak as a proton donor in DMF, because of association between DMF and water.[51] In DMSO, this effect operates very strongly, as for example shown by (cyclooctatetraene)$^{\cdot -}$ being unaffected by a water concentration as high as 5 M.

Table 5. Rate constants (k_p) for protonation of carbanions in different solvents[32-35]

Compound	Solvent	Proton donor	Temperature/°C	$k_p/M^{-1}s^{-1}$
$PhCH_2^-$ (free)	THF	Water	24	$0.53 \cdot 10^8$
$PhCH_2^-Na^+$ [a]	THF	Water	24	$55 \cdot 10^8$
$PhCH_2^-$ (free)	THF	MeOH	24	$2.3 \cdot 10^8$
$PhCH_2^-Na^+$ [a]	THF	MeOH	24	$58 \cdot 10^8$
$PhCH_2^-$ (free)	THF	EtOH	24	$1.4 \cdot 10^8$
$PhCH_2^-Na^+$ [a]	THF	EtOH	24	$37 \cdot 10^8$
$PhCH_2^-$ (free)	THF	t-BuOH	24	$0.16 \cdot 10^8$
$PhCH_2^-Na^+$ [a]	THF	t-BuOH	24	$13 \cdot 10^8$
Triphenylmethanide, K^+ [a]	PhH/t-BuOH (1:1)	t-BuOH	30	10^7-10^8
Triphenylmethanide, K^+/dicyclohexyl-18-crown-6	t-BuOH	t-BuOH	30	10^6
Triphenylmethanide (free)	DMSO	i-PrOH	25	$6 \cdot 10^4$
Triphenylmethanide	MeOH	MeOH	45	10^8 [b]

[a] Contact ion pair. [b] Estimated value.

of critical importance. This comparison shows that carbanion protonation is $\sim 5 \times 10^4$ (ion pair) and $\sim 2 \times 10^4$ (free ion in THF vs ion in THF/tetraglym) faster than that of the anion radical. Comparing triphenylmethanide ion with (anthracene)$^{\dot{-}}$ gives corresponding ratios of 10^4–10^5 and 10^5, respectively. Finally, the rate of protonation of triphenylmethanide ion in DMSO can be compared to that of a closely related anion radical, DPA$^{\dot{-}}$, using an electrochemically determined k_p in DMSO with 2,4,5-trimethylphenol as proton donor.[36] Assuming that a Brönsted relation between protonation rate constant and pK of the proton donor with the same α for different radical anions is valid, it can be estimated from these data that the protonation rate constant for DPA$^{\dot{-}}$ by ethanol in DMSO is $\leq 10^{-3}\ M^{-1}\ s^{-1}$, to be compared to that of triphenylmethanide ion by 2-propanol, $6 \times 10^4\ M^{-1}\ s^{-1}$. The ratio is here $> 10^7$.

Concluding, the protonation of radical anions is 10^4–10^7 times slower than that of carbanions of similar structure. Looking at one of the dianions in Table 4, Pe^{2-}, we find that the protonation rate, albeit high, still is lower than that of benzyl anion and triphenylmethanide ion, in spite of the double negative charge of Pe^{2-}. Thus the remarks made by earlier investigators and quoted above are entirely borne out by comparison with more extended studies on carbanions. We suggest that this unusually slow protonation process is due to restrictions imposed by the D–Z rules upon the transition state between a proton and a $4n+3$ radical anion. Radical anions of the $4n+1$ type should not behave anomalously in this respect, and indeed it has been shown[36] that (cyclooctatetraene)$^{\dot{-}}$ is protonated much faster by 2,4,5-trimethylphenol in dimethyl sulfoxide than such typical $4n+3$ systems as (anthracene)$^{\dot{-}}$, (phenanthrene)$^{\dot{-}}$ and (pyrene)$^{\dot{-}}$ (protonation rate constant ~ 3000 vs 75, ~ 900 and $130\ M^{-1}\ s^{-1}$). It was also commented by the authors of this paper that (cyclooctatetraene)$^{\dot{-}}$ was protonated at a rate "considerably higher than would have been anticipated from electron densities".

Acknowledgement—we thank the Swedish Natural Science Research Council for financial support.

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