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One Electron More, One Electron Less. What Does It Change? Activations Induced by Electron Transfer. The Electron, an Activating Messenger.

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OUTLINE

Introduction 6194
1. One electron more 6197
  1.1. Diatomic molecules 6197
    1.1.1. Selected cases of homonuclear diatomic molecules 6197
      1.1.1.1. H_2, H_2^-, H_2^+, H_2^* 6197
      1.1.1.2. One electron added to heavier homonuclear diatomic molecules 6200
    1.1.2. Selected cases of heteronuclear diatomic molecules 6204
  1.2. Triatomic and tetraatomic molecules 6207
  1.3. Pentaatomic molecules with a central atom 6209
  1.4. More complex molecules classified by radical types 6210
    1.4.1. σ^* type radical anions without unsaturation in α– or β-position 6211
    1.4.2. σ^* type radical anions α– or β– to an unsaturation 6212
      1.4.2.1. Approaches to selectivity in the cleavage of σ^* anions containing unsaturations. The reactive mixed valence approach 6212
      1.4.2.2. The very rapid formation of some 3e bonds. Consequences for the design of ETC system 6223
    1.4.3. π^* type radical anions 6225
      1.4.3.1. Structural modifications caused by the addition of one electron to a π system 6225
      1.4.3.2. Associative activation in the reactivity of π^* radical anions 6228
        1.4.3.2.1. Associative activation toward σ systems 6228
        1.4.3.2.2. Associative activation toward π systems 6228
    1.4.4. π and σ radicals 6232
      1.4.4.1. β-cleavage in radicals, carbenium ions and carbanions 6232
      1.4.4.2. Reactive mixed valence approach applied to β-scission. Captodative *versus* polar approach 6236
      1.4.4.3. The strange case of benzyne *versus* σ radicals 6239
      1.4.4.4. α-cleavage in π radicals and their hyponomers 6240
      1.4.4.5. Associative activation in σ and π radicals 6241
      1.4.4.6. Aspects of the reactive mixed valence approach applied to bimolecular homolytic substitution (SH2) 6245
      1.4.4.7. Remarks on the nomenclature of mechanisms. Outer-sphere.Inner-sphere. Electron shift. SH2. SN2 viewed in perspective 6247
2. One electron less 6251
  2.1. Homonuclear and heteronuclear diatomic radical cations 6251
  2.2. More complex molecules classified by radical types 6251
    2.2.1. σ type radical cations without unsaturation 6253
      2.2.1.1. Radical cations of alkanes and stannanes 6253
      2.2.1.2. Radical cations of alkyl and stannyl halides 6255
      2.2.1.3. Radical cations of strained hydrocarbons 6257

2.2.2. σ type radical cations obtained from the ionization of a lone pair 6258
    2.2.2.1. General considerations 6258
    2.2.2.2. Radical cations centered on N 6259
2.2.3. Radical cations with unsaturation 6264
    2.2.3.1. Associative activation 6264
    2.2.3.2. Dissociative activation 6267
3. Prospective 6272

Introduction

For a long time, chemists have enjoyed counting electrons and correlating the number obtained with some observable properties. It began with rare gas inertness[1] in atoms. It then continued with molecules and the octet rule[2], the aromatic sextet[3], the Hückel approach to aromaticity[4], the 14e rule[5], the isoelectronic relationship[6], the 18e rule for transition metal-centered organometallic complexes (EAN: Effective Atomic Number)[7] and to even larger numbers, once the structural chemistry of clusters was better understood[8,9]. All these different ways of counting share a common feature: it seems as if chemists are unable to count one by one, and all these counting techniques involve only even numbers. Exceptions to this would be the apparent special stability associated with half-filled subshells (p^3, d^5)[10a] and the prediction of ion bond lengths related to those of the corresponding neutral systems[10b].

It may seem strange that a question as simple as the one formulated in the title has never been addressed as such in its entirety. We began to realize this while writing a paper[11a] whose main purpose was to show the occurrence of electron transfer catalysis (ETC) beyond the artificial barriers of organic, inorganic and organometallic[11b] chemistry. During this study, the variety of substrates involved[14], the transformations[12] and the chemical compositions[13] appeared to be related by a single unique idea: reactivity induced in a substrate by the attachment or the removal of an electron. The idea of comparing the reactivity of molecules differing only by one electron, simple as it is, was not readily accepted. We still remember a discussion we had with an excellent physical chemist who defended the point of view that, comparing the reactivity of molecules whose only difference was the electron number was like comparing apples and oranges. More precisely, his point was that the only "fruitful" comparisons in chemistry had come out of comparisons involving small perturbations (Hammett's approach, Taft's approach, PMO approaches etc..). The addition or removal of an electron is such an important change however, that no useful information should emerge from comparisons involving species differing only by their electron number. Our reply was that, as long as the question has not been studied, it is difficult to guess whether or not it would prove useful. Thus, the main incentive for this Tetrahedron Report is:

1) to collect the widely dispersed relevant information

2) to extract valuable rules from the presently available material

3) to underline the unanswered questions and draw attention to areas where there is a lack of knowledge.

There is a lack of concise terminology which is available to describe one electron reduced or one electron oxidized counterparts of a given molecule. Throughout the text, we will use the expressions hypernomers and hyponomers to indicate molecules whose only difference is their electron number (plus or minus one electron). For example, the radical cation of benzene is its hyponomer, and the radical anion of benzene is its hypernomer. The hypernomer of a neutral radical is an anion. and its hyponomer is a carbocation.

One of the most clear examples known originates from the chemistry of transition metal complexes[15] :

$$[Cr^{III}(H_2O)_6]^3 + H_2O^{\bullet} \xrightarrow[k = 3 X 10^{-6} Mol^{-1}s^{-1}]{} [Cr^{III}(H_2O^{\bullet})_6]^{3+} + H_2O \quad [1]$$

$$[Cr^{II}(H_2O)_6]^{2+} + H_2O^{\bullet} \xrightarrow[k = 10^{9} Mol^{-1}s^{-1}]{} [Cr^{II}(H_2O^{\bullet})_6]^{2+} + H_2O \quad [2]$$

In this example, we can see that a substrate undergoes the same reaction; the only difference is the oxidation state of chromium. There is a large increase in the rate of ligand substitution associated with the addition of an electron. The addition (substraction) of an electron to (from) a substrate often changes its reactivity so dramatically that the normal reactivity for a compound is completely overshadowed by a different kind of reactivity in its hyponomer or hypernomer. No quantitative prediction of reactivity for a given transformation is possible.

A shorthand term for the "enhancement of reactivity" is the word "activation"[16]. This word covers a wide range of situations. Its most general meaning is "to render a substrate reactive which, under the same conditions of temperature, pressure and medium, would have been inert". We would now like, to make the term more precise by specifying that induced reactivity corresponds to either the same overall transformation (homoactivation, see preceding example of equations [1], [2]) or to an overall transformation completely absent in the one electron reduced (oxidized) species. This second case often corresponds to an act of Umpolung[17a] but, the term "Paractivation" must be introduced to account for all the observed facts (**Section 1.1.1.2.**). "Homoactivation", "Umpolung" and "Paractivation" are all covered by the general term "Activation." To keep this Report within a reasonable length, "Umpolung"[17b] will be treated far more superficially than "Homoactivation". Later. we will speak of associative activation when the addition or removal of an electron increases the tendency of the substrate to form a new bond. The expression dissociative activation will indicate cases where addition or removal of an electron increases the tendency towards bond cleavage (either mono or bimolecular) in the substrate. Partial weakening of a bond will also be labelled "dissociative activation". This can be associated with electron attachment on a double bond which facilitates $E \rightleftarrows Z$ stereomutation. This is an example of bond weakening without total cleavage of the bond.

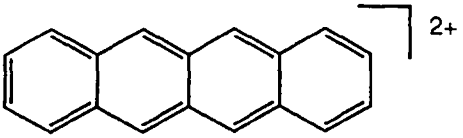
The emphasis of this Report will be on organic substrates, but several examples from inorganic or organometallic fields will be included when necessary. Others authors[18] as well as ourselves[11-14] have shown the benefit of comparisons between inorganic and organic chemistry and the transposition of concepts. In the field of mechanisms, each area has developed its own vocabulary. It is worthwhile to recall the correspondences shown in Table 1[19,20]:

Table 1: Correspondence between inorganic and organic nomenclature for substitution mechanisms.

	Evidence for an intermediate with a lower coordination number	No direct evidence for an intermediate		Evidence for an intermediate with a higher coordination number
Stoichiometric mechanism	D	I		A
Intimate mechanism	D	I_D	I_A	A
Ingold definition	SN1 (Lim.)	SN1	SN2	SN2 (lim.) SNAr
Sensitivity rate to nature of entering group	Rate independent of nature of entering group		Rate dependent on nature of entering group	
Homolytic substitutions	SH1	SH2 I.s.e.t.		Associative SH2 (see ref. 331) I.s.e.t

Extrapolated from M.L. Tobe, Ref. 20a and extended to Paramagnetic Species. D stands for Dissociative; I for Interchange; A for Associative; I_D for Dissociative Interchange; I_A for Associative Interchange; SN1 for Nucleophilic Monomolecular Substitution; SN2 for Nucleophilic Bimolecular Substitution; SNAr for Nucleophilic Substitution on Aromatic Substrates; SH1 for Monomolecular Homolytic Substitution; SH2 for Bimolecular Homolytic Substitution; I.s.e.t. for Inner-sphere Electron Transfer; see **Section 1.4.4.7.** for discussion of this Table .

Guthrie[21] has proposed a nomenclature which takes these considerations into account. Unfortunately, these proposals have not yet been adopted by the chemical community.



: B^{2+}

$$B^{2+} \longrightarrow B^{1+} \longrightarrow B \longrightarrow B^{-1} \longrightarrow B^{-2} \qquad \text{(ref. 22c)} \qquad [3]$$

When redox equilibria cover several successive oxidation states of the same substrate, the situation is described by the term "redox series"[22a], or by "ionic series" in theoretical chemistry[10b]. Some structural aspects have been discussed previously [22b-g].

Which species should be the starting point for the electron count so that the question of "one electron more, one electron less" can be examined ? The octet rule[1] will be used as much as possible to give the "natural state" of the substrate. Some substrates, however, do not conform to these rules[23,24]. So, we will also rely on experimental data to determine the "natural" state.

1. One Electron More.

1.1. Diatomic molecules.

1.1.1. Selected cases of homonuclear and heteronuclear diatomic molecules.

1.1.1.1. H_2, H_2^-, H_2^+, H_2^*.

The title of this section shows that, for this molecule, we intend to put aside the general dichotomy of this Report (one electron more, one electron less). Our aim for this simple molecule will be to:

1) find analogies between the different states

2) try to outline the appropriate models for a consistent treatment of sets of hyponomer-neutral-hypernomers species (redox [22a] or ionic series[10b]).

In **Figures** 1 and 2, the potential energy curves of H_2, H_2^-, and H_2^+ and some excited states of these species are represented. This drawing is a synthesis of figures 14 in ref. 25 and figures 13.1 and 13.2 in ref. 26 . The potential energy curves for H_2^- are the result of theoretical calculations performed to explain electron scattering observations[27]. The state labelled $a^2\Sigma_g^+$(11.4 eV) (labelled **3** in **Fig. 1**) corresponds to the electron in the field of the $c^3\pi_u$ excited state (labelled **7** in **Fig. 1**) and called parent state of H_2. The main configuration involved in this H_2^- state seems to be $(1s\sigma_g)(2p\pi_u)^2$; this configuration reminds us that the elaborate treatment of H_2 has to use a basic set of atomic orbitals which includes orbitals of higher energy as well as the classic 1s atomic orbitals[28a]. Here it is worthwhile to recall that a fair description of radical ions usually requires[29] interaction of the configuration; therefore, $(1s\sigma_g)(2p\pi_u)^2$ should be considered as a label rather than as an accurate description.

In terms of the simplest LCAO model, the description of the $^2\Sigma^+_g$ resonance state of H_2 would have only one electron in the stablest molecular orbital and two electrons in molecular orbitals of higher energy. Such a description comes as a surprise for the average chemist used to thinking in terms of bonding and antibonding orbitals; indeed, these terms suggest that such a species could not possibly exist. Nevertheless, the internuclear distance for this $^2\Sigma^+g$ state of H_2^- has been calculated to be 0.97 Å[26]; this value is 1.31 times that measured for ground state H_2 ($^1\Sigma^+_g$) and 0.94 times that evaluated[30a] for the $c^3\pi_u$ parent state. This $^2\Sigma^+_g$ state of H_2^- is not dissociative, and from the shape found in **Figure** 1, D_0 for this state could be estimated as being approximately 2eV (~ 50 kcalMol^{-1}).

This value is approximate because even fairly elaborate treatments[31] of H_2 give unsatisfactory results[28a] for D_0 of H_2. A simple MO (molecular orbital) description would have hinted at the similarity of geometries associated with $c^3\pi_u$ (excited state of H_2) and $^2\Sigma_g{}^+$ state of H_2^-. Indeed, the electronic excitation in excited H_2 leaves a hole in a bonding MO and populates an antibonding one. In contrast, the radical anion H_2^- is described as having two electrons in the bonding MO and one in an antibonding MO. The bond order for H_2^* therefore appears to be 0, and that of H_2^- to be 1/2. This expectation for geometries is not substantiated by the curves 2 and 7 in **Figure 1**: the distance between H nucleus is greater for the $^2\Sigma^+{}_g$ state of H_2^- than for the $c^3\pi_u$ state of H_2.

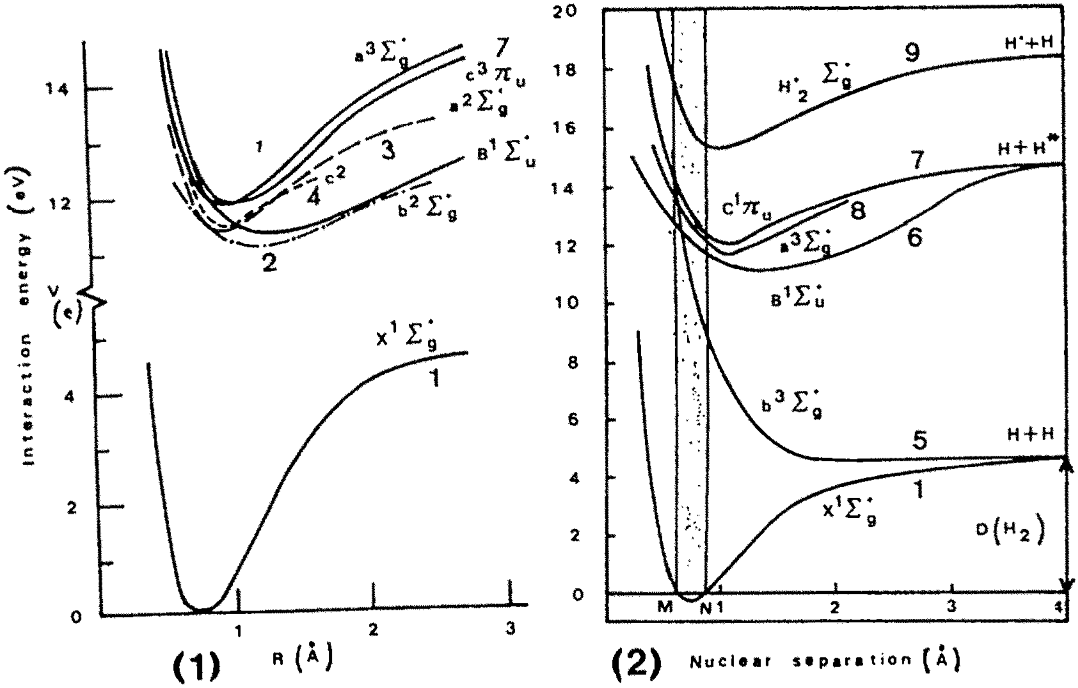


Figure 1 and 2: **Relative situations of ground and excited states of H_2 and its hypernomer and hyponomer in their fundamental and excited states.**

(1): ground and excited state of H_2 (full line) *plus* ground and excited states of H_2^- (broken line); (2): ground state of H_2 *plus* excited states of H_2 *plus* ground state of H_2^+. If (2) was extended at higher energies, a dissociative $^2\Sigma_u{}^+$ state of H_2^+ would appear (crossed by the Franck-Condon region in the range 27-32 eV). This Franck-Condon region appears as a shaded area in (2). Described states: 1 $X^1\Sigma_g{}^1$ of H_2; 2 $b^2\Sigma_g{}^+$ of H_2^-; 3 $a^2\Sigma_g{}^+$ of H_2^-; 4 $c^2\pi_u$ of H_2^-, apparent only in D_2 molecules; 5 $b^3\Sigma_u{}^+$ lowest triplet state of H_2; 6 $B^1\Sigma_u{}^+$ singlet excited state of H_2; 7 $c^1\pi_u$ singlet excited state of H_2; 8 $a^3\Sigma_g{}^+$ lowest stable triplet state of H_2; 9 $^2\Sigma_g{}^+$ ground state of the molecular ion H_2^+.

Three dissociative attachment processes to H_2 have been studied[58a]. None of them is displayed in **Fig.1** because, here, the unstable state reached after the electron/H_2 collision directly dissociates (no actual resonance). The energies of electrons used in creating all the preceding resonance radical anion states and dissociative attachment processes are far from the thermal energies used in "beaker chemistry". They nevertheless teach us that there are already several different states for the hypernomer of the simplest known diatomic molecule. The measurement of their equilibrium geometry or their potential energy curves as a function of internuclear distances suggests that the system of two protons better supports a cloud of 3 electrons than the simple bonding-antibonding LCAO model would have suggested.

Interestingly, the set of hyponomer states for H_2 lies at a higher energy than the set of hypernomer states. Indeed, in **Fig. 2** the $^2\Sigma^+_g$ state of H_2^+ (ground state) lies at about 15eV above the ground state of H_2 (curve 9). It is not dissociative, as Franck-Condon transitions from H_2 reach a part of the H_2^+ potential energy curve at a lower point than the continuum of the dissociation leading to H^+ and H. The dissociation energy of H_2^+ amounts to 2.79 eV(≈64 kcalMol^{-1})[28b]; this value would suggest that adding an electron to H_2 destabilizes it more than substracting one does ($D_0 \approx$2eV for H_2^- resonance at 12eV)[27a]. This concurs with the simplest MO models where the interaction of two atomic orbitals yields two molecular orbitals: one bonding and the other antibonding. The second one is generally more destabilizing than the first one is stabilizing.

Let us now turn to the second aim of **Section1.1.1.1**: "outline appropriate models to consistently treat sets of hyponomers-neutral-hypernomers species". On the one hand, some authors defend the point of view that only very elaborate calculations may be trusted for this type of problem[33]. For example, Gutsev and Boldyrev[33a] recall that to obtain an agreement between calculated and experimental Electron Affinities (EA) within 0.1-0.3 eV (2-6 kcalMol^{-1}), it is necessary to "use bases not less than double zeta with inclusion of diffuse and polarization functions as well as to account for all the terms of the pertubation theory up to the fourth order or, equivalently, all the singly and doubly excited configurations in the configuration interaction expansion". For the calculation of EA for larger systems, these authors estimate that the Hartree-Fock-Roothan method[34] provides Electron Affinity with an inaccuracy of 3-4 eV (70-100 kcalMol^{-1}). They therefore prefer the Xα method[35] for which they estimate this inaccuracy to be only 0.5-1eV (11-23 kcalMol^{-1}). For a chemist, the figures associated with this degree of inaccuracy are amazingly large, even for the best treatments. The same type of problem limits the treatment of positive ions created by ionization of neutrals, and Eland[36a] clearly discusses them with respect to photoelectron spectroscopy. The still unsatisfactory state of the field is illustrated by the number of different approximate treatments of the problem[37-46].

Semi-empirical theoretical methods have also been used to rationalize physical or chemical evolution in redox series[22b]. The general shapes of polyatomic neutral-hyponomer-hypernomer sets of species may often be satisfactorily[47] considered in terms of the simple EHT treatment (**Section 1.2.**)[48]. In a study on the use of EHT calculated HOMO and LUMO, we found a good correlation between *ab initio* and EHT calculated HOMO. A limited set gives an r (correlation coefficient) of 0.930, and this could be improved if compounds with an HOMO greater than 12.5 eV were excluded (also iodo and bromo derivatives are poorly treated[50]). Thus, both elaborate and semi-empirical models are significant so we will follow the philosophy stated in the preface to Burdett's book[47] "to use molecular orbital results from much cruder molecular orbital methods.... and try to find a symmetry or overlap explanation whenever possible". When elaborated treatments are available, then we will try to give the reference. Finding an explanation is not equivalent to finding the explanation.

1.1.1.2. One electron added to heavier homonuclear diatomic molecules.

For all the species concerned, the following formula can be used:

$$B.O. = 1/2\,(N_B - N_A)$$

N_B number of valence electrons occupying bonding orbitals

N_A number of valence electrons occupying antibonding orbitals.

These bond orders and other information concerning diatomic homonuclear molecules are summarized in **Table 2**. In **Figure 3**, the MO diagrams calculated using EHT are given.

To find whether the theoretically calculated EA is negative or positive, it is simply necessary to consider the energy of the neutral MO where the electron can go to obtain the corresponding radical anion (**Fig. 3**). For example, in the case of Li_2, the LUMO is at -4.57 eV; therefore, the electron affinity of Li_2 should be positive in agreement with experimental results (**Table 2**). There is a high concordance for the whole series of homonuclear diatomic molecules (**Table 2** *vs* **Fig. 3**).

J.P. Lowe[51] proposes the following qualitative rule. If the LUMO of A_2 is bonding then $EA(A_2) > EA(A)$. If the LUMO is antibonding, then, $EA(A_2) < EA(A)$. This qualitative rule provides the correct EA trends for 12 out of the 13 homonuclear diatomic molecules examined (Li_2 is the exception).

The comparison of Li_2^- and H_2^- makes it possible to correct an inaccurate statement sometimes found in literature. This statement is that stronger bonds better withstand the addition of an electron when dissociation is considered. That this is clearly not true is illustrated by the following figures: dissociation energies D_0^0: (H_2) 103.25 kcalMol^{-1}; (Li_2) 25,3 kcalMol^{-1}; nevertheless, the $^2\Sigma^+_u$ state of H_2^- is rapidly dissociative (**Section 1.1.1.1.**), while the dissociation energy of the Li_2^- ground state (20 kcalMol^{-1}) is just slightly less than that of Li_2[53]. Along the same lines, Li_2^- internuclear equilibrium distance is only 12% longer than that of Li_2 (respectively 3.1Å and 2.67 Å). This example concurs with the simple LCAO rule of the thumb: the greater the antibonding character of the LUMO welcoming the electron, the higher the destabilizing effect of the bond associated with this electron addition.

Table 2: Experimental and theoretical data on diatomic homonuclear molecules and their hypernomers.

	H_2	Li_2	B_2	C_2	N_2	O_2	F_2
Bond order in the neutral	1	1	1	2	3	2	1
Equilibrium internuclear distance a)	0.74	2.67	1.59	1.31	1.10	1.21	1.43
D_0^0 (eV) a)	4.476	1.03 or 1.05g)	2.84g)	(3.6) or 6.25g)	7.37 or 9.75g)	5.08	< 2.75 or1.59g)
Ground state in the neutral a)	$^1\Sigma_g^+$	$^1\Sigma_g^+$	$^3\Sigma_g^-$	$^3\pi_u$	$^1\Sigma_g^+$	$^3\Sigma_g^-$	$^1\Sigma_g^+$
Energy of MO where the electron is added b)	4.2	-4.57	-10.0	-11.6	-13.0	-12.9	-10.7
Energy of the AO of the element in the separated atom limit	-13.6	-3.5	-8.5	-11.4	-13.4	-14.8	-18.1
Electron Affinity (eV) c) (experimental)	< O	0.35	1.8	3.3	- 1.8	0.4	2.8
Calculated EA sign	-	+	+	+	+	+	+
Eq. Distance in the hypernomer (radical anion)	d)	3.10 e)		1.27 e)	1.17 f)	1.25 g) j)	h)
Ground state hypernomer	$^2\Sigma_u^+$			$^2\Sigma_g$	$^2\pi_u$	$^2\pi_u$	$^2\Sigma u^+$
Bond order radical anion	0.5	0.5	1.5	2.5	2.5	1.5	0.5
D_0^0 (eV) in the hypernomer	1.5i)	0.98i)		8.5i)	8.2i)	4.05i)	1.3i)

a) From ref. 30 b b) in eV (see **Figure** 3) c) From ref. 33b d) From ref. 27a
e) Ref. 57a f) Ref. 59 g) Ref. 61, 66 h) Ref. 64, 72
i) taken from ref. 51 j) For reviews on O_2^- see ref. 67.

For theoretical calculations on these diatomic molecules and their hypernomers, see: H_2 (28, 31), H_2^- (27); Li_2 (52), Li_2^- (53); B_2 (54), B_2^- (55); C_2 (56), C_2^- (57); N_2 (58), N_2^- (60); O_2 (61), O_2^- (62); F_2 (63), F_2^- (64). Although not stable, Be_2 has been calculated (68) as has Be_2^- (69). More data are available in ref. 59.

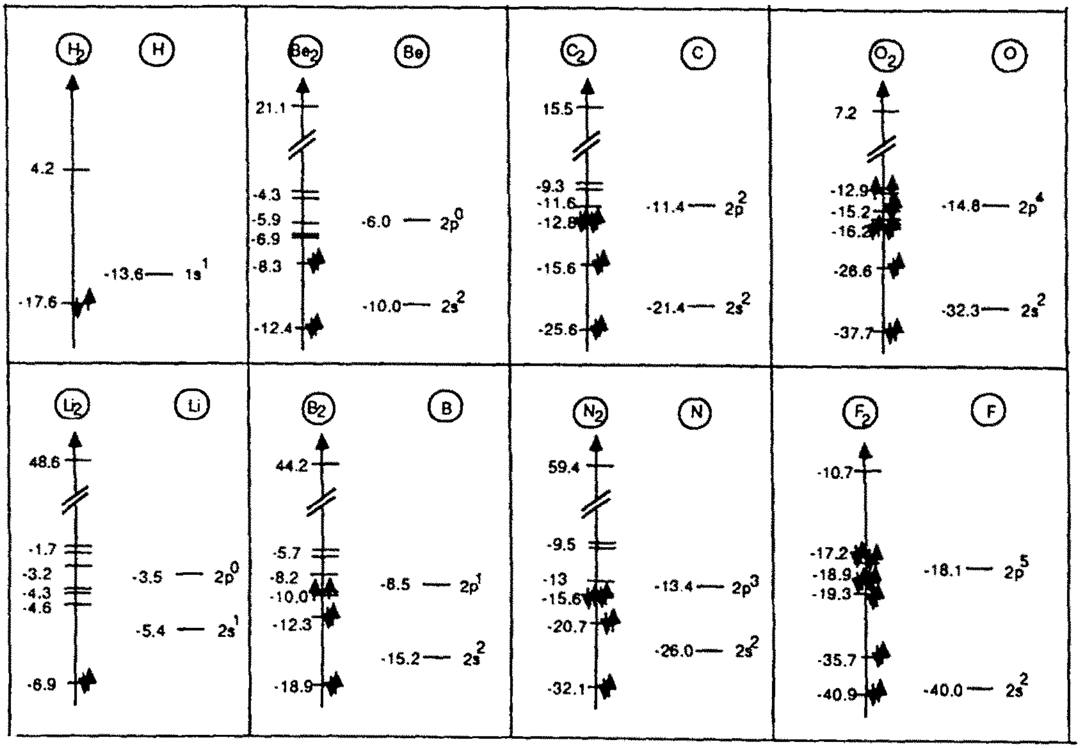


Figure 3 : MO diagrams of homonuclear diatomic molecules (energies in eV)

Table 2 compares the properties of homonuclear diatomic molecules with the properties of their hypernomers. Beside these data, some interesting observations on the chemical effects of adding one electron may be highlighted.

In the gas phase, an interesting activation toward association has been proposed. While O_2 displays a weak only tendency toward dimerization[70a], Phelps et al.[70b] have proposed the following reaction (**equ. [4]**) to explain experimental observations in the variation of O_2^- mobilities in an environment of O_2 molecules. Recently[71], O_4^- species were also reported in H_2O solution.

$$O_2^- + O_2 \rightleftharpoons O_4^- \qquad [4]$$

The chemistry of $X_2^{\bullet -}$ radical anions (X=halogen) has been reviewed[73]. A pseudopotential method was developed to calculate the ground and low-lying excited electronic states of $F_2^{\bullet -}$, $Cl_2^{\bullet -}$, $Br_2^{\bullet -}$ [74]. This method provides an evaluation of D_o and equilibrium bond lengths. The relevant values are displayed in **Table 3**. The authors observed that the binding energy calculated from the interaction of (X^-... X) and (X....X^-) valence bond structures decreased with decreasing vertical electron affinities of the atoms. As the electronic configuration of the $^3\pi_o+_u$ excited state of X_2 $(\sigma_g)^2(\pi_u)^4(\pi_g)^3(\sigma_u)^1$ differs from that of $X_2^{\bullet -}$ only by the absence of one weakly antibonding π_g electron, the properties of $X_2^{\bullet -}$ can be expected to be very similar to those of $X_2^{\bullet}$ ($^3\pi_{ou}$ +). This expectation is substantiated by the values given in **Table 3**, apart from the dissociation energies which are higher for $X_2^{\bullet -}$ than for the corresponding $^3\pi_{ou}$ + excited states.

The experimental study of the reactivity of $X_2^{\bullet -}$ species is complicated because these species are often formed in the presence of $X^{\bullet}$, X_2, $XOH^{\bullet -}$. An associative activation, however, seems to be clearly displayed by $I_2^{\bullet -}$. In fact, although I_4 is not known as such, $I_4^{\bullet -}$ has been identified in flash photolysis[75] experiments:

$$I^{\bullet} + I_3^{-} \rightleftharpoons I_4^{\bullet -} \rightleftharpoons I_2^{\bullet -} + I_2 \qquad [5]$$

Shida et al.[76] interpreted the ESR spectra of $I_4^{\bullet -}$ as suggesting a perpendicular configuration of the $I_2^{\bullet -}$ and I_2 moieties. It should be noted at this point that D_0 values (**Table 2**) are not necessarily the most important parameter when equilibrium in solution is considered. Protic solvents able to solvate X^- will shift equilibrium [6] towards the right, while aprotic solvents favor the $X_2^{\bullet -}$ species[73]:

$$X_2^{\bullet -} \rightleftharpoons X^{\bullet\bullet -} + X^{\bullet} \qquad [6]$$

Table 3: **Estimated and observed properties of X_2 and $X_2^{\bullet -}$**

	D_e a)	b)	r_e c)	d)	Redox properties f)
$F_2^{\bullet -}$				1.91	
Cl_2	2.48	1.38	1.99	2.19	0.43b)
$Cl_2^{\bullet}$ e)	0.32		2.47		
$Cl_2^{\bullet -}$	1.2 ± 0.5	1.24	2.6 ± 0.1	2.71	2.29a)
Br_2	1.97	1.07	2.28	2.36	0.41b)
$Br_2^{\bullet}$ e)	0.46		2.66		
$Br_2^{\bullet -}$	1 ± 0.5	1.20	2.8 ± 0.1	2.90	1.77a)
I_2	1.54	0.84	2.67	2.87	0.06 or 0.172 (ref. 77)
$I_2^{\bullet}$ e)	0.54		3.02		
$I_2^{\bullet -}$	0.7 ± 0.3	1.08	3.1 ± 0.1	3.28	1.00a)

a) estimated ($X_2^{\bullet -}$) and measured (X_2) D_e (dissociation energy)(eV); **b)** calculated D_e (pseudopotential); **c)** r_e equilibrium distance in Å (experimental); **d)** calculated r_e by the pseudo-potential method (ref. 63b, 64a and 64b); **e)** excited $^3\pi_{ou}+$ state from ref. 30. See also ref. 59 and 73a; **f)** standard reduction potentials for the reactions: a) $X_2^- + e \rightleftharpoons 2X^-$ and b) $X_2 + e^- \rightleftharpoons X_2^-$ from ref. 73, 77 (1eV = 23.06 kcalMol^{-1}).

P. Neta et al.[78] have explored the reactivity of $Cl_2^{\bullet -}$, and have shown that this radical anion may react in SH2 type reactions (H abstraction), as well as in unsaturated compounds and oxidations, by electron transfer. The rate constants for hydrogen abstraction range from 10^3 to 10^5 lMol^{-1}s^{-1}. Here we see an example of a totally new reactivity associated with the addition of an electron.

