A theoretical approach to understanding the fragmentation reaction of halonitrobenzene radical anions[†]

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We present a semiempirical AM1 study of the radical anions of *o*-, *m*- and *p*-halonitrobenzenes and some alkyl substituted derivatives in relation to their σ–π orbital isomerism and the energy of their interconversion ($\Delta E_{\sigma\pi}$). Halobenzene radical anions are also included for comparison. The results obtained with the RHF/CI(5) formalism account for the differences observed in the fragmentation rate of these radical anions under thermal and photochemical conditions. Based on the calculated $\Delta E_{\sigma\pi}$ the intramolecular thermal electron transfer from the π system to the σ* C–X bond involved in the fragmentation of the intermediates into an aromatic radical and the anion of the leaving group occurs with considerable energy for the *p*-, *m*- and *o*-chloronitrobenzenes (**1a**–**c**) and the *p*- and *m*-bromo (**2a**, **b**) derivatives. The fragmentation of these radical anions is favoured either from the first or from higher energy excited doublet states. On the other hand, the intramolecular thermal electron transfer is favoured for the *p*-, *m*-, *o*-iodo (**3a**–**c**) and *o*-bromo (**2c**) derivatives. The results obtained for some alkyl substituted halonitrobenzene radical anions are in agreement with their known experimental fragmentation rates.

Introduction

Radical anions (RAs) of haloaromatic compounds have been proposed as intermediates in different types of reactions. The intermediates have an enhanced reactivity with respect to their parent neutral compound in the carbon–halogen bond breaking reaction,[1] which has been shown to depend on the halogen leaving group and the type of substitution present on the aromatic moiety. Their fragmentation rates, determined electrochemically[2] or by pulse radiolysis,[3] range from 10^{10} s^{-1} for phenyl halides to 10^{-2} s^{-1} for some halonitrobenzenes. Thus, while the rate of the reaction for some aryl halide RAs is too high to be measured electrochemically, the fragmentation of more stable RAs such as those of 1-bromo- and 1-iodo-anthraquinone,[4] *p*-[5–7] and *m*-bromo-[8] and *p*-[5,6] and *m*-chloronitrobenzenes[8] occurs at considerably lower rates and the reaction is favoured from their photoexcited states. Aryl halide RAs may present σ–π orbital isomerism depending on the orbital symmetry of their singly occupied molecular orbital (SOMO).[9] Such a proposal is based on theoretical and experimental evidence.[10,11] The isomerism is possible when the excitation of the unpaired electron from the singly occupied to a low lying unoccupied MO of different symmetry, gives rise to a species that differs in geometry from the initial state, both being different local minima on the ground state surface.[12] The π–σ isomerization of these RAs can thus be interpreted in terms of an intramolecular electron transfer (intra-ET) from the π system, corresponding to the generally more stable and initially formed RA, to the σ* C–halogen bond (σ RA). This reaction is possible through the avoided crossing of both electronic states, accompanied by internal coordinate rearrangement.[13] From the two possible RAs, it is proposed that only the σ dissociates into an aromatic radical and the anion of the leaving group.[10a] On the basis of these considerations, the fragmentation of haloaromatic RAs can be viewed as an intra-ET reaction [eqn. (1)].

$$\mathrm{Ar{-}X} + e^- \longrightarrow \underset{\pi\ \mathrm{RA}}{{}^{-\bullet}(\mathrm{Ar}){-}\mathrm{X}} \xrightarrow{\text{intra-ET}} \underset{\sigma\ \mathrm{RA}}{\mathrm{Ar}\overset{-\bullet}{-}\mathrm{X}} \longrightarrow \mathrm{Ar}^{\bullet} + \mathrm{X}^- \qquad (1)$$

A relatively limited number of theoretical studies have been reported on haloaromatic RAs.[14] Recently, a detailed theoretical inspection of the potential surface of the RAs of halobenzenes, halobenzonitriles and *o*-, *m*- and *p*-haloacetophenones was published.[15] In this study it is proposed, within the Marcus theory, that the difference in energy between both RAs could be correlated with their experimental fragmentation rates, considering the intra-ET from the π to the σ system as the limiting step of the cleavage reaction.[15]

In the present paper we investigate the relevant potential hypersurfaces for the intra-ET of RAs of the halonitrobenzene family and some alkyl substituted derivatives. These intermediates, which have a highly stabilised π system, fragment with relatively low rates in the ground state but can undergo a photochemical cleavage. The results obtained for the family are compared with studies performed for the halobenzene RAs for which the thermal intra-ET is favoured.[2,16]

Computational procedure

All calculations were carried out with the semiempirical AM1 method as implemented in AMPAC.[†,17] The equilibrium geometries were obtained with complete optimization without applying symmetry conditions. Stationary points were characterized by calculating their Hessian matrices with the usual criteria.[18]

