Application of the Dewar–Zimmerman Rules to the Reactions Between Radical Cations and Nucleophiles

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Summary The reaction between a $4n+1$ aromatic radical cation and a nucleophile, the interacting orbital of which must be used suprafacially in the transition state, should be 'forbidden' by the Dewar–Zimmerman rules.

THE reactivity of radical cations toward nucleophiles presents some puzzling features which have so far eluded rational explanation.[1] The reactions of the radical cations of perylene,[2,3] thianthrene,[4,5] phenothiazine,[5] and dibenzodioxin[6] are representative of the complexities involved (Table). There are two types of competing reactions, namely electron transfer oxidation of the nucleophile (ET), and nucleophilic attack upon the radical cation (N). No systematic reactivity pattern is discernible, however, when one considers all four systems and tries to relate reactivities to, *e.g.*, oxidation potentials of the nucleophiles.

In this Communication it is proposed that the Dewar–Zimmerman rules[7,8] give testable predictions about the reactions between radical cations and nucleophiles. The underlying assumption is that nucleophilic attack occurs *via* a transition state in which there must be a strong interaction between the two reacting components (a new bond must be formed) whereas the transition state of the competing ET reaction does not require any such interaction

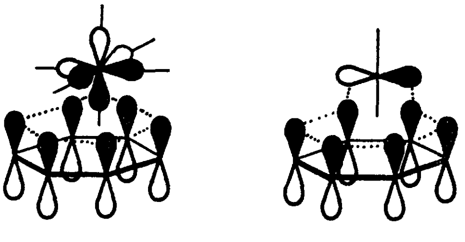

FIGURE. Orbital representation for the transition state of the reaction between a benzene radical cation and (a) a nucleophile interacting suprafacially (exemplified by a halide ion) or (b) a nucleophile interacting antarafacially.

(electron tunnelling, no bond formation). It is the former type of transition state on which the Dewar–Zimmerman treatment imposes restrictions in certain situations. To illustrate the reasoning, let us consider the perylene radical cation (Pe^+).

Pe^+ would first be replaced by the system having one more electron, *i.e.*, perylene itself, following the recommendation[8,9] that an odd-electron system should be treated as that with one more electron added. The two uniquely single bonds are then dissolved[7] to give two naphthalene entities, one of which is considered for interaction with the nucleophile. The attack of the nucleophile is assumed to occur perpendicular to the ring plane at the midpoint of a C–C bond along the periphery.

TABLE. Reactivity patterns of radical cations *vs.* nucleophiles[1,3–6]

Nucleophile ($E_{1/2}$/V)[a]	Reaction type[b]			
	[Perylene]$^+$	[Thianthrene]$^+$	[Phenothiazine]$^+$	[Dibenzodioxin]$^+$
F^- (2·5)	No reaction	—	No reaction[c]	—
Cl^- (0·8)	ET	N	N	—
Br^- (0·4)	ET	—	N	—
I^- (0·2)	ET	ET	ET	ET
NO_2^- (0·7)	N	—	N	N
CN^- (0·7)	N	ET	ET	ET
$MeCO_2^-$ (1·4)	N	—	—	—
$PhCO_2^-$ (1·3)	N	—	—	—
H_2O (1·1)	N	N	N	N
Pyridine (1·8)	N	N	N	N
H_3N, amines (1·2)	—	N	—	ET

[a] *Vs.* Ag/Ag^+ (0·1 M) reference electrode. [b] ET, electron transfer; N, nucleophilic reaction; —, not known. [c] F^- acts as a base toward the phenothiazine radical cation.

If the nucleophile now must use its interacting orbital in a suprafacial manner, it is easily seen that the transition state with naphthalene will be equivalent to an 11-centre Hückel system containing 12 electrons, *i.e.*, a $4n+3$ anion. This has antiaromatic character[7] and hence corresponds to an unfavourable pathway. On the other hand, for nucleophiles which can use their interacting orbitals in an antarafacial manner, the transition state is equivalent to an anti-Hückel $4n+3$ anion and represents a favourable process.

Halide ions, being monoatomic species with a closed shell of electrons, must interact suprafacially *via* one *p*-lobe with the other component, as shown in the Figure (a) for benzene. One therefore predicts that halide ions should not undergo nucleophilic reaction with radical cations derived from $4n+2$ parent systems (which in turn could be derived from larger systems by dissolution of single or multiple bonds according to Dewar's rules).[7] Thus, either electron transfer or no reaction should take place in this situation. On the other hand, nucleophiles, such as the remaining ones in the Table, which can interact antarafacially *via* *p* or sp^n orbitals [Figure (b)] should be capable of undergoing nucleophilic reaction with this type of radical cation. Since in this case no restriction is imposed upon any of the two competing processes, ET is also possible and there is at present no way of telling which route will predominate. Perhaps fortuitously but nevertheless encouraging, the reactivity pattern of Pe^+ defines a sharp line of demarcation between the two types of nucleophiles.

The isoconjugate species of the remaining radical cations in the Table is anthracene dianion. Application of the Dewar–Zimmerman rules to this $4n$ species shows that no restriction is imposed in any of the two situations corresponding to the Figure (a and b). Thus a radical cation derived from $4n$ systems should be capable of undergoing nucleophilic attack by any kind of nucleophile. Indeed, phenothiazine radical cation seems to react readily with Cl^- and Br^- to give nucleophilic substitution products.

Radical anion reactions with electrophiles should be governed by the same rules (anion radical + electrophile is isoconjugate with radical cation + nucleophile). Here it is predicted that protonation of a radical anion derived from a $4n+2$ system should lead to an antiaromatic transition state and thus be a less favourable process. On the other hand, anion radicals derived from $4n$ systems should undergo protonation easily. Experimental evidence, although scarce, favours this; protonation of naphthalene[10] and anthracene[11] anion radical occurs at anomalously low rates (k_{20} = 300 and 5·6 l mol^{-1} s^{-1}, $\Delta H^{\ddagger}$ 17 and 16 kcal mol^{-1}, respectively) as compared to similar carbanions (rates essentially diffusion controlled). Protonation of perylene radical anion takes place *via* the dianion,[12] even though the equilibrium constant for the process $2R^- \rightleftharpoons R^{2-} + R$ is very small[13] (10^{-10}—10^{-11}).

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