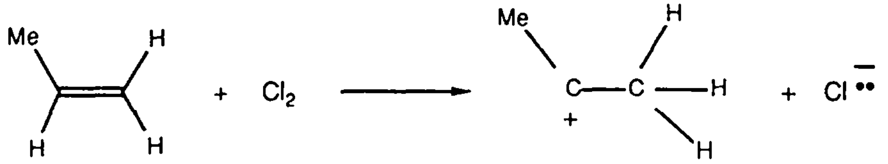
$$Cl_2 + H\text{-}C \xrightarrow{\quad X \quad} \text{no reaction if } Cl_2 \text{ is not dissociated into } Cl^{\bullet} + Cl^{\bullet} \qquad [7]$$

$$Cl_2^{\bullet -} + H\text{-}C \longrightarrow Cl_2H^- + {}^{\bullet}C \qquad [8]$$

The rates of this bimolecular homolytic substitution (SH2) range from $<10^3 Mol^{-1}s^{-1}$ (e.g. tBuOH) to $2x10^6 Mol^{-1}s^{-1}$ observed for HCO_2^-. This corresponds to an activation which cannot be described as "homoactivation" in the sense that the studied elementary step does not exist in the neutral substrate but appears in the hypernomer. This is not an "Umpolung"[17a] because the induced reactivity does not correspond to an inversion of polarity in the substrate. This activation is better associated with the appearance of paramagnetism in the substrate, and later we will look at the oxidative counterparts of this activation. A shorthand description could be paractivation. In the present case, this activation is associative as the $Cl_2^{\bullet -}$ species is now more "eager" to form a bond with H. Later, we shall see examples of dissociative paractivation. In contrast with the preceding abstraction reactions, both Cl_2 and $Cl_2^{\bullet -}$ react with olefins (solvent H_2O). Olefinic compounds react with Cl_2^- three orders of magnitude faster than their saturated analogs (10^5 to 10^8 $Mol^{-1}s^{-1}$). This reaction produces the chlorine atom adduct:

[9]

The mechanism of chlorination by Cl_2 in polar solvents, such as acetic acid and alcohols, seems to follow an electrophilic pathway[79], in contrast with mechanisms proposed in apolar solvents[80-82].



[10]

The reported rates[79a] for bimolecular coefficients in acetic acid at 25°C are about 10^5 times slower than the ones found by Neta for similar substrates reacting on $Cl_2^{\bullet -}$. This ratio is approximate as the solvents are different. Solvents play an important role in this reaction as shown by the almost total inertness of Cl_2 toward ethylene in the vapor phase at room temperature[83] and the drastic effect of trace water upon some halogenations[82b]. These reaction rates hint at a reaction which is easier to perform on the $Cl_2^{\bullet -}$ radical anion than on its hyponomer. This is a reductive activation toward dissociation.

1.1.2 Selected cases of heteronuclear diatomic molecules

As the emphasis of this report is on organic chemistry, in this section we will only treat the case of HCl for the gas phase studies. Many more examples may be found in ref. 84 or in the 1987 Chem. Rev. issue devoted to temporary anion states and related phenomena[33c].

In electron resonance scattering experiments, the alignment of the HCl dipole axis and the approaching electron means that the approaching electron sees a potential which is attractive or repulsive in the long run depending on the direction. This interaction is important for electron energies smaller than 1 eV. The dipole potential acts as a channel which ensures that the electron only approaches the attractive end of the molecule.

There are two non-dissociative states HCl^- $1^2\Sigma^+$ and $2^2\Sigma^+$. The more stable ($1^2\Sigma^+$) state lies very close to the ground state of HCl. This state, however, does not actually correspond to a valence state, but is more similar to a Rydberg state (diffuse electron + HCl). Recent theoretical calculations[85] provide interesting insights into the $1^2\Sigma^+$ state of HCl^-. The two relevant facts provided are:

$$D_{o(HCl^-)} \approx 0{,}09 \text{ eV } \{D_{o(HCl)} = 4.62 \text{ eV}\} \text{ and } r_e \approx 2.1 \text{ Å } \{r_{e\,(HCl)} = 1.275 \text{ Å}\}.$$

Although these values cannot been taken too seriously because of the difficulty in obtaining theoretically precise D_o and r_e values for radical anions, they clearly show an important trend. This trend is: the destabilization caused by the addition of an electron in the LUMO of HCl is greater than the one respectively caused in the corresponding homoatomic molecules $\{D_{o(H2)} = 4{,}48$ eV; $D_{o(H2^-)} = 1.5$ eV; $D_{o(Cl2)} = 2.48$ eV; $D_{o(Cl2^{\bullet -})} = 1.2$ eV; see **Tables 2 and 3**$\}$. In an exhaustive theoretical study of 1e and 3e bonds, T. Clark[86] demonstrated a very interesting pattern of behavior for heteronuclear uneven bonds. Although the studied bonds all correspond to positive ions (either ionization of a 2e σ bond or complexation of a base by a radical cation), the displayed trends may tentatively be extended to neutral and negative 3e bonds. The general behavior would be:

$$D_{AB} = [(D_{AA} + D_{BB})/2] \exp(-\lambda_A \lambda_B \Delta_{IP}) \qquad [11]$$

* D_{AB} stands for the bond energy in $kcalMol^{-1}$) of a one electron bond ($Li...BeH^{\bullet +}$; $Li...CH_3^{\bullet +}$; $H_2B...CH_3^{\bullet +}$ etc) or of a three electron bond ($H_3N...OH_2^{\bullet +}$; $H_3N...ClH^{\bullet +}$; $HF...PH_3^{\bullet +}$ etc..).

* D_{AA} and D_{BB} are the bond dissociation energies (in $kcalMol^{-1}$) of the complexes $A...A^{\bullet +}$ and $B...B^{\bullet +}$ respectively. For the preceding one electron bonds, they would be, $D_{Li...Li}{}^{\bullet +}$ and $D_{HBe...BeH}{}^{\bullet +}$; $D_{Li...Li}{}^{\bullet +}$ and $D_{H3C...CH3}{}^{\bullet +}$; $D_{H2B...BH2}{}^{\bullet +}$ and $D_{H3C...CH3}{}^{\bullet +}$. For the preceding three electron bonds, they would be $D_{H3N...NH3}{}^{\bullet +}$ and $D_{H2O...OH2}{}^{\bullet +}$; $D_{H3N...NH3}{}^{\bullet +}$ and $D_{HCl...ClH}{}^{\bullet +}$; $D_{HF...FH}{}^{\bullet +}$ and $D_{H3P...PH3}{}^{\bullet +}$

* λ_A and λ_B are positive parameters depending on the elements or groups involved. λ varies from 0.057 (H, F) to 0.190 (Argon). Representative values are CH_3: 0.066; NH_3: 0.119; HCl: 0.177; Li: 0.137; BeH: 0.096; OH_2: 0.062.

* Δ_{IP} is calculated energy ($kcalMol^{-1}$) for the reaction:

$$A^{\bullet +} + B \longrightarrow A + B^{\bullet +} \qquad [12]$$

where A is the fragment of lower ionization potential. Δ_{IP} is therefore calculated by $IP_B - IP_A$. For example $IP_{Li^\bullet} = 122.9$ $kcalMol^{-1}$; $IP_{BeH} = 186.8$ $kcalMol^{-1}$. $\Delta IP = 63.9$ $kcalMol^{-1}$ for D_{AB} of $Li...BeH^{\bullet +}$.

Figure 4 displays a typical variation for $[D_{AA} + D_{BB} / 2] = 30$ kcal, when Δ_{IP} and $\lambda_A\lambda_B$ vary continuously. The maximum value of the exponential term is 1 (for $\Delta_{IP}=0$). The greater the IP variation, the smaller the D_{AB} value with respect to D_{AA} and D_{BB}. If a comparable type of behavior were present for negatively charged 3e bonds, D_{HCl^-} should be much smaller than D_{H2^-} and D_{Cl2^-}, because

$\Delta IP = IP_{(Cl^-)} - IP_{(H^-)}$ is remarkably large. As the IP of groups are grossly correlated with their atomic or molecular electronegativity[87,88], a simplified and qualitative rule of the thumb can be seen.

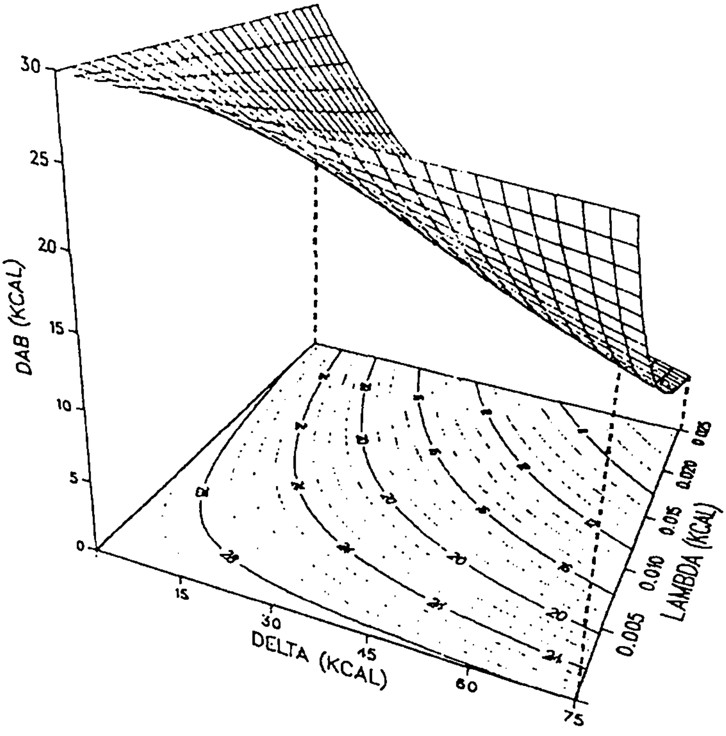


Figure 4: **Three dimensional representation of the effect of Δ_{IP} and $\lambda_A\lambda_B$ variations on the energy of a bond AB.**

With the addition removal of one electron, the labilization of an heteropolar σ bond AB with respect to that expected from the simple consideration of the labilizations of AA and BB will be maximum when the difference in the electronegativity of its constituting elements or fragments is maximum. This would hint at a contrasting behavior for even and odd bonds: for the former, Pauling[1] has shown that the D_{AB} values were always larger than expected from D_{AA} and D_{BB}; for the latter, D_{AB} values are always smaller than expected from D_{AA} and D_{BB}. This trend is consistent with a simple MO representation of heteropolar bonds. The bond strengths in the series

$$D_{HI} < D_{HBr} < D_{HCl} < D_{HF}$$

hint at a more stable bonding σ molecular orbital (and therefore more antibonding σ^* counterpart) for HF. Clark's otherwise excellent report[86] definitively shows that chemists are not used to thinking in terms of +/-1e comparisons. Nowhere, in this report are the energies of the 1e bond compared to their 2e counterparts, and the same holds true for the 3e bonds.

1.2. Triatomic and tetraatomic molecules.

At the present time, the tools for the qualitative understanding of structure modifications are the Walsh-Mulliken diagrams[47,89], improved by the critical use of canonical orbital energies and Koopman's review[90]. The Buenker-Peyerimhoff approach[90] is so well done that there is no point in duplicating it. We direct the reader to this reference for an explanation of the underlying principles and limits of the Walsh-Mulliken approach. This section is limited to **Tables 4** and **5**, which compile the known informations on the structural effects of adding one electron to triatomic and tetraatomic molecules.

Table 4: **Structural instability *versus* stability of triatomic molecules upon electron attachment** (AH_2, AHY, AY_2 [a])

	Instabilities	Examples					Ref.[e]
From	10e to 11e [b]	HCN	180°[c] ---->	HCO	119°	(AHY)	91
	16e ----->17e	CO_2	180° --->	FCO	135°	(AY_2)	92
	17e -----> 18e	NO_2	134° --->	ClNO	116°	(AY_2)	
	Stabilities						
From	11e -----> 12e	HCO	119° ---->	HNO	108°	(AHY)	
	12e -----> 13e	C_3	180° ---->	CCN	180°	(AY_2)	
	13e -----> 14e	CNC	180° ----->	NCN	180°	(AY_2)	
	14e -----> 15e	CCO	180° ----->	N_3	180°	(AY_2)	
	15e -----> 16e	N_3	180° ----->	N_3^-	180°	(AY_2)	
	18e -----> 19e	FNO	110° ----->	NF_2	104°	(AY_2) [d]	
	19e -----> 20e	ClO_2	117° ----->	Cl_2O	110.8°	(AY_2)	

[a] A: central atom; H: hydrogen; Y: atom heavier than H; [b] Number of valence electrons; [c] apex angle; [d] Weak instabilities are also observed (see Table 2 in ref. 90); the numerical values of angles are taken from ref. 47 and 90; [e] The references provided describe geometrical changes reported after adding an electron rather than changing the number of valence electrons by modification of an atom.

Although we have mainly concentrated here on heteroatomic molecules, the existence of homoatomic should also be recalled, as shown by a short enumeration of the relevant references: H_3[93] and H_3^-[94], Li_3[95] and Li_3^-[96], Be_3[97] and Be_3^-[98], Na_n and Na_n^-[96b]. These cluster anions are the prototypes of a class of compounds, whose gas-phase experimental study became possible with the advent of gas-phase nozzle beam techniques[99].

Concerning the reactivity of hypernomers, for the $H_2O^{\bullet -}$ anion, the added electron would occupy a molecular orbital of σ^* symmetry , therefore $H_2O^{\bullet -}$ should be dissociative. This agrees with *ab initio* calculations[100] and dissociative attachment experiments in the gas phase[101], which have revealed three negative-ion states. All three resonance states have potential-energy surfaces which are repulsive in the Franck-Condon region. The situation is complicated, however, because H_2O has a dipole moment of 1.8 Debye, which is greater than the critical dipole moment of 1.6 Debye (see **Section**

1.1.2) and should therefore have an infinite number of bound anion states. In these anion states, the electron is so loosely bound that it is not able to "follow" the rotating dipole and rotational-to-electronic energy transfer causes the electron to detach[102]. Thus, even for a triatomic molecule such as H_2O, the situation of "one more electron " may already involve a variety of states, as shown by adding the possibility of negatively charged water clusters[103] to the preceding considerations. Pulse radiolysis experiments have never directly detected $H_2O^{\bullet -}$ ions as such, (however see ref. 160c), and pulses of electrons in water directly create OH^- and $H^\bullet$ [104a].

$$e_{aq}^- + H_2O \longrightarrow H^\bullet + OH^-_{aq} \qquad [13]$$

The rate is 6 $Mol^{-1}s^{-1}$ at a pH of 8.3-9. This is a relatively slow rate, which suggests that the highly dissociative $H_2O^{\bullet -}$ creates a kind of bottleneck in this mechanism. However, if this rate is compared with that in the reaction:

$$H_2O \longrightarrow H^+ + OH^- \qquad [14]$$

whose value has been determined[105] as 10^{-5} s^{-1}, it must be assumed that, for this solvolytic reaction (compare equ. [1] and [2]), the addition of an electron to the substrate highly activates it towards solvolysis.

The example of CO_2 illustrates the kind of activation possibly displayed when the LUMO in the substrate has a π symmetry and is delocalized on the whole σ framework. The theoretical study of the structures and stabilities of the $(CO_2)_2^-$ ion[106] suggest that the addition of an electron to CO_2 activates it towards association. This expectation is substantiated by both pulse radiolysis and electrochemical studies[107]. The radical anion of SO_2 displays the same tendency toward dimerization[108].

Table 5: **Structural instability versus stability of AH_3 and AY_3 molecules upon electron attachment .[a]**

	Instabilities to		Examples			Ref[d]
From	6e ----->	7e [b] (AH_3)	CH_3^+ (planar)	----->	BH_3^- (pyramidal) [c]	109,110
From	24e ---->	25e [b] (AY_3)	CO_3^{2-} (planar)	----->	ClO_3 (pyramidal)	
		Quasi Stabilities or Stabilities				
From	4e ----->	5e (AH_3)	Be H_3^+ (distinctly non planar)	----->	Be H_3 (planar)	
From	7e ----->	8e (AH_3) [c]	BH_3^- (pyramidal)	----->	CH_3^- (pyramidal)	
From	5e ----->	6e (AH_3)	CH_3^{2+} (planar)	----->	CH_3^+ (planar)	
From	25e ---->	26e (AY_3)	BrO_3 (114°)	----->	$SOBr_2$ (pyramidal<100°)	91c, 111

[a] A: central atom; H: hydrogen; Y: atom heavier than H; examples taken from ref. 47 and 90; [b] Number of valence electrons; [c] Here, the differential form of Koopmans' theorem[90] and Walsh diagrams differ in their predictions; [d] The references provided describe geometrical changes reported after adding an electron rather than changing the number of valence electrons by modification of an atom.

The comparison of, on the one hand, carbocations and radicals and, on the other hand, carbon centered radicals with carbanions will be discussed in **Section 1.4.4.1.**. At this point, it is already interesting to note that if $CH_3^\bullet$ dimerizes very quickly ($k \approx 10^9$ $Mol^{-1}s^{-1}$)[112]; CH_3^+ has never been reported to do so. It is sometimes argued that this reluctance originates in the repulsive effect of positive charges. The equilibrium:

$$2\,NO_2^{2-} \rightleftharpoons N_2O_4^{4-} \qquad [15]$$

where the dimer is strongly favored[91b], shows that electrostatic repulsions are not strong enough to inhibit dimerization when the dimer is orbitally favored. The hyponomer NO_2^- (18e) displays no tendency towards dimerization. Therefore, an associative paractivation operates both for NO_2^{2-} and $CH_3^\bullet$; this paractivation (see **Section 1.1.1.2.**) largely transcends electrostatic effects.

On the side of dissociative activation, electron attachment to OH_3^+ provides OH_3; OH_3 species have never been identified, even in the fastest pulse radiolysis experiment[113]. They are highly dissociative. Their existence has been reported in the gas phase however[114], and theoretical calculations even hint at the existence of OH_3^- species[115].

1.3. Pentaatomic molecules with a central atom.

CF_4 and CH_4 (8e) are of tetrahedral symmetry (Td); SF_4 (10e) has a butterfly-like shape (C_{2v}); XeF_4 (12e), as well as CH_4^{2+} (6e), are thought to be planar. Two lines of rationalization have been offered to explain these data: one is based on the energy gaps in **Figure 5** and first or second order Jahn-Teller distortions[47]; the other is based on united atom calculations[116]. Let us examine the first. The important value of the $2a_1$-$1t_2$ gap precludes any second order Jahn-Teller distortion for CF_4 and CH_4. In contrast, the small $2a_1$-$2t_2$ gap allows such a Jahn-Teller distortion to occur. Finally, XeF_4 (two electrons in $2t_2$) and CH_4^{2+} (4e in $1t_2$) are first order Jahn-Teller unstable distortions (see recent theoretical approach to further examine this point[117]).

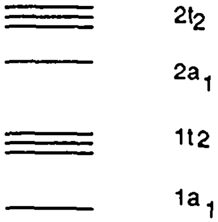


Figure 5: **Molecular orbital diagram for a tetrahedral AH_4 or AX_4 molecule (Td).**

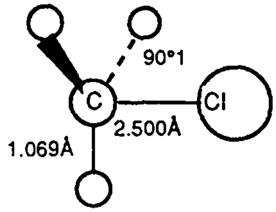
The importance of the $2a_1$-$1t_2$ gap hints at a highly energetic CH_4^- state. Along with this expectation, there is no low-lying resonance in methane. Very short lifetime resonance states in the region of 8 and 18.5 eV[118] have been observed. These values clearly show that anion radicals of CH_4 do not play any role in thermal solution chemistry, as is also shown by pulse radiolysis data[119]. There are three ways to decrease the $2a_1$-$1t_2$ gap: replace C by Si, substitute H by halogens or other electronegative groups, introduce the CH_2 fragment in a saturated ring. SiH_4 shows evidence for shape-resonance formation below 5 eV where the electron occupies a σ^* orbital[120]. The substitution by halogens or other electronegative groups (except OH, OR or NR_2) spectacularly enhances the reactivity of CH_4 towards e^-_{aq}[119]. The alkyl halides are particularly reactive ($k \approx 10^{10}$ $Mol^{-1}s^{-1}$) and the reactivity increases in the following order: $F \ll Cl < Br < I$.

The third way of lowering the σ^* orbital in saturated hydrocarbons is to pass from a linear framework to a cyclic one ; the electron transmission spectra of cyclopropane through cyclohexane all display structures associated with two anion states below 10 eV:

cyclohexane (4.11 eV) < cyclopropane (5. 29eV) < cyclobutane (5.8 eV) < cyclopentane (6.14 eV)[121].

Most of the pentaatomic like molecules with a C central atom are highly dissociative towards electron attachment. The best way to increase their lifetime seems either to introduce a substituent which prevents the electron from coming into contact with the central carbon (p-CN or p-NO_2 benzyl halides and related compounds[122], see **Section 1.4.2.1.**) or to load it with atoms which have low lying orbitals accessible to the electron. The methyl halide series is on the side of highly unstable radical anions. Theoretical calculations of $CH_3Cl^{\bullet-}$ suggest that these species could exist in the gas phase[123]. On the experimental side, $CH_3X^{\bullet-}$ (X = F, Cl, Br, I) has never been observed at room temperature. In low temperature rigid aprotic media, ESR clearly shows the presence of loose $[CH_3^{\bullet}\ X^-]$ complexes[124]. Experimental spin density and theoretical calculations[123a] suggest the following structure for these complexes:

Scheme 1



To reach the other side of relatively stable pentaatomic carbon-centered radical anion species, all the hydrogens of CH_3X must be successively replaced by halogen atoms[125]. The radical anions of CBr_4[125a], CF_3X[125b], CCl_4[125c] have been observed as distinct species by low temperature ESR experiments (≈70°K). The ESR results for $CBr_4^{\bullet-}$ suggest a geometry distorted towards a pentagonal trigonal bipyramid in which one ligand is replaced by the radical center. This experimental work also suggests that CBr_4 is better able to accommodate an extra electron than is CCl_4.

1.4. More complex molecules classified by radical types.

M.C.R. Symons[111] has proposed a nomenclature for radicals which is convenient:

σ^*, ex: $[Cl-Cl]^{\bullet-}$, $[R_3PPR_3]^{\circ+}$ π^*, ex: $[C_6H_6]^{\bullet-}$

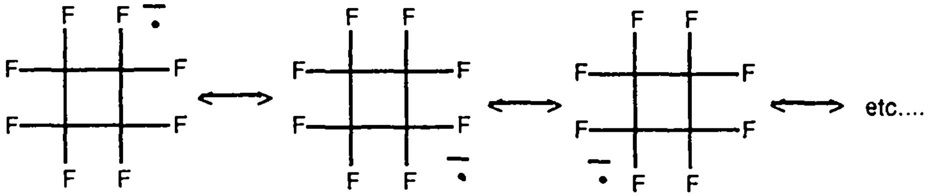
n.b. π ex: $^{\bullet}CH_3$, $^{\bullet}NH_2$ n.b.σ ex: $^{\bullet}NO_2$, $^{\bullet}CF_3$, $^{\bullet}SiR_3$ (n.b. = non bonding) π, ex: $[C_6H_6]^+$, $[C_2H_4]^+$ σ, ex: $[Ag.Ag]^+$, $[Me_3C.CMe_3]^+$

We shall see that often the classification is not very strict, since a radical anion may begin as a π* radical and then evolve specifically when "the electron has migrated to another part of the molecule to become a dissociative σ* radical anion". This section does not attempt to be exhaustive: only illustrative examples will be selected. Furthermore, the focus on activation gives a biased view of the chemistry of some substrates. To compensate for this, we will direct the reader as often as possible to more complete reviews.

1.4.1. σ* type radicals without unsaturation in α- or β-position.

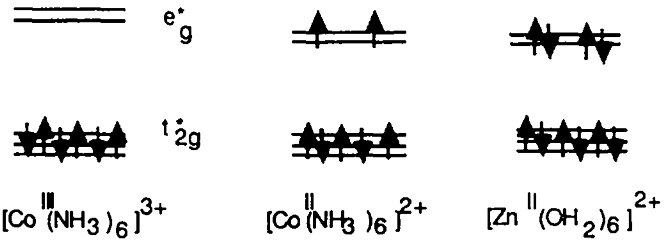
Among the diatomic molecules with 3e bonds studied by T. Clark[86], $F_2^{\bullet-}$ is the most stable with a bond energy of less than 30 kcalMol^{-1} (UHF and MP2 methods yield different values). Considering that 3e bonds between atoms of different electronegativity are expected to be even weaker, it is not surprising that σ* radical anions are highly dissociative. Two types of exceptions undermine this statement as illustrated by examples given in **Section 1.3.**. The first type corresponds to something which could be called σ delocalization (see also **Section 2.2.1**). Williams[127a] has observed the ESR spectra of the radical anion of $C_4F_8^{\bullet-}$. This astonishing result may tentatively be rationalized by writing the mesomeric forms shown in **Scheme 2**:

Scheme 2



The second type of exception is usually found in octahedral hexacordinated transition metal complexes. The simplified molecular orbital diagrams of the frontier orbitals in some typical inorganic complexes (**Scheme 3**) support this proposition[7b]:

Scheme 3

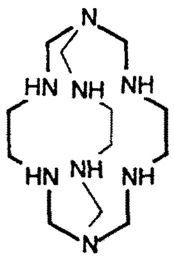


In this frontier diagram, t^*_{2g} corresponds to a π* symmetry and e_g^* to an a σ* symmetry. The case of $[Co^{II}(NH_3)_6]^{2+}$ is quite spectacular in terms of geometrical variation due to the addition of one electron.

For this complex, the Co^{II}-N length has been determined to be 2.11Å, while in its hyponomer, whose configuration is π^{*6}, it is only 1.94 Å[19b].

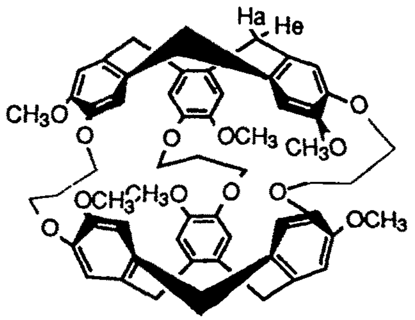
Another interesting fact emerges from the recent body of knowledge provided by research on inorganic substrates. Pt^{III} complexes are highly labile complexes when classical ligands such as Cl$^-$ coordinate the central metal[128]. However, Bond[129] et al. have been able to obtain highly inert Pt^{III} complexes by including them in cryptate ligands such as the one displayed in **Scheme 4a**:

Scheme 4a



sepulcrate (sep)

Scheme 4b



Considering the recent work by Collet et al.[130] cn cryptophanes (**Scheme 4b**) which are able to complex polyhalomethanes, one may hope to isolate stabilized σ* organic bonds in the near future. For the specific case of cryptophanes the problem would be to find out whether the extra electron actually remains in σ* antibonding orbitals or if it is mainly localized in the LUMO of the cryptand.

1.4.2. σ* type radical anions α- or β- to unsaturation.

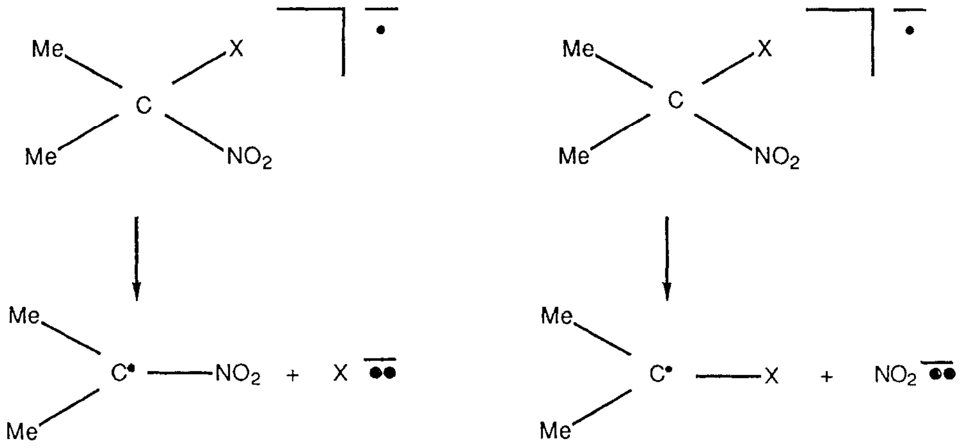
From what has been seen in the previous sections, these types of radicals can be expected to display primarily dissociative activation with respect to their hyponomers. This reactivity is probably the most widely illustrated in the chemistry of radical anions[126b]. We are going to propose a very general unifying pattern of reactivity in these substrates: the unsaturated group of the substrate usually acts as a captor (electrophore) during the primary act of electron transfer; the electron then migrates intramolecularly to a σ part of the substrate, which is activated toward dissociation. It is as if the *electron* were an activating messenger.

1.4.2.1. Approaches to selectivity in the cleavage of σ* anions containing unsaturations. The reactive mixed valence approach.

When dealing with more complex molecules, interesting problems of intramolecular selectivity of cleavage appear after electron attachment. These problems have not yet been solved, as shown by the variety of rationalizations which have been provided to explain these selectivities.

Bowman has experimentally studied these problems in detail for the 2-substituted-2-nitropropanes, and gives an overview of this topic in a recent review devoted to photoinduced nucleophilic substitutions at sp^3 carbon[131]. ESR spectroscopy at low temperatures for matrix isolated radical anions shows the following pattern of cleavage in radical anions[132] (**Scheme 5**). Bowman proposes that the location of the unpaired electron in the radical-anion has only a small influence on the rate and direction of these dissociations. Bond strength (compare with **Section 1.1.1.**) and nucleofugacity are the main parameters to explain the observations[131].

Scheme 5

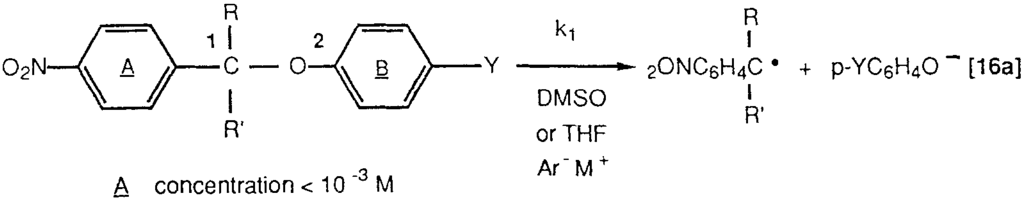


If $X = I, Br, Cl, NO_2, SCN, S(O)R, SO_2R, SR$, N-diazoles, S-thioamides

If $X = CN, CO_2Et, NO_2, COEt, CH_3, p\text{-}NO_2C_6H_4, p\text{-}NO_2C_6H_4N{=}N$

minor ← If $X = N_3$ → major

These problems of selectivity in cleavage have been examined from a different point of view in the series of aromatic ethers. Two types of experimental data are provided by these studies: cleavage rates and selectivity of cleavage[133] (equ. [16]). The possible cleavages are shown in **Scheme 6**.