The configuration interaction (CI) calculations for the ground and first excited states (generally up to the lower quadruplet) were performed with the AM1/RHF Hamiltonian within the subspace of all possible excitations of five electrons into five molecular orbitals, from SOMO − 2 up to SOMO + 2 (100 configurations, CI = 5). The hypersurfaces were obtained by varying two geometric parameters simultaneously (the C–X bond length and its dihedral angle with respect to the aromatic ring), with full geometry optimization for the $3N - 6 - 2$ remaining internal coordinates. The AM1-UHF formalism was

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[†] Key stationary points archive files for the AMPAC calculations are available as supplementary data (SUPPL. NO. 57511, pp. 68) from the British Library. For details of the Supplementary Publications Scheme, see 'Instructions for Authors', *J. Chem. Soc.*, *Perkin Trans. 2*, available *via* the RSC web page (http://www.rsc.org/authors). For direct electronic access see http://www.rsc.org/suppdata/p2/1999/1003/.

Table 1 AM1/CI Heats of formation and main geometric parameters for halobenzene radical anions[a,b]

	Chlorobenzene		Bromobenzene		Iodobenzene	
	RAπ[c]	RAσ	RAπ[d]	RAσ	RAπ*[e]	RAσ
ΔH_f	−6.9 (23.7)	31.7[f]	26.7 (59.9)	51.0 (68.5)	93.5 (100.6)[g]	65.6 (95.6)
r(C–X)	1.765 (1.77)	2.030	1.975 (1.93)	2.062 (2.06)	2.030 (2.05)	2.118 (2.16)
d(X < Ph)	150.3 (163.5)	179.8	151.6 (159.3)	180.0 (178.8)	180.0 (177.6)	157.1 (179.9)
q(X)	0.28 (−0.20)	−0.74	−0.33 (−0.21)	−0.56 (−0.48)	−0.03 (−0.02)	−0.52 (−0.41)

[a] ΔH_f in kJ mol^{-1}; bond distances in Å [r(C–X)]; C–X dihedral angle with respect to the phenyl ring in degrees [d(X<Ph)]; charge density on the halogen in atomic units [q(X)]. [b] AM1/UHF values in parentheses (see ref. 15). [c] The C_S π structure is the absolute minimum on the ground state surface. A C_{2v} plane π structure was characterized as the transition state for the interconversion between the two equivalent bent structures. The barrier for the interconversion is 17.5 kJ mol^{-1}. [d] The barrier for the interconversion of the two equivalent bent structures is 22.2 kJ mol^{-1}. [e] Excited doublet state (root 2). [f] Not clearly localized by UHF. [g] Ground state AM1/UHF.

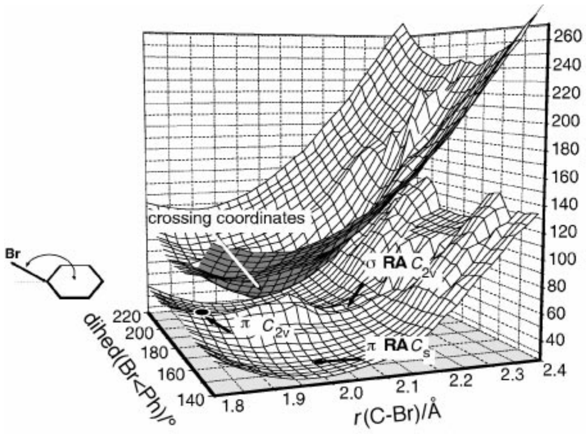


Fig. 1 Potential energy surfaces for the fragmentation of bromobenzene RA. The ground and first excited states are presented as a function of the C–X bond length and its dihedral angle, defined as the bent angle with respect to the phenyl ring along the symmetry plane. The ground state absolute minimum (π C_S RA), the π C_{2v} structure (transition state for the two equivalent bent π RAs), the σ ground structure and the approximate coordinates of the crossing point are indicated.

also applied; the procedure used to find π and σ RAs was as previously described.[12b,15]

No sensitive improvement was achieved with higher CI subspaces. On the other hand, with this level of CI good reproducibility in the symmetry ordering of the excited states was obtained. Semiempirical AM1/RHF-CI has been successfully used in studies of reactivity of open shell systems, among them, ET reactions in radical cations and reactions with biradicals as intermediates.[19,20]

Results

Halobenzene family

The RHF-CI heats of formation and main geometric parameters obtained for the RAs of the family (PhX, X = Cl, Br, I) are summarized in Table 1 together with the previous[15] AM1/UHF results. CI gives isomers with geometry, relative stabilities, charge and spin distributions similar to those of UHF. The calculated hypersurfaces are presented in Fig. 1 for bromobenzene RA, taken as being representative.

