# THEORETICAL STUDY OF FREE-RADICAL MIGRATIONS

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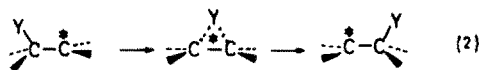Groupe de Recherche No. 12, C.N.R.S., 2 rue H. Dunant, 94320 Thiais, France

**Abstract**—Free-radical migrations have been investigated by *ab initio* molecular orbital theory to account for the facts that 1,2-migrations are observed for Cl-atoms, aryl or vinyl groups, whereas for H atoms only 1,5- and 1,6-migrations have been seen in contrast to the easy 1,2-hydride shifts in cations. The optimum geometry and energy models of the transition states of 1,2- and 1,5-migrations, and of their corresponding initial states have been determined using the Gaussian 70 STO-3G RHF method. The calculated activation energies $\Delta E$ are in agreement with experimental observations. The main features of the 1,2-migration reactions are (i) $\Delta E$ is more important for elements of the first and second row of the periodic classification than for those belonging to the third row; (ii) protonation strongly reduces $\Delta E$. For both 1,2- and 1,5-migrations a correlation exists between $\Delta E$ and the energetic change of the frontier orbital, $\Delta \epsilon_{SOMO}$: the reactions are under frontier orbital control.

Y-Migration from carbon to carbon (eqn 1) is frequently observed when $-\overset{*}{\underset{|}{C}}-$ is a carbocation $(* = +)^{1,2}$ for

$$\underset{R_1}{\overset{R}{\underset{|}{C}}}\!\!\overset{Y}{\underset{|}{C}}-(C)_{\overline{n}}\overset{*}{\underset{R}{\overset{|}{C}}}\!\!\overset{R_3}{\underset{R_4}{\sim}} \longrightarrow \underset{R_1}{\overset{R}{\underset{|}{C}}}\!\!\overset{*}{\underset{|}{C}}-(C)_{\overline{n}}\overset{Y}{\underset{R_4}{\overset{|}{C}}}\!\!\overset{R_3}{\sim} \quad (1)$$
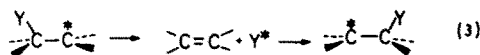
Y-migrating groups such as hydride, halogen, hydroxyl, alkyl, vinyl, aryl, etc., and chiefly occur, but not exclusively, when n = 0. On the other hand with an anion $(* = -)$ 1,2-migrations have only been observed when Y is a vinyl[3] or an aryl group.[4] In free radicals $(* = \cdot)$, these latter groups have been seen to undergo 1,2-migrations, and, in addition, for Y = aryl, 1,4- and 1,5-shifts have been observed.[5] In contrast to the easy 1,2-hydride migrations observed in cations, such facile 1,2-hydrogen shifts have not been seen in solution,[6] in contradiction to the frequently noted 1,5- and 1,6-migrations.[10] Paradoxically 1,2-chlorine migration, a very fast process depending on the structure of the free-radical, is observed,[11-13] whereas 1,5- and 1,6-migrations have not been detected.[14,15] To date, migrations involving groups such as Y = F, OR, NR₂ or CR₃ have not been reported.
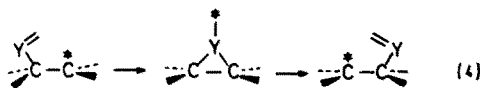
Three possible mechanisms may be envisaged for 1,2-migrations: (a) A direct migration (eqn 2) through a

$$\underset{\sim}{\overset{Y}{C}}-\overset{*}{\underset{\sim}{C}} \longrightarrow \underset{\sim}{\overset{Y}{C}}\cdots\overset{*}{\underset{\sim}{C}} \longrightarrow \underset{\sim}{\overset{*}{C}}-\overset{Y}{\underset{\sim}{C}} \quad (2)$$

bridged structure which could be a real intermediate. It has been shown[16] and confirmed by calculation[17] to be the case with cations. In free-radicals, the chlorine as the migrating atom seems to be the sole example of such a process.[18] (b) A two step elimination-addition migration (eqn 3) as postulated in free-radicals, when Y is a
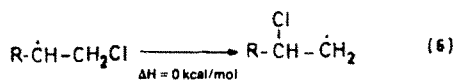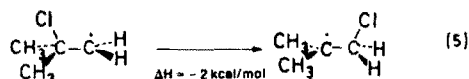
$$\underset{\sim}{\overset{Y}{C}}-\overset{*}{\underset{\sim}{C}} \longrightarrow \underset{\sim}{\overset{}{C}}=C\underset{\sim}{\overset{}{}}+Y^* \longrightarrow \underset{\sim}{\overset{*}{C}}-\overset{Y}{\underset{\sim}{C}} \quad (3)$$