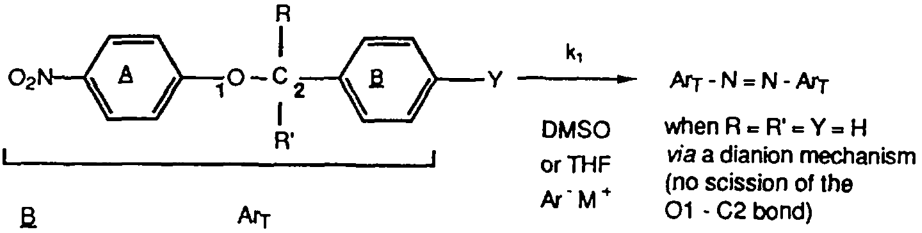


A concentration < 10^{-3} M

$Y = H, Me, Cl$; $R = H$; $R' = H, Me, Ph$ (133a)

Ar^- = 2,4,6-tritertiobutylnitrobenzene radical anion

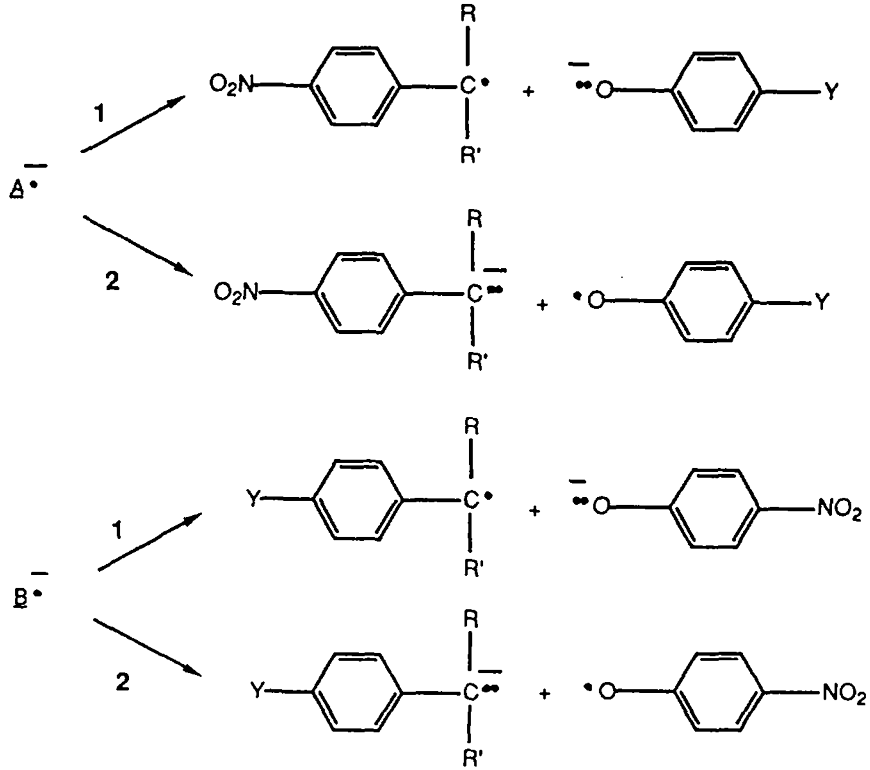
$M^+ = K^+$ or Li^+



[16b]

The authors expected that between the $A^{\bullet-}(1)$ and $B^{\bullet-}(1)$ pathways, the second pathway should be favored because of its greater ΔH° of reaction (more stable products). In fact, just the opposite is observed: $B^{\bullet-}$ evolves with no visible cleavage of the C-O bond, while $A^{\bullet-}$ evolves 10^4 times more rapidly with the expected direction of cleavage for the C-O bond ($A^{\bullet-}(1)$). To explain this result, Guthrie and Maslak proposed the concept of regioconservation of spin density.

Scheme 6



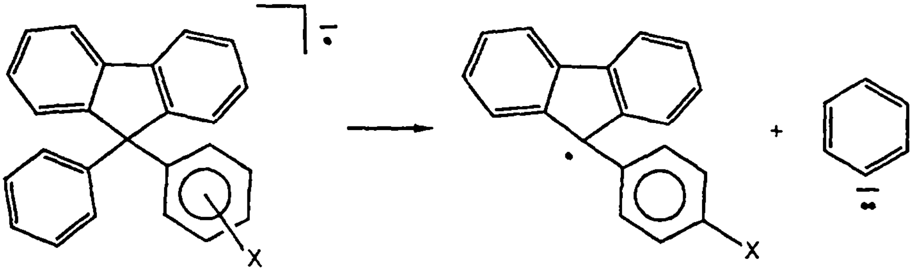
An inherent preference for radical anion scission reactions would occur with regioconservation of spin density, i.e., where the unpaired electron remains on the same side of the scissible bond throughout the fragmentation process"[133a].

One problem is associated with the concept of regioconservation of spin. This concept relies heavily on the localization of the extra electron in the aromatic ring for which the LUMO is deepest, either because of substituents or of its own structure. It is from the unsaturated part where its remains the longest that the electron apparently best plays its activating role towards dissociation. There is another dimension, however: in the aromatic ring where the electron remains the longest because of a strongly electrophoretic substituent (NO_2 for example), this same substituent may keep the electron away from the σ bond that should be activated. When a cyano group replaces the nitro group in p-nitrobenzyl halides, the rate of dissociation of the radical-anion measured by pulse radiolysis[134] increases by at least five orders of magnitude. The same kind of effect has been reported by Todres in the reactivity of benzene sulphene amide with the trichloro silylanion[135,136].

The concept of regioconservation of spin does not seem to apply to substrates such as $[(Me)_2C(NO_2)(CN)]^{\bullet -}$; the most probable location of the extra electron is in NO_2 and the cleavage reported in **Scheme 5** does not correspond to regioconservation of spin. However, a difference exists between the aromatic substrates and nitromethane radical anions; for the aromatic substrates, the electron probably first enters the LUMO of the phenyl ring and then migrates towards the σ^* antibonding orbital. In contrast, for substrates such as chloronitromethane, the electron enters a molecular orbital which is a combination of the π^* MO of the NO_2 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, and the radical anion fragments without any barrier[123e] (see also **Fig. 7**).

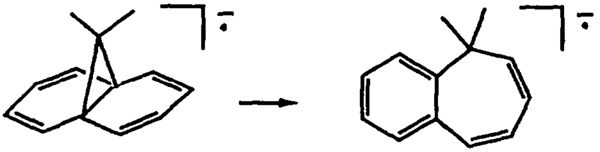
The cleavage of C-C bonds in radical anions of fluorenyl substrates was studied by Walsh[137a], who showed that the involvement of dianions in this cleavage may be a complicating factor. For the part of cleavage following the radical anion pathway, the regioconservation of spin concept applies (**Scheme 7**).

Scheme 7

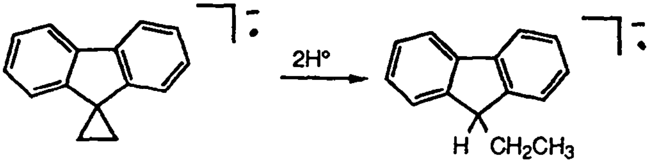


The overlap between the π^* radical-anion (mainly localized in the fluorene moiety) and the σ^* antibonding C-C orbital is drastically increased for these substrates, compared to that present in alkylbenzenes. The same kind of stereoelectronic influence is also observed for 9-methoxyfluorene[137b].

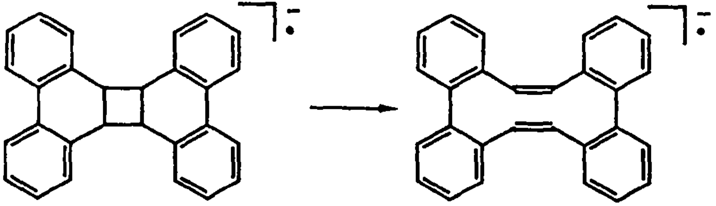
The intervention of dianions in C-C bond cleavage has also been elegantly demonstrated by Kiesele[138]. This author showed that the electron transfer induced rearrangement of 1,1'-spirobiindene into 7H-benzo[c]fluorene no longer takes place in the presence of the crown ether which complexes the K^+ cation. This results have been confirmed very recently [139]. The problem of the intervention of dianions in the cleavage of C-C bonds is a very critical one. Indeed, Walsh[137a] clearly points out that the dianion may be the cleaving species, even if its concentration is too low to allow direct detection. The factors which discourage dianion formation are well treated in Holy's review[140]. Besides the effect of appropriate crown ethers already discussed, these factors are: small cations, low temperatures (but see ref. 141) and solvents such as DME or HMPA which form strong associations with the cations. The free radical anions usually do not disproportionate, and all the preceding parameters favoring loose ion pairs discourage disproportionation. Nevertheless, the possibility of dianion intervention when a C-C bond cleavage apparently occurs in a radical anion, is pervasive[142]. As a general rule, C-C bonds present in alkyl aromatic radical anions[143] are rather reluctant to cleave. Some cases where C-C cleavage has been reported are shown by **equ. [17]** to **[19]**:



(ref.144) [17]



(ref.141) [18]



(ref.145) [19]

The same type of C-C cleavage has been reported[146-154]. **Equ. [17]** to **[19]** suggest that stereoelectronic factors are important in these types of cleavage: the cleavage appears to be easier when the overlap between the π system of the electrophore and the axis of the cleaved σ bond is optimized. The reactive mixed valence approach (next paragraph) naturally rationalizes these observations.

Symons[111], Bunnett and Rossi[155-157] have proposed that the cleavage of C-X bonds in halogeno- aromatic radical anions may be seen as the result of electron transfer from the π^* radical anion to the σ^* arylnucleofugal bond by an orbital crossing (**Figure 6**).

The orbital crossing is made possible by lengthening or out-of-plane wagging motion of the C-X bond (vibronic interactions. Compare with ref. 158a,c). In terms of selectivity, the fragmentation rates of these radical anions also depend on the position of the nucleofugal group on the aromatic ring[159,160]. Thus, the fragmentation rates of o- and p-chloroacetophenone radical anions in dimethylformamide are greater than 10^4 s^{-1}, while the fragmentation rate of the m-chloroacetophenone radical anion is only 5 s^{-1}. This positional selectivity of cleavage for bonds directly connected to the ring (α-scission) is also found for β-scission. The rates of dissociation for nitrobenzyl chloride radical anions are[134] :

$$\underset{10^4\ s^{-1}}{o\text{-}NO_2\text{-}C_6H_4CH_2Cl^{\bullet -}} > \underset{10^3\ s^{-1}}{p\text{-}NO_2\text{-}C_6H_4CH_2Cl^{\bullet -}} \gg \underset{\text{less than } 5\ s^{-1}}{m\text{-}NO_2\text{-}C_6H_4CH_2Cl^{\bullet -}}$$

Steric effects also play an important role, as shown by the following order of the decomposition rates for the anion radicals of halonitrobenzenes[161]: o-iodo > o-bromo >> p-iodo > m-iodonitrobenzene. There is clearly a release of strain when the o-iodonitrobenzene radical anion cleaves.

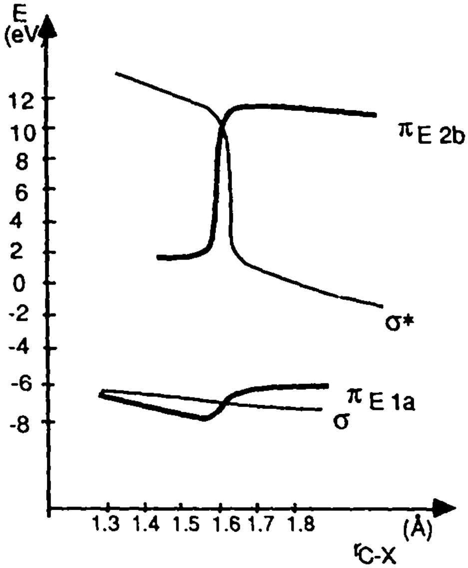
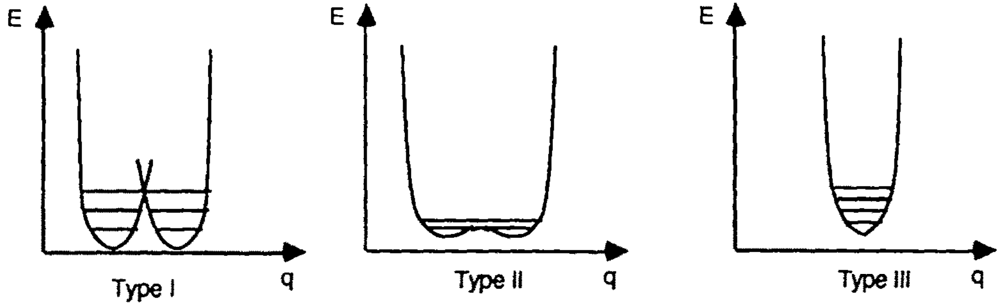


Figure 6: **Variation of the frontier orbital energy along the reaction coordinates for the Ph-F)•(-) system (from ref. 157).**

For the α- as well as for the β-scission, there seems to be two main parameters governing the aromatic radical anion lifetime (when solvent and steric or conformational effects are kept constant). First stage, a π* radical anion is formed which is stable as such with respect to dissociation: it only becomes dissociative when an intramolecular electron transfer has transformed the π* radical anion into a σ* one. The probability of transition from the π* state to the σ* state depends on the coupling between these states. As an initial approximation, this coupling is a direct function of the overlap between the σ* orbital and the π system, ponderated by the spin density in the position of the α or β ring to the scissible bond. In the preceding sentence, "as an initial approximation" means that Miller and Kozak[162] believe that spin density is not sufficient to explain the relative rates of cleavage of ortho, meta and para-substituted nitrobenzyl chloride anion radicals. It also means that, as the successive approaches[163] to spin densities in p-substituted benzyl radical[164] have shown, the problem of calculating spin densities in paramagnetic species has not yet been totally solved. Once the electron has been transferred, two cases still remain to be considered: either the σ^* state is highly dissociative (carbon-halogen bond) or it displays the lifetime associated with certain 3e bonds. One must, indeed, restrain from jumping to the conclusion that, as soon as the electron has switched from the aromatic part to the C-X part, one reaches a dissociative state. Although **Fig. 7** and **8** suggest this, the question has not yet been solved as the C-X bond which welcomes the electron has little to do with the C-X bond associated with alkyl halides. As it is probably longer (**Fig. 6**), its antibonding character could be weaker than the one displayed by a typical alkyl halide C-X bond. Therefore, a very shallow Morse curve could represent the situation as accurately as the dissociative one shown in **Fig. 8**. Here, the selectivity may also depend on this lifetime. The theoretical formulation[158] of these types of mixed valence compounds starting from the 3 Robin-Day cases[165] has been thoroughly treated for inorganic models (**Figure 7**).

a) Mixed Valence Isomers



b) Reactive Mixed valence Isomers

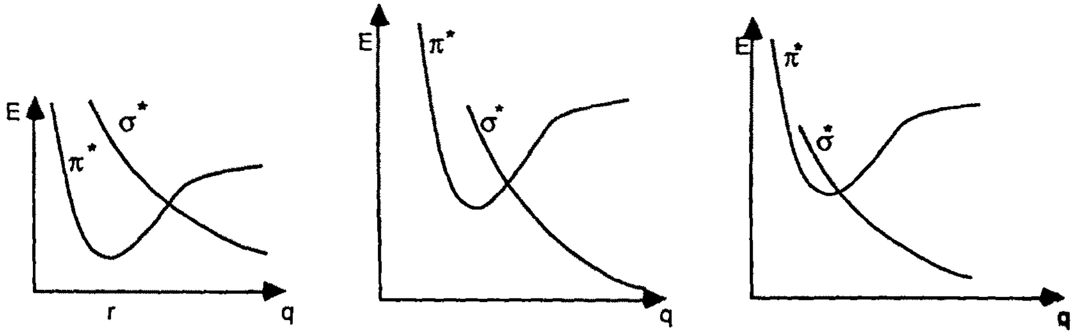
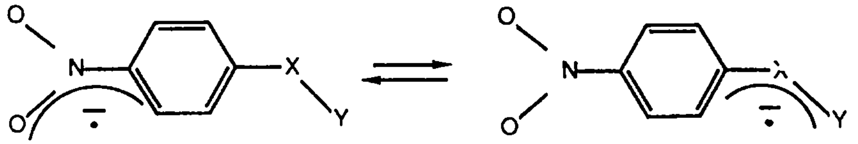
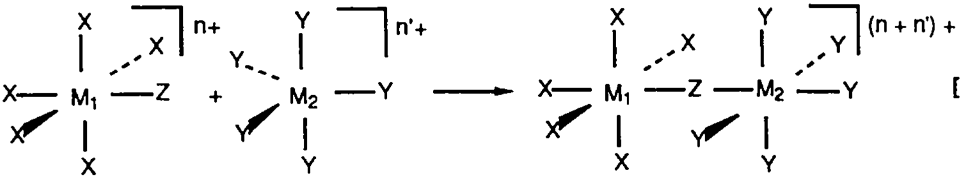


Figure 7: **Reactive Mixed Valence Isomers in comparison with stable Mixed Valence Isomers**. The main information in this figure is the analogy between the value of the barrier for intramolecular electron transfer. This barrier is high for Type I, average for Type II, very low ($\approx$200 calMol^{-1}) for Type II (see ref.165). The dissociative curve could be transformed into a very shallow Morse curve under appropriate conditions (see **Figure 9**). In terms of potential energy surfaces[166], the Type II Mixed Valence Isomers may be generalized to situations where several shallow valleys are connected to one or several cols of low energy (see **Scheme 21**).

There is certainly room for cross-fertilization between these experimental[167,168] and theoretical[158] inorganic approaches, and the wide range of data accumulated on unsaturated organic radical anions. If viewed as mixed valence compounds, aromatic radical anions with a potential leaving group show a specific property: one of the two isomers is highly dissociative (**equ. [20]**):



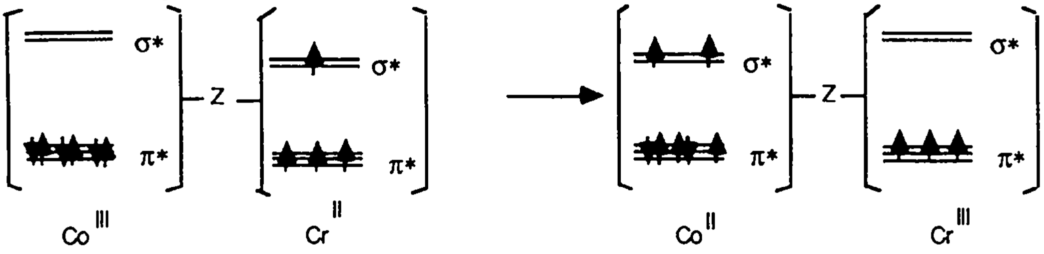
[20]



[21]

In contrast, most of the identified inorganic or organic[169] valence isomers possess two stable forms; the class of isolable inorganic mixed valence isomers with one reactive isomer has just began to be recognized[170]. The word "isolable" is important; without it, the wide class of bridged intermediates involved in inner-sphere electron transfer has to be considered, which closely parallel the behavior of aromatic radical anions. One of their isomers (the one on the product side) is usually highly dissociative[167b] (**equ. [21]**).For $X = NH_3$, $Y = OH_2$, $Z = Cl$, $M_1 = Co^{III}$, $M_2 = Cr^{II}$, the approximate frontier orbital diagram representation of electron transfer is shown in **Scheme 8** (Z is presumed to be almost identical to X and Y):

Scheme 8



Scheme 8 shows that, in reactive mixed valence, there is a net electron flow towards the σ* orbital of the oxidizing part of the reactive mixed valence isomer. It is this flow which underlies the "exchange" usually observed in inner-sphere electron transfer reactions: the oxidizing complex adds an electron, but loses a ligand (there are exceptions[171,172]).

For the aromatic halide radical anions, the graphic representation of the transition $\pi^* \rightarrow \sigma^*$ given in **Figure 8** explains some of the variations to be expected in this type of reaction. The $\Delta H^{\neq}$ activation energy mainly depends on the relative positions of the π* and σ* curves : when the crossing point "C" is energetic with respect to v = o the rate of $\pi^* \rightarrow \sigma^*$ transformation is low. This would be the case for α and β C-C bonds, but we have seen that (**equ. [17]** and **[18]**) that a C-C bond which is almost perpendicular to the electrophoretic π system may fragment. The intrinsic reluctance of the σ* C-C bond to temporarily accept the extra electron (see **Section 1.3.**) has been compensated by an excellent overlap angle between the π* and σ* systems.

An approximate idea of the ΔE value may be obtained from the LUMO energy in the hyponomer of the radical anion considered when compared to the energy of the σ* orbital to be populated in the σ* state. **Figure 8** also shows that this is not the unique parameter, but there is hopefully a compensation in the other factors when comparing a series of structural analogs.

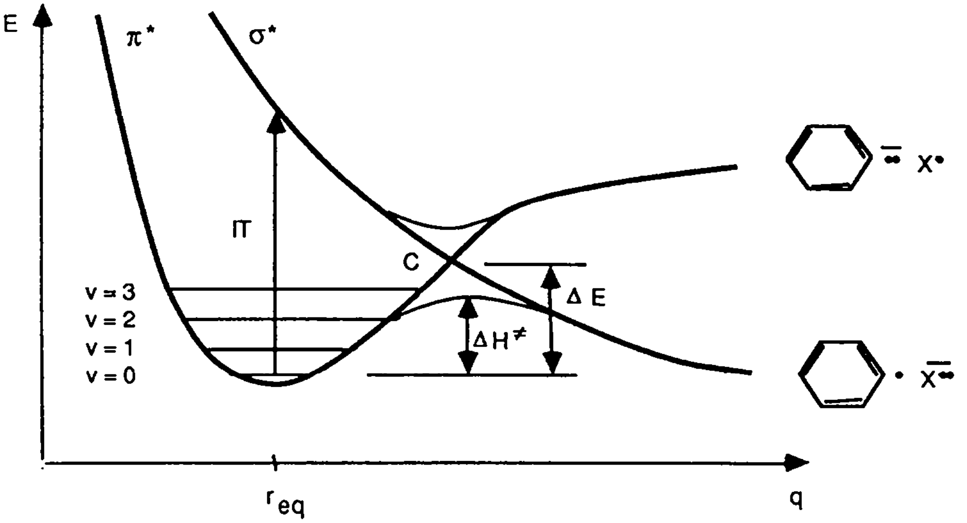
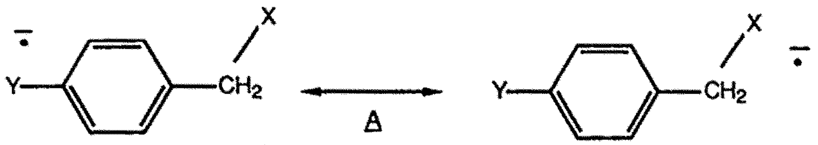


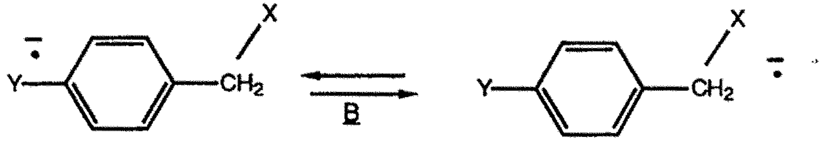
Figure 8: Reactive Mixed Valence formulation for the case of halobenzene radical anions.
IT stands for the photochemical pathway (intervalence transition[168b]) not yet studied in organic reactive mixed valence species, but which has been studied in depth in their inorganic counterparts (ref. 168b, 170). For application to reactive E.D.A. complexes, see ref. 173 p. 186.

This is indeed what has been measured by Saveant's group[174]. The experimental rates of cleavage of series of aromatic halide anion radical series roughly correlate with the standard potential of the $ArX/ArX^{\bullet -}$ couple. The easier it is to reduce ArX, i.e. the deeper its LUMO is, the slower the cleavage rate. In terms of **Fig. 8**, this means correlating the rate of cleavage with the of ΔH≠ or ΔE value. This set of rates spans a range of 10 log units from the least reactive p-$NO_2C_6H_4Cl$ radical anion (logk ≈ -2) to the most reactive one p-CNC_6H_4 Cl (logk ≈ + 8). This wide range of rates clearly shows that there is an activation energy necessary to pass from the π* state to the σ* one. Returning to the mixed valence analogy, this is certainly a Type I or II Day system. **Figure 7** shows, however, that for some terms of the series (the easiest to cleave), point C would be close enough to v_0 so that the equilibrium arrow $\pi^* \rightleftarrows \sigma^*$ would be transformed into $\pi^* \longleftrightarrow \sigma^*$ (type III Day system). This mixed valence analogy is interesting to apply to the p-substituted benzyl halides. Bowman[131,132c] prefers the A representation rather than B for them (**Scheme 22**). We believe that B is a better representation because there is definitely an activation energy necessary to pass from the π* state to the σ* one as shown by the following representative cleavage rates (k, s^{-1}):

p-NO_2-$C_6H_4CH_2Br$: 1.7 x 10^5	p-CN-$C_6H_4CH_2Br$: 6 X 10^7 (10^{10}?)
p-NO_2-$C_6H_4CH_2Cl$: 4 x 10^3	m-NO_2-$C_6H_4CH_2Br$: 60



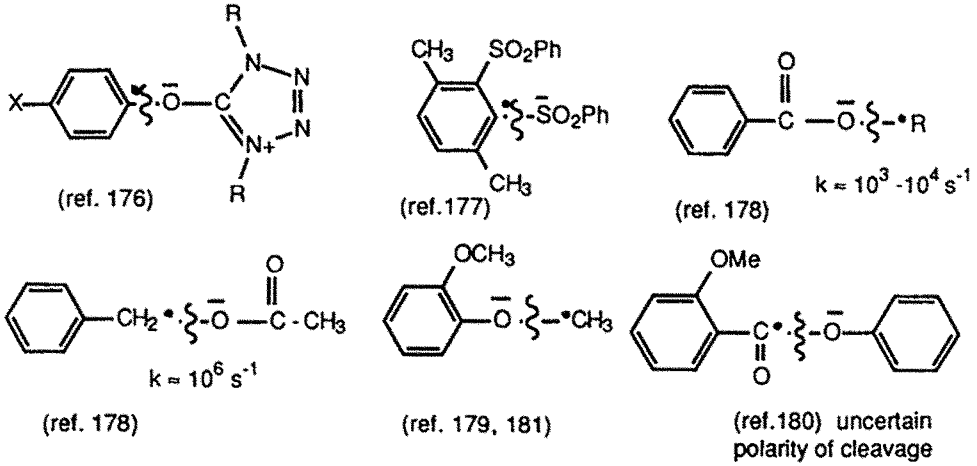
[22a]



[22b]

However, for some special substituents on the phenyl ring or for some other aromatic systems[175], the **[22a]** representation may become predominant. The comparison of C-X α– and ß-induced cleavages shows that for this situation, ß-cleavage seems easier in the radical anion. This ß selectivity is rather general: α-cleavage may become competitive when the α bond is strongly bent out of the π plane (fluorenyl, indenyl systems, **equ. [17, 18]**). **Scheme 9** shows the preferred selectivity which seems to be mostly ß-cleavage (for aromatic esters the C=O is integrated to the aromatic conjugation, so that the reported cleavage results in a β-scission):

Scheme 9

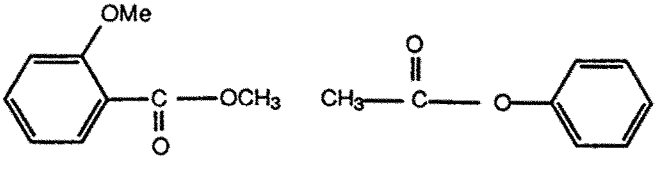


(ref. 176) (ref.177) (ref. 178)

(ref. 178) (ref. 179, 181) (ref.180) uncertain polarity of cleavage

The sulfoxide[177] and the methoxy substituted esters[180] illustrate the possible difficulties expected when several substituted aromatic rings are present in the radical anion.

Scheme10



LUMO = -9.43 eV (EHT) LUMO = -8.756 eV (EHT)

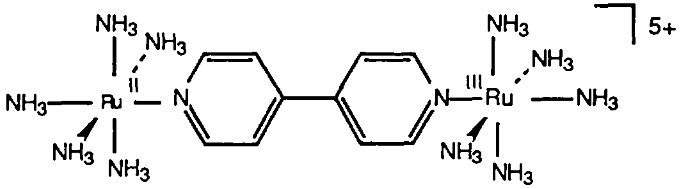
A rule of the thumb for finding which ring should be the one where the extra electron remains, is to isolate each ring with its simplified substituents and search the lowest lying LUMO using a well parametrized Molecular Orbital method (**Scheme 10**).

The preceding discussion has concentrated on the intramolecular factors involved in these cleavages. It should be clear that solvent effects and counterion effects[181] have their role to play as well: V. Parker[182] has found that the cleavage rate of the 9-cyano-10-bromoanthracene anion radical increases by a factor of 15 from butyronitrile to acetonitrile. The effect of protic solvents should even be higher as they can enter into hydrogen bonding[183,184] interactions with the radical anions and could increase leaving group abilities by specific solvation or protonation. Thus, protonation on NO_2 decreases this rate, while the protonation of the leaving group increases it[184]. When the excess of charge travels from the π^* system to the C-X bond, the cation associated with the radical anion must change its position to optimize electrostatic interactions. In some inorganic mixed valence compounds, this parameter has been shown to be important[185a], and Kosower has suggested a predominant influence of solvent effects on intramolecular electron transfer rates[185b].

Finally, as expected from **Fig. 8**, the correlation of log k versus E° shows some scattering[174]. Part of it may be assigned to cleavage assisted by steric strain release; on the other hand it would be interesting to verify if the introduction of a correction for the vibronic contribution[186] (stretching and bending frequencies of the C-X bonds in different structures) may improve the quality of the correlation.

One may wonder if, within the reactive mixed valence approach, it would be feasible to master the α *versus* β selectivity. Indeed, for the classical mixed valence compound in D_2O solution (**Scheme 11**), absorption of light at 9800Å induces the intervalence transfer[187](IT in **Figure 8**).

Scheme 11



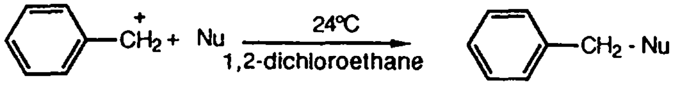
To obtain the same reaction in **Fig.8**, one would have to irradiate at an energy equal to IT. If an ITα were associated with the photochemical α-scission and an ITβ associated with the photochemical β-scission, one could hope to select the correct λ (lasers in this λ range may be tuned with a fair precision) to cleave the radical anion selectively in the desired position[188]. The recent Symons and Bowman's report[132c], showing the stability of p-nitrobenzyl halide radical anions at low temperature, opens the way for this type of photochemical study on organic reactive mixed valence structures.

The mixed valence isomer approach extended to intramolecular dissociative electron transfer also reveals a fascinating aspect of the relationship between thermodynamic stability and reactivity in these reactions. These substituted aromatic compounds have a positive electron affinity, and the radical anion has a higher thermodynamic stability than its hyponomer. A naive reasoning would lead to the conclusion that this overall gain in stability is evenly distributed among all the constitutive bonds of the radical ion and an intuitive expectation of decreased reactivity would follow. Of course, the molecular orbital approach reminds us that with the extra electron occupying an antibonding molecular orbital, some destabilization could, in fact, occur. But this is not sufficient; indeed, the first order molecular orbital approach tells us that the LUMO is mainly localized on the aromatic framework and we will see in **Section 1.4.3.2.** that the typical π^* activation is associative rather than dissociative. This means that, in **Fig.8**, the first order molecular orbital approach describes the situation for v=0. To explain reactivity, the C point has to be reached. In N dimensional potential energy surfaces[189], this means populating vibrational levels of appropriate symmetry (vibronic approach). An equivalent,but more revealing approach, is to consider the electron as an activating messenger. In the radical anion, the extra electron occupies a part of the space where it spends the greatest part of its time (electrophore part). However, there are parts of the space where it spends far shorter amount of time, but which play a critical role in terms of reactivity, because they correspond to strongly antibonding properties for a given σ bond.

Miller and Kozak[162] have proposed an interesting physical description of the succession of events which occur during the C-Cl bond cleavage of p-$O_2NC_6H_4CH_2Cl$. They suggested: "if on a time scale much shorter than the chemical event (bond cleavage), we regard the electron as a particle migrating from site to site on the radical anion, then the mean lifetime τ of the electron before reaction occurs at, say, the para site can be determined by calculating the *ensemble average of all possible displacements of the electron* (our italics), starting from some initial position (e.g. the site of electron attachment) or, given delocalization, from all possible positions defining the reaction space of the system, before its trajectory terminates at the para position". The italicized part of the citation explains our label of "messenger" for the electron; the adjective "activating" is supported by the body of data that we have collected in this Tetrahedron Report. We will return later to the consequences of viewing the electron as an "activating messenger"; the point we want to stress now is that it already provides us with a fresh physical view of the reactivity behavior associated with the data we have gathered under the unifying label of "reactive mixed valence species".

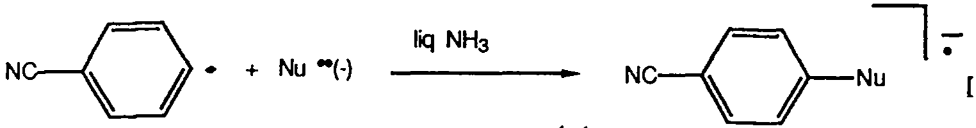
1.4.2.2. The very rapid formation of some 3e bonds. Consequences for the design of ETC systems.

One puzzling fact in terms of thermodynamic thinking is that these 3e species, which violate one of the most widespread rules of chemistry: the octet rule[2-9] and its extensions, may be formed so rapidly. The rapid reaction of nucleophiles with carbocations[190, 191] is well accepted and **equ. [23]** gives an idea of the rates measured in this case:


(ref. 190) [23]

Nu	k ($Mol^{-1}s^{-1}$)
Cl^-, Br^-, I^-	$6x10^{10}$
tri-n-butylamine	$7x10^{6}$
MeOH	$7x10^{7}$

Reactions between σ radicals and nucleophiles (equ. [24]) show that the suppression of electrostatic attraction between the reacting partners and the formation of products which violate the octet rule are not particularly damaging to the reaction rate[192].


