Fragmentation Rates of Aromatic Radical Anions and the $\pi^* - \sigma^*$ Orbital Crossing Point

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The reaction coordinate of the fragmentation of aromatic radical anions with nucleofugal groups was studied by the INDO and MNDO techniques. The reaction coordinate turned out as the stretching between the nucleofugal group bonded to the carbon atom of the aryl moiety. It was found that to fragment a π^* radical anion, the odd electron has to be transferred to the σ^* molecular orbital of the aryl-nucleofugal bond by an orbital crossing, which is reached by the lengthening of this bond. There is a qualitative agreement between the length of the bond to reach the orbital crossing point and the experimental fragmentation rates of the aromatic radical anions. Finally, some considerations about the $\sigma - \pi$ coupling are made, since it is defining the possibility of a transfer from the π^* to the σ^* molecular orbital.

Introduction

When an aromatic substrate with a nucleofugal group receives an electron, a radical anion is formed (1) and there are many evidences that it fragments according to (2) when X is a halogen, trimethylammonium ion, etc. [1]

$$\mathrm{Ar\,X} + e^- \rightarrow (\mathrm{Ar\,X})^{\dot{-}}, \quad (1)$$

$$(\mathrm{Ar\,X})^{\dot{-}} \rightarrow \mathrm{Ar}^{\cdot} + \mathrm{X}^- . \quad (2)$$

However, the fragmentation rate varies depending on the aromatic moiety and the nucleofugal group X. For instance, the radical anion of meta and parahalonitrobenzenes decomposes very slowly, or not at all [2].

The fragmentation rates of radical anions not only depend on the aromatic moiety and the nucleofugal group, but also on its position in the molecule [3]. The electrochemical reduction of haloacetophenones in dimethylformamide is one electron reduction which forms unstable radical anions that fragment to form aryl radicals and halide ions. The fragmentation rates of o- and p-chloroacetophenone radical anions are greater than $10^4\,\mathrm{s}^{-1}$, whereas the fragmentation rate of the meta chloroacetophenone radical anion is only $5\,\mathrm{s}^{-1}$ [4].

There are experimental evidences that if the odd electron is located in the π^* molecular orbital (MO), it has to be transferred to the σ^* MO associated to the aryl-nucleofugal bond, thus this bond becoming unstable and the system fragmenting [5]. The radical anion fragmentation rates are very important in $S_{\mathrm{RN}}1$ chemistry. The coupling of an aryl radical with a nucleophile forms a radical anion, and this is one of the propagation steps of the $S_{\mathrm{RN}}1$ mechanism [6]. The radical anion thus formed can follow different reaction pathways. One is the electron transfer to give the substitution product [6] or, if the radical anion has a low lying σ^* MO, fragments to give a new radical and nucleofugal group. It has been demonstrated that the competition of electron transfer or fragmentation of the radical anion intermediates depends on fragmentation and not on the electron transfer rates [7].

It has been suggested that, when an aryl radical approaches to the nucleophile, the three-electron interaction forms a σ and σ^* MO's of the bond being formed, and as they approach each other, the σ MO decreases its energy as the σ^* MO increases it. If there is in the reacting species a low lying MO, by orbital crossing the electron of the σ^* MO is transferred to the π^* MO, and finally the radical anion formed has the odd electron in the π^* MO [8].

That is the case observed in the coupling of a methyl anion with a phenyl radical studied by the INDO method [9], leading to a stable toluene radical anion, which is a π^* radical anion. The same

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result is obtained in the coupling of a fluoride ion with a phenyl radical, leading to a fluorobenzene radical anion with the odd electron in the π^* MO. However, the fluorobenzene radical anion fragments into a phenyl radical and a fluoride ion [1], in contrast with the toluene radical anion. These differences in behaviour were attributed to the distance between the orbital crossing point $\pi^* - \sigma^*$ and the equilibrium position of the radical anion, which is far from the toluene radical anion, but it is near the equilibrium distance in the fluorobenzene radical anion, and vibrations allow the orbitals to mix ($\pi^* - \sigma^*$), and from the σ^* state the radical anion fragments [9]. Similar results were obtained in an ab initio study of the fragmentation of the methyl chloride radical anion [10]. In the equilibrium position, the odd electron is on a diffuse orbital mainly localized on carbon, but as the C–Cl bond distance increases, the odd electron is transferred in the intersection from this diffuse orbital to the σ^* MO of the C–Cl bond, which then fragments into a methyl radical and a chloride ion [10].

