

THE APPLICATION OF THE DEWAR-ZIMMERMAN RULES TO THE REACTIONS
BETWEEN AROMATIC RADICAL CATIONS AND FLUORIDE ION.

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Recently Ebersson¹ has come to the conclusion that reactions between a $(4n+1)\pi$ -electron aromatic radical cation (ARC) and halide ions X^- are restricted only to electron transfer and that nucleophilic attack of X^- upon ARC should be forbidden by the Dewar-Zimmerman rules².

This conclusion seems to be controversial, and therefore let us examine Ebersson's argument. The attack of the nucleophile is assumed to occur perpendicular to the ring plane at the midpoint of a C-C bond along the periphery¹. There are two types (Fig.I,a,b) of interaction, a suprafacial attack (the orbital of X^- interacting with π -system is symmetrical) and an antarafacial attack (the orbital of X^- is anti-symmetrical). The transition states will be equivalent to a 7-centre Huckel system (a) and an anti-Huckel system (b). The odd-electron system should be treated as that with one more electron added, following the recommendation of Zimmerman³ and Woodward and Hoffmann⁴. Accordingly the transition state (b) is aromatic and corresponds to a favourable process and the transition state (a) is anti-aromatic and corresponds to an unfavourable pathway and should be forbidden by the Dewar-Zimmerman rules.

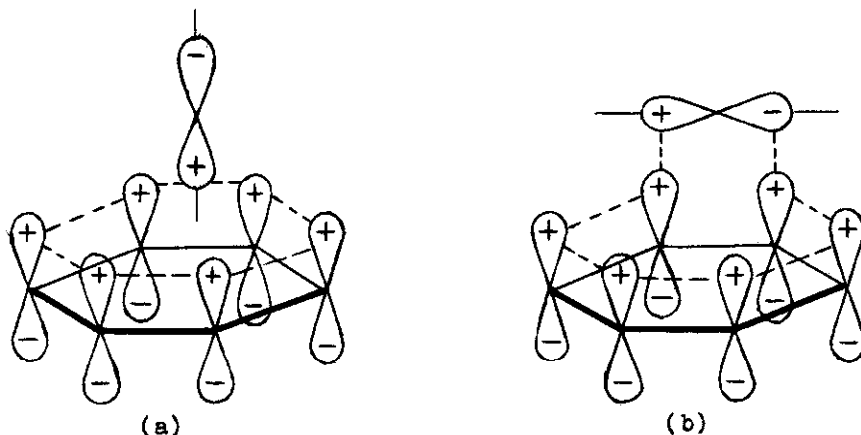


Figure I. Orbital representation for transition state of the reaction between a benzene radical cation and a nucleophile (a) interacting suprafacially or (b) antarafacially.

The weak point of this argument consists in the selection of the nucleophile orbitals interacting with ARC. For example Ebersson has took into account only the p_z -orbitals of the halide ions (Fig.2). Nevertheless the evaluation of overlap integrals (S_x, S_z)⁵ shows that the interactions of the p_x - and p_z -orbitals of X^- with a p_z -orbital of a carbon atom are comparable in value (Table I). Thus, in spite of the prohibition of the suprafacial interaction the nucleophilic attack of X^- may take place as a result of the antarafacial interaction of the p_x -orbital of X^- with the π -system of the ring.

Table I. Overlap Integrals (S) of $2p_z$ -orbital of carbon atom and p-orbitals of halide ion

$R_{\text{C-X}^-}$ Å	F		Cl	
	S_x	S_z	S_x	S_z
1.49	0.169	0.232	-	-
1.76	-	-	0.179	0.306
2.00	0.053	0.118	0.126	0.262

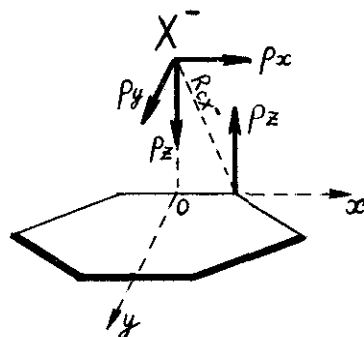


Figure 2. Representation of p-orbitals of halide ion and carbon atoms of ARC.

Consequently the conclusion¹ that halide ion should not undergo nucleophilic reaction with radical cations derived from $4n+2$ parent system seems to be wrong.

Indeed it has been shown earlier⁶⁻¹⁴ that fluoride ion is capable of nucleophilic attack on an ARC with the formation of a C-F bond. The anodic oxidation of aromatic compounds in the presence of fluoride ion have led to the fluorine containing products *via* intermediate ARC⁶⁻¹¹. Nucleophilic attack on an ARC by F^- has been proposed in the reactions between aromatic compounds and XeF_2 ¹²⁻¹³ and high valency metal fluorides¹⁴⁻¹⁵.