[24]

$Nu^{\bullet\bullet}(-)$	k ($lMol^{-1}s^{-1}$)
$PhS^{\bullet\bullet}(-)$	$1.4 x 10^{10}$
$(EtO)_2PO^{\bullet\bullet}(-)$	$8 x 10^{9}$
$CN^{\bullet\bullet}(-)$	$9.6 x 10^{8}$

Application of the microreversibility principle to **Fig.8** helps to understand this surprisingly high reactivity. The driving force for the reaction is the formation of a π* radical anion from the initial σ* one obtained in the transition state. This very high reactivity in the formation of some three electron bonds is not confined to organic substrates. It is also found for organometallic[24,36,193] and inorganic reagents[11a,73,194] and it is worth verifying whether the reactive mixed valence approach applies here as well.

A direct consequence of these high reaction rates is that, in the well known SRN1 like processes and related chain reactions[195], whose importance in synthesis keeps increasing[156,196,197], selectivity often results from competition between reactions which nearly reach the diffusion control limit. This may give rise to macroscopic effects, difficult to understand in classical terms[198]. A second consequence relates to the design of E.T.C. cycles. At the begining of the study of electron transfer induced chain reactions, the emphasis was essentially laid upon the necessity of the electron transfer propagation step being feasible. The condition was written as[199]:

$$E^o_s > E^o_p$$

where E^o_s is the standard reduction potential of the couple ArX / $(ArX)^{\bullet -}$ and E^o_p is the standard reduction potential of the substitution product ArNu/ $(ArNu)^{\circ -}$:

$$ArX + e \rightleftarrows (ArX)^{\bullet -} \qquad E^o_s \qquad [25a]$$

$$ArNu + e \rightleftarrows (ArNu)^{\bullet -} \qquad E^o_p \qquad [25b]$$

It then appeared that in terms of generalized SRN1 (ETC[11a]), this condition may be bypassed if the propagating step is of the inner-sphere type[14]. It now becomes clearer that for ETC building, it is necessary to obtain 3e type $RNu^{\bullet -}$ intermediates with long enough lives to propagate the cycle:

$$R^{\bullet} + Nu^{\bullet\bullet -} \longrightarrow [RNu]^{\bullet -} \qquad [26a]$$

$$[RNu]^{\bullet -} + RX \longrightarrow R^{\bullet} + X^{\bullet\bullet -} + RNu \qquad [26b]$$

This lifetime increases with the depth of the LUMO in RNu for systems following the behavior described by **Fig.8**. On the other hand, the rate of electron transfer from $RNu^{\bullet -}$ to RX (**equ. [26b]**) decreases with this depth. A fine balance[200] has therefore to be reached in designing efficient cycles (high turnovers). Maximum shaped dependence of turnovers has been reported in the photooxidation of X-$C_6H_4CH_2OH$ catalyzed by various flavins[201]. This type of maximum shaped rate has been kinetically justified in catalysis by Boudart[202]. The range of electrophilic substrates not working in SRN1 reactions of substituted aromatic[203] (YC_6H_4X does not work for Y = Me_2N, O^-, NO_2) also hints at the possibility of bell shaped behavior for these substrates.

1.4.3. π* type radical anions.

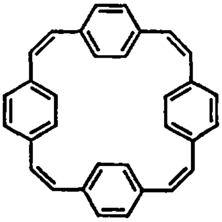
With **Sections 1.4.2.1.**, and **1.4.2.2.**, it might appear that the activation of unsaturated systems by the addition of an electron has already been widely treated. All the chemistry described in these sections, however, occurred after an intramolecular electron transfer from the π part of the structure to the σ one. In this section, we will show that, with the exception of the electron transfer induced geometric isomerization of olefins[204] and the disproportionation processes[205], the only direct activation induced by adding an electron to a π system is associative in character.

1.4.3.1. Structural modifications caused by the addition of an electron to a π system.

Most of the structural data available on the geometrical consequences of adding an electron to a π system have been obtained in cyclic compounds. In a typical π aromatic system, the addition of an electron changes the overall structure very little[206,207], illustrating one of the multiple[208] criteria retained as characteristic for aromaticity: "one of the most striking phenomena related to aromaticity is the unusual tendency of aromatic systems to remain so"[209]. However, the crystalline complex bis (tetramethylenediamine) lithium naphthalene dianion shows that the dianion, with 4 atoms 15 pm off the mean plane of the group[210], is no longer planar. At the level of radical anions containing several aromatic groups, this structural stability of aromatic rings generally means that conformational distortions, when present, take place in the non-aromatic part of the molecule. For example, in the radical anion of [2.2.2.2.] paracyclophane-1,9,17,25-tetraene[211] shown in **Scheme 12**, the geometry of aromatic rings is normal whereas the olefinic part deviates from olefinic plane.

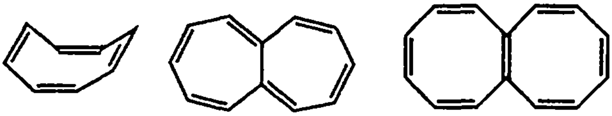
W. Huber and K. Müllen[212] recently gave an excellent review of their contributions to the study of conformational changes induced by the successive addition of electrons to selected annulenes. Taking ion pairing[205,213] factors as constant, or uniformally compensated, some interesting trends emerge in series.

Scheme 12



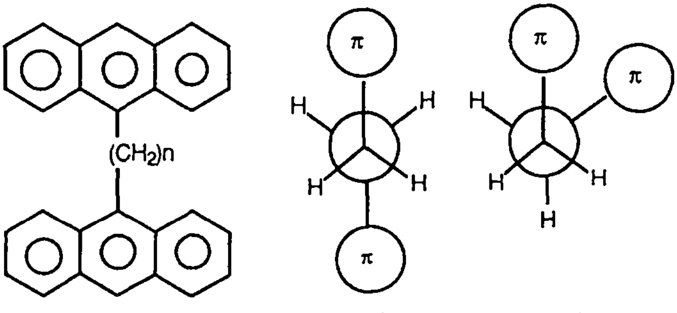
A general phenomenom is the flattening of annulenes after electron addition to the π system. The cyclooctatetrene[214] and its fluoroderivatives[215] are textbook examples, where the neutral molecule is tub-shaped and the anion or dianion are both planar. Müllen et al. have shown the wide application of the effect, by extending it to heptalene[216] and octalene[217] (**Scheme 13**):

Scheme 13



The case of dianthryl alkanes[218] provides a natural transition with the following Section, dealing with associative activation induced by electron addition to π systems. Indeed, for these systems, face-to-face arrangement of anthracenes is more or less feasible, depending on n in the formula (**Scheme 14**).

Scheme 14

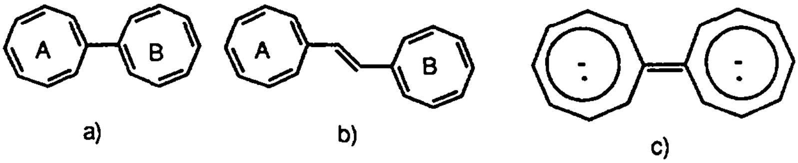


anti type *syn* type

Huber and Müllen[212] have studied the various possibilities of what occurs, when successive electrons are added to this system for various lengths of the methylenic chain connecting the two anthracenyl moieties. For dianthrylethane (n=2) the role of the counterion and solvent are determinant on the localization *versus* delocalization of the extra electron in the anthryl subunits. A tight interaction of the radical anion with its counterion (methyltetrahydrofuran, MTHF as solvent) favors localization within one ring. In contrast, the solvent system dimethoxyethane-hexamethyl- phosphorotriamide favors a situation where the extra electron rapidly exchanges between the two anthryl subunits. When such a delocalization occurs, the preferred conformation corresponds to an eclipsed or partially eclipsed arrangement (*syn* type) of π systems, which enforces the intramolecular through-space interaction of the anthryl subunits. Passing to the dianion, one obtains a singlet state, where the excess π charge is uniformly distributed over the two anthryl moieties; for this singlet state, the favored conformation is again a *syn* type, despite coulombic repulsion. In contrast, for the triplet state of this dianion, observed at -170°C, the *anti* type conformation is preferred. The trianion, even in solvents such as dimethoxyethane-hexamethyl phosphorotriamide, displays ESR and ENDOR spectra very similar to those recorded for the radical anion in MTHF. Therefore, a spin localized structure is indicated for this system. This tendency towards spin localization with increasing charge is confirmed by the spectral properties of the tetraanion of dianthrylethane.

The uniform delocalization of the excess π charge in the dianion of dianthryl ethane contrasts with the localization reported for the contact ion pairs of dianions derived from the two systems[219] shown in **Scheme 15**, where, at low temperature (-80°C in NH_3), both electrons occupy one planar eight- membered ring, while the other ring adopts a distorted tub conformation. At higher temperatures, electron exchange between the two rings takes place at a rapid rate on the NMR time scale, with each ring simultaneously changing from a planar to a folded conformation.

Scheme 15

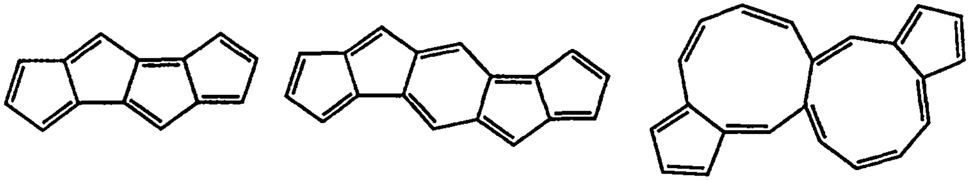


A very interesting outcome of the study of this system is that the delocalization in this case apparently does not involve species such as those displayed in **Scheme 15c** where one electron would have jumped from a doubly charged A ring to the neutral B one. Experimentally everything occurs as if both extra electrons were "jumping" from ring A to ring B. Every attempt to directly observe the preceding totally delocalized dianion of **Scheme 15c** has been inconclusive. The price of reorganization energy for passing from the U shaped conformation to the planar one has to be paid[220]. As soon as the delocalized dianion is formed, both rings are planar, and the second electron transfer to obtain the two electrons localized in ring B is favored by the energetic bonus expected from once again reaching a situation where one of the two rings has a 10 π e "aromatic" configuration.

Other examples of such situations, where a first electron transfer apparently activates the substrate towards a second electron transfer in the same direction, are known[221,222].

The specific structural aspects associated with the biradicaloid[223] character of some dianions and the effect of tending towards aromatic or away from aromatic π systems have been discussed at length in ref. 4b,208d, 223. They will not be treated here. Some non-alternant non-branched systems (**Scheme 16**), have vacant bonding orbitals [4b]; the addition of one electron to them should provide radical anions with increased stability.

Scheme 16



1.4.3.2. Associative activation in the reactivity of π* radical anions.

The dianthrylethane system, discussed in the preceding paragraph, has shown that, depending upon the medium and the counterion, aromatic radical anions can display an associative activation toward themselves or toward their hyponomer present in the solution. This paragraph will provide other examples of such an associative activation.

1.4.3.2.1. Associative activation toward σ systems.

The most trivial one that we may describe as enhanced reactivity toward electrophiles is quite well documented. The π basicity of biphenyl measured is very low[224] but when one passes to its radical anion, the obtained base is strong enough to abstract a proton from compounds having a pKa of about 33[225]. More data on the pKa of radical anions and rates of protonation may be found in ref. 226-231.

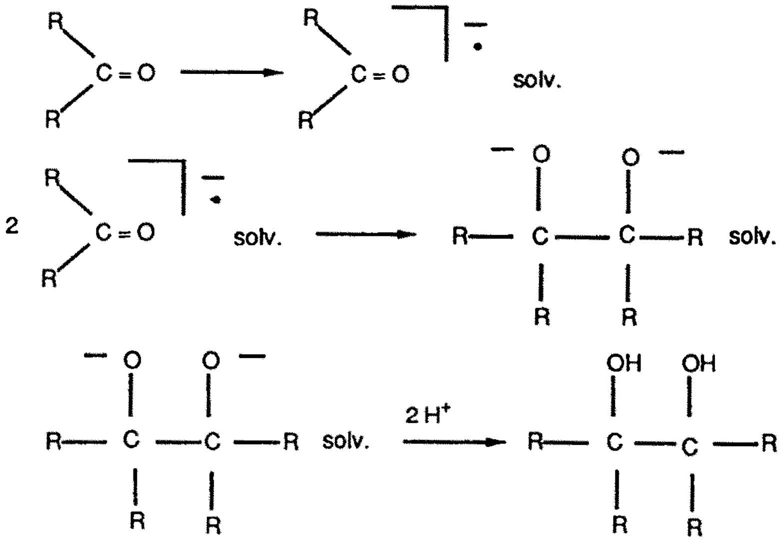
An important step toward the understanding of the border between the polar SNAr mechanism and its SET counterpart[232] would be quantitative data on the rate of radical addition to aromatic radical anions. Garst[233] has proposed such a step in the reaction between naphthalene radical anion and alkyl radical, but experimental rate constants are not yet available.

1.4.3.2.2. Associative activation toward π systems

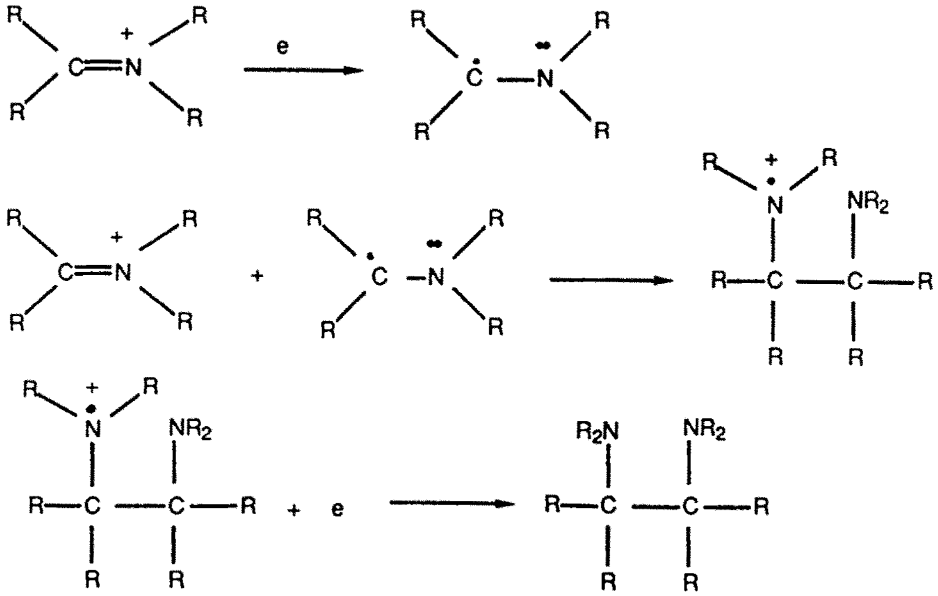
When π* radical anions are opposed to other π systems, the associative activation does not demand a preliminary localization of the π system. We will successively examine non-aromatic and then, aromatic systems.

One of the earliest identified examples is the reductive dimerization of activated olefins and carbonyl groups[234], but the mechanistic subtleties of the chronology of adsorption, proton transfer, electron transfer and dimerization steps required a long time before they could be disentangled. The reference articles in electrochemistry for this mechanistic puzzle originate from Saveant's[235], Bard's[236] and Evans's[237] groups. The main pathways are summarized in **Schemes 17** to 19[235a]. The first (**Scheme 17**) is R.R.C. (radical-radical coupling) usually met for activated olefins in aprotic solvents; the intermediate dimer dianion is stabilized by rapid protonation. The second (**Scheme 18**) is R.S.C. (radical-substrate coupling) operating in electrohydrodimerization of compounds containing the immonium group. The third (**Scheme 19**) is I.S.C. (ion-substrate coupling) which was the first mechanism proposed for electrodimerizations; a di-reduced species attacks the substrate.

Scheme 17

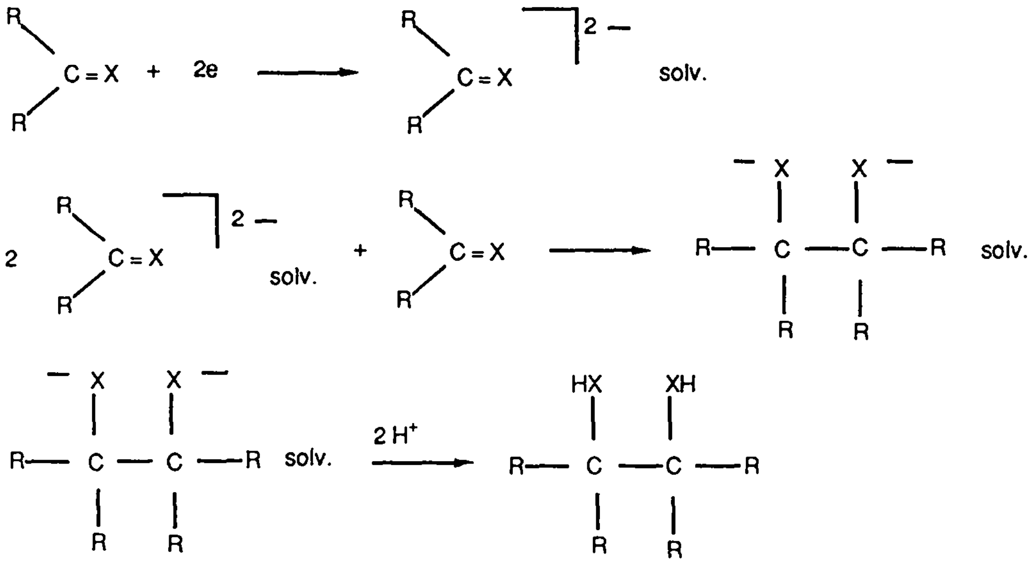


Scheme 18

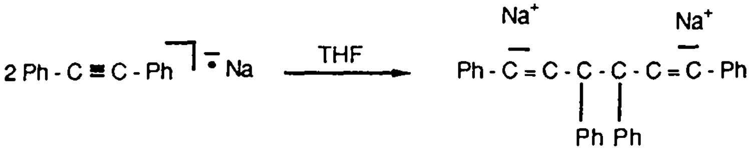


Variations around these main mechanisms may be induced by specific solvent or structural modifications. For example, in the R.R.C. mechanism, the protonation steps may either follow the R.R.C. step or flank it[235a]. The importance of associative activation is shown in **Scheme 17** where association of negatively charged species precedes their protonation in the succession of events. This is particularly noteworthy, if one recalls the pKa range (9 to 12) of typical carbonyl radical anions in water[238].

Scheme 19

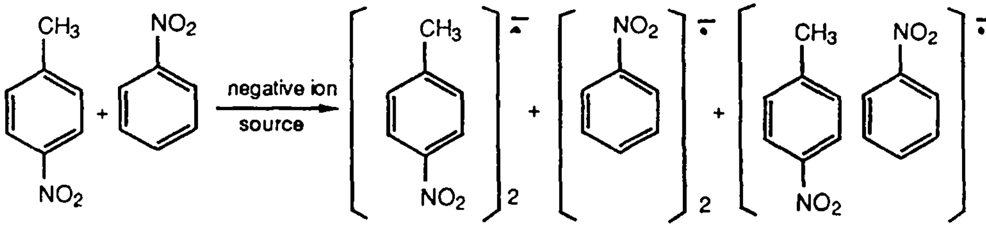


Under special conditions, non-activated π bonds are also subject to associative reductive association. **Equation** [27] illustrates the operation of such a reductive associative activation; more examples may be found in references 145 and 240-243.



$$2\,\mathrm{Ph{-}C{\equiv}C{-}Ph}\,\rceil^{\overset{-}{\bullet}}\mathrm{Na}\xrightarrow{\text{THF}}\mathrm{Ph{-}\overset{-}{C}{=}C{-}\underset{Ph}{C}{-}\underset{Ph}{C}{-}C{=}\overset{-}{C}{-}Ph}\quad(\mathrm{Na^+},\ \mathrm{Na^+})$$

(ref. 239) [27]

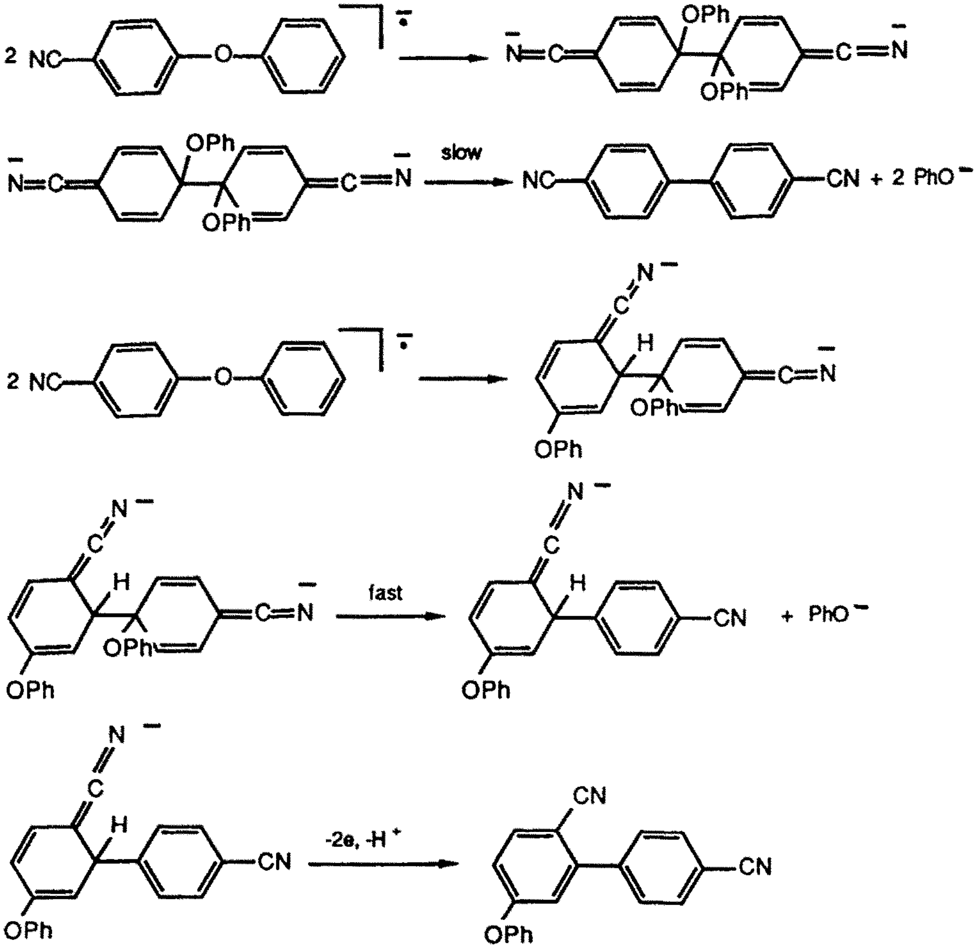


[28]

As ion pairing appears to be important in these dimerizations, the choice of the solvent may be critical: in hexamethylphosphorotriamide, there is no detectable dimerization of diphenylacetylene radical anion. **Equ. [28]** shows, however, that in the gas phase, reductive associative activation may also take place[244].

In solution, Bartak's et al. electrochemical studies have shown the manifestation of such an associative activation[245]. The radical anions of 4-cyano and 2-cyanodiphenylether undergo dimerization in DMF, the first one irreversibly (k_2=1.1x10^2 $Mol^{-1}s^{-1}$), the second one reversibly ($k_{forward}$=1.2x10^3 $Mol^{-1}s^{-1}$, $k_{backward}$ =9.5x10^{-2} $Mol^{-1}s^{-1}$). The proposed overall mechanism for the 4-cyanodiphenylether is shown in **Scheme 20**.

Scheme 20



Such a dimerization of aromatic radical anions is also reported for 2-fluorobenzonitrile, 2-cyanoanisole[246] and heptafulvalene where it is reversible[247]. The regioselectivity of coupling would be controlled by a coupling at carbon sites of the highest unpaired electron density[248] (provided by

ESR[249] and theoretical calculations[250] of the radical anion). The overall result of the reaction is a carbon-oxygen bond cleavage under reductive conditions. The first experimental hint at such a bimolecular mechanism is that the decomposition of the radical anion is dependent on concentration. This contrasts with the simple unimolecular cleavages examined in **Section 1.4.2.1.**. Walsh[137a] proposed that such an experimental result may also be reconciled with the participation of a disproportionation step involving the radical anion. Arai's pulse radiolysis studies[251] of benzene derivatives at low temperature in methyltetrahydrofuran did not reveal dimerization of the radical anion. Arai suggested that unsaturated systems substituted by groups of high electron affinity (CN, CO_2Et, NO_2) have radical anions more prone to dimerization with their hyponomer. Other examples of reductive associative activation of aromatics may be found in ref. 182 and 252-254.

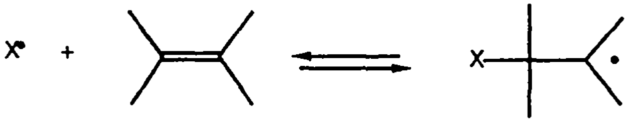
Among the preceding associative activations, some involved the dimerization of the radical anion whereas others involved the reaction of the radical with its hyponomer. One could guess[135] that, because of coulombic repulsion, the first type of dimerization is considerably slower than the second. This is not true for 1,1-diphenylethylene (D). Szwarc and colleagues[255a] have measured the two types of rates and the effect of ion pairing and they found that $D^{\bullet-}$ self dimerizes faster ($k=10^5$ $Mol^{-1}s^{-1}$) than it adds to its hyponomer ($k=10^4$ $Mol^{-1}s^{-1}$). In these reactions, as in disproportionations, cation affinity and ion pairing may play a determinant role[255b].

1.4.4. π and σ radicals

The addition of an electron to a carbocation yields a radical. The distinction between π radicals and σ radicals is not very clear cut. Thus, $CH_3^\bullet$ is almost planar and may therefore be considered to be a π radical, while $CF_3^\bullet$ is pyramidal[256], and is better classified as a σ radical. The distinction becomes clearer for vinylic[257] or aromatic carbocations[258]. For these cases, the addition of an electron to the carbocation provides a radical whose σ character is well defined. Treating the structure and reactivity of both classes of intermediates through the filter of "one electron more" would clearly demand a review in itself. We will therefore only select some illustrative examples. More could be said by a comparison of the standard books and reviews dealing with carbenium ions[259-262] and radical[263-265] chemistry. To maintain continuity with the preceding sections, we will consider a planar carbenium ion as the smallest unsaturated fragment imaginable. We should again therefore search for dissociative activation (α or β to the unsaturation) and associative activation when one electron is added to these systems. In many respects, radicals are situated in between their hyponomers (for a carbon centered radical: carbenium ions) and their hypernomers (for a carbon centered radical: carbanions). For this **Section 1.4.4.**, we treat simultaneously "one electron more " and "one electron less".

1.4.4.1. β-cleavage in radicals, carbenium ions and carbanions.

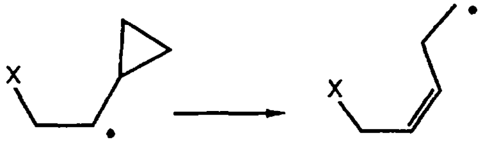
The cleavage of bonds situated in the β-position with regard to a carbon centered radical is a well identified reaction in radical chemistry. It is the reverse of the addition of a radical to a double bond (equ. [29]):



[29]

X = R_3Sn, RS [266,267]

The equilibrium may be driven to the left if a bond is introduced in β' of the radical and this bond cleaves faster than the C-X bond [268,269] (equ. [30]):

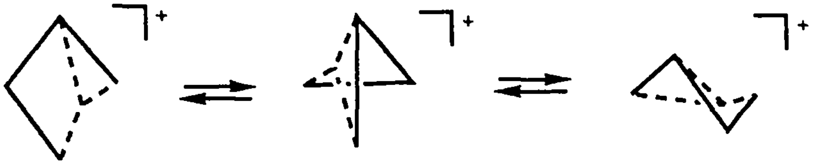


[30]

The driving force in this specific case is the relief of strain associated with the opening of the cyclopropyl ring. This type of β-cleavage is pervasive in radical chemistry[173,270-273]. It has been reviewed[274] and its stereoelectronic aspects have been clearly demonstrated[275].

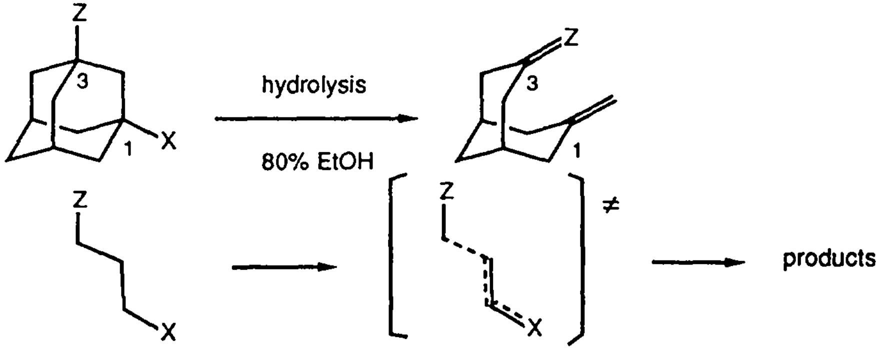
We now consider the β-fragmentation of carbocations. The cyclopropylcarbinyl cation has been thoroughly studied and Ahlberg's review[261b] provides an excellent description of the thermodynamic, theoretical and kinetic aspects of its rearrangement between bicyclobutonium like ions, bisected cyclopropylcarbinyl cations and related structures. The main relevant information for our purpose is that the barrier for interchange shown in **Scheme 21** is less than 3 kcalMol^{-1} [262a]. The potential energy surface for $C_4H_7^+$ is certainly very flat[262b]. It is not known if the barrier could be as low as the one which has been proposed for the norbornyl cation studied at 5°K (≈200 calMol^{-1})[262c]. It would seem, in terms of Day's mixed valence nomenclature[165a], that the cyclopropyl carbinyl cation would be on the border between class II - class III dynamic processes. The norbornyl cation would illustrate a class III dynamic process (i.e. a mesomeric one). In 1979, while writing ref. 11a, we were bewildered by the lack of communication which exists between organic and inorganic chemists. The classical *versus* non classical ion controversy[276] put in perspective with the mixed valence approach[165a], gives another striking example of this phenomenon. Here again, two important groups of bright scientists strive towards the same elaborate

Scheme 21



mechanistic objective and, to our knowledge, none of the reviews on this common objective written by either group aknowledges the efforts and contributions made by the other group.

There are identified cases where the ß-cleavage in carbenium ions provides two fragments rather than an intramolecular rearrangement. The first are Grob's fragmentations[259b,277-279a]. When 3-substituted 1-adamantyl bromides are hydrolyzed, the effect of strong electron donors (Z = NH_2, NMe_2, O^-, S^-) on the rate is higher than expected from their polar substituent constants. The bond ß to the positive carbon is cleaved and fragmentation products are obtained[280a,b] (**equ. [31]**):

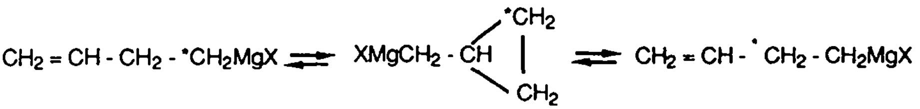


[31]

The transition state proposed for this solvolysis involves five atomic centers participating in a concerted mechanism. The carbanionic counterpart of this fragmentation has recently been reported on Al_2O_3[281]. There is never a full development of the carbenium ion on 1-carbon. Such a full development is observed in unimolecular fragmentations (F1)[282].

In all the carbenium ions undergoing fragmentation in solution, there is clearly a flow of electronic density towards the carbenium site. The radicals are half-way between carbenium ions and carbanions. Therefore, one has to inquire "what happens to carbanions in terms of ß-scission ?".