A quite different result was obtained in an ab-initio study of the fragmentation of the chloronitromethane radical anion. In this case, although there is a nitro group that may accept the odd electron in the π^* MO to form a "stable" radical anion, the fragmentation is spontaneous and exothermic. This result was interpreted in terms of an in phase mixing of the π^* MO of the nitro group with the σ^* MO of the C–Cl bond. Thus, when the radical anion is formed, there is no orbital crossing between occupied and unoccupied orbitals, the odd electron being delocalized between the π^* MO of the nitro group and the σ^* MO of the C–Cl bond, which fragments without any barrier [11].

We have studied by semiempirical methods (INDO, MNDO) the fragmentation of several aromatic radical anions with nucleofugal groups in order to know the factors on which their fragmentation rates depend.

Method

Radical anions were studied by semiempirical techniques: the INDO [12] method for open shell systems and the MNDO [13], with half electron model [14], were used. All calculations were done in double precision [15].

Both methods seem to be adecuate for the treatment of this class of compounds, since they suitably reproduce the properties of this systems at the equilibrium positions (for instance, the proper energetic isomer is given) compared to ab-initio calculations [16].

For the INDO calculations an approximate molecular geometry was taken. It was found that the use of an improved geometry does not lead to any noticeable change in the parameters treated in this work. For the MNDO analysis the molecular geometry was optimized by the Davidon-Fletcher-Powell procedure [17] at each point on the reaction coordinate (minimal energy pathway).

The reaction coordinate is the stretching between the nucleofugal group bonded to the carbon atom of the aryl moiety. This procedure gives a regular shape curve that represents the total energy of the system as a function of the reaction coordinate which was done as previously reported [9].

Discussion

All the systems studied show, as in the example previously analyzed, the existence of an orbital crossing point $\pi^* - \sigma^*$ in the reaction coordinate; that is, at the equilibrium position of the radical anion, the odd electron is in the π^* MO of the aryl moiety, but becomes at this point a σ^* MO of the aryl-nucleofugal bond, which gives after this point the aryl radical and the nucleofugal group. As an example, the energy of the MO's involved in the reaction coordinate of the fragmentation of p-cyanofluorobenzene radical anion is shown in Figure 1.

The σ^* MO belongs to the a_1 irreducible representation, when a C_{2v} punctual group is considered;

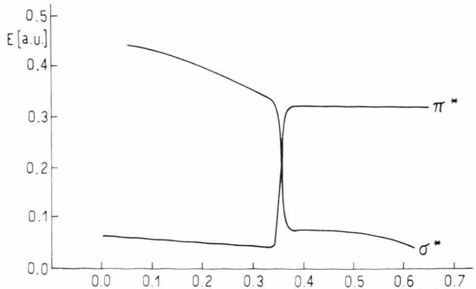

Fig. 1. Energy of the frontier orbitals of the p-fluorobenzonitrile radical anion as a function of the reaction coordinate distance from equilibrium (INDO method).

when an out of plane vibration occurs it becomes a' in the C_s punctual group. The π^* MO is usually a_2, so it becomes a'' when the symmetry is reduced. Thus from the symmetry point of view, the crossing is allowed if a vibronic coupling happens, since it involves an a' a'' orbital crossing. It can be observed that in the systems studied, the distance of the orbital crossing point from the equilibrium position of the radical anion varies as the aromatic moiety varies, and there is a qualitative agreement with the experimental fragmentation rates of the radical anions (Table 1). It is known that these rates vary with the solvent and the temperature [18], and these data are from different sources so that it is not expected to find a quantitative correlation between them, but the trend observed is important to show that a longer distances, there is a slow fragmentation rate which increases as the distance of the orbital crossing point becomes shorter. The results with MNDO technique show the same behaviour and trend, although the values of the orbital crossing point are larger than those from the INDO technique.

Table 1. Fragmentation rates and the orbital crossing point of aromatic radical anions.

Radical anion derived from	lg K	Orbital crossing point [a]
4-fluorobenzophenone	Not observed [b]	2.0
toluene	Not observed	0.55 [c]
m-fluoronitrobenzene	−2.70 [d]	0.49
p-fluoronitrobenzene	−2.52 [d]	0.45
p-fluorobenzonitrile	1.05 [e]	0.35
p-fluorobenzoate ion	5.78 [f]	0.33
p-fluorophenylacetylene		0.30
fluorobenzene	6.0 [g]	0.30 [c]
p-bromobenzonitrile	10.0 [h]	0.26 [i]
m-difluorobenzene		0.25
o-difluorobenzene		0.24
p-difluorobenzene		0.22
chlorobenzene	fast	0. [c]

[a] Measured in A from the equilibrium position, using INDO technique.