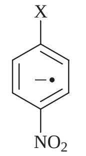
For bromo- and chlorobenzene, the most stable ground state RAs are of the π type with C_S symmetry. In these intermediates the C–X bond, considerably bent with respect to the aromatic plane, has a bond distance similar to that of the neutral molecule and the aromatic ring shows bond alternation (cyclohexa-2,5-dienyl type). The C_{2v} π species were located as the transition states for the C–X bending of the most stable C_S intermediates. The σ RAs, with a slightly elongated C–X bond, usually have C_{2v} symmetry and small C–C bond alternancies. This intermediate is a minimum on the ground state diabatic surface for X = Cl, Br and it is the most stable RA for X = I.

Even though π and σ spatial symmetry may be lost because of C–X deviation from planarity, the RAs were named on the basis of their charge and spin distribution. Thus, π RAs have the extra electron and the negative charge mainly delocalized over the aromatic system while in the σ RAs the halogen bears a higher negative charge with a radical character at the carbon of the C–X bond.

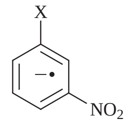
The avoided crossing of the π surface with that of the second eigenvector of our CI treatment (root 2, upper surface in Fig. 1) rationalizes the π and σ regions of the ground state surface. The change in orbital symmetry in the vicinity of the crossing zone was followed by monitoring the spin density on the carbon or the charge density on the halogen of the breaking bond. The π RA smoothly becomes σ by slight variations of the C–X bond length and dihedral angle. This is possible with relatively low energies and not far from its equilibrium geometry due to its proximity to the intersecting state (Fig. 1). As can be seen the CI predictions are similar to those of UHF in relation to the presence of π and σ regions on the ground state surfaces. These regions are connected through a dissociative adiabatic path of lower energy by CI. The adiabatic surface for the intra-ET reaction of these RAs showed dissociative endergonic behaviour. The fact that the fragmentation of the σ species is calculated as endergonic by AM1 can be ascribed to deficiencies of the method to reproduce the heat of formation of the halide anions.[21] A similar but exergonic pattern has been reported for chlorobenzene RA at the PMP2/6-31G*//UHF/6-31G* *ab initio* level.[14g,22]

Halonitrobenzenes and related compounds

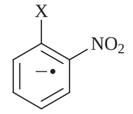
The RHF-CI and UHF main geometric parameters and heats of formation for the most relevant states of the *o*-, *m*-, and *p*-halonitrobenzene RAs (**1**–**3**) are presented in Table 2. The absolute minimum on the ground state surface, either by UHF or CI, is always π with the C–X bond and the nitro group *coplanar* or slightly twisted with respect to the phenyl plane. The coupling of the nitro and phenyl π systems is structurally evidenced by a shorter C–N bond length (around 1.41–1.43 Å) either with respect to the neutral molecule or to the σ RAs



1a X=Cl
2a X=Br
3a X=I



1b X=Cl
2b X=Br
3b X=I



1c X=Cl
2c X=Br
3c X=I

Table 2 Halonitrobenzene radical anions. AM1 Heats of formation and main geometric parameters for ground and first excited doublet states[a]

	CI					UHF				
	RA type	r(C–X)	d(X < Ph)	q(X)	ΔH_f	RA type	r(C–X)	d(X < Ph)	q(X)	ΔH_f
1a	π	1.713	180.0	−0.099	−143.7	π	1.711	180.0	−0.105	−115.3
	π*	1.732	180.0	−0.094	−45.1					
	σ*	1.922	179.9	−0.561	1.3		—	—	—	—
1b	π	1.721	179.6	−0.104	−114.8	π	1.721	180.0	−0.109	−110.7
	π*	1.716	180.0	−0.118	−35.5					
	σ*[b]	1.932	180.0	−0.567	14.0		—	—	—	—
1c	π	1.708	180.0	−0.056	−111.6	π	1.709	180.0	0.066	−87.1
	π*	1.708	178.0	−0.068	−24.5					
	σ*[c]	1.904	179.9	−0.522	19.9	σ[c]	1.906	180.0	−0.468	31.4
2a	π	1.841	167.3	−0.039	−83.4	π	1.876	179.9	−0.045	−71.0
	π*	1.889	174.9	−0.054	17.3					
	σ*	2.037	180.0	−0.511	10.1	σ	2.041	180.0	−0.433	9.7
2b	π	1.892	180.0	−0.140	−66.1	π	1.889	180.0	−0.049	−63.5
	π*	1.916	153.3	−0.279	−1.1					
	σ*	2.055	180.0	−0.520	23.8	σ	2.049	180.0	−0.442	18.7
2c	π	1.881	180.0	−0.001	−35.1	π	1.883	176.5	−0.013	−31.6
	σ*[c]	1.953	161.7	−0.383	28.7	σ[c]	2.040	180.0	−0.420	32.1
3a	π	2.018	169.9	0.018	−31.4	π	2.021	180.0	0.040	−23.5
	σ*	2.134	180.0	−0.461	40.4	σ	2.147	180.0	−0.367	38.6
3b	π	2.034	180.0	0.043	−18.4	π	2.032	180.0	0.037	−16.7
	σ*	2.150	180.0	−0.469	54.1	σ	2.154	180.0	−0.375	46.2
3c	π	2.030	180.0	0.080	16.0	π	2.033	179.7	0.071	18.5
	σ*[c]	2.153	174.6	−0.442	66.5	σ[c]	2.154	179.7	−0.355	63.7