The interconversion of cyclopropyl carbinyl and allyl carbinyl Grignard reageants provides the carbanionic counterpart of the cyclopropylcarbinyl carbenium rearrangement[283,284] (**equ.[32]**):



$$CH_2=CH-CH_2-{}^{*}CH_2MgX \rightleftharpoons XMgCH_2-CH\begin{matrix}{}^{*}CH_2\\ |\\ CH_2\end{matrix} \rightleftharpoons CH_2=CH-{}^{*}CH_2-CH_2MgX \qquad [32]$$

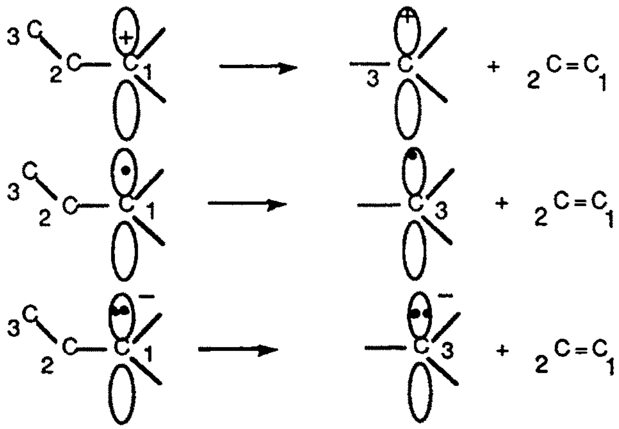
The rearrangement occurs at -24°C in dimethyl ether and, starting from cyclopropylcarbinyl bromide, 57% of the starting product is opened after 1 hour[283]. The authors estimate a free energy of activation of 19 kcal for this rearrangement. The same carbanionic rearrangement also takes place with cyclopropylmethyl lithium at -70°C in diethyl ether[285]. As expected, cation effects and ion pairing considerably change the rate. The rearrangement of 3-methyl-3-butenyl lithium is much faster than that of 3-methyl-3-butenylmagnesium bromide and this rate increases with increasing solvating power of the solvent[286].

The E_1cb (Elimination, unimolecular from the conjugate base[279,287]) and the Ad-E (Addition Elimination [279,288]) of vinyl halides confirm that ß-scission is also feasible with a flow of electronic density away from the carbon of the carbanion. In these cases, the flow of electronic density is driven by an electronegative element. This driving force is absent in methylcyclopropyl systems.

In a pioneering paper, Zimmerman and Zweig applied the Hückel molecular orbital theory to predict that "other factors being equal, [1,2] sigmatropic rearrangements will occur with decreasing ease along the series: carbenium ion > free radical > carbanion"[289] (see also ref. 283 for an excellent discussion of this point). This prediction is fully substantiated by the sigmatropic rearrangements of cyclopropylmethyl species. Indeed, we have seen that on the carbenium side the rearrangement has been shown to occur even at -152°K. Kochi and Krusic[290] have reported that the cyclopropylmethyl radical rearranges very rapidly at -120°C. Further experimental studies provide the rate constant $10^8 s^{-1}$, for this rearrangement at room temperature[291]. The cyclopropylmethyl radical is clearly situated between its hypernomer and its hyponomer. The difficulty is in knowing whether the radical is closer to the carbanion or to the carbocation. One way of evaluating the situation is to take the average (ionization potential + electron affinity) of each of the three species ($CH_3^{\bullet\bullet-}$, $CH_3^{\bullet}$, CH_3^{+}). Approximate values obtained from **Annex 1** would give respectively: 0 +/-1 eV; 5 +/-1 eV; 20 +/-5 eV. This points towards a greater similarity between the carbanion and the radical in the absence of substituent effects. These data would have to be corrected in solution, because strong solvation or ion pairing may deactivate both carbanions and carbocations. Radicals are not so prone to strong solvatation or ion pairing effects.

Scheme 22, which shows the relation between substituent effects when comparing *plus* and *minus* 1e series. This illustrates the type of studies which should be explored for rearrangements including sigmatropic rearrangements[292].

Scheme 22

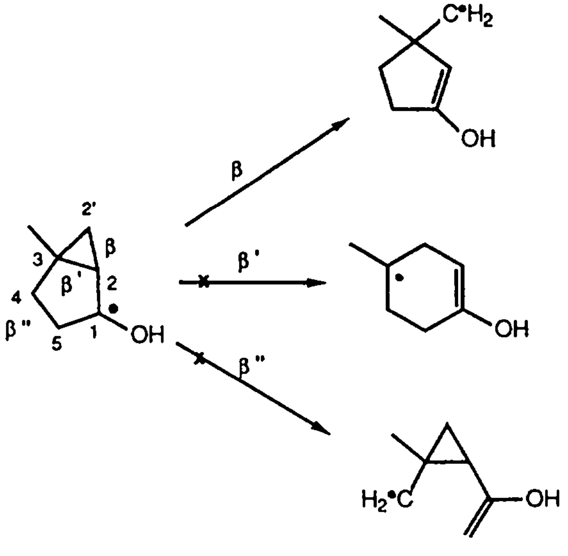


For the specific case of the cyclopropylcarbinyl system, molecular orbital calculations suggest that the ring closed structure is more stable than the acyclic structure for the case of carbenium, about equal in energy for the radical and less stable for the carbanion[293].

1.4.4.2. Reactive mixed valence approach applied to ß-scission. Captodative *versus* polar approach.

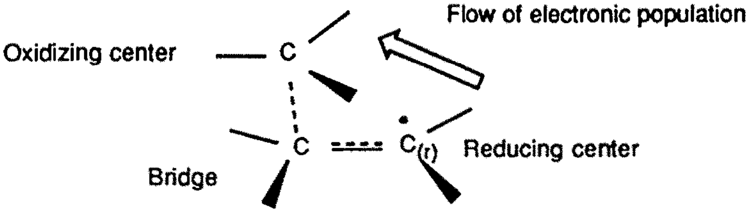
The preceding section suggests that radical ß-scissions could formally be viewed according to 3 patterns of reactivity: 1) ß-scissions in which the electron flow is toward the paramagnetic center (carbenium like); 2) ß-scission in which the flow is away from the paramagnetic center (carbanion like); 3) those where the flow is difficult to estimate and which could be called isopolar. The whole field of ß-cleavages on carbon centered radicals, as shown by the measured rates[294] of ß-scission, does not cover a wide range in terms of reactivity (from $10^6\ s^{-1}$ to $10^9\ s^{-1}$). When their rate is relatively slow, another type of event occurs such as addition, electron transfer or dimerization.

Scheme 23



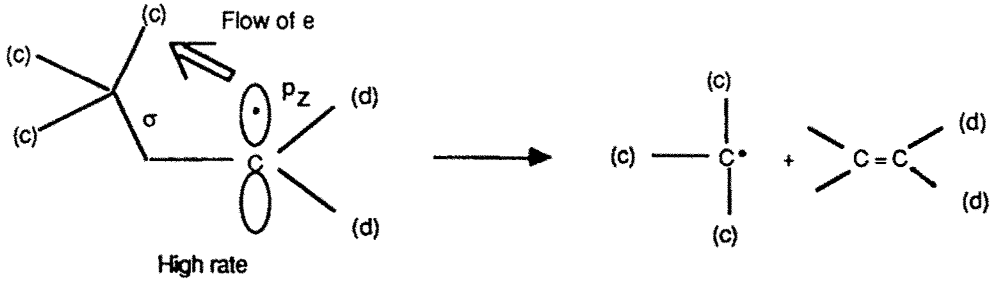
Some features of the reactive mixed valence model apply both to carbenium-like and to carbanion-like radicals. The stereoelectronic aspect of ß-cleavage[275c] **(Scheme 23)** is especially revealing. Experimentally, ß-cleavage prevails over ß'-cleavage although the latter would be thermodynamically favored. The β"-cleavage, which, apart from its stereoelectronic handicap, does not benefit from the energetics associated with the strain release[295] in the opening of the cyclopropyl ring, is highly unfavored. **Scheme 23** therefore provides another situation where the overlap between the σ^* antibonding orbital and the p_z orbital carrying the single electron is a very critical parameter in cleavage selectivity , when scissible bonds are of the same type. Here we have not considered the direction of the electronic flux of electron density which is probably as indicated by the arrow in **Scheme 24** (carbanion like). The arrow makes it possible for us to pictorially describe the reactive mixed valence approach in the framework of **Fig.8**. In this case, the electron rich site (the reductor) would be C1(because of the OH substituent), the bridge would be C2 and the electron poor site would be the σ orbital of the C2-C2' bond (**Scheme 23**). A good overlap between the p_z orbital and the C2-C'2 bond increases the resonance term in **Fig.8** so $\Delta H^{\neq}$ is decreased. The good overlap makes it easier for the electron to pass from the electron rich site to the electron poor one as an activating messenger. The same stereoelectronic argument would obviously hold true for a typical carbenium like radical. At this point, the reactive mixed valence model is exactly equivalent to Beckwith's excellent stereoelectronic approach[275].

Scheme 24



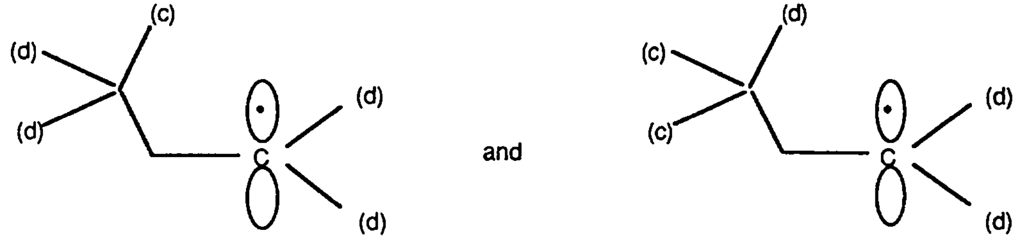
In a reactive mixed valence complex, making the reducing center more reducing and/or the oxidizing center more oxidizing should increase the reaction rate. In the reactive mixed valence approach there are three partners: the electron rich site, the bridge[167d], and the electron poor site. If polar effects predominate then only once we have decided which is the electron rich part and which is the electron poor one for a given substrate, can we begin to think of the effects of electronic substituents on the reaction rate. For a carbanion-like paramagnetic center, other parameters being kept constant, the most favorable situation may be represented as in **Scheme 25**.

Scheme 25: Favorable substitutent effect for a carbanion-like β-cleavage. c and d stand for capto and dative as in ref. 296. We define c as the substituent which makes respectively deeper the σ^* or the p_z orbital; d describes the opposite situation.



This scheme only describes a situation of cooperativeness of the substituents with the electron flow density. These substituents make the electron poor center poorer and the electron rich center richer. In contrast, the application of the **c-d** effect would lead to the recognition of this situation as unfavorable. Thus, keeping the same (**d**) substituents on the paramagnetic center (i.e. keeping the stability of the olefinic part constant), one would guess that the most favorable situations for ß-cleavage are the ones displayed in **Scheme 26** because they would yield radicals which are stabilized by **c-d** effect. The reactive mixed valence model shows that polar effects and **c-d** effects work in opposite directions, and this suggests the type of experiment necessary to try to discriminate between them. In this sense it converges with the Arnold and Creary approaches[297], which measure the importance of the polar contribution with respect to spin delocalization through the value of a ρ/ρ^* parameter . In every situation where the Arnold model hints at a strong polar contribution, the **c-d** effect could be overcome by the polar effects. Another possible way to express this is that captodative effects could be expected to work primarily when the radical ß-scission is essentially "isopolar" in terms of electron flux. At this point, it should be recalled that we are not actually affirmative about the direction of electronic flow in β-scissions of C-C bonds. We have reasoned using the hypothesis of a carbanion-like cleavage, but there are polar effects described in the literature which suggest on the contrary a carbenium like flow of electron density[298]. The reversal of flow would not change the main point of our argument. When polar effects predominate, the **c-d** effect is not applicable.

Scheme 26



As shown by Beckwith's report[274], the rationalization of ß-cleavage rates and selectivities as well as their opposite (addition) is a field of study in itself. Before reaching the stage where experimental results can be related to theory, one has to answer the preliminary questions:

a) Is there any reversible step[299c,d,300]?

b) Does the overall selectivity result from thermodynamic or kinetic effects[275]?

c) Can we reverse the selectivity by changing the temperature[301]?

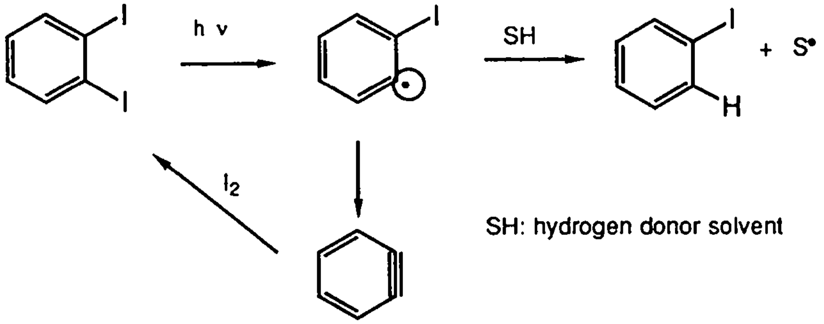
d) Is the observed reaction a straightforward one or is the ß-scission or radical addition integrated into an overall chain mechanism[273]?

After this preliminary stage, if one is sure that entropy is not the source of selectivity, one can begin to think of interpreting the observed results in relation to some of all the factors already discussed including the steric treatment[302]. The exercise of quantitative interpretation in this field is still an art and is often a highly controversial.

1.4.4.3. The strange case of benzyne *versus* σ radicals.

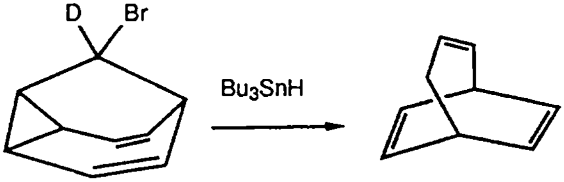
Up until now we have studied the ß-cleavage mainly in π type radicals. The word "mainly" is used here because the bending angle in carbon centered radicals depends on the electronic nature of its substituents[303,304]. Adamantyl and phenyl type radicals are typical σ radicals. In phenyl like radicals, ß-cleavage should provide benzynes. This possibility has been explored by F. Greene[305], N. Kharasch[306], Kampmeier[307], Cadogan[308] and Friedman[309].

Scheme 27

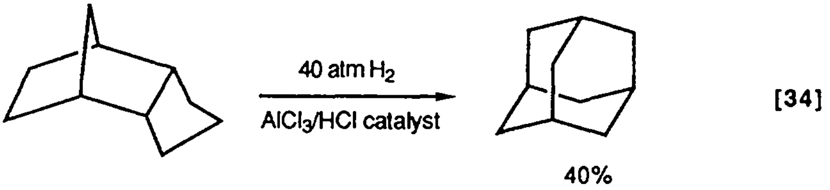


Most of the dehydrobenzene formed adds to I_2 and reverts to the starting material. However, if the reaction is performed in the presence of tetracyclone, up to 16% of dehydrobenzene is trapped[306,307]. In the monograph[310] devoted to dehydrobenzene and derivatives, the main method of formation of dehydrobenzene is scission ß from a carbanion and, no method based on phenyl cations[258b] is described. Apparently here is a situation which is the opposite of the one prevailing with π radicals. For the latter, and in agreement with Zimmerman's[289] prediction, ß-cleavage was fastest for the carbenium ions followed by the radicals and by the carbanions. It would be interesting to explore the reasons for this behavior; could benzynes be generated using the principle of Grob's fragmentation[280a] (equ. [31]) ?

σ Radicals may be generated under mild conditions. When 9-deuterio-9-bromo barbaralene is reduced at 5°C with tributyl tin hydride, bicyclononatriene is formed with the deuterium associated with all nine carbons[311] (equ. [33]):



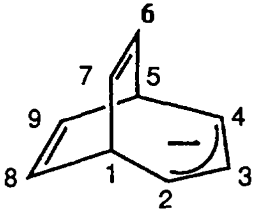
[33]



The adamantane rearrangement (equ. [34]) discovered by Schleyer in 1957[312], shows that carbocationic analogs of these radical rearrangements are available.

P. Ahlberg et al. have studied the 9-barbaryl cation rearrangement which parallels the 9-barbaryl radical rearrangement[313], which occurs under even milder conditions. The 9-barbaryl cation generated from the bicyclic alcohol at -135°C in FSO_3H/SO_2ClF, displays only a sharp singlet [$(CH)_9^+$ ion] in its ^2H NMR spectrum. Double isotopic labelling (^{13}C and D) made it possible to disentangle some of the complexities of this rearrangement[313]. The same group also studied the rearrangement of the bicyclo [3.2.2.] nona-3,6,8-trien-2-yl anion, $(CH)_9^-$ anion (**Scheme 28**)

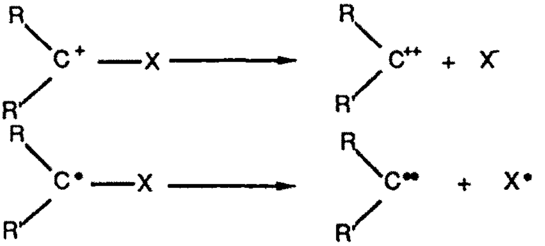
Scheme 28



which uses the 9-barbaralyl anion as an intermediate[314,315]. The degenerate rearrangement of the K and Li salts in 1,2-dimethoxyethane takes place at 25°C; NMR spectra recorded at -27°C show a slow rearrangement at this temperature. Although Washburn's results[311] were not calibrated under the same conditions, it would seem as if the pattern of decreasing reactivity carbenium > radical > carbanion is also observed here. A rich field of quantitative investigations would be to compare the rates of rearrangements found in a radical and involving ß-scission to the ones found in hypernomers and hyponomer counterparts. Lack of space prevents the discussion of other rearrangements, but the reviews covering this topic in carbenium[216b,316-319], radical[293,320-322] and carbanion[283,323] centered mechanisms make it possible to extend the preceding approach to further cases.

1.4.4.4. α-cleavage in π radicals and their hyponomers.

In aromatics, the addition of an electron apparently activates more towards α-cleavage than toward ß-cleavage. Thus, the relative rates of solvolysis of p-nitrobenzyl chloride ($\approx 10^{-5}$ s^{-1})[324] and of its radical anion counterpart (10^8 s^{-1})[134b] yields an activation of about 10^{13}. To evaluate the same activation for the ß-cleavage in the carbocation-radical couple, it is necessary to know the ß-scission rates in carbocation: the upper limit of 10^{13} s^{-1} for the methyl cyclopropyl cation yields an activation of about 10^5. On the side of α-scission of radical anions, the activation figures are very large. The rate of solvolysis of aromatic halides has recently been estimated as (10^{-24} $Mol^{-1}s^{-1}$)[325]. Compared to the 10^{8} $Mol^{-1}s^{-1}$determined by Saveant's group and confirmed by photochemical[326] and pulse radiolysis techniques. These rates provide the highest figures of activation found in this Report. The activation toward α-scission in C-centered radicals is not known. To obtain it ,one would have to compare the rates of **equations [35a]** and **[35b]**:



[35a]

[35b]

To our knowledge, the formation of carbenes has never been rationalized as in **equ. [35b]**[327]. There is, however, a special case where α-scission has been described both in radicals and their hyponomers:

$Me_3C-C^+=O \longrightarrow Me_3C^+ + CO$ (ref. 328-329) **[36a]**

$Me_3C-C^\bullet=O \xrightarrow[k = 10^3\ s^{-1}]{} Me_3C^\bullet + CO$ (ref. 330) **[36b]**

Quantitative data are lacking for the estimation of the activation associated with **equations [36]**.

1.4.4.5. Associative activation in σ and π radicals

Two levels must be considered here. The first is rather simple : radicals are usually very highly activated toward self association when compared either to their hyponomers or to their hypernomers. Neither carbenium ions nor carbanions display any tendency towards dimerization. Organolithium compounds certainly display a strong tendency toward aggregation[332], but the driving force is provided by Li. This tendency of radicals toward dimerization may be counteracted by electronic[296] or steric effects[333] but is generally very strong. Rather than considering it as an umpolung[17a] which would lay the stress on its electrostatic character, we prefer to see it in terms of paractivation (see **Section 1.1.1.2.**). The main driving force here is spin pairing rather than a decrease in electrostatic repulsion, as shown by the dimerization rate of the $^+NH_3CH_2^\bullet$ radical ($2k = 1.8 \times 10^9$ $Mol^{-1}s^{-1}$)[334].

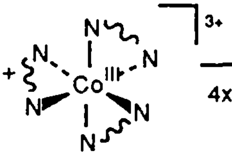
The second level is more subtle, it involves the reactivity of radicals toward diamagnetic substrates. This reactivity may correspond either to their addition to a π system (which results in a substitution if a radical then leaves: homolytic aromatic substitution) or their addition to a σ system (which may also result in a substitution: bimolecular homolytic substitution SH2). The addition of radicals to unsaturations is a field in itself[335,336] and a great number of rate constants have been measured[337]. Some illustrative examples showing the spread of rates follow:

$CH_3^\bullet + CH_2=CH_2 \xrightarrow[5 \times 10^3\ Mol^{-1}s^{-1}]{} CH_3CH_2CH_2^\bullet$ (ref. 338) **[37a]**

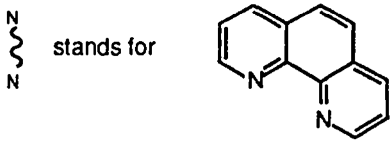
$$CH_3^\bullet + CH_2=CH-CH=CH_2 \xrightarrow[1 \times 10^6\ Mol^{-1}s^{-1}]{} CH_3CH_2C^\bullet HCH=CH_2 \quad \text{(ref. 338)} \qquad [37b]$$

$$^\bullet C_2H_5 + CH_2=C(CH_3)_2 \xrightarrow[17\ Mol^{-1}s^{-1}]{} n\text{-}C_3H_7C^\bullet(CH_3)_2 \quad \text{(ref. 339)} \qquad [37c]$$

$CH_3C^\bullet HOH$ +



$\xrightarrow[4 \times 10^9 Mol^{-1}s\text{-}1\ \text{Å}]{}$ Addn on the phenanthroyl ligand (ref. 340) **[37d]**



The scarce quantitative data concerning the reactions of carbocations towards nucleophiles[190] show that the reaction of nucleophiles such as FSO_3^- toward carbocations is a diffusion limited process ($k \approx 10^{10}\ Mol^{-1}s^{-1}$). Carbanions do not react on unactivated olefins[341]. Therefore, with some modulations resulting from substituent or medium effects, radicals are activated toward π association when compared to their hypernomers and deactivated when compared to their hyponomers. This statement is limited to π generalized bases. If ones considers π generalized acids such as BF_3[12b], radicals will display the opposite pattern of activation-deactivation. Given the higher reactivity of carbenium, in comparison with their hypernomers, toward π clouds, one could have expected a greater selectivity of attack of radicals on substituted aromatics; apparently the reverse holds true[342b].

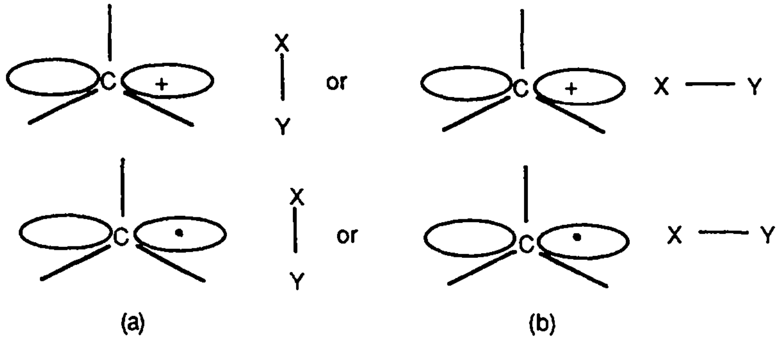
Radicals generally also add to electronic clouds of n.b.σ symmetry. This leads to the formation of 3e bonds, whose stability depend strongly upon the electronegativity difference of the elements involved in the bond[86] and upon the possibility of delocalization of the extra electron. The whole range of possibilities is found here depending upon the partner: a) the radical has a very low electron affinity (e.g. $NH_2CH_2^\bullet$, see **Annex 1**) and the σ system has a very high one (e.g. CBr_4); in this case, an outer-sphere electron transfer to the σ* orbital followed by a dissociative activation may occur; b) the radical has an electronegativity similar to the atom with which it interacts or there is a possibility of delocalization of the 3e bond; in this case, an addition of intermediate of a given lifetime may form (**equ.** [38]):

$$RO^\bullet + P(OR)_3 \longrightarrow (RO)_4P^\bullet \quad \text{(ref. 331)} \qquad [38]$$

In this situation, if an α-cleavage is the most probable fate of the intermediate, one obtains a substitution product. The substitution shown in **Table1** is an Associative Substitution (identical in timing with SNAr, nucleophilic substitution at an aliphatic trigonal carbon[277] or with ligand substitution in a Pt^{II} tetracoordinated complex)[20]; c) the radical begins to form a 3 e bond (or a 1 e bond: attack on H), and when the extra electron (or hole) begins to delocalize, it carries a "dissociative message". There is a more or less concerted formation of a new bond and the cleavage of an old one. Depending on the exact timing, the terms I_A or I_D (**Table 1**) describe this substitution.

What happens on the hyponomer side of the radical during the interaction with a cloud of σ symmetry? Two directions of interaction must be considered[259c] (**Scheme 29**):

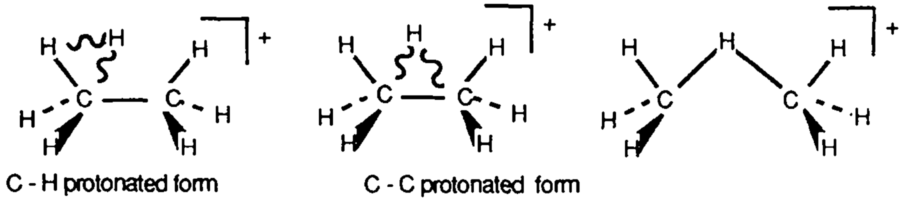
Scheme 29



The perpendicular direction (a) is apparently feasible only with the carbocations when either X or Y are H; it yields the [2e-3 center] bonds described by Olah[343]. The only radicals which could possibly enter into such an interaction are the ones with a very deep SOMO (see **Annex 1**).

The linear direction (b) is not an absolute necessity: the bridged cation with an hypercoordinate hydrogen atom $(CH_3 - H \cdots CH_3)^+$ can be stabilized in a configuration with a linear or bent bridging bond. Mass- spectrometric[344] study of $C_2H_7^+$ in the gas-phase hinted that two stable ions differing in energy by 7-8 kcalMol^{-1}, corresponded to the C-H and C-C protonated isomers (**Scheme 30**).

Scheme 30



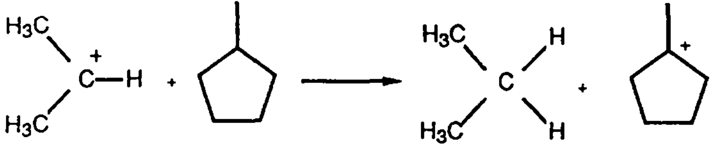
Pople calculated that the bent structure with a bridging H was the most stable[345], and further theoretical studies[346] confirmed this result. This structure is calculated to be 4-10 kcalMol^{-1} more stable than the C-H protonated form and 2-5 kcalMol^{-1} more stable than the linear H-bridged form. Gas-phase ion-molecule reactions also made fluoride[347], chloride[348], bromide[349], methide[350] and ethide[351] transfers evident (**equ. [39]**):

$$R1^+ + X\text{-}R2 \rightleftharpoons R1X + R2^+ \qquad [39]$$

with X = F, Br, CH_3, CH_3CH_2

In solution, hydride transfers have been the most studied[352].

Secondary alkyl cations in SbF_5/SO_2ClF react with methyl cyclopentane at -78°C to give the more stable tertiary methylcyclopentyl cation[353] (equ. [40]):

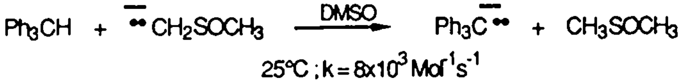


[40]

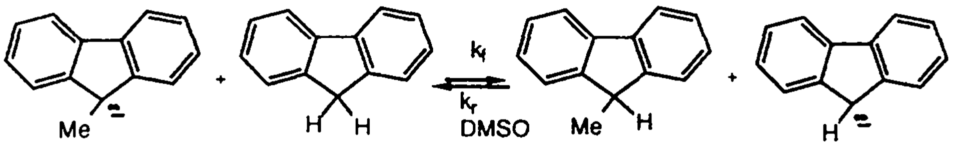
The rate of such intermolecular hydride shifts has been assumed to be diffusion limited when the hydride donor is cyclohexane and the hydride acceptor is the ethyl cation (CH_2CD_2F in SbF_5/SO_2)[354]. Brownstein measured the rate of transfer from isobutane to the t-Butyl cation in sulfur dioxide: $E_a < 4$ kcalMol^{-1} [355]. These very low values have been confirmed by Kramer and al[355b].

Therefore, the reactivity of carbon centered radicals toward H centers in an SH2 process is apparently lower than that of their hyponomers. Quantitative data in the gas phase suggest[348] that hydride transfer is slower than the corresponding chloride transfer. The relatively high reactivity of carbon centered radicals toward Cl atom in an SH2 process[356] hints that the preceding deactivation is less important for chloride transfers. Both carbon centered radicals and their hyponomers display very little, if any, intermolecular reactivity toward the saturated carbons in alkanes and substituted alkanes. The modulations to be anticipated in terms of structural variations are probably connected with the relative values of hydride and halide affinities[259d] and homolytic bond dissociation energies of C-H bond in various structural situations[259e,357].

To examine the hypernomers of carbon centered radicals, the whole chemistry of carbanions[358-360] would have to be considered. Only the dominant features will be summarized here. First, carbanions do not react with an unactivated alkane, while their hyponomers do. Only activated C-H bonds may be attacked by carbanions. Ritchie has investigated the rates of such reactions (equ. [41] and [42]) in dimethyl sulfoxide and some representative rates follow[361,362]:



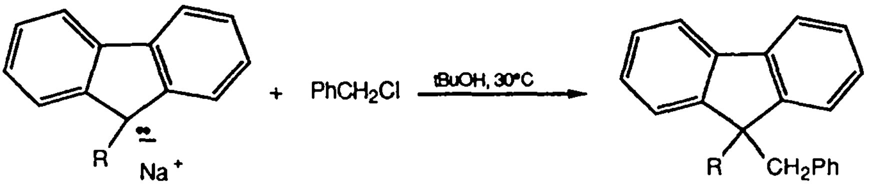
$$Ph_3CH + {}^{\bar{\bullet\bullet}}CH_2SOCH_3 \xrightarrow[25°C\,;\,k=8\times10^{3}\,Mol^{-1}s^{-1}]{DMSO} Ph_3\bar{C}^{\bullet\bullet} + CH_3SOCH_3 \qquad [41]$$



[42]

25°C $k_f = 2.7\times10^{-2}$; $k_r = 16\times10^{-2}$ Mol^{-1}s^{-1}

Therefore, radicals are generally activated towards attack on H with respect to their hypernomers. The reverse holds true when the attack towards C is considered. Bimolecular homolytic substitutions on C are virtually unknown[363], while carbanion attack on an electrophilic carbon is one of the best known reactions for forming C-C bonds[364] (equ. [43]):

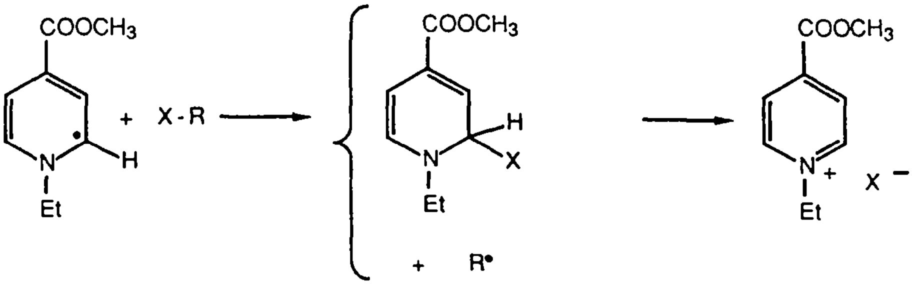

[43]

R	k ion pair	k ion (Mol⁻¹s⁻¹)
CO_2Me	0.124	4.27
CN	0.2	4.1

Zefirov and Makhonkov[365] have coined the term "X-philic substitutions" for nucleophilic reactions taking place at the halide end of the C-X bond, considered as an ambident electrophile. Although their report does not deal with bimolecular homolytic substitutions occurring on an X atom, it is convenient to extend the label (spin transfer or homolytic X-philic substitution) to these cases as well. Carbon centered radicals react with the halogen end of a C-X bond in a range of rate constants, which overlaps those associated with the attack on the H end of the C-H bond[366]. Taking the rate of abstraction of H on toluene as the unit value ($k \approx 1$ $Mol^{-1}s^{-1}$)[367], the relatives rates of homolytic X-philic substitution when $CH_3°$ is the attacking species are[368]: CH_3Br: $6x10^{-3}$; CH_2BrCl: 0.9; CF_3I: 21500 (or 800); CCl_4: 4.1; $CBrCl_3$: 7400; $(CH_3)_3CI$: 1680. On the side of X-philic reactions where the nucleophile is a carbanion, the rates are also increased when the leaving carbanionic species is substituted by electron withdrawing groups[369]. Such X-philic attacks have been recognized in the reactions of stannanions with sterically hindered alkyl bromides[370,371], but little is known about rate constants. Therefore, at this point, it is difficult to tell if for X-philic attacks the change from the radicals to their hypernomers corresponds to an activation or to a deactivation.