bromine atom or SR group.[19,20] (c) A cyclisation-ring opening mechanism (eqn 4) which occurs in cations,

$$\underset{\sim}{\overset{Y}{C}}-\overset{*}{\underset{\sim}{C}} \longrightarrow \underset{\sim}{\overset{Y}{C}}\overset{*}{\underset{\sim}{C}} \longrightarrow \underset{\sim}{\overset{*}{C}}-\overset{Y}{\underset{\sim}{C}} \quad (4)$$
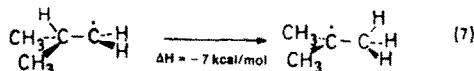
anions and free-radicals when X contains unsaturation (Y = aryl, vinyl, etc.).

From a general point of view, free-radical reactivity is interpreted by three main factors: thermodynamic, steric and polar.[21,22,23] Clearly, however, these factors, either separately or together, cannot give a complete explanation of the experimental data. For example, 1,2-migration of a chlorine atom has been noted where $\Delta H$ is slightly favourable[11] (eqn 5) and also where it is unfavourable[18] (eqn 6).
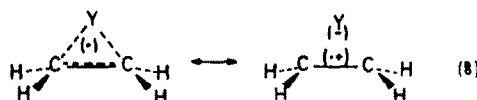
$$\underset{CH_3}{\overset{CH_3}{\underset{|}{C}}}\overset{Cl}{\underset{|}{C}}-\dot{C}\cdots\overset{}{\underset{H}{}}H \xrightarrow[\Delta H = -2\,kcal/mol]{} \underset{CH_3}{\overset{CH_3}{\underset{|}{C}}}\dot{C}-\overset{Cl}{\underset{|}{C}}\cdots\overset{}{\underset{H}{}}H \quad (5)$$

$$R-\dot{C}H-CH_2Cl \xrightarrow[\Delta H = 0\,kcal/mol]{} R-\overset{Cl}{\underset{|}{C}}H-\dot{C}H_2 \quad (6)$$

If $\Delta H$ is the determining factor, 1,2-migration of H atoms should be seen, since in this case (eqn 7), $\Delta H$ is even more favourable.[24]

$$\underset{CH_3}{\overset{CH_3}{\underset{|}{C}}}\overset{H}{\underset{|}{C}}-\dot{C}\cdots\overset{}{\underset{H}{}}H \xrightarrow[\Delta H = -7\,kcal/mol]{} \underset{CH_3}{\overset{CH_3}{\underset{|}{C}}}\dot{C}-\overset{H}{\underset{|}{C}}\cdots\overset{}{\underset{H}{}}H \quad (7)$$

Entropy considerations also fail to account for the observed data, since the entropy of activation should not be greatly influenced by the nature of the various Y-groups. Furthermore, from a seric point of view, we might expect bulky groups to be disfavoured from participating in a bridged intermediate and this is the direct opposite of the behaviour noted above (Cl atom migration vs H atom migration).

When free-radical reactivity cannot be explained by thermodynamic and/or steric factors, polar effects are invoked. From a polar point of view the transition state could be represented as a resonance hybrid of the two canonical forms (eqn 8). (Note that where Y is elec-

$$\underset{H}{\overset{}{\underset{}{H}}}-\!\!-\!\!\overset{Y}{\overset{(-)}{C}}\cdots\overset{}{C}\cdots\overset{}{\underset{H}{}}H \longleftrightarrow \underset{H}{\overset{}{\underset{}{H}}}-\overset{\overset{Y}{(-)}}{C}\cdots\overset{}{C}\cdots\overset{}{\underset{H}{}}H \quad (8)$$

tropositive with respect to the rest of the molecule, the charge-separated canonical form will show a reversed

polarity). According to these polar considerations, migrations involving F atoms or OR groups should occur in preference to those involving Cl atom, but this is not the case.

Since the classical factors have failed to adequately explain such free-radical migrations, theoretical studies have been performed in order to find an analysis in terms of orbital effects.