[a] Bond distances in Å [r(C–X)]; C–X dihedral angle with respect to the phenyl ring in degrees [d(X < Ph)]; charge density on the halogen in atomic units [q(X)]; heat of formation in kJ mol^{-1} (ΔH_f). The π* and σ* RAs were localized on the first excited doublet potential surface (root 2) unless indicated. [b] Minimum on root 3. [c] Nitro group plane bent with respect to the phenyl ring. These rotamers are *ca.* 13 kJ mol^{-1} more stable than the totally planar ones.

(*ca.* 1.49–1.50 Å); the other main geometric parameters (C–X distances and degree of C–C bond alternancies) being similar to the halobenzene case. The charge and spin distribution remains mainly on the nitrophenyl moiety as indicated in Fig. 2 for all the unsubstituted halonitrobenzene RAs.

The shape of the potential hypersurface for the fragmentation of these RAs is presented in Fig. 3a for **2a**, taken as a model system. In Fig. 3 the three lower CI states (roots 1, 2, 3) are shown. The hypersurface was also monitored by following the charge density on halogen as indicated in Fig. 3b. The vertical excitation from the ground state π RA leads to excited π* and σ* electronic doublet states, the latter being of higher energy. The π* RA located on the first excited surface, [r(C–Br) = 1.889 Å and halogen–aromatic ring dihedral angle of 174.9°], crosses the σ* surface to afford a local minimum corresponding to a σ* RA [r(C–Br) = 2.037 Å and halogen–aromatic ring dihedral angle of 180.0°]. The change in charge density on halogen that accompanies this crossing can be seen in Fig. 3b. Beyond the crossing point the charge density on the halogen in root 2 increases (π*→σ*) while the inverse occurs in root 3 (σ*→π*). A similar general behaviour was observed for *m*-bromo- (**2b**) and *p*-, *m*- and *o*-chloronitrobenzene RAs (**1a**–**c**). For these RAs the σ* intermediates are of higher energy than the π* isomers with the exception of **2a**.

The intra-ET of these RAs is calculated as dissociative on the ground state surface with a gradual charge displacement from the nitrophenyl π system to the σ* C–X bond. The crossing between both electronic states (root 1 and 2) requires higher energies than for the halobenzene RAs and is located at longer C–X distances [*e.g.*: C–Br *ca.* 2.4 Å, see Fig. 3a and b (ground state)].

For **1a**–**c** and **2a**,**b**, the UHF energy difference between both RAs ($\Delta E_{\sigma\pi}$) or the CI energy difference between the π RA and the point at which the crossing with the σ* potential surface occur follow the order: *p*-bromo (**2a**) ≅ *m*-bromo (**2b**) < *p*-chloro (**1a**) ≅ *o*-chloro (**1c**) < *m*-chloronitrobenzene (**1b**) as shown in Table 3. As within CI the crossing point cannot be clearly determined in all cases, the energy difference between the π and the σ* RAs was used as indicative.

Table 3 AM1 $\Delta E_{\sigma\pi}$ for halonitrobenzene radical anions and experimental fragmentation rates

	$\Delta E_{\sigma\pi}$/kJ mol^{-1}		k_{frag}/s^{-1}	
	CI[a]	UHF	Thermal[b]	Photochemical[c]
1a	145.0		$\leqslant 10^{-2}$	0.041
1b	[d]		$< 5 \times 10^{-3}$	0.03 [0.022]
1c	131.5	118.5		
2a	93.5	80.7	$\leqslant 10^{-2}$ (1.4×10^{-3})	0.07 [0.052]
2b	89.9	82.2	$< 5 \times 10^{-3}$	0.12 [0.10]
2c	63.8	63.7	(250)	
3a	71.8	62.1	1.1 (7.17)	
3b	72.6	62.9	0.3 (0.92)	0.37 [0.40][e]
3c	50.5	45.2		

[a] Taken between the heats of formation of the π ground state and first σ* RA (see text). [b] In acetonitrile, see refs. 5–8. Values determined in DMF (in parentheses), see refs. 25, 26. [c] Fragmentation rates at $\lambda_{330-335}$ nm. Fragmentation rates at $\lambda_{470-490}$ nm in brackets (see refs. 5–8). [d] Higher than **1a**. A σ* state appears on the 3rd excited surface and its crossing with the ground state cannot be determined. [e] Mixed photochemical and thermal rate constant (ref. 8).