[b] L. Nadjo and J. M. Saveant, J. Electroanal. Chem. **30,** 41 (1971).

[c] From Ref. [9].

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[i] Using CNDO/3R technique.

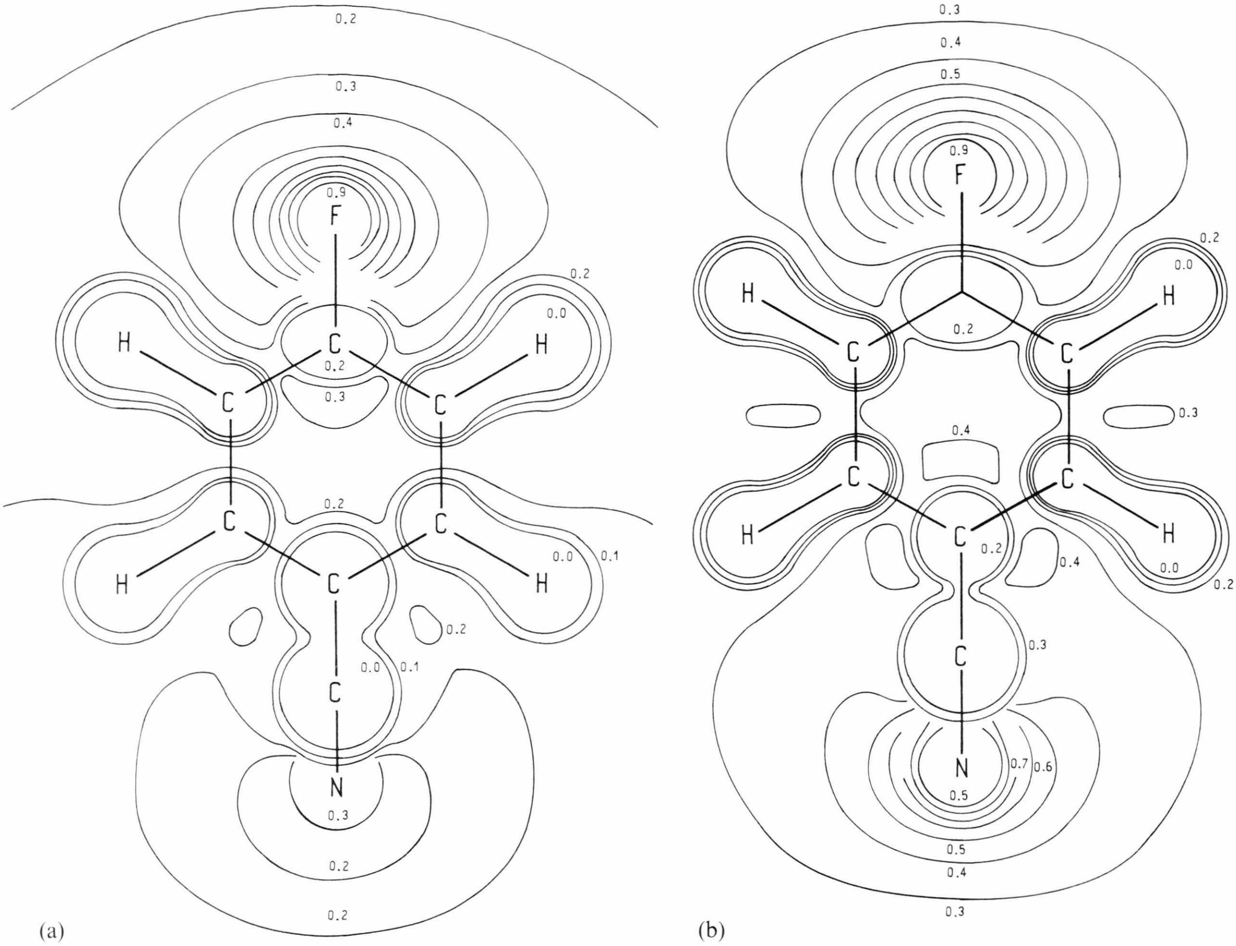
Table 2. Bond index and dipole moments for p-fluoroacetylene radical anion as a function of the carbon fluorine stretching using INDO technique.