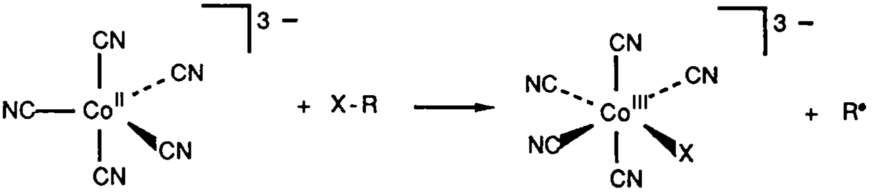
1.4.4.6. Aspects of the reactive mixed valence approach applied to bimolecular homolytic substitutions (SH2).

Kosower[372] studied the rates of reaction between 1-ethyl-4-carbomethoxy-pyridinyl radical and various halogeno alkanes in acetonitrile (equ. [44]):


[44]

X	R	k ($Mol^{-1}s^{-1}$)
Cl	CH_3	$1x10^{-12}$
Cl	CH_2Cl	$2x10^{-8}$
Cl	$CHCl_2$	$2x10^{-5}$
Cl	CCl_3	3
Br	CH_2Cl	$5x10^{-5}$
I	CH_2Cl	$1x10^{-1}$
I	CH_3	$4.7x10^{-6}$

Nearly concurrently, Halpern[373] measured the reaction rates of the pentacyanocobaltate ion with organic halides in water at a pH greater than 12 (**equ. [45]**):

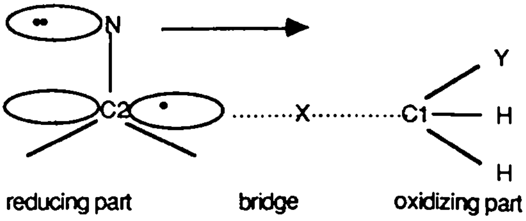


[45]

X	R	k ($Mol^{-1}s^{-1}$)
Cl	CH_2COO^-	$2x10^{-4}$
Cl	$CHClCOO^-$	$2x10^{-2}$
Cl	CCl_2COO^-	$4x10^{-1}$
Br	CH_2COO^-	$3x10^{-1}$
I	CH_2COO^-	890

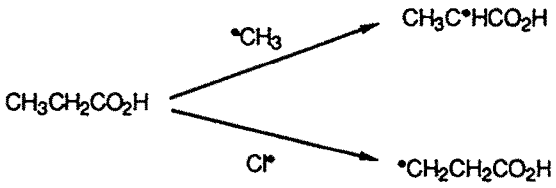
Structural effects are more important in the purely organic reaction than in the inorganic-organic mixed one. Kosower proposes that the main cause of rate differences in **equ. [44]** is a difference in bond energy, as long as the reaction rates which produce the same radical product (same leaving group) are compared. We believe that Kosower's results are not incompatible with an interpretation (**Scheme 31**) based on polar effects, viewed under the perpective of reactive mixed valence species (**Section 1.4.4.2.**). The first explanation focused on the ΔG° of reaction, the other one on its $\Delta G^{\neq}$, yet both converge. The substitution of hydrogen by halogens in the polyhalogenomethane clearly increases the oxidizing ability of the C1 site, and therefore acts cooperatively with the flow of electronic population density shown by the arrow.

Scheme 31

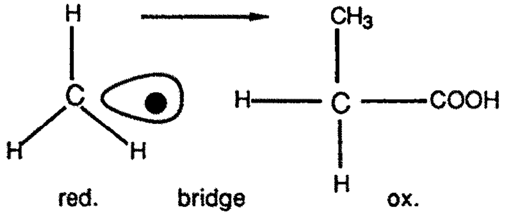


Along the same lines, the reactive mixed valence model provides an easy rationalization of the examples of selectivity provided by Tedder[335] for various reactions (**Scheme 32**):

Scheme 32

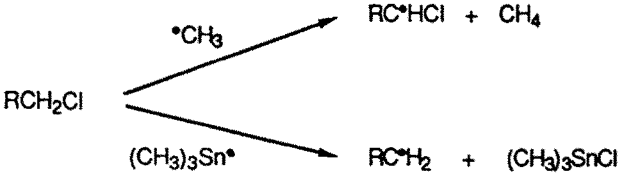


Scheme 33



Considering that the electron flow for $CH_3^{\bullet}$ is in the direction equivalent to $CH_3^{\bullet}$ as a reducing center in the corresponding reactive mixed valence complex (**Scheme 33**), it is clear why the H α to the CO_2H group is selectively attacked by $CH_3^{\bullet}$. When the attacking species is $Cl^{\bullet}$, the direction of electronic flow is reverted, and so is the attack selectivity. Another example of selectivity, which closely parallels inorganic examples, is given in Tedder's review[335] (**Scheme 34**):

Scheme 34



The effect of changing bridges on the rates of inner-sphere electron transfers is discussed in detail in ref. 168c. It is clear, from Cannon's discussion, that depending upon the polarizability of the reducing and oxidizing parts of the reactive mixed valence involved, a given ranking of bridging efficiency or its reverse may be found.

1.4.4.7. Remarks on the nomenclature of mechanisms. Outer-sphere, Inner-sphere, Electron Shift, SH2, SN2 viewed in perspective.

In the preceding sections, we have studied displacement reactions. The general situation for the set hyponomer-radical-hypernomer may be illustrated as follows for a carbon centered radical:

$$C_1^+ + Y\text{-}C_2 \longrightarrow C_1\text{-}Y + C_2^+ \qquad [46a]$$

$$C_1^\bullet + Y\text{-}C_2 \longrightarrow C_1\text{-}Y + C_2^\bullet \qquad [46b]$$

$$C_1^{(-)\bullet\bullet} + Y\text{-}C_2 \longrightarrow C_1\text{-}Y + C_2^{(-)\bullet\bullet} \qquad [46c]$$

The situation is reminiscent of what we have described for ß-cleavages (**Section 1.5.4.4.**): in terms of an inorganic analogy this would mean comparing sets of reactions such as **[47a]** to **[47c]**:

$$Cr^{III} + Y\text{-}Co^{III} \longrightarrow Cr^{III}Y + Co^{III} \qquad [47a]$$

$$Cr^{II} + Y\text{-}Co^{III} \longrightarrow Cr^{III}Y + Co^{II} \qquad [47b]$$

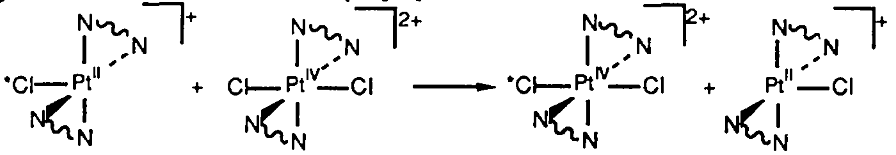
$$Cr^{I} + Y\text{-}Co^{III} \longrightarrow Cr^{III}Y + Co^{I} \qquad [47c]$$

This analogy would be valid for Y = electronegative atom; for Y = H, one would have to turn toward organometallic hydrides.

For inorganic substrates, the first term of the series is practically unknown as a one step process: Co^{III} would first have to exchange Y with the medium and only then could Cr^{III} possibly exchange one of its ligands for $Y^{\bullet\bullet}(-)$[19f]. The second term is well known: it corresponds to the very wide class of inner-sphere electron transfer processes. The third one is not known for the couple Cr^{I}-Co^{III}, but has been proposed for the couple Pt^{II}-Pt^{IV} [374-376]. Other two electron couples (Tl^{I}-Tl^{III}, Sn^{II}-Sn^{IV}, Rh^{I}-Rh^{III}) are described in Cannon's monography on electron transfer[168]. In organic chemistry, they would correspond to carbanions involved in so-called X-philic reactions[365] (**equ. [48]**):

$$C^{(-)\bullet\bullet} + X\text{-}CX_4 \longrightarrow C\text{-}X + CX_3^- \qquad [48]$$

A natural question which arises here, given the success of the electron shift approach to mechanisms[377], is: "are we dealing with a two electron transfer shift "? The answer is very probably "no", and here we find one of the fundamental ambiguities attached to redox numbers that we already pointed out in ref. 11a (p. 14). Let us return to charges carried by the metal in Pt^{II} and Pt^{IV}. Chatt remarks[378] that the "actual" charges (this is not an observable but has a definitive physical meaning[379]) will never exceed +/- 0.3 e, which tells us that there is no fundamental difference, in terms of orbital following[19g], between the Pt^{II}-Cl-Pt^{IV}electron transfer and the Cr^{II}-Y-Co^{III} reactive mixed valence compound. The overall reaction described for the so-called two electron transfer[19h] involving Pt^{II} and Pt^{IV} is[374] shown in **equ. [49]**:



[49]

•Cl : labelled chloride

Use of steric effects and isotopic labelling have shown that it is an inner-sphere electron transfer process, where the bridge is Cl[374b]. There is no ambiguity in the charge count procedure to determine the oxidation numbers displayed in **eq. [49]**. If one now represents the reaction in terms of outer-sphere electron transfer, to try to escape the transfer *versus* exchange ambiguity associated with inner-sphere electron transfer, one obtains the series of reactions shown in **equations [50]**:

$$[{}^{\bullet}\mathrm{Cl\text{-}Pt^{II}}]^{+} + [\mathrm{Cl\text{-}Pt^{IV}}]^{2+} \xrightarrow{\text{e.t.}} [{}^{\bullet}\mathrm{Cl\text{-}Pt^{III}}]^{2+} + [\mathrm{Cl\text{-}Pt^{III}}]^{+} \qquad [50a]$$

$$[{}^{\bullet}\mathrm{Cl\text{-}Pt^{III}}]^{2+} + [\mathrm{Cl\text{-}Pt^{III}}]^{+} \xrightarrow{\text{e.t.}} [{}^{\bullet}\mathrm{Cl\text{-}Pt^{IV}}]^{3+} + [\mathrm{Cl\text{-}Pt^{II}}]^{0} \qquad [50b]$$

$$[\mathrm{Cl\text{-}Pt^{II}}]^{0} \longrightarrow \mathrm{Cl}^{\bullet\bullet}(-) + [\mathrm{Pt^{II}}]^{+} \qquad [50c]$$

$$[{}^{\bullet}\mathrm{Cl\text{-}Pt^{IV}}]^{3+} + \mathrm{Cl}^{\bullet\bullet}(-) \longrightarrow [{}^{\bullet}\mathrm{ClPt^{IV}Cl}]^{2+} \qquad [50d]$$

Two electron transfer *plus* one decomplexation step, *plus* one complexation step lead to the same overall result; the chronology of events, which is just formal, may be permuted at will. One could, without problem, apply the same formal process for the X-philic reaction (**equ. [48]**). Applied to the inner-sphere electron transfer process, $\mathrm{Cr^{II}}$--Y--$\mathrm{Cr^{III}}$ (**equ. [47b]**), the same procedure would yield:

$$[\mathrm{Cr^{II}}]^{2+} + [\mathrm{YCo^{III}}]^{2+} \xrightarrow{\text{e.t.}} [\mathrm{Cr^{III}}]^{3+} + [\mathrm{YCo^{II}}]^{+} \qquad [51a]$$

$$[\mathrm{YCo^{II}}]^{+} \longrightarrow \mathrm{Y}^{\bullet\bullet}(-) + [\mathrm{Co^{II}}]^{2+} \qquad [51b]$$

$$\mathrm{Y}^{\bullet\bullet}(-) + [\mathrm{Cr^{III}}]^{3+} \longrightarrow [\mathrm{YCr^{III}}]^{2+} \qquad [51c]$$

Here, the overall result is obtained by the formal succession of one electron transfer *plus* one decomplexation step, *plus* one complexation step. It is understandable why inorganic chemists call the $\mathrm{Pt^{II}}$-$\mathrm{Pt^{IV}}$ case "a two electron transfer mechanism", in contrast with the $\mathrm{Cr^{II}}$-$\mathrm{Co^{III}}$ case, labelled "one electron mechanism". But the label is artificial[376]: it says, " when a ligand is added or removed from a complex, there is no change in oxidation state", even if one knows that the charge on the atom considered is probably changed by the addition or removal of ligand. The real ambiguity can be seen when one looks at substitution on carbon (SN2). Pross describes this event as a one electron shift and, approximately following our earlier nomenclature without knowing it (ref. 11b p. 126), further clarifies this picture by labelling it an inner-sphere electron transfer, where the role of bridge is played by the carbon[377]. Let us see a classical SN2 substitution under this angle:

$${}^{\bullet}\mathrm{Cl}^{\bullet\bullet-}(-1) + \mathrm{C\text{-}Cl}(-1) \longrightarrow {}^{\bullet}\mathrm{Cl}(-1)\text{-}\mathrm{C} + \mathrm{Cl}^{\bullet\bullet-}(-1) \qquad [52]$$

In terms of oxidation degrees, the count has not changed in any of the involved chlorine atoms. A blind defendant of the oxidation number system would never call this equation an electron transfer process. If one thinks in terms of transfer of electronic population densities, however, such a transfer does occur. The labelled chloride certainly carries a less negative charge when it is linked to a carbon than when it is under its anion form. For any chemical event, there is a change in the electronic population of the elements involved. Thus, any mechanistic event could be labelled an electron transfer shift. But, without any specific application, it looses its interest as a label. At least, it was important to show that fuzzy meanings (oxidation states) can easily become misleading. One has to keep in mind, speaking of inner-sphere processes ("tight" transition states as opposed to very loose ones), that SH2 covers the interaction of paramagnetic reagents with diamagnetic centers whereas SN2 covers the interaction of diamagnetic reagents with diamagnetic substrates. This has certainly consequences in terms of potential energy surfaces.

On the question of nomenclature, we would like to call attention to the recent Saveant's, possibly misleading, nomenclature[380]. This author proposes, in agreement with an earlier suggestion (table 3 in ref. 11a), to extend the inorganic nomenclature of electron transfer processes to organic cases. But, in so doing, he distorts the original inorganic meaning of outer-sphere ano inner-sphere processes[381]. His proposition that "synonyms of outer-sphere and inner-sphere electron transfer could thus be bond-conserving and bond-changing electron transfer" does not concur with the body of knowledge gathered on inorganic and organometallic substrates. There are several examples where an inner-sphere electron transfer does not cause direct bond changing as illustrated by the following equations:

$Co(CN)_5]^{3-} + [Ir^{IV}Cl_6]^{2-} \longrightarrow [Co(CN)_5(H_2O)]^{2-} + [Ir^{III}Cl_6]^{3-}$ (ref. 171) **[53a]**

$R_4Sn + [Ir^{IV}Cl_6]^{2-} \longrightarrow R_4Sn^{\circ}+ + [Ir^{III}Cl_6]^{3-}$ (ref. 172) **[53b]**

A consequence of this nomenclature is then to consider every part of the redox couple as having either an inner-sphere or outer-sphere behavior. We believe that the original inorganic meaning does not dissociate the couple in its two partners : the redox reaction is either inner-sphere or outer-sphere for the overall couple. "Outer-sphere" conveys the idea of weak overlapping during the act of electron transfer, whereas "inner-sphere" conveys the opposite meaning. We are aware that there probably exists a grey area between these extremes (ref. 11b, p.199), but we believe that for this sensitive mechanistic area, it is better to modify the old nomenclature (conservative outer-sphere electron transfer opposed to dissociative[383a] or associative outer-sphere electron transfer) than to blurr it by using it outside of its original meaning.

Saveant's publication is part of a very important mechanistic stream whose aim is to explore the "terra incognita" lying between clearly identified inner-sphere processes (SN2[11b,382-385], additions to unsaturations[384a,386], SNAr[232], Diels-Alder[387], electrophilic aromatic substitutions[383]) and outer-sphere ones. Another label for this search is the "border between polar and electron transfer processes". Elsewhere we have compiled[11a] the information added to this problem by organometallic substrates.Some inorganic references are also devoted to this topic. In the reaction between $Cl_2^{\bullet -}$ and $[Fe^{II}(OH_2)_6]^{2+}$, inner-sphere and outer-sphere paths coexist[389a]. This inorganic contribution is only one of many[389-394] examining the grey area between outer-sphere and inner-sphere pathways. Here again, there is room for cross fertilizations, though not much communication has been established between the potential partners.

Collecting the information given in ref. 11b (p. 212) and the trends displayed in ref. 19i, 220, 394, 384-392, one could try to give tentative rules of the thumb for predicting situations where low k^{IS}/k^{OS} values should prevail. These are: a) Donor acceptor couples which, by application of Marcus theory, suggest a high rate of outer-sphere electron transfer; b) Poor mixing of orbitals (overlap) in the reactive mixed valence model describing the transition state. This criterion must be used with caution: some reactions which had been described as unfavored in their inner-sphere version because of Dewar Zimmerman's rules, have then been measured as being very fast[395]; c) Steric effects inhibiting the best overlap in the substrate-reagent couple. This criterion must be applied with caution as well. Many reactions involving sterically hindered substrate-reagent couples still operate through an inner-sphere pathway[396]. This is because the outer-sphere channel is so unfavored that even when k^{IS} decreases, it still does not reach the threshold where outer-sphere would begin to manifest (ex: most of the SN2 on carbon). These are just trends; actually, a large "terra incognita" seems to exist . For every reaction type, a different map is expected to appear in terms of the relative importance of outer and inner-sphere channels. For some reactions, the part of the map close to outer-sphere will remain small, and for these the body of classic knowledge will remain almost unchanged; in contrast, for those reactions where the part of the map devoted to outer-sphere is of considerable importance, new insights on the very roots of reactivity will emerge.

2) One electron less.

This part will be far shorter than Part 1 because: a) the basic principles and more specifically the theoretical treatment of uneven bonds has been dealt with in **Section1.1**; b) H_2 and radicals (σ or π) have been treated with respect to both their hyponomers and their hypernomers; c) the geometrical changes introduced in triatomic, tetraatomic and pentaatomic molecules (**Sections 1.2.** to **1.3.**) implicitly treated the effect of adding and substracting one electron to a molecule within the Walsh model; d) the basic principles of the reactive mixed valence model have been exposed and applications have been given in **Sections 1.4.2.1**. In this section, we will therefore concentrate only on the aspects of activation which are specific to the removal of an electron. The photochemistry of radical cations, explored by Haselbach[397] and Shida[398a], reviewed in the context of orbital control of reactions paths by Dunkin and Andrew[398b], will not be treated here.

2.1. Homonuclear and heteronuclear diatomic radical cations.

The data from **Table 6** display two main differences from the situation encountered with radical anions. First, several radical cations have stronger bonds than their hypernomers: this is the case for Be_2^+, O_2^+, X_2^+ (X: halogen). This situation occurs when the electron removed occupied an antibonding orbital. Secondly, the removal of a bonding electron from a σ bond usually destabilizes this bond less than the addition of an electron to the corresponding σ^* antibonding orbital. A more detailed discussion of the trends in the periodic table may be found in ref. 51.

For heteronuclear diatomic radical cations, the main result in terms of bond stability of radical cations is provided by Clark's theoretical approach[86] to bonds with an uneven number of electrons (see **Section 1.1.2.**).

2.2. More complex molecules classified by radical types.

We will now examine some general trends for radical cation structure and reactivity, using the classification proposed by Symons (see opening of **Section 1.4.**). We will start from the radical cations where the formation of the hole demands the greatest energy: radical cations of alkanes and alkyl halides. The transition towards more easily obtained radical cations will be provided by the study of strained cycloalkanes whose ionization potentials are lower than linear alkanes.

Table 6: Experimental and theoretical data on diatomic homonuclear molecules and their hyponomers (compare Table 2 for notations)

	H_2	Li_2	Be_2	B_2	C_2	N_2	O_2	F_2
Equilibrium internuclear distance <u>re</u> [a]	0.74	2.67	[b]	1.59	1.31	1.10	1.21	1.43
$D_0°$ (eV)[a]	4.476	1.03 or 1.05[c]		2.84[c]	3.6 or 6.25[c]	7.37 or 9.75[c]	5.08 or 1.59[c]	<2.75
Energy of MO where the electron is removed[d]	-17.6	-6.9	-8.3	-10.	-12.8	-15.6	-12.9	-17.2
Ionization Potential [f]		5.15 (PI)	21.1 (EI)	12 (EI)	15.6 (S)	12.07 (PI)		15.7 (PI)
Ground State of the hyponomer[g]	$[1\sigma_g]$	$[He_2 2\sigma_g]$	$[Be_2 1\pi_u]$		$[Be_2 1\pi^3]$	$[Be_2$ $1\pi^4 2\sigma_g]$	$[Be_2 2\sigma_g^2$ $1\pi_u^4 1\pi]$	$[Be_2 2\sigma_g^2$ $1\pi_u^4 1\pi_g^3]$
$D_0°$ (eV) in the hyponomer[h]	2.64	1.3		1.8	5.2	8.72	6.48	3.32

[a] from ref. 30 b in Å

[b] non existent

[c] from ref. 61

[d] see **Figure 3**

[e] removal from the lone pair

[f] from ref. 399; EI: Electron Impact; PI: Photoionisation; S: Spectroscopy

[g] from ref. 30

[h] from ref. 51 in eV

* For theoretical calculations on the hyponomers, see Li_2^+ (ref.400-402), Be_2^+ (ref. 403-405), B_2^+ (ref. 403), C_2^+ (ref. 403,406), N_2^+ (ref. 403,407-410), O_2^+ (ref. 401, 403, 411-414), F_2^+ (ref. 406, 415). For the calculation of dionized O_2, N_2, Be_2 and F_2 see ref. 416.

* Ref. 30b, 59 and 417 also provides data for heavier diatomics and their hyponomers.

As with anions radical (**Section 1.4.2.**), we will then see that, when an easily ionized HOMO is available (unsaturation, lone pair of electrons), the triggering event for reactivity is the ionization of this HOMO; if there is no scissible σ bond in α or ß position to the HOMO, or if an efficient associative activation of the radical cation is feasible, the chemistry will be that of π* radical cation (mainly associative); if there is a strong opportunity for the hole to act as a dissociative activation messenger toward a σ bond, then the chemistry will be that of a σ* radical cation (mainly dissociative). There is an important difference for this latter case, however: the activation toward dissociation is often weaker after removal of an electron than by addition. Therefore, in the radical cation, this dissociation will often have to be assisted by a nucleophile, while it was often unimolecular for radical anions and radicals. Various aspects of the chemistry of radical cations in the gas phase[418] and in solution[419-455] have been exhaustively reviewed.

2.2.1. σ Type radical cations without unsaturation.

2.2.1.1. Radical cations of alkanes and stannanes.

In contrast to the negative ions of alkanes, which are reported only for cycloalkanes, the radical cations of alkanes have been generated both in the gas phase[456] and in rigid solutions. Only the second type of results will be discussed here.

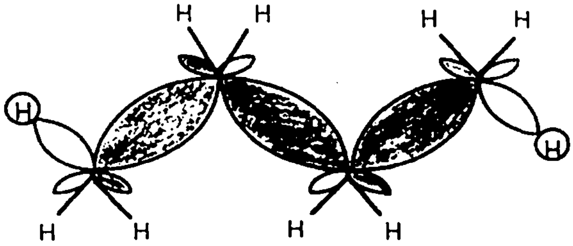
The simplest radical cation is that of methane but, because of the high ionization potential of this alkane (12.6 eV), it was observed only in 1984 by Knight and Steadman in a neon matrix[457]. Because of the triple degeneracy of t_2 orbitals, four possible Jahn-Teller type of distortion could occur for $CH_4^{+\cdot}$

The joint experimental-theoretical interpretation of ESR for CH_4^+, $CD_2H_2^+$, CDH_3^+ made it possible to unambiguously define the ground electronic state of the radical ion as being C_{2v}. Distortions according to D_{2d}, or C_{3v} had been respectively found from non empirical calculations[458] and semi-empirical ones[459]. A recent theoretical calculation of the ground state potential-energy surface of CH_4^+ analyzes the complex dynamic Jahn-Teller behavior revealed by these ESR matrix results at 4K[460].

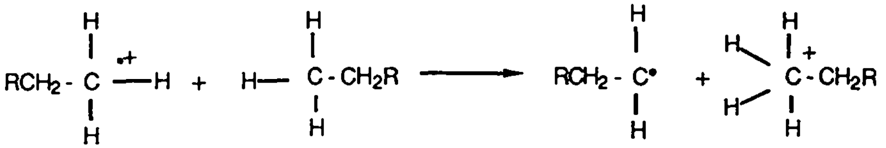
SnH_4^+ exists in two conformations at 77K; the predominant one corresponds to the unpaired electron in the σ orbital, composed primarily of an sp hybrid atomic orbital on tin and the s orbital on a unique hydrogen atom (overall symmetry C_{3v}). The less abundant conformation (C_{2v}) corresponds to two equivalent hydrogens in equatorial position, the other two occupy the axial position[461]. Structural studies aiming at understanding Jahn-Teller effects in radical ions, have also been performed on $C_2H_6^+$ (C_{2h})[462], c-C_3H_6 (C_{2v})[463], Si Me_4^+ (C_{2v})[464], $GeMe_4^+$ (C_2v), CMe_4^+ (C_{3v})[462], c-$C_4H_8^+$ (C_{2v})[465a], cubane+ [465b] and $SnMe_4^+$ (C_{3v})[466], as well as in benzenic derivatives[467]. One may recall that SnH_4^- has a C_{2v} structure[468].

One interesting feature of these radical cations is σ delocalization[469] (compare **Section 1.4.1.**). Such a σ delocalization is suggested by the low temperature (4.2K and 77K) ESR spectra of linear alkane cations $[H(CH_2)_n]^+$ (n up to 10). The unpaired electron in the in-plane σ molecular orbital delocalizes over the entire chain (**Scheme 35**), with a large spin density on the two in-plane end hydrogens[470,471]. In contrast to this σ delocalization, branched alkanes do not show this type of delocalization: in $Me_3CCMe_3^+$, the unpaired electron is strongly localized in the central C-C bond[472].

Scheme 35



The most fascinating results on these alkane radical cations are the ones obtained on reactivity. The old term "paraffin" reminds us that alkanes were for a long time taken as typical examples of inert compounds, and we teach our students that cracking butane at 435°C is feasible only if an appropriate catalyst is present[23b].



$$RCH_2-\overset{H}{\underset{H}{C}}{}^{+}\!\!-H \;+\; H-\overset{H}{\underset{H}{C}}-CH_2R \longrightarrow RCH_2-\overset{H}{\underset{H}{C}}{}^{\bullet} \;+\; {}^{H}_{H}\!>\overset{H}{\underset{H}{C}}{}^{+}-CH_2R \qquad [54]$$

Recently, confirming earlier observations, Iwasaki's group showed that radical cations of n-C_6H_{14} react at 4K with their hypernomers to yield a radical and a carbonium ion[473] (equ. [54]). This reaction occurs by the dimer formation between the radical cation and its hypernomer maintained in a head-to-tail position in the narrow zeolite channels (5-6 Å) where the formation of the radical cation takes place. The presence of the zeolite is, however, not compulsory. The same reaction has been observed in crystalline neat linear alkanes irradiated at 4K[474]. Gas phase acidities evaluated from $\Delta H°_f$ and expressed as proton affinities(PA) of the conjugate base of the radical cation (i.e. $CH_3^\bullet$ for CH_4^+)[475] (equ. [55]):

PA(kcalMol^{-1})

$CH_4^{+\bullet} \rightleftharpoons CH_3^\bullet + H^+$ 124 [55a]

$C_2H_6^{+\bullet} \rightleftharpoons C_2H_5^\bullet + H^+$ 142 [55b]

$PhCH_3^{+\bullet} \rightleftharpoons PhCH_2^\bullet + H+$ 195 [55c]

show the very high acidity induced per electron removal as shown by comparison with more familiar acids (equ. [56]):

$CH_4 \rightleftharpoons CH_3^- + H^+$ PA(CH_3^-): 124 [56a]

$C_2H_6 \rightleftharpoons C_2H_5^- + H^+$ PA($C_2H_5^-$): 142 [56b]

$PhCH_3 \rightleftharpoons PhCH_2^- + H^+$ PA($PhCH_2^-$): 195 [56c]

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ PA(CH_3COO^-): 348 [56d]

This acidity is even higher than the one evaluated for CH_5^+: PA(CH_4) = 131.6 kcalMol^{-1}. These results, if confirmed (see Symons' remark[440] on the possibility of basic impurities), are breathtaking for a solution chemist. Everything occurs as if, provided the reageants are optimally oriented in the space, reactions which usually require a given activation energy had become without activation (≈200 calMol^{-1}). We may open a short parenthesis at this point, to recall that the preceding observation is not unique and should be connected with similar facts. The 4K norbornyl cation rearrangement[262c], the halogenation of olefins through charge transfer complexes at very low temperature[82b], the very fast (≈3 ps) electron transfer between porphyrin stacks of chlorophyll[476] all share a common feature: the reageants seem to have been spatially disposed to allow the easiest possible flow of electrons.

The chemistry of CH_4^+ in SF_6 was studied at 77K although its chemistry begins below this temperature[477]. CH_4^+ is deprotonated in an ion-molecule reaction:

$$CH_4^{+\bullet} + SF_6 \longrightarrow CH_3^\bullet + SF_6 + H^+ \qquad [57]$$

The deprotonation could possibly go through the formation of a complex between the "base" SF_6 (lone pairs on F) and the "acid" $CH_4^{+\bullet}$. Another equivalent description is to say that the hole is shared between solute and solvent[478]. This complex would then decompose to release $CH_3^\bullet$ at temperatures higher than 110K. Such a behavior is specific of CH_4^+; the other radical cations of alkanes are also deprotonated in SF_6, but at temperatures higher than 100K and without observation of fluoride adducts of alkyl radicals. Under the same conditions, besides dedeuteriation, CD_4^+ undergoes, a series of reactions leading to the formation of minor amounts of $^\bullet CFD_2$, $^\bullet CF_2D$ and $^\bullet CF_3$. These byproducts could result from the formation of CH_2^+; carbene radical cations and carbene radical anions have been proposed for more usual reactions[479]. In these alkane radical cations, the cleavage of C-C bond at 77K apparently does not occur, even for the radical cation of hexamethylethane, where the unpaired electron is mainly confined to the central C-C bond[472]. This relative inertness is consistent with Clark's calculation of 1e C-C bond[86] ($\approx$45 kcalMol^{-1}). It contrasts with the behavior of stannane radical cations[480].

2.2.1.2. Radical cations of alkyl and stannyl halides.

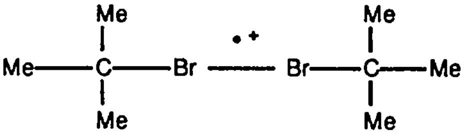
Two new structural features are introduced when one examines alkyl or stannyl halides. The first one is the presence of lone pairs on the halogen atom, which could be first ionized in most structures[481] Semi-empirical calculations, using the MNDO-UHF, method suggest that, for most alkyl chlorides, bromides and iodides, the HOMO was formally a halogen np_π lone-pair orbital[482a]; but there is considerable overlap between the halogen np_π orbitals and the p_π orbitals of the α-carbon[483]. Miller and Watkins[484] suggested, however, that the anodic carbon-bromine bond cleavage in adamantyl derivatives involves initial electron transfer from an orbital primarily located on the adamantyl moiety. In $SnMe_3Cl$, the ionization which takes place in solution is that of the tin-carbon σ bond rather than that of chlorine[480]. The second structural feature is the presence of a bond between atoms of rather different electronegativity (at least for the lighter halogen terms); therefore, Clark's relationship[86] hints at weaker bonds in these radical ions if the hole is located in a C-X σ bond. The first structural feature will be the basis for activation toward self-association: indeed, ionization of lone pairs often promotes the association between the neutral and its hyponomer. The second structural feature will be the basis for dissociative activation. This dissociative activation is, however, far less pronounced that the one associated with the addition of an electron. The MNDO-UHF calculations[483], in agreement with gas phase data, predict direct halogen atom loss only for the sterically hindered Me_3CX^+ (X: Cl, Br) while radical anions of methyl halides are predicted to be at the border of stability and have never been experimentally observed (see **Section 1.4.2.**).