A different general pattern is observed for *p*-iodo-, *m*-iodo-, *o*-iodo- (**3a**–**c**) and *o*-bromonitrobenzene (**2c**) RAs. For these intermediates the first excited surface is of the σ type. The first two states calculated for **3a** are shown in Fig. 4. The relevant crossing between the π ground and the σ* states requires lower energies than for the above discussed partners. The lowest corresponds to the *ortho* isomers and from them to the iodo derivative (**3c**) (Table 3).

A special feature was observed for the *ortho* RAs. In all the π intermediates the rotation of the nitro group is restricted due to its coupling with the phenyl π system. This is not the case for the σ structures, in which the C–N bond elongates.[23] The σ RAs of the *ortho* derivatives **1c**–**3c** can reach a less repulsive conformer with the plane of the nitro group twisted (CI) or perpendicular (UHF) to the phenyl plane. Thus, destabilization due to repulsion with a steric *ortho* group affects the stability of the π and σ RAs to a different extent. It raises the energy of the

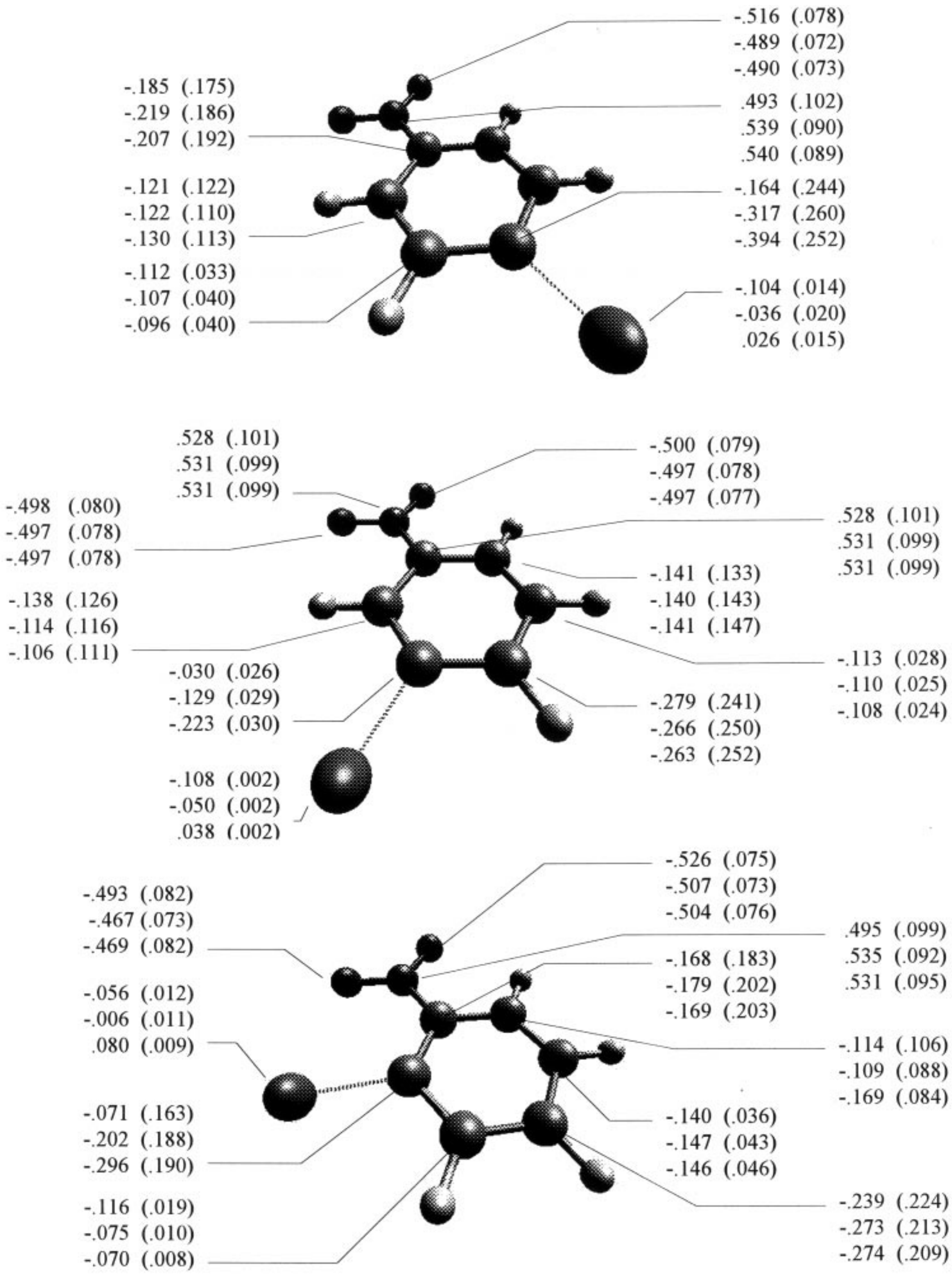


Fig. 2 Point charges and π spin density (in parentheses) for all the halonitrobenzene ground state RAs. For each geometry the data presented correspond from top to bottom to X = Cl, Br, I. A small σ spin density contribution can arise in those intermediates in which the halogen is considerably bent.