Now we present some additional evidence for the nucleophilic reaction between fluoride ion and an ARC generated by anodic oxidation. It is known¹⁶ that electro-oxidation on Pt of 9,10-diphenylanthracene (DPA) in CH_3CN containing tetra-alkylammonium perchlorate involves two discrete steps. The transfer of the first electron produces a rather stable radical cation (RC) and transfer of the second electron generates the dication. Accordingly the cyclic voltammogram contains the first oxidation peak (Ox_1) at 0.92v (vs. Ag/Ag^+ 0.1M) and the second peak (Ox_2) at 1.32v. On reversing the direction of the scan at 1.1v, the cathodic peak (R_1) is observed at 0.85v which is due to reduction of the RC formed at the first oxidation peak Ox_1 ¹⁶. We have reproduced these results under the following conditions: Pt-anode 1.7mm², Pt-cathode 400mm², reference

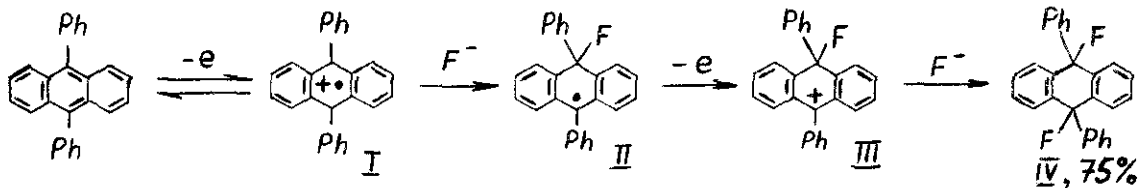
electrode - an Ag wire diameter 5mm; The electrolyte contains 5.4mg DPA, 69mg $\text{AgClO}_4 \cdot 3\text{CH}_3\text{CN}$, 0.22g Et_4NBF_4 , 1 ml C_6H_6 and 20 ml CH_3CN . Under these conditions the correlation of cathodic and anodic peak currents $I_{p,c}/I_{p,a}$ depends on the sweep rate and approaches 1 at high sweep rates (Table 2, a).

The addition of 19mg $\text{Et}_4\text{NF} \cdot 3\text{HF}$ to the electrolyte leads to very significant changes in the cyclic voltammograms of DPA (Table 2, b). The anodic peak potential ($E_{p,a}^*$) is slightly displaced and anodic peak current ($I_{p,a}^*$) increases markedly and becomes to correspond to a two electron transfer process. The electro-oxidation of DPA in the presence of fluoride ion becomes an irreversible process and no cathodic peak is detected at 25° on reversing the direction of the scan. At a lower temperature (-30°) the oxidation process is only partly irreversible and a cathodic peak current can be detected.

Table 2. Cyclic voltammetry of DPA in acetonitrile containing (a) Et_4NBF_4 and (b) $\text{Et}_4\text{NF} \cdot 3\text{HF}$

V $\text{v} \cdot \text{sec}^{-1}$	a				b		
	Ox_1 (mv)	$I_{p,a}$ (μa)	R_1 (mv)	$\frac{I_{p,c}}{I_{p,a}}$	Ox_1^* (mv)	$I_{p,a}^*$ (μa)	$\frac{I_{p,a}^*}{I_{p,a}}$
0.04	905	4.27	830	0.60	859	8.0	1.87
0.08	908	5.66	830	0.70	872	11.0	1.93
0.16	914	8.50	830	0.76	878	15.4	1.82
0.25	915	10.10	830	0.82	883	17.4	1.72
0.50	921	14.55	814	0.81	903	23.8	1.64
1	920	21.30	812	0.81	903	34.5	1.62
2	920	30.25	808	0.83	905	42.5	1.41
4	937	42	800	0.87	905	59.7	1.42
8	943	61.5	800	0.88	907	76	1.24
16	943	91	798	0.93	907	107.5	1.18

The results collected in Table 2 support unequivocally the nucleophilic attack of fluoride ion upon the DPA radical cation (I). The adduct of I and F^- (the intermediate radical II) is oxidized more easily than the original hydrocarbon. Thus, the primary one-electron transfer is followed by the chemi-



cal reaction with fluoride and a second electron transfer occurs at the same electrode potential. The generated benzenium ion (III) reacts further with the second fluoride ion producing 9,10-difluoro-9,10-diphenyl-9,10-dihydroanthracene (IV). Controlled potential electrolysis (at 0.95v) was conducted on a solution of DPA (1.15 g) in acetonitrile (74 ml) containing 8 g $\text{Et}_4\text{NF} \cdot 3\text{HF}$ and 1 ml C_6H_6 in the cell¹¹. After passing 2F/mol of electricity the electrolyte was added to 50 ml H_2O and filtered. The precipitate was recrystallized (C_5H_{12} , C_6H_6) and 750mg of DPA and 334mg of IV (m.p.227° with decomposition) were obtained. Earlier⁹ IV had^{been} obtained by electro-oxidation of DPA at the potential of the second oxidation peak (Ox_2).

It should be noted that the very high oxidation potential of F^- (2.5v vs Ag/Ag^+ 0.1M) excludes the possibility of the formation of IV *via* the radical fluorination of DPA. Neither could a disproportionation mechanism of the DPA radical cation present a satisfactory explanation for the formation IV. In this case one would expect an extremely quick reaction between F^- and the DPA dication. Moreover the kinetics of the anodic pyridination of DPA also excludes the disproportionation of radical cation^{17,18}.

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