Distance [a]	Bond indices [b]	Dipole moment (in Debyes)
0.65	0.2287	8.801
0.55	0.2261	8.584
0.45	0.2607	8.291
0.35	0.2814	7.902
0.33	0.2865	7.810
0.31	0.2882	7.739
0.30	0.2951	7.661
0.29	0.7573	0.072
0.28	0.7611	0.114
0.25	0.7661	0.309
0.00	0.8572	1.969

[a] Measured in A from the equilibrium position.

[b] Reference [20].

This orbital crossing point is important not only in the nature π^* or σ^* of the radical anion, but also in other drastic changes in the molecule. The dipole moment of the system changes strongly from one to another side of the orbital crossing point at least by 4 Debye units. When the odd electron in the radical anion is in the π^* MO, the charge is dispersed over the whole molecule, and in the orbital crossing point the charge is transferred to a localized point, that means that a strong dipolar moment is created. This charge transfer point is actually a strong re- estructuration of charges in the system, as we can see in the electrostatic isopotential maps (Figure 2). Similar behaviour has been observed in other charge transfer processes [19]. There are also other changes in the orbital crossing point in the system, such as the strong changes in the bond index [20] between the aryl moiety and the nucleofugal group (Table 2). The total energy curve as a function of the aryl nucleofugal bond distance presents a second minimun after the orbital crossing point (Figure 3). This second minimun was not found in the examples studied previously [9]. This second minimun may suggest that an aryl radical and a nucleophile (or nucleofugal) group may form an adduct that has a certain stability, which may progress to the orbital crossing point and forms a π^* radical anion, or may diffuse appart giving the free aryl radical and the nucleofugal group (Figure 4). It was suggested that the reaction of phenyl radical with benzene thiolate ion that is one of the less reactive nucleofiles in the $S_{RN}1$ mechanism, forms an encounter complex that reverts to the starting



(a) (b)

Fig.2. (a) Isopotential curves before the orbital crossing point generated by the electrostatic potential of the p-fluorobenzonitrile radical anion. The numbers represent fractions of the minimum negative potential. (b) Isopotential curves after the orbital crossing point.

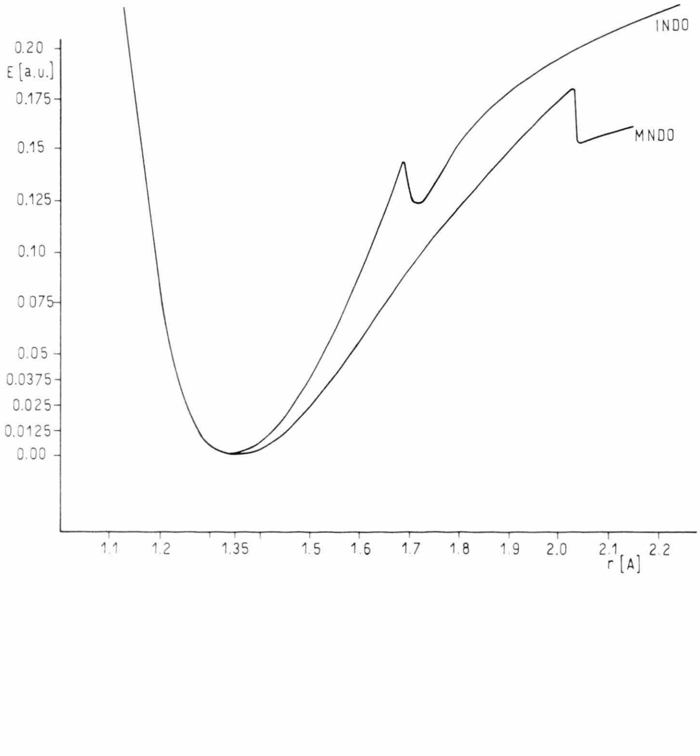


Fig. 3. Total energy as a function of the reaction coordinate. (a) INDO method; (b) MNDO method (optimized energy at each point).