coplanar π RAs leading to a net decrease in the $\Delta E_{\sigma\pi}$ difference. The effect is stronger the bigger the halogen. A similar behaviour has been reported for *o*-haloacetophenone RAs.[15] The study was extended to include alkyl substituted halonitrobenzene RAs. The ΔH_f values calculated for these intermediates are presented in Table 4. The presence of alkyl substituents *ortho* to the halogen or the nitro group usually decreases the $\Delta E_{\sigma\pi}$ with respect to the unsubstituted parent halonitrobenzene RAs. This effect is more important the bigger the alkyl group (Table 4).

Discussion

The $\Delta E_{\sigma\pi}$ calculated for halobenzene, haloacetophenone and halobenzonitrile RAs, has been shown to correlate with their experimentally determined fragmentation rates, considering the intra-ET as the rate limiting step of the cleavage reaction [eqn. (1)].[15,24] The results presented here follow this general trend.

According to the present study the energy required for the π ground state to cross the σ upper surface is considerably higher for the halonitrobenzene than for the halobenzene RAs and so the latter will undergo a very fast thermal fragmentation in the order chloro < bromo < iodobenzene (k_{frag} from $4.0 \times 10^7\ \text{s}^{-1}$ for chlorobenzene RA up to diffusion controlled for iodobenzene RA).[2,16] On the other hand, it would be expected that the *o*-bromo- and all the iodonitrobenzene RAs will undergo a lower thermal fragmentation, following the relative reactivity order: *m*-I < *p*-I ≪ *o*-Br < *o*-I. This is in agreement with the thermal fragmentation rate constants known for these RAs (Table 3). The correlation between the $\Delta E_{\sigma\pi}$ calculated for these compounds and the logarithm of their thermal fragmentation rate, determined in different solvents and under different experimental conditions,[6–8,25,26] is shown in Fig. 5 in which the alkyl substituted derivatives are included.[27]

The $\Delta E_{\sigma\pi}$ calculated for the thermal intra-ET step of the bromo (**2a**,**b**) and the chloro (**1a**–**c**) RAs are the greatest. Accordingly, it is known that these RAs do not fragment thermally under the previous experimental conditions and timescale. For example, the *p*-bromo- (**2a**) fragments *ca.* 6000