Asmus[485] and Symons's[486] group contributions clearly illustrate the associative activation following ionization. Asmus' group generated the alkyl iodide cations in acidic aqueous solution by pulse radiolytic methods[485a] and showed the existence of the equilibrium shown in **equ. [58]**:

$$RI^{\bullet+} + RI \rightleftharpoons RIIR]^{\bullet+} \qquad [58]$$

An intramolecular three electron iodine-iodine bond was characterized in the radical cation of 1,3-diodopropane: this species displays a broad absorption band at 405 nm[485,487]. Symons' group γ-radiolysis study of alkyl halides was the first data clearly showing the propensity of alkyl halides radical cations to combine with their hypernomers at 77K in matrices[486]. This dimerization apparently has the ability to stabilize otherwise dissociative species: the Me_3CX radical cations are difficult to observe, even at low temperatures; however, the ESR spectrum of the dinuclear cation shown in **Scheme 36** has been characterized[486a]. All these associative activations may be viewed in the context of generalized acid base chemistry. Lewis[488] and particularly Usanovitch[489] would have been very pleased to see the lone pairs of halogens in an alkyl halide "salifying" the electron deficient center constituted by the hole created by ionization. This generalization would have consequences such as:

Scheme 36



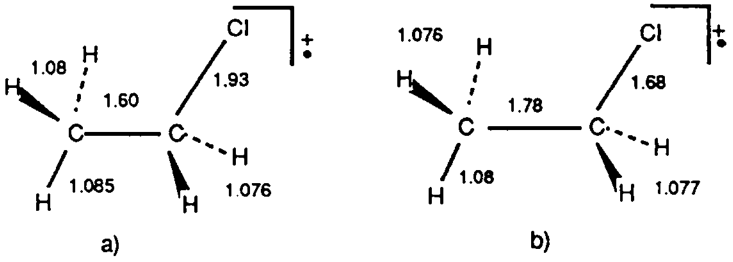
$$Me_3C{-}Br \overset{\bullet +}{\text{———}} Br{-}CMe_3$$

1) classification of the used matrices in terms of acidic (SF_6) and basic (e.g. $FCCl_3$) and consideration of their specific role as such (e.g. induced eliminations)

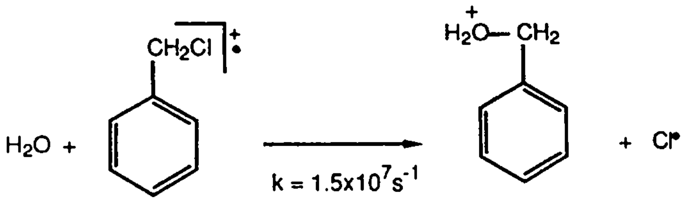
2) consideration of the non-classical structures associated to some of the paramagnetic super acidic species generated by ionization.

The structural consequences of ionization may be simulated in detail by *ab initio* methods[490,491]. The Franck-Condon ionized state (a) and its adiabatic counterpart (b) are shown for ethyl chloride radical cation in **Scheme 37**. This theoretical work excellently illustrates how *ab initio* calculations now make it possible to simulate all the intermediates and transition states involved in intramolecular evolution of radical ions generated in the gas phase.

Scheme 37 : Geometrical modifications between the Frank-Condon (a) (same geometry as fundamental) and adiabatic (b) (after vibrational relaxation) states of $CH_3CH_2Cl^{+\bullet}$ (ref. 490).



An approximate measurement of oxidative dissociative activation is given by the laser flash photolysis study of benzyl chloride in water. Benzyl chloride radical cation reacts with H_2O to form a chlorine atom and benzyl alcohol[492] (equ. [59]):



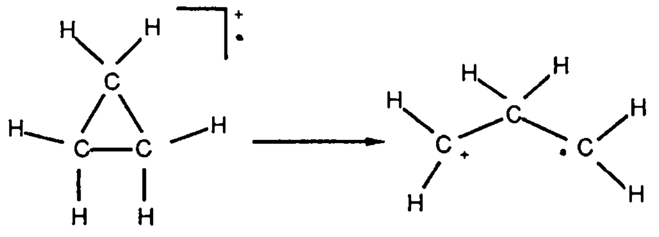
[59]

This corresponds to an estimated activation greater than 10^{10}.

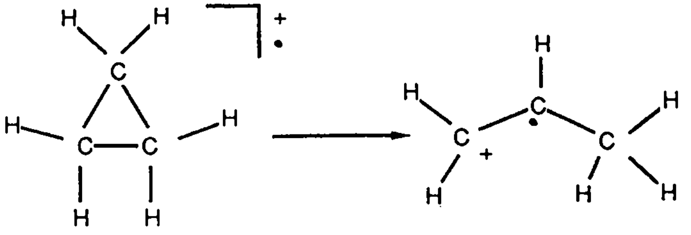
2.2.1.3. Radical cation of strained hydrocarbons.

This section will be short because this topic has recently been reviewed by Gassman[430a] and Roth[430b]. Cyclopropanes and derivatives are oxidized in the same potential range as their olefinic analogues[493]. The chemistry of these radical cations constitutes an hot meeting point for the gas phase[494], low temperature matrix[495], theoretical[496], photon[430,497] and electrode[493] chemistry.

In SF_6 at 4K, the cyclopropane cation is stable but, because the HOMO is degenerate in its hypernomer (3e'), it displays a static Jahn-Teller effect which distorts the original D_{3h} symmetry into a C_{2v} one[495] with an associated stabilization energy of about 3400 cm^{-1} [498]. Two types of distortions may be observed in the radical cation, depending upon the structural environment[430b]; the first one corresponds to the lengthening of the bond between one pair of carbons; the second one corresponds to the lengthening of the two bonds, where the third one is shortened (**see equ. [60]**). At higher temperatures in CF_2ClCCl_2F, however, F. Williams and al observed an opening of this cyclopropane radical cation to yield the trimethylene radical cation[495a,499]. This result has been questioned on the basis of *ab initio* calculations[496] which describe the irreversible opening of the ring as being too energetic, while the rearrangement of this cyclopropyl radical cation to a propene radical cation is predicted to occur (**equ. [61]**) without appreciable activation energy and to be exothermic.



[60]

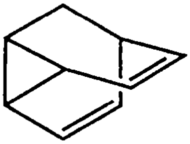


[61]

These theoretical calculations also reject the possibility of a conrotatory ring opening in the trimethylene radical cation, followed by hydrogen migration to yield the most stable propene radical cation. They propose a transition state with a C_1 symmetry, where hydrogen migration accompanies ring opening. The only way to reconcile these highly sophisticated calculations with the inescapable ESR spectroscopic evidence provided by the low temperature matrice experiments[495a,499], is to suppose that a very strong stabilizing interaction exists between a nucleophile and the carbocationic methylene group. Several propositions have been made concerning the nature of this nucleophile [495a,496b,500-502]. The important point for our evaluation of whether the removal of an electron from these strained bonds is sufficient to cause a direct cleavage, is that the answer is very probably negative. Thus, a one electron C-C bond, even situated in a strained structure, is still stable. To cleave it requires either the intervention of further structural stabilizing effects[430b,497] or the intervention of an external nucleophilic reagent.

A particularly striking example of the effect of electron removal must be given, which has been discussed in Roth's review[430b]. The example is that of barbaralane (**Scheme 38**]. This compound undergoes rapid degenerate Cope rearrangement even at -150°C, and its potential energy surface has a double well[502a].

Scheme38



In contrast, its radical cation assumes a structure with a single minimum[502b]. For the barbaralane system, the homoaromatic structure is a transition state on the potential energy surface; it becomes a minimum on the potential energy surface of the radical cation.

2.2.2. σ Type radical cations obtained from the ionization of a lone pair.

2.2.2.1. General considerations.

In **Section 2.2.1.2.** (alkyl halides) we have seen that both associative and dissociative activations could follow the removal of an electron for these types of structures. For dissociative activation, depending on the alkyl halide considered, this activation was either sufficient in itself to cause a monomolecular cleavage or only partial, in which case an intermolecular attack was necessary to cleave the activated bond. An important general conclusion is given in Symons' review[440] on radical cations in condensed phases. When lone pair centered radical cations are formed, the ones centered on third and subsequent row elements (P, S, Se, Cl, Br, I) display a far greater tendency to form dimers than the corresponding second row radical cations (O, N, F). One may be tempted to propose that this dichotomic behavior strongly suggests a symbiotic behavior[503,504] of the soft-soft type for 3 e bonds.

But if we want to do so, we must abandon the line of thinking opened by Clark. In Clark's theoretical approach, there is no hint of a preferential soft-soft interaction as shown by the following calculated D_{AB} values for 1 e and 3 e bonds[86]:

$Li — Li^{\bullet(+)}$	28.8 $kcalMol^{-1}$	$H_3N — NH_3{}^{\bullet(+)}$	24.0 $kcalMol^{-1}$
$Na — Na^{\bullet(+)}$	22.1 $kcalMol^{-1}$	$H_3P — PH_3{}^{\bullet(+)}$	18.5 $kcalMol^{-1}$
$HBe — BeH^{\bullet(+)}$	48.1 $kcalMol^{-1}$	$H_2O — OH_2{}^{\bullet(+)}$	16.3 $kcalMol^{-1}$
$HMg — MgH^{\bullet(+)}$	31.4 $kcalMol^{-1}$	$H_2S — SH_2{}^{\bullet(+)}$	18.2 $kcalMol^{-1}$
$H_2B — BH_2{}^{\bullet(+)}$	39.3 $kcalMol^{-1}$	$HF — FH^{\bullet(+)}$	19.9 $kcalMol^{-1}$
$H_2Al — AlH_2{}^{\bullet(+)}$	28.8 $kcalMol^{-1}$	$HCl — ClH^{\bullet(+)}$	28.8 $kcalMol^{-1}$

The HSAB's appeal is increased by the basic observation that, in the ambident selectivity of SRN1 type processes, the most polarizable end of the ambident anion is preferentially selected by the carbon centered radical. For this observation, the simple difference in electronegativity between the partners of the 3e bond contained in Clark's approach is still sufficient to rationalize the observation. At this point, the question must therefore remain open: is there any specific stabilization in uneven bonds formed between polarizable elements or groups (π clouds for example)?

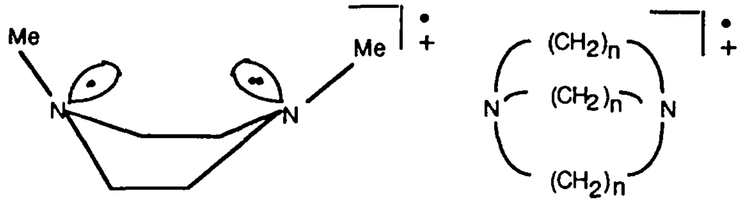
The structural effects caused by the removal of an electron from a lone pair are well dealt with in Symons's review[440], and we will therefore concentrate only on reactivity in this section. Taking into account the lack of space and the apparent dichotomy between second row centered and other elements, we will treat only the group of nitrogen centered radical cations. This element is probably the one for which the most amount of information is available. The chemistry of radical cations centered on O, P, S is well treated in Parker[419], Shines[439], Asmus[421], Musker[422], Pienta[432] and Tordo[423b] reviews.

2.2.2.2. Radical cations centered on nitrogen.

Radical cations of amines are probably planar[440,505,506]. This was expected from the Walsh treatment (see **Section 1.2.**). Conformational effects ($Et_3N^{\bullet+}$) reminiscent of what has been observed in alkyl groups linked to sp^2 C[507a,b] also agree with this planarity. In contrast, the phosphine[508a] and arsine[509a] ionized forms are pyramidal.

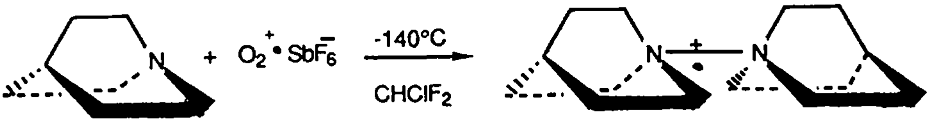
On the side of associative effects, electron removal obviously decreases the tendency to protonation. In contrast, weak σ^* bonds are formed between $NH_3{}^{+\bullet}$ or alkylamine radical cations[507c] and halide anions (Cl^-, Br^-, I^-). Formation of 3e N-N bonds apparently occurs only if the two involved nitrogens pertain to the same structure and are correctly oriented in space to permit a good overlapping [508b-d] (**Scheme 39**):

Scheme 39



(ref.493) (ref.500)

Dinnocenzo and Banach[509b] (equ. [62]) were recently successful in overcoming this apparent reluctance toward intermolecular dimerization (compare with ref. 510):



[62]

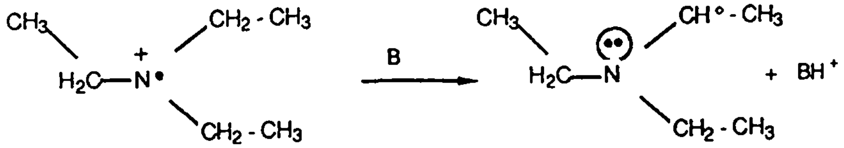
This reluctance to form 3 e N-N bonds of σ symmetry can be contrasted with the well known stability of the 3 e π bonds (2 bonding π electrons and 1 electron in antibonding π* orbital) formed by ionization of hydrazine derivatives. Nelsen's recent review covers both structural and chemical aspects of hydrazine cation radicals[424b].

Associative paractivation is illustrated by the chemistry of aminium radical cations, which are able to abstract hydrogen intermolecularly or intramolecularly[511] (equ. [63]):

[63]

This intramolecular hydrogen abstraction has been recently simulated by *ab initio* molecular theory, to evaluate the efficiency of hydrogen abstraction as a function of the alkyl chain length. The preference for the abstraction corresponding to a 1,5 hydrogen shift corresponds to the best possible overlapping (C-H-N angle=151°) between the ionized lone pair and the C-H bond: a 14 kJMol^{-1} barrier is found for the hydrogen abstraction, when the optimal conformation is taken as the initial geometry[512].

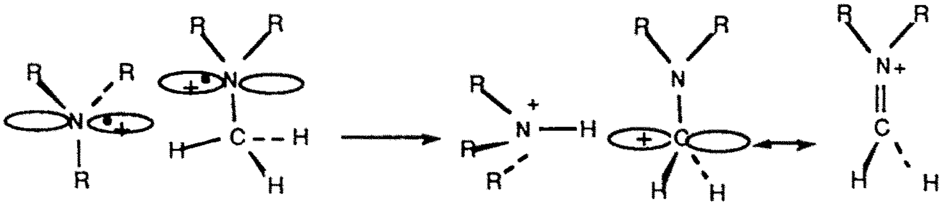
The reviews dealing with the chemistry of aminium radicals[432,513] identify deprotonation as the main mechanistic pathway of the aminium radical (equ. [64]):



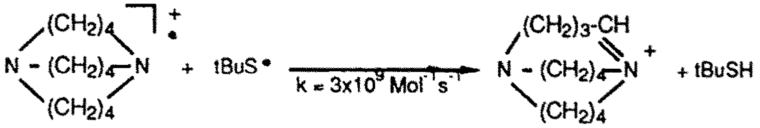
[64]

Nelsen and Ippoliti have recently challenged the theory of deprotonation, suggesting that an equally reasonable pathway could compete with deprotonation. This pathway is SH2 on the H in ß-position of the paramagnetic center[514] (**Scheme 40**):

Scheme 40



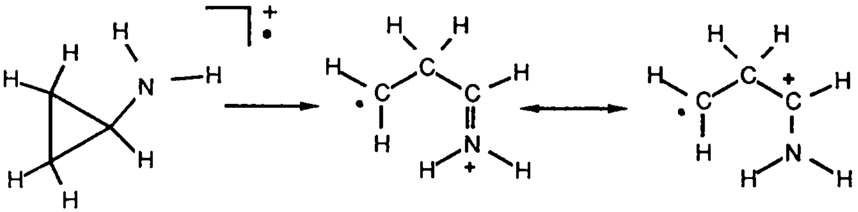
A possible estimate of the rate of this disproportionation could be 10^6 Mol^{-1}s^{-1} (Activation energy≈5 kcalMol^{-1}) for the case of $Me_2NH^{+\bullet}$[515]. Stereoelectronic effects obtained for the best eclipsing of the C-H bond and the half filled lone pair, could increase this rate, provided that the structural factors which increase this intramolecular overlapping do not overly inhibit the intermolecular approach of the reactive species. The considerable weakening of the ß-C-H bond is shown by the reaction rates[515] (**equ.[65]**):



[65]

Applying the reactive mixed valence aproach to this SH2 reaction reveals that one could increase the rate of these reactions by introducing electron withdrawing groups on the starting amine ($EtN(CF_2CF_3)_2$). Rate data are lacking to precisely estimate under which conditions the disproportionation channel will take precedence over the deprotonation one. Common sense suggests that under basic conditions and/or in diluted solution, ß-deprotonation should remain the dominant route.

Could this weakening of ß-bonds to the half filled lone pair activate C-C bonds? A tentative positive answer was provided by Resonance Raman Spectroscopic studies on the radical cation of 1,4-diazabicyclo [2.2.2.]octane in aqueous solution[516]. Although this work probably ignored the presence of dimers[510], their conclusion on C-C_β weakening probably is still true, though it is underestimated. Results from low temperature matrice experiments, photochemistry and mass spectrometry do support the idea of weakening, though the main remaining unknown is: to what extent ? William's group recently studied the ring opening of cyclopropylamine radical cation in CF_3CCl_3 or $CFCl_3$ at temperatures between 80 and 140K[517] (**equ. [66]**):

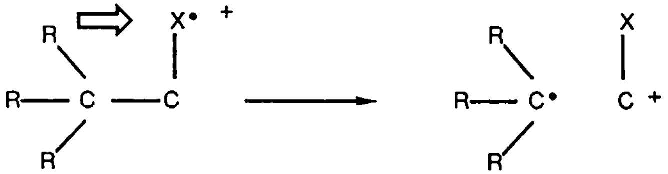

[66]

distonic radical cation: charge and spin are carried by different atoms when written under a classical form[518]

The opened radical cation displays a new structural feature, when compared to the open form of the unsubstituted form of the cyclopropyl radical cation (**equ. [66]**). This new structural feature is the stabilization of the carbocationic part of the structure: the dilemma shown by *ab initio* treatment of the cyclopropane radical cation is no longer present (see **Section 2.2.1.3**).

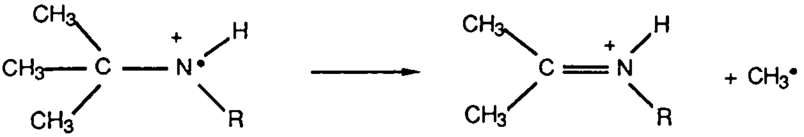
On the side of photochemistry, oxidative photofragmentations illustrate the weakening effect exerted by radical cations on C-C bonds in ß-position:

Scheme 41



Ci and Whitten recently reviewed this topic[519] Here, the basic structural features discussed in the reactive mixed valence approach can be found (see **Section 1.4.2.1.**). Also, the structural effects would work in the opposite direction depending on whether one concentrates on the transition state or on the formed products. In the transition state, in terms of electron flow, dative R and electron withdrawing X would favor the reaction. In the formed products, capto dative sets of R would stabilize the formed radical and electron donor substituents would stabilize the formed carbocation. Here also, the same experimental difficulties must be overcome to disentangle these structural effects, because they also play a role in the competitive reaction (mainly deprotonation for amines). The best studied cases of oxidative photofragmentation all include an aromatic part in their structure; they will be treated in **Section 2.2.3.2.**.

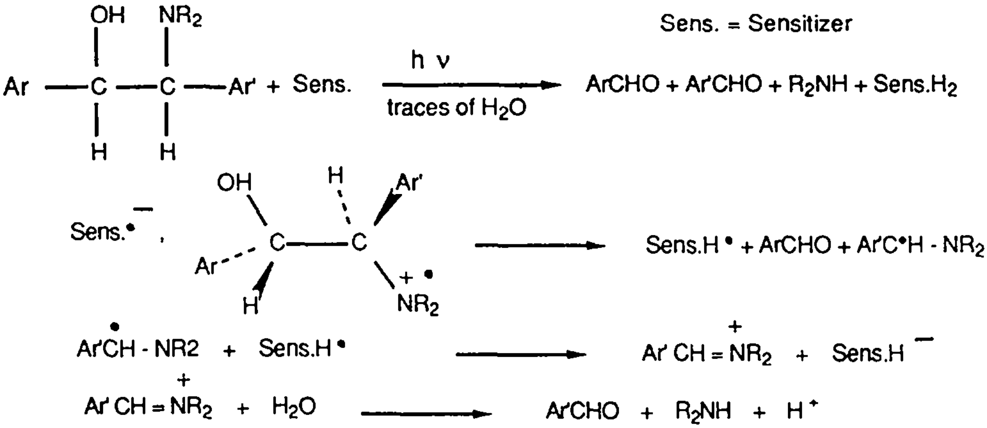
The so called α-cleavage of tertiary amines in the gas phase[520] provides the third evidence for bond weakening in ß position with respect to the radical cation center (**equ. [67]**):


[67]

Hammerum and Derrick[520b] have shown that these reactions occur with the specific release of considerable energy. Another interesting result from these gas phase studies is that, even for aminium radical cations bearing long alkyl chains, α-cleavage (Mass Spectrometric nomenclature) is faster than H abstraction in any position of the alkyl chain[520b]. Since *ab initio* calculations[512] predict a rather low energy barrier for these H abstractions and provided that entropic factors are not the main source of this absence of H abstraction in the gas phase, this suggests a rather low barrier to α-cleavage in these radical ions.

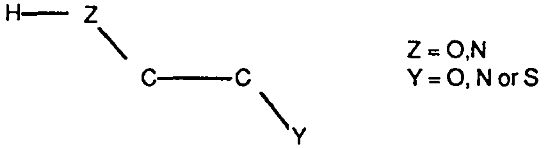
Ci and Whitten[519b] studied the parameters at work in the photoinduced electron fragmentation of aminoalcohols displayed in **Scheme 42**:

Scheme 42



This scheme shows only the fate of the *erythro* isomer and does not display the back electron transfer between the radical cation of the aminoalcohol and the radical anion of Sens. This system has brought important information about fragmentation. First, the best stereochemical situation for the cleavage of the C-C bond is an antiperiplanar relation between the alcohol, the C-C bond and the amine cation radical. This situation is easier to attain for the *erythro* isomer. Second, the fragmentation occurs faster for the aminoalcohol than for its ether. This increase in reactivity is viewed as the consequence of the merging of one and two electron processes in the fragmentation step. In this step, the radical anion of the Sensitizer would assist the C-C bond cleavage by deprotonation of the OH group. Rapid fragmentation is coincident with radical anion of the Sensitizer, deprotonating the aminoalcohol radical cation[519c]. This electron transfer induced dehydrofragmentation is quite general and may be applied to structures such as those shown in **Scheme 43**. Results discussed in **Section 2.2.3.2.** show that its scope is even wider. The anodic oxidation of N-benzyl-N-ethanolamines was the electrochemical precedent of this photochemical reaction[521].

Scheme 43



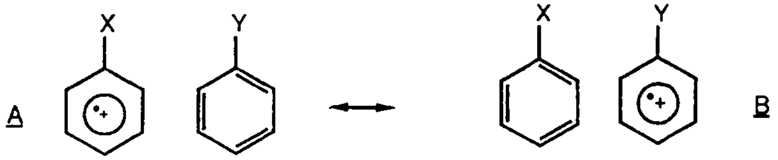
2.2.3. Radical cations with unsaturation.

This label is rather artificial because many structures simultaneously contain heteroatoms with lone pairs, double or triple bonds and aromatic or heteroaromatic groups. It would be helpful for our focus on understanding the roots of activations associated with the removal of an electron, to be able to know if the electron has been initially removed from a lone pair, from an unsaturation or from a π system. This is often not possible, so we will select examples where this decision is apparently simplified. The second point is that creation of a hole often activates a given substrate in different directions. This is even more important for the radical cations dealt with in this section: the overall selectivity of the process is often the result of complex competitive reaction schemes. This important aspect has been excellently dealt with in Parker's[419] and Shine's[439] reviews, and in other reviews[419-455] dealing with radical cations.

2.2.3.1. Associative activation.

Radical cations formed from unsaturated compounds are highly prone to dimerization. On the side of aromatic structures, the dimeric complexes (neutral + hyponomer) are more stable than the complexes obtained between the neutral and the hyponomer of any of the substituted neutrals[522]. Meot-Ner has ascribed the origin of this extra stabilization to a "no-bond resonance" **(Scheme 44)**:

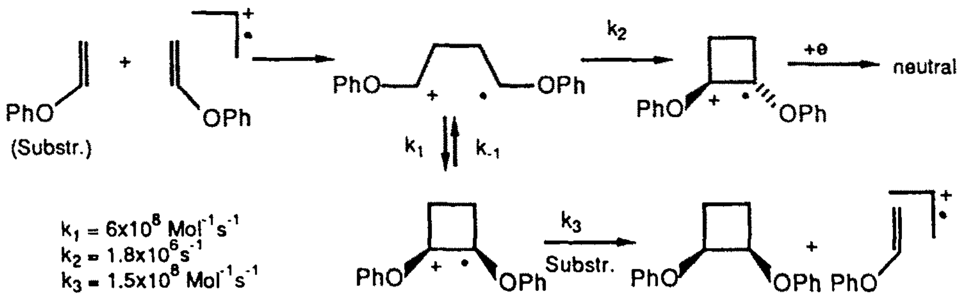
Scheme 44



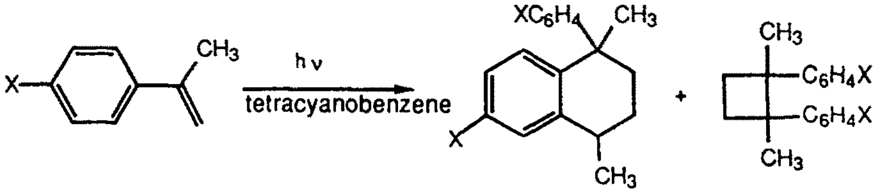
When the difference in energy between the two resonance structures A and B is closest to zero, the complex is the most stabilized. This obviously converges with Clark's approach to uneven electron bonds[86], as when X and Y are similar (best situation), the ionization potentials of the two partners are identical. This again may be seen as an illustration of symbiotic behavior[503] (see **Section 2.2.1.2.** for the discussion of this point). It is interesting to note that for bromobenzenes, dimerization does not take place through the π systems, but rather through the bromine groups[523]. Semi-empirical SCF-MO calculations show, however, that in alkyl bromide radical cation dimers the SOMO is heavily localized in the Br-Br bond, whereas in $(PhBr)_2^+$ the SOMO is still of σ type but is mainly confined to the C-C bonds of the aryl rings[483].

Non aromatic carbon-carbon multiple bonds, whose radical cation chemistry has been superbly reviewed by Lewis[427] also display this type of associative activation (**Scheme 45**):

Scheme 45



The kinetic study of photochemically induced dimerization of phenylvinyl ether shows that, after a very fast dimerization, the competition between ring opening and the propagation step of this chain reaction determines the cis/trans dimer ratio[524].



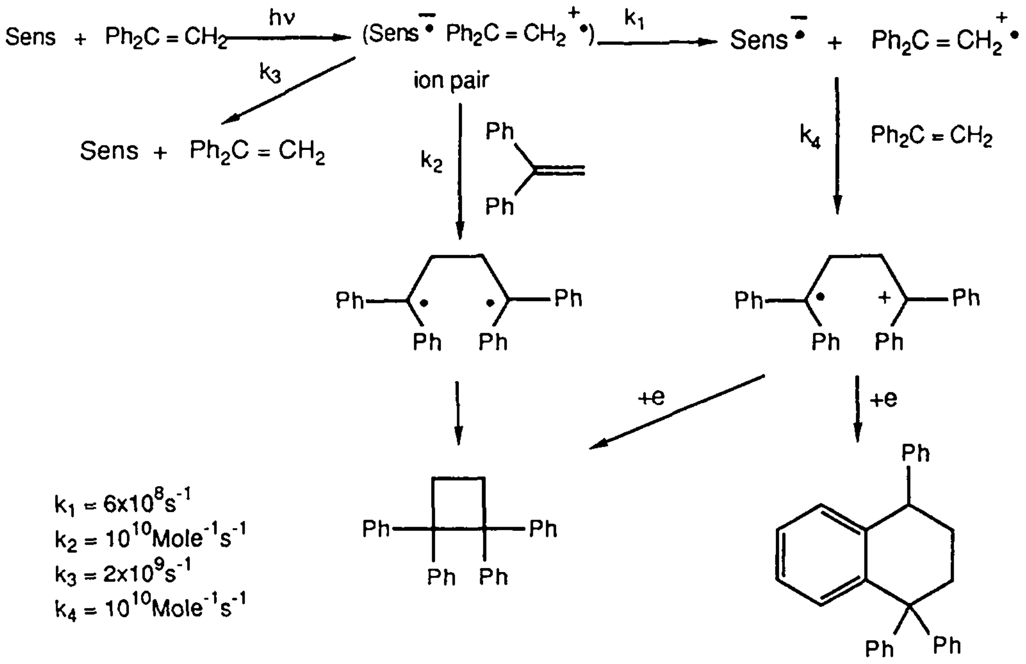
[68]

dominant if X = H, Me   dominant if X = OMe

In the [4+2] dimerization of styrene derivatives, two types of associative activation compete[525]. If only symbiotic effects were at work, only [2+2] dimer would be formed: actually, they are mainly formed when styrenes of lower ionization potential are considered. For the styrenes with higher ionization potentials, the [4+2] dimerization is preferred[526] (**equ. [68]**). This competition between [4+2] and [2+2] reactivity permeates the chemistry of thermally[527], photochemically and electrochemically generated radical cations of olefins. It may be part of a wider range of fast competing reactions involving protonation of the π cloud[528], deprotonation of α-carbons to the radical cation and polymerizations[529].

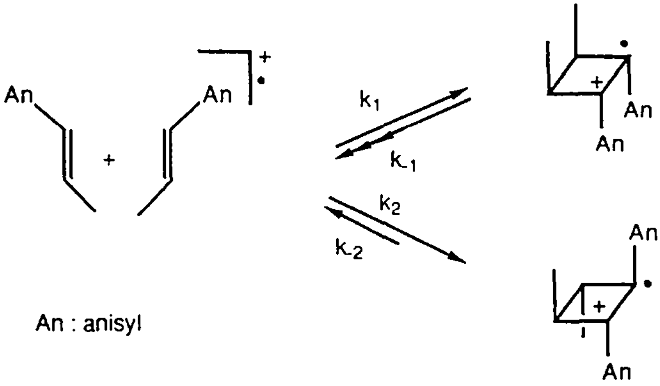
Mattes and Farid[530] conducted a kinetic analysis of the [2+2]*versus* [2+4] selectivity for the dimerization of 1,1-diphenylethylene in acetonitrile as shown in **Scheme 46**. Reaction of 1,1-diphenylethylene with the ion pair yields the [2+2]dimerization while cage-escaped cation radical yields both [4+2] and [2+2] dimers. The values of measured rate constants shows that the competition is settled between chemical processes, which are all characterized by very low activation energies.

Scheme 46



Very recently, Lewis and Kojima investigated the reactivity of *cis* and *trans* anethole hyponomers[531]. They found that the neutral-hyponomer dimerization takes place with retention of the olefin configuration and yields a mixture of *syn* and *anti* head-to-head dimers. The stereochemical outcome of this dimerization led them to discard the acyclic 1,4-cation radical as a precursor of any of the observed products (**Scheme 47**).

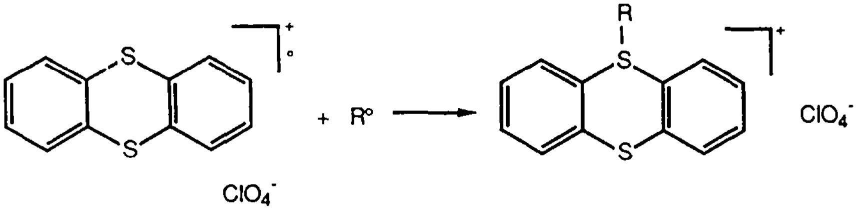
Scheme 47



Rather, they suggested that the formation of the *cis* An-An radical cation is formed more reversibly than its *trans* isomer. The rate evaluated for k_2 ($\approx 2\times10^6$ $Mol^{-1}s^{-1}$) in this case, is far lower than the one reported for the 1,1-diphenylethylene case (**Scheme 47**).

Bauld[527] proposed very high numbers (10^{23} and 10^{49}) to explain the associative activation involved in the Diels-Alder radical cation reaction. Controversial approaches have been developed to treat these reactions within the scope of Woodward-Hoffman rules[532,533]. The transition state of these Diels-Alder radical cations are probably non-synchronous. All the preceding examples show a dissymmetry in the compared reactivity of π radical anions and radical cations: radical cations are far more activated toward self-association than radical anions. The only exception to this statement can be found in heteropolar unsaturations (C=O, C=N, etc..).