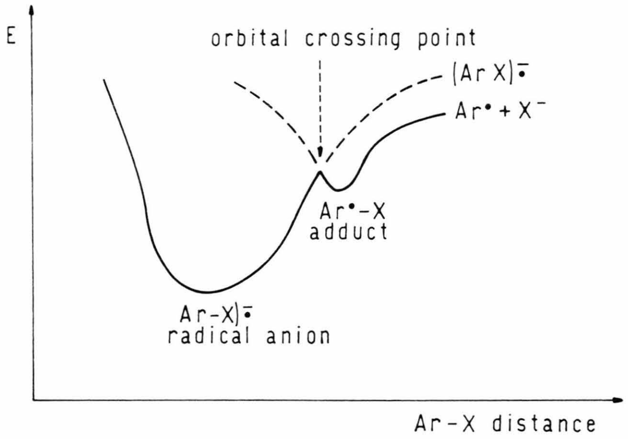


Fig. 4. Schematic representation of the formation of an adduct, the orbital crossing point, and the radical anion intermediate.

materials faster than it progresses to form the radical anion of the substitution product in a reversible step Eqs. (3) and (4) [21].

$$\mathrm{Ph^{\cdot} + {}^{-}S\,Ph \rightleftarrows \underset{\text{encounter complex}}{(Ph^{\cdot}\,{}^{-}S\,Ph)}} \qquad (3)$$

$$\mathrm{(Ph^{\cdot}\,{}^{-}S\,Ph) \rightarrow \underset{\text{radical anion.}}{(Ph\,S\,Ph)^{\overset{\cdot}{-}}}} \qquad (4)$$

Gamma irradiation of alkyl bromines or iodines to form alkyl radicals (Eq. (5)) does not always give the ESR signal of the expected alkyl radical at 77 K, but frequently grows by annealing [22].

$$\mathrm{RX + e^{-} \rightarrow R^{\cdot} + X^{-}}. \qquad (5)$$

It was suggested that by electron capture the alkyl halide forms an adduct, that was interpreted in terms of charge transfer complex between the alkyl radical and the halide ion, giving the observed ESR spectra, but that upon warming, the adduct dissociates as free particles [22].

Let us briefly consider the facts that make the in plane CX stretching the minimun energy pathway. This is easily understood in terms of the pi energy. For instance, if the system dissociates through an out of plane reaction coordinate the CX bond would loose its pi energy (given by the mesomeric effect) in a more rude way than it would do if the nucleofugal group remained in the molecular plane, until the neighbourhood of the orbital crossing point.

If an out of plane vibration, coupled with the CX stretching were considered there would be an increase of the activation energy of about 5 K cal./mole for each degree that the bond were lifted from the molecular plane.

Out of plane vibration of	Energy[a]
fluorine	5.
orto carbon	1.0
meta carbon	1.2
para carbon	4.0
CN group	5.5

Table 3. Energy excess required for an out of plane vibration necessary to allow the $\sigma^* - \pi^*$ coupling for the p-fluorobenzonitrile.

[a] The energy is in K cal./mole and for each degree from the molecular plane.

The importance of the mesomeric effect is also noticeable from the experimental point of view, since the more overlapped the "p_π" orbital of the nucleofugal group is to the aromatic moiety, the more stable the system becomes. For example, the p_π orbitals of fluorine, are more overlapped to the p_π orbital of the carbon atom, than those of chlorine, so, their radical anions are more stable than those of chlorine, when attached to the same aromatic moiety; this may be seen through the decomposition constants. Another relevant aspect is that the more extended the pi conjugation becomes the more stable the system is.

Both factors show the importance of the pi energy in the character of the carbon-nucleofugal bond. This remarks the impossibility of throwing away the pi energy of the bonding from the very begining in order to allow the states to mix up gradually. This is the reason why the system prefers a symmetry forbidden pathway. In Table 3, we show off the energy excess required to allow the $\sigma - \pi$ coupling, which became $a' - a''$ as a result of the reduction in the symmetry. There are many possibilities for such coupling and any of them would throw a succesful "σ" – "π" coupling.

This results show an agreement with the experimental data, if there is an intramolecular electron transfer as it was suggested experimentally [23].

Conclusion

From these studies it is concluded that to fragment a π^* radical anion, the odd electron from the π^* MO has to be transferred to the σ^* MO of the aryl-nucleofugal bond in the orbital crossing point, and this point is reached by lengthening the σ bond. The fragmentation rate depends on how far the orbital crossing point is from the equilibrium distance. In this orbital crossing point a strong change of charges is observed, and the dipole moment of the system increases by more than 4 D units. In some radical anions the total energy of the system as a function of the aryl-nucleofugal group distance may present a second minimum, and this may suggest that an adduct is formed between an aryl radical with the nucleofuge (or nucleophile). This adduct progresses to form the radical anion, or diffuses appart giving the free particles.

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