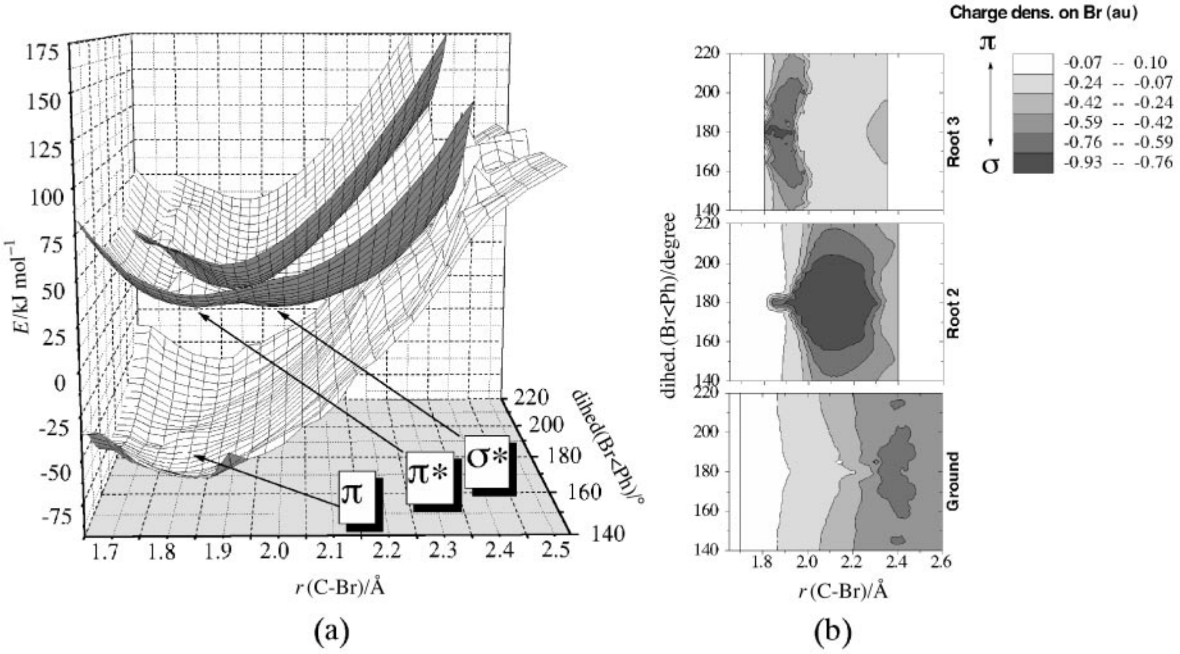


Fig. 3 (a) First three calculated adiabatic surfaces for *p*-bromonitrobenzene RA (**2a**). The π ground state RA and the two excited π* and σ* RAs are indicated. (b) The σ (dark) or π (light) zones of the surfaces shown in (a) are evidenced on the halogen point charge contour plots.

Table 4 AM1 Heat of formation and experimental fragmentation rates of substituted halonitrobenzene RAs

$R(X)C_6H_4NO_2$	RA type	ΔH_f/kJ mol^{-1}		k_{frag}/s$^{-1\,a}$
		CI	UHF	
X = 3-I	π	−41.9	−41.4	9.8
R = 6-Me	σ	21.7	23.3	
X = 4-I	π	−53.7	−47.1	1.4
R = 3-Me	σ	16.2	13.0	
X = 3-Br	π	−93.1	−91.9	0.085
R = 4-Me	σ	−4.7	−11.6	
X = 3-Br	π	−116.3	−115.0	0.15
R = 4-*t*-Bu	σ	−35.6	−45.8	
X = 4-Br	π	−101.0	−95.8	0.013
R = 3-Me	σ	−16.4	−17.4	
X = 4-Br	π	−123.7	−120.1	3.1
R = 3-*t*-Bu	σ	−48.4	−53.3	

[a] From ref. 27.

times more slowly than the *p*-iodo (**3a**) RA. Other studies confirm the stability of the *m*-chloro (**1b**) RA which has a lifetime of several minutes and can even accept a second electron to form a stable dianion under adequate experimental conditions.[28] The fragmentation of these RAs has been reported to be favoured photochemically.[5–8]

Since light absorption for the originally formed π RA is a Frank–Condon vertical transition, it is expected that the energy and orbital symmetry of the excited surfaces at the equilibrium geometry of the π ground state RA should play an important role in the photochemical fragmentation of these intermediates. The following general trend has been observed in the energy ordering of the diabatic excited states of RAs **1a**–**c** and **2a**,**b** within the active CI subspace: (*i*) a lowest excited doublet of π type (unpaired electron in the SOMO + 1 MO); (*ii*) excited doublet of the σ type with the unpaired electron in the SOMO + 2 MO; (*iii*) first quadruplet and (*iv*) a π doublet very close in energy to the quadruplet formed by excitation of an electron from SOMO − 1 to SOMO.

One photochemical pathway may be the high energy fragmentation through a doublet (*iv*)–quadruplet (*iii*) intersystem crossing with the possibility that the latter metastable state would decay to a σ* surface (Scheme 1, part a). This is possible for almost the whole set of compounds under study and for which a σ* minimum of lower energy than the quadruplet was characterized. *p*-Cyanonitrobenzene RA which, based on our