Eberson applied the Dewar-Zimmerman rules[534] to the interaction between aromatic radical cations and nucleophiles[231], noting that a nucleophile orbital which interacts suprafacially with the ion should correspond to an antiaromatic transition state. He proposed that, for some nucleophiles, the pathway where no overlapping is involved (outer-sphere electron transfer), could become dominant. Eberson's proposition has its proponents and opponents (see ref. 535-541). It can be proven that, in some cases, the reaction of aromatic radical cations with nucleophiles is extremely fast[539b], although the general question remains unanswered: which nucleophile-aromatic radical cation couples follow an inner sphere pathway, and which follow an outer-sphere ? Much work remains to be done in this area , as it bears a direct connection to the problem of electrophilic reactivity of aromatics[542-545].



[69]

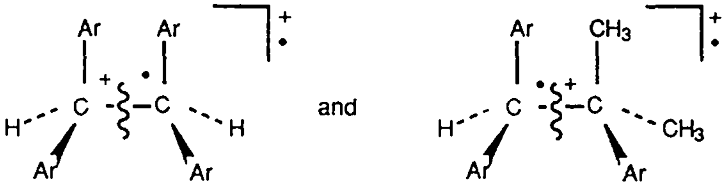
One aspect of unsaturated radical cations which has received comparatively little attention is their activation or inactivation toward radicals. Shine recently proposed a reaction which fills this gap[546] (equ. [69]). This reaction is found in the reaction of Grignard reagents toward the thiantrene radical cation. As rate constants for R° adding to the hypernomer are not available, it is difficult to decide if there is oxidative activation toward this associative reaction.

2.2.3.2. Dissociative Activation.

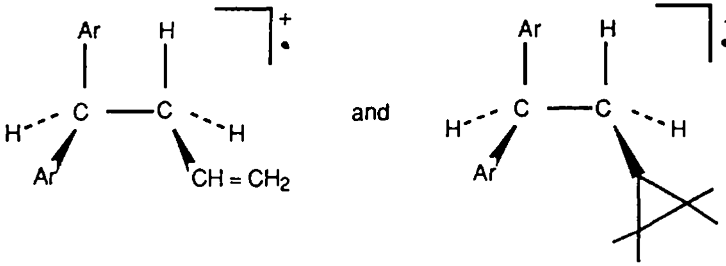
For carbocations, the main competitive pathway for nucleophilic reactivity (inter or intramolecular) toward the positively charged carbon is attack of the nucleophile on the β-hydrogen. The same type of activation toward C-H attack by nucleophiles is true for radical cations: using thermodynamic cycles, Arnold has shown that the pKa of toluene is increased by 60 pKa units when one electron is removed[547]. This activation is not always as high (see ref. 548b), but in any case, is often sufficient to transform a rather inert hydrogen into a center whose reactivity approaches diffusion controlled rates· As Nelsen pointed out for the case of amines the next question is: will this activation lead to an acidic compound or to an excellent hydrogen donor? The use of thermodynamic cycles[259,547-549] is a first step towards a response; the only drawback of the method is that, depending upon the cycle concerned, the estimation error may easily reach ±3 kcalMol^{-1}. This is not sufficiently precise to select between two pathways, when both are expected to be very fast. At this point, on the experimental side, it would seem as if the activation toward proton removal for unsaturated substrates has played a more important role than activation toward hydrogen removal[536-538]. Such an activation is expected to be even more stronger in dications [395].

The electron transfer sensitized C-C bond cleavage has been touched on in **Section 2.2.2.2.**. It probably results from ionization of a lone pair (N, O, P, S) followed by intramolecular hole transfer. One may wonder if special structures can be designed where the "holephore" would be an unsaturation and where the activating hole would then cleave a bond ß to the unsaturation. An excellent report by Okamoto, Snow and Arnold[550] provides a positive answer to this question. These authors have shown that C-C bond cleavage occurs between 10°C and 80°C in the radical cations shown in **Scheme 48**, although it does not occur for those shown in **Scheme 49**.

Scheme 48



Scheme 49



The careful discussion made in the original report allows us to focus on only the ß-scission step. The study of temperature dependence of cleavage efficiency for the two first radical cations, completed by the inclusion of these results in thermochemical cycles, gives an idea of the strength of the cleaved C-C bond. For the tetraaryl derivative, it amounts to 11.3 kcalMol^{-1}. These figures allow us to give a graphic representation of the comparative situations of radical anion bond cleavages that we discussed in **Fig. 8** and the radical cations. **Figure 9a** shows that for most of the aromatic radical anions where intramolecular electron transfer leads to ß-cleavage, the state reached after the C point is probably directly dissociative. In contrast, for the presently discussed radical cations, the situation is probably better represented by **Figure 9b**. The reason why the second set of substrates (derivatives with 2 Ar) do not cleave, may therefore either be that the C crossing point has too much energy, or that the radical cation formed after passing the col is too stable to dissociate. Within the second hypothesis, one could hope to observe, under selected structural and medium conditions, isomeric radical cations in equilibrium (**equ. [70]**) or respectively stabilized by appropriate substitution.

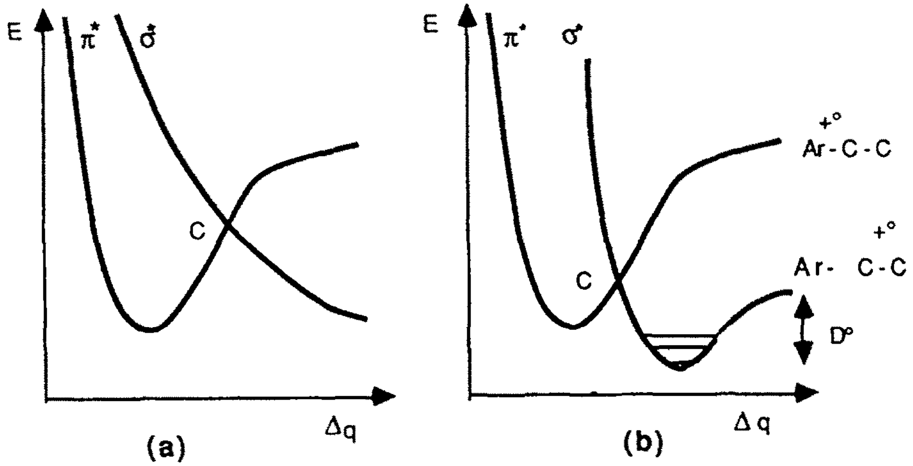
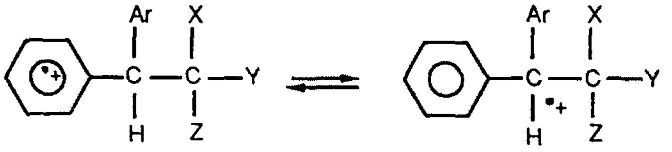


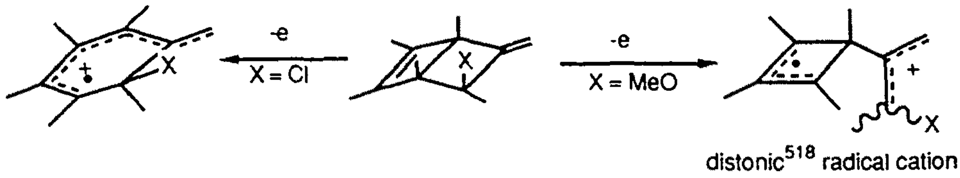
Figure 9: **Reactive Mixed Valence formulation**
(a) origin of bond cleavage in halobenzene radical anions (see **Fig. 8**)
(b) origins of bond cleavage in the radical cations, studied in ref. 550.



[70]

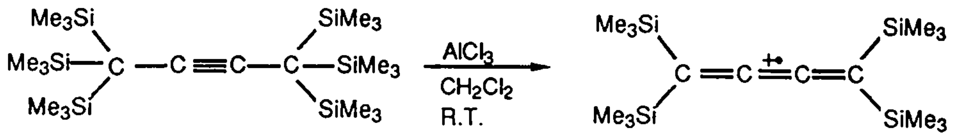
Isomeric forms of radical cations have been proposed by Roth[430,551] for the radical cations of 6-X-5-methylene-1,2,3,4,6-pentamethylbicyclo[2.2.0]hexene (**Scheme 50**).

Scheme 50



Here is a kind of conflicting situation, where stabilizing the carbon sp^3-carbon sp^3 centered radical cation, leads to a lowering of C energy in **Fig. 9b**, but could also simultaneously lead to a higher dissociation energy of this radical cation. (a) and (b) cases in **Figure 9** are obviously extreme situations; structural or medium perturbations should make it possible to cover all situations between the two.

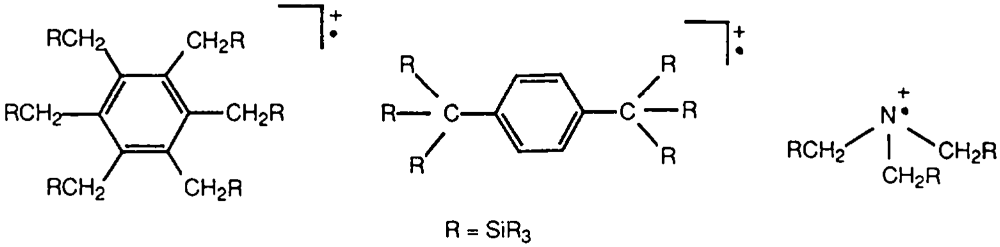
When one compares these results with those of Clark[86], it clearly appears that, depending on its structural environment, a one electron C-C bond may display D° values ranging from 45 kcal to almost zero. In fact, we believe that substituents such as NR_2 drastically lower the value of this D°, even when substituted on the aromatic part[552]. This belief is based on the rapid opening of the radical cation of cyclopropylamine (**equ. [66]**). The same remark applies to substituents such as OR, capable of stabilizing a carbenium ion[487]. An interesting experiment would be to simulate electronic substituent effects on one electron C-C bond strengths using Clark's approach. Clark's results for one electron Si-Si bonds ($D^\circ \approx 29$ kcalMol^{-1}) suggest that Si-Si or C-Si bonds have a more efficient oxidative cleavage than their C-C isostructural counterparts. Bock and Kaim's results only partially substantiate this. The room temperature C-Si bond cleavage in the radical cation of **equ. [71]** converges with the theoretical results[553]:



[71]

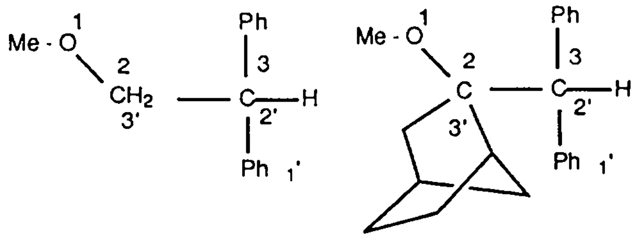
But the persistence of radical cations[425] shown in **Scheme 51** suggests that the theoretical treatment does not yet include all the features associated with one electron removal. As shown for the radical cation, the radical anion of the silyl derivative of butyne cleaves to yield the radical anion of the cumulene[425] shown in **equ. [71]**.

Scheme 51



The radical cations shown in **Scheme 52** :

Scheme 52

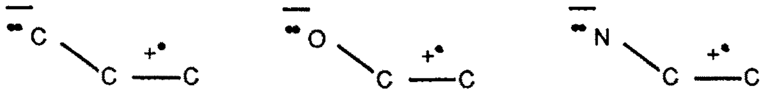


MeO in endo
and exo position

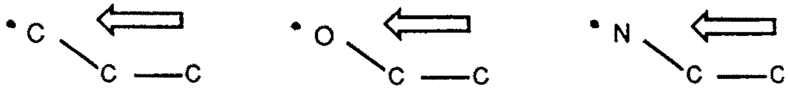
cleave under far milder conditions (< 10°C) than their structural counterparts, where the MeO group has been replaced by an hydrogen (no cleavage even at 80°C)[550]. This confirms that a substitutent with lone pairs considerably labilizes a one electron C-C bond.

An extreme situation would be provided by the structures included in **Scheme 53**, where one recognizes (see **Section 1.4.2.1.**) the situation reached, when an intramolecular electron transfer in the direction indicated by the arrow (**Scheme 54**) has taken place.

Scheme 53

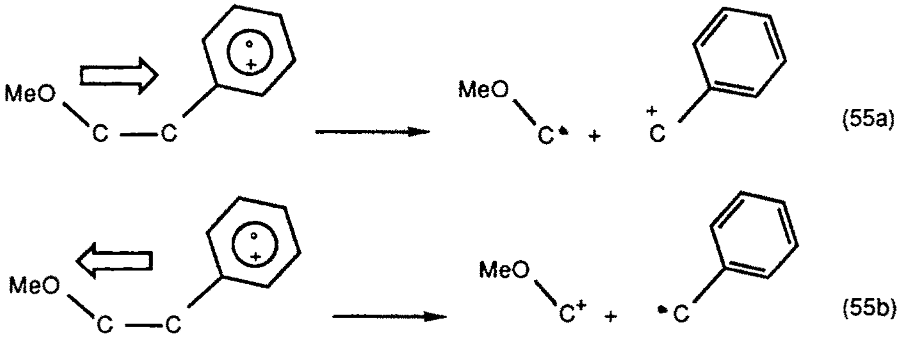


Scheme 54



The next question, in terms of the reactive mixed valence approach applied to these β-cleavages, is whether we should consider that the holephore in these structures is the aryl system or the oxygen lone pair ? The answer provided by Okamoto, Snow and Arnold[550] and by Reichel et al.[553], indicates that the diphenylmethyl moiety is the main component of the SOMO in the cation radical.

Scheme 55



In **Scheme 55**, we find the same type of dilemma as the one found for the concept of regioconservation of spin for the cleavage of radical anions (**Section 1.4.2.1.**). The nature of the dilemma is that, looking at the substrate, one would suppose that (a) is the predominant pathway (because of SOMO localization), but when we look on the product side, (b) is clearly preferred, as the formed carbenium ion is highly stabilized by the methoxy group[552]. The experimental difficulty of the dilemma, well identified by Arnold's group, is that the simple observation of final products is not sufficient, as the final products which suggest a (b) path could simply be the result of an (a) path being followed by a very fast electron transfer from the electron rich radical to the carbocation. Such an electron transfer has less time to occur in the gas phase (faster diffusion of the cleaved fragments); in the gas phase, methyl 2,2-diphenylethyl ether cleaves to yield predominantly the diphenylmethyl cation, which corresponds to the (a) channel. In contrast, the radical cation of this ether in acetonitrile-methanol solution, shows no trace of methyl diphenylmethyl ether (**equ. [72]**):

$$Ph_2C^+H + MeOH \xrightarrow{\text{unobserved}} Ph_2CHOMe + H^+ \qquad [72]$$

The difference between cleavage in the gas phase and in solution would hint at a very fast electron transfer following the cleavage, but the evidence is not totally compelling because solvent effects may play an important role in intramolecular electron transfers[185b]. To trap the radical formed in **Scheme 55** one could think of very fast free radical clocks, but the only appropriate ones would be those for which the rearranged product could not form at the cation stage.

Lack of space makes it impossible to discuss C-C bond cleavages in radical cations formed from unsaturated substrates, and in reactions such as cycloreversion and rearrangements. This topic is well covered in recent reviews[427, 428,430,438a,446,454].

3. Prospective.

This Tetrahedron Report has not nearly exhausted the question raised in its title. Apart from the actual facts we have certainly missed in the published literature, there are a host of topics that we did not treat despite their relevancy.

The following questions show that the topic "the electron, an activating messenger?" is heuristically rich. When one electron, under light excitation, leaves one relatively localized OM to reach another OM with a given localization of the transferred electron, what are the chemical consequences viewed in terms of activation[553]? In these light induced events, the electron "travels" far faster than the nuclei (Franck-Condon principle). It has been recently suggested, however, that for some proton transfers inside hydrogen bonds[554], the proton travels faster than the electron. Can the proton become a faster messenger than the electron?

Can we apply thermodynamic cycles[259d,547-549] to transition states, when predicting changes in reactivity inside redox series? It is known that the introduction of certain ligands in transition metal complexes may exert as much effect on a given type of reactivity as would exert the addition or the removal of one electron[11a]. What type of equivalence exists between structural substitution (attempt to substitute a carbon by 4 electron rich groups) and addition or removal of one electron? We have seen (**Section 1.4.2.1.**) that the addition of an electron may shift a substitution from the field of interchange mechanisms to that of dissociative substitutions. Are there leaving groups where the reverse may be occur (remove an electron and shift from the dissociative area to the interchange one)?

With the advent of computer graphics, are we going to see pictures of potential hypersurfaces[5,166] of reactive events calculated for homogeneous redox series?

In this Report, the focus has been mainly on the electron (or the hole) acting as activating messengers in intramolecular events. What about intermolecular reactive events? We have seen the importance of adding or substracting an electron on stable structural units and the drastic changes that it causes in reactivity; on the other hand, for aromatics (**Section 1.4.2.**), we have proposed that its intramolecular transfer corresponds to a message of activation. What about intermolecular acts of reactivity? S. Shaïk[555] proposed that both TS geometries and barriers reflect the nature of the SN2 reaction as a transformation involving synchronous single electron shift and bond interchange. The electron, viewed as an activating messenger provides a fresh view in the controversial problem of polar *versus* SET mechanisms of transformation. The competition between these two basic schemes of reactivity would be ruled by a bidimensional approach. The two main dimensions (keeping steric effects constant) would be 1) respective E° of the partners of the DA couple; 2) importance of the activation induced by electron transfer. The clear cut cases would correspond to extreme situations: a) when ΔE° between D and A is large, and activation induced by electron transfer is small, one would have a typical situation of outer-sphere electron transfer; b) on the opposite, when ΔE° is small, and activation induced by electron transfer is important, one would go toward a generalized inner-sphere type of mechanism (i.e. SN2, SNAr, nucleophilic additions, and more generally reactions where steric effects are shown to play an inhibiting role when they interfere with the approach of the partners). For such situations, everything goes as if the activated substrate was "so eager to receive the message" that it does not wait the end of this message to get transformed. As expected, the in-between cases (medium ΔE° and medium activating effects) would be more difficult to study, but also richer in informations.

The study of Rydberg states shows that states with principal quantum numbers up to n=520 can be observed; their "size" is about 2×10^5 Å[557]. At this size, the most external electron still "belongs" to the nucleus. In terms of reactivity, would it be any difference between such Rydberg states and a solvated electron?

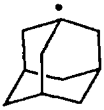
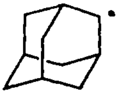
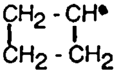
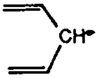
In biological structures, the evidence that electrons make long distance trips is well known[476]. Does Nature use the activating dimension of the electron for specific purposes in supramolecular machines?

We have tried to remain as phenomenological as possible in this report, but molecular orbitals do appear throughout the text. Some have begun to wonder about what happens to Woodward-Hoffmann rules when they are applied to redox series[12,398b, 532,533]. However, much more remains unknown, and despite the pervasiveness of electron transfer catalysis, not much has been done to answer the question: what results from the application of isolobal principles[18a,b] to redox series?

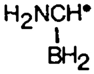
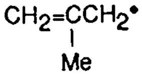
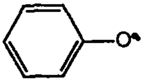
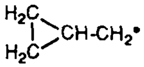
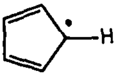
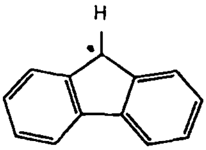
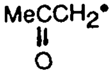
Acknowledgements

We would like to thank Mrs S. Roussel for her patience and ability in creating a difficult camera ready version of this report. It is a pleasure to acknowledge the stimulating discussions with Dr. C. Amatore, A.T. Balaban, J. Fossey, J.F. Gal, M. Santelli and L. Stella. Wise advice and comments on the written English from Professor Ollis considerably improved the first submitted manuscript. A NATO grant on the theme "Activation induced by electron transfer" has made the realization of this Report easier. Despite the size of the cited literature, we are certain to have missed data relevant to the question asked in the title of this report. We would greatly appreciate any supplementary information, and apologize for any serious omissions.

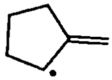
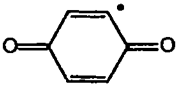
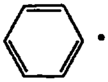
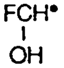
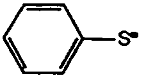
Annex 1: SOMO, IP, EA, E° of representative radicals

	Radicals	SOMO (eV)	IP (eV)	EA (eV) **y)**	$E^\circ_{(R^\circ/R^{\circ\circ}(-))}$**z) ab)**
1	Na		5.1	0.5 +/- 0.2	
2	$Nb(allyl)Cp_2$		5.7 **q)**		
3	$Mo(CO)Cp_2$		5.9 **q)**		
4	cyclopropenyl•		5.8 **ad)**, 7.6 **w)**		
5			6.2, 6.4 **l)**		
6	$CH_2(CH_2)_5CHCH_2^\bullet$		6.6 **h)**	0.8 +/- 0.5	
7	$p\text{-}MeOC_6H_4CH_2^\bullet$		6.9 **h)**		
8			6.7, 7 **l)**		
9	$p\text{-}MeC_6H_5CH_2^\bullet$		6.96 **m)**	0.7 +/- 0.2	
10	$Ph_2CH^\bullet$		7.3 **h)**	0.9 +/- 0.5	-0.9 **z)**, 0.35, -1.14 **ab)**
11	$PhCH_2^\bullet$		7.2 **f) m)**, 7.8 **h) w)**	0.73, -1.45 **ab)**	
12	α-naphthyl$CH_2^\bullet$			1 +/- 0.2	0.47, -1.27 **ab)**
13	$CH_2{=}CHCH^\bullet CH_3$		7.5, 7.7 **k)**		
14	$(CH_3)C^\bullet$		7.5 **b)**, 6.7 **l)**, 6.9 **l)**	0.21 +/- 0.4	-2.1 **z)**, 0.09 **ab)**
15	 $\begin{matrix} CH_2 - CH^\bullet \\ \vert \quad\quad \vert \\ CH_2 - CH_2 \end{matrix}$		7.5, 7.7 **k)**		
16		-7.6 **a)**		1 +/- 0.3	0.80, -1.50 **ab)**
17	$Si^\bullet H_3$		7.6 **b)**	2.2 +/- 0.5	

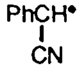
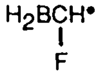
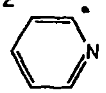
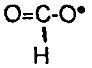
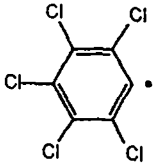
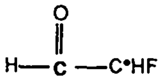
Annex 1: SOMO, IP, EA, E° of representative radicals *(continued)*

	Radicals	SOMO (eV)	IP (eV)	EA (eV) y)	$E°_{(R^\bullet/R^{\bullet\bullet(-)})}$z) ab)
18	 $H_2N\underset{BH_2}{C}H^\bullet$	-7.8 a)			
19	$(CH_3)_3CCH_2^\bullet$		7.9, 8.2 j)		
20	cyclohexyl•			0.3 +/- 0.3	
21	$(CH_3)_2CH^\bullet$		7.9 b), 7.4 l), 7.7 l)	< 0 aa)	
22	 $CH_2{=}\underset{Me}{C}CH_2^\bullet$		7.9, 7.95 k)		
23	$H_2NC^\bullet HF$	-8 a)			
24	$CH_3CH_2CH_2^\bullet$		8.15 o), 8.4 j) w)	0.7 +/- 0.4	
25	$CH_2{=}CHCH_2^\bullet$		8.2 b) h) w)	0.4 +/- 0.5	-1.3 z)
26	$CF_3CF_2CF_2^\bullet$			2.3 +/- 0.2	
27	$CF_2(CF_2)_5CFCF_2^\bullet$			3.9 +/- 0.4	
28	cyclopropyl•		8. w)		
29	$HOCH_2^\bullet$	-9.8 a)	8.1 h), 8.5 w), 7.6 ad)		-0.24 (OMe) ab)
30	$H_2NCH_2^\bullet$	-8.1 a)	7.6 w)		-1.03 (NMe_2) ab)
31	$CH_3O^\bullet$		11.9 w)	1.5 +/- 0.3	0.8 z)
32	$tBuO^\bullet$			1.9 +/- 0.3	0.3 z)
33			8.7 c), 8.8 w)	2.4 +/- 0.3	
34				0.5 +/- 0.3	
35	$CH_2{=}CHCH_2CH_2^\bullet$		8.5 k)		
36			8.6 b), 8.7 w)	1.8 +/- 0.2	-0.2 z)
37				1.9 +/- 0.2	-0.6 z), 0.76, 0.76 ab)
38	$CH_2(CH_2)_3CHCH_2^\bullet$		8.7 h)		
39	$MeC^\bullet{=}O$		8.1 u) v), 11.9 w)		
40	 $Me\underset{O}{\underset{\Vert}{C}}CH_2^\bullet$		8.8 b)		

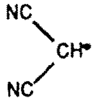
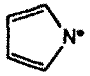
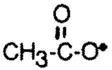
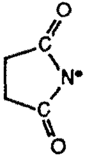
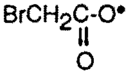
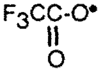
Annex 1: SOMO, IP, EA, E° of representative radicals *(continued)*

	Radicals	SOMO (eV)	IP (eV)	EA (eV) y)	$E^\circ_{(R^\bullet/R^{\bullet\bullet(-)})}$z) ab)
41				1.6 +/ - 0.2	
42	$CH_3CH_2^\bullet$		8.8 b), 8.4 l) n), 8.5 l) n) w), 8.15 n)	0.9 +/- 0.3 <0 aa)	
43	$CF_3CF_2^\bullet$			2.4 +/- 0.4	
44	$F_2CH^\bullet$			0.6 +/- 0.2	
45	$H_2C{=}C{=}CH^\bullet$		8.34 w)	2.3 +/- 0.3	
46	$Cl_3C^\bullet$		8.8 g)	1.5 +/- 0.3	
47	$Br_3C^\bullet$			1.7 +/- 0.2	
48			9.2 t)	2.0 +/- 0.3	
49			9.2 w)	2.0 +/- 0.3	(-0.1)
50	$F_3C^\bullet$		9.2 b)	2.0 +/- 0.5	
51	$O_2NCH_2CH_2^\bullet$			2.1 +/-0.3	
52	$ON^\bullet$		9.3 b) w)	0.4 +/-0.4	
53	$O{=}C^\bullet H$		9.3 w), 8.14 ac)		
54	$O{=}C^\bullet{-}CF_3$			0.5 +/- 0.2	
55	$H_2C{=}CH^\bullet$		9.5 h) w)	1.5 +/-0.5	(-0.3) z)
56	$F_2C{=}CF^\bullet$			2.0 +/-0.22	
57	 $FCH^\bullet(OH)$	-9.5 a)			
58	$ClCH_2^\bullet$		9.3 h)	0.30	
59	$CH_3^\bullet$	-10.3 a)	9.9 b), 9.8 l)	0.3 +/- 0.7 < 0 aa)	-0.5 +/- 0.2 z)
60	$CH_3S^\bullet$		8.1 b)	1.7 +/- 0.3	
61	$HS^\bullet$		10.5 b)	2.3 +/- 0.2	
62	$tBuS^\bullet$			2.1 +/- 0.3	
63				2.5 +/- 0.2	-0.2 z)
64	$I^\bullet$		10.5 b)	3.2 +/- 0.2	
65	$NO_2^\bullet$		9.8 ad), 11.5 w)		

Annex 1: SOMO, IP, EA, E° of representative radicals *(continued)*

	Radicals	SOMO (eV)	IP (eV)	EA (eV) y)	$E^{\circ}_{(R^{\bullet}/R^{\bullet\bullet}(-))}$z) ab)
66	$NCS^{\bullet}$				0.7 z)
67	$H_2BCH_2^{\bullet}$	-10.8 a)			
68	$NCC^{\bullet}(CH_3)_2$			1.0 +/- 0.2	0.3 z)
69	$NCCH_2^{\bullet}$		10.9 e), 10 w)	1.3 +/- 0.3	
70	 $PhCH^{\bullet}(CN)$			1.9 +/- 0.3	
71	$N_3^{\bullet}$		11.2 w)		
72	 $H_2BCH^{\bullet}(F)$	-11.0 a)			
73	$Me_2N^{\bullet}$		11.2 b)	0.8 +/- 0.4	
74	$H_2N^{\bullet}$		11.2 b) 11.1 p), 12.4 w)	0.8 +/- 0.4	
75	$H_3CC{=}C^{\bullet}$			0.9 +/- 0.5	
76	$HC{\equiv}C^{\bullet}$		11.6 r), 12 s)	2.5 +/- 0.3	
77	$F_2N^{\bullet}$			1.6 +/- 0.8	
78				2.4 +/- 0.2	
79	$F_3Si^{\bullet}$			2.7 +/- 0.5	
80	$Br_3Sn^{\bullet}$			3.0 +/- 0.3	
81	 $O{=}C(H){-}O^{\bullet}$			3.5 +/- 0.5	
82				2.7 +/- 0.2	
83	$(CH_3)_2C^{\bullet}{-}NO_2$				0.9 z)
84	 $H{-}C({=}O){-}C^{\bullet}HF$	-11.2 a)			
85	$FCH_2^{\bullet}$	-11.3 a)		0. +/- 0.5	
86	$HOO^{\bullet}$		11.5 d) w)	1.4 +/- 0.3	
87	$CN{-}C^{\bullet}HF$	-11.5 a)			
88	$(CH_3C{=}O)_2C^{\bullet}H$			2.9 +/- 0.3	1 z)
89	$(HC{=}O)_2C^{\bullet}H$	-11.6 a)			

Annex 1: SOMO, IP, EA, E° of representative radicals *(continued)*

	Radicals	SOMO (eV)	IP (eV)	EA (eV) **y)**	$E°_{(R^{\bullet}/R^{\bullet\bullet(-)})}$**z) ab)**
90	$Br^{\bullet}$		11.8 **b)**	3.4 +/- 0.3	1.2 **z)**
91		-12 **a)**		2.3 +/- 0.3	0.6 **z)**
92				2.4 +/- 0.3	
93	$F_2C^{\bullet}H$	-12.7 **a)**			
94	$NCO^{\bullet}$		11.5 **w)**		
95	$FC{=}C^{\bullet}$			3.4	
96	 $F_3C\underset{O}{\underset{\|}{C}}\text{-}\underset{O}{\underset{\|}{C}}C^{\bullet}H_2$			3.5 +/- 0.5	
97	$HO^{\bullet}$		12.9 **b)**, 14.9 **w)**	1.7 +/- 0.3	1.1 **z)**
98	 $CH_3\text{-}\overset{O}{\overset{\|}{C}}\text{-}O^{\bullet}$			3.3 +/- 0.2	1.3 **z)**
99				2.4 +/- 0.3	
100	$H^{\bullet}$		13.6 **b)**	0.7 +/- 0.1	
101	$O_3N^{\bullet}$			3.7 +/- 0.2	1.6 **z)**
102	 $BrCH_2\underset{O}{\underset{\|}{C}}\text{-}O^{\bullet}$			4.0 +/- 0.3	
103	$NC^{\bullet}$		14.2 **b) w)**		
104	$Cl^{\bullet}$		14.5 **b)**	3.6 +/- 0.2	1.6 **z)**
105	 $F_3C\underset{O}{\underset{\|}{C}}\text{-}O^{\bullet}$			4.5	1.1 **z)**
106	$F^{\bullet}$		17.4 **b)**	3.4 +/- 0.3	2.4 **z)**
107	$O_3P^{\bullet}$			4.5 +/- 0.5	
108	CH_2^{+}		18.9 **w)**		
109	NH_3^{+}		23.5 **w)**		

a) ref. 556 **b)** ref. 399a **c)** ref. 558 **d)** ref. 559 **e)** ref. 560 **f)** ref. 561 **g)** ref. 562
h) ref. 261a **i)** ref. 563 **j)** ref. 564 **k)** ref. 565 **l)** ref. 566 **m)** ref. 567 **n)** ref. 568

o) ref. 569 p) ref.570 q) ref. 571 r) ref. 572 s) ref. 573 t) ref. 574 u) ref. 575
v) ref. 576 w) ref. 577 x) ref. 578 y) ref. 33b (this reference contains many more EA of radicals; the values reported here are often an average value obtained from Tables in ref. 33b, completed by an estimation of the associated error which gives an idea of the scattering of tabulated values).

z) ref. 579 *vs* NHE (see this reference for the aprotic solvent used in the experimental determination).

aa) ref. 549 and 580 *vs* SCE; add 0.24 to value *vs* SCE to obtain values *vs* NHE. For these two references, $E_{1/2\ ox}$ and $E_{1/2\ red}$ are given in this order. ab) ref. 581 ac) ref. 582 ad) ref. 583

( ) values are uncertain; underlined numbers in IP represent adiabatic values.

Useful geometrical, vibrational and thermodynamic data on radicals may be found in ref. 59, 259e, 570, 357, 584, 585, 586, 587, 588.

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