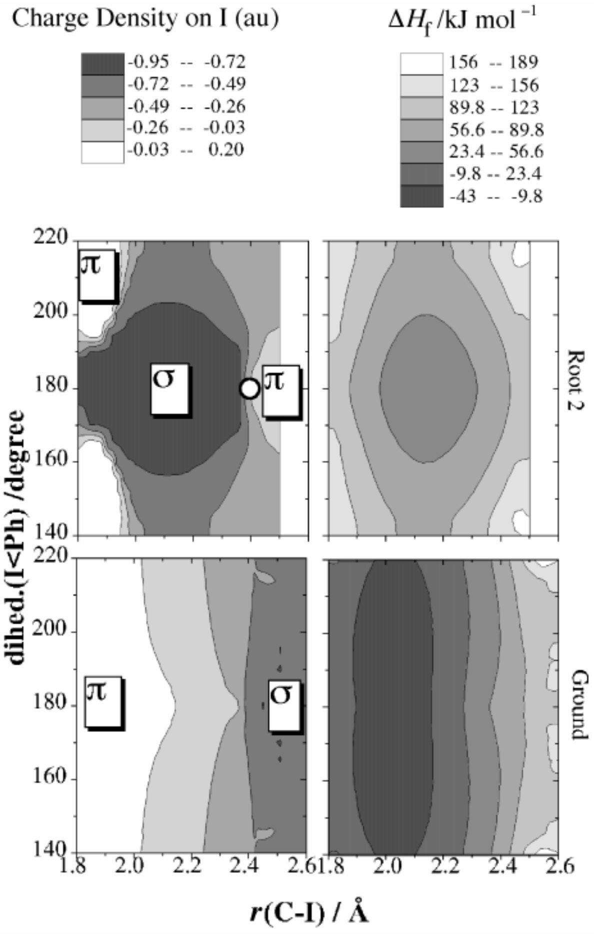


Fig. 4 Charge density on halogen (left) and energy (right) contour plots for the fragmentation of the *p*-iodonitrobenzene RA (**3a**). The minima on the ground and on root 2 (π and σ* respectively) are presented together with their crossing point (light circle on the charge density contour plot).

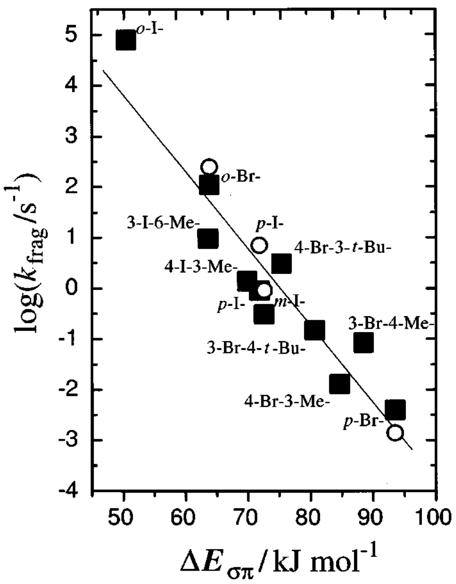
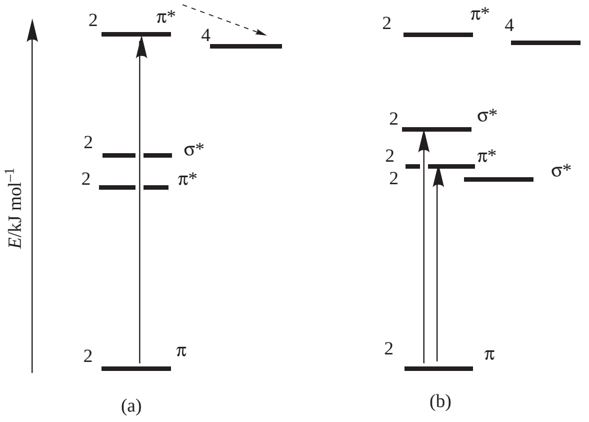


Fig. 5 Correlation between the logarithm of the experimental rate constant and the AM1-CI values of $\Delta E_{\sigma\pi}$ for substituted and unsubstituted halonitrobenzene RAs in DMF: (■) from ref. 27; (○) from different experiments, refs. 25, 26.

calculations, lacks such a σ* state, does not fragment thermally or photochemically.[8]

At lower energies the photochemical fragmentation could involve promotion to a π* state that can cross to a close σ* doublet or direct promotion to a σ* doublet state (Scheme 1, part b). These pathways are spin allowed, at variance with the doublet–quadruplet crossing and so they are expected to be favoured. For example, **2a** and **2b** which have π* and σ* states close in energy, can be effectively dehalogenated at 480 nm, this band being more effective than that of high energy at 330 nm.[5–8] For the *p*-chloro- (**1a**), it was not possible to find a vertical σ* state, so it is expected that this RA would fragment through a doublet (*iv*)–quadruplet (*iii*) intersystem crossing of high energy. These results are in agreement with recent experimental information which indicates that **1a** does not fragment at 480 nm but at 330 nm.[6]



Scheme 1

Conclusions

The intra-ET in RAs of halobenzenes was found to be a dissociative process which occurs through the avoided crossing of the π and σ states close in energy according to our AM1/RHF-CI treatment.

The CI treatment for halonitrobenzene RAs allowed us to explain the pathway followed by the family upon fragmentation under thermal conditions, in terms of the $\Delta E_{\sigma\pi}$ calculated, and for the photoinduced reaction, in terms of the electronic nature of the excited potential surfaces. Even when their $\Delta E_{\sigma\pi}$ energy difference is considerably bigger than in families previously studied, a good correlation with the experimental fragmentation rates was obtained with the inclusion of some alkyl substituted derivatives. The presence of these substituents *ortho* to the halogen or the nitro group usually decreases the $\Delta E_{\sigma\pi}$. This effect is in agreement with the fragmentation rates known for the intermediates.

In general, the CI results are equivalent to those obtained within the UHF formalism but the former allowed us to build a more complete picture of the intra-ET process through the calculation of all the adiabatic states involved in the reaction.

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