The theoretical approach most frequently met in the literature[25,26] derives from the Hückel method and compares the energies of a triangular and a linear arrangement for $H_3^+$, $H_3^{\cdot}$ and $H_3^-$.[27,28] From the calculated energies the answer is clear in the case of $H_3^+$ and $H_3^-$, but for $H_3^{\cdot}$ the energy difference between the two structures is very small. Despite this small energy difference, the linear structure is generally assumed, since, in this form, the Singly Occupied Molecular Orbital (SOMO) is non-bonding whereas in the alternative triangular structure the SOMO is antibonding.[25,26] Moreover, *ab initio* calculations show that the transition state of the reaction $H^{\cdot} + H_2$ is more likely linear than triangular.[29] Nevertheless, it is questionable how realistic it is to transfer the results of the model $H_3$ to systems of greater complexity. For example, it has been necessary to invoke the participation of vacant d-orbitals to explain Cl atom migrations in free-radicals.[30]

Only 1,2-migration of vinyl,[31] $OH^{32}$ and $OH_2^{+33}$ have been studied for free-radical reactions by *ab initio* calculations, but from these few results it is still difficult to bring out the factors which control such reactions. In particular, they do not tell us why hydrogen atoms cannot easily achieve a 1,2-shift in regard of the 1,5- and 1,6-ones, or why fluorine atoms do not migrate, whereas chlorine atoms do.

### METHODOLOGY

A direct 1,2 $XH_n$ migration has to pass through a bridged structure. In order to remove the $\Delta H$ term which contributes to the relative ease of the free-radical reactions[22,23] we studied the simplest model as represented in eqn (9).
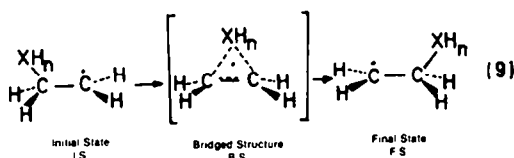
This bridged structure (B.S.) owing to the $C_s$ symmetry group could be either the transition state or an intermediate state of the reaction, but in any case its energy level is the least energy to be reached by the system in order to achieve the direct 1,2-migration. Therefore the purpose of this study was to establish whether or not, depending on $XH_n$, the bridged structure is a possible transition state. In order to obtain a fuller understanding of this phenomenon, we have chosen some simple groups from the first, second and third rows of the Periodic Table: H, $CH_3$, $NH_2$, OH, F, SH, Cl. In addition, the protonated forms $NH_3^+$ and $OH_2^+$ have been investigated so that our results can be compared with those of Golding and Radom.[33]

Also it was interesting to study a model corresponding to 1,5- and 1,6-migrations, where in contradiction to 1,2-shifts, migrations of H atoms have been noted,[10] but shifts of Cl atoms have not.[14,15] The 1,5- and 1,6-migrations pass through a linear transition state,[10] and in order

to simplify the calculations we investigated the following reactions (eqn 10) for $XH_n = H$ and Cl. In addition we have taken X as the middle of the C–C bond of the transition state ($D_{3h}$ symmetry group).
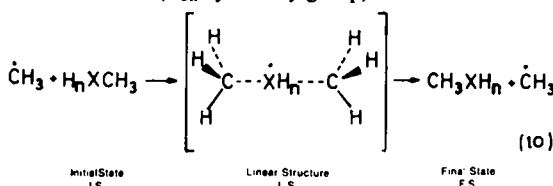
The *ab initio* calculations reported here used the Gaussian 70 program.[34] In this version of the program, free radicals can be treated either by the unrestricted Hartree–Fock method or by a restricted Hartree–Fock method similar to that of Binkley *et al.*[35] We employed the minimal STO-3G basis function[36] with the RHF method for the calculation of molecular equilibrium geometries.

In order to show the consistency between the RHF method and the UHF one, we report for some cases the STO-3G UHF energies calculated from the RHF optimized geometries.

### RESULTS

*Reaction I: 1,2-migration*

(a) *Initial state: β-substituted ethyl free-radicals.* In our study we have met 4 kinds of structure A, B, C, D (see Fig. 1) depending on the number of H atoms branched on X.

The equilibrium geometry of the ethyl free radical ($XH_n = H$) has been established by Pople *et al.*[38] Its most stable conformation (belonging to the $C_s$ symmetry group) is such that one of the $C_2$–H bonds eclipses the 2p singly occupied orbital of $C_1$ with a slightly out-of-the-plane bending of the $C_1$–H bonds towards X (here $XH_n = H$).[37]

We assumed the same conformation regardless of the identity of $XH_n$. When X bears 1 to 3H atoms we choose the conformations around the $C_2$–X bond indicated in Fig. 1. All parameters were optimized (see Table 1) except for $r(C_1$–H), $r(C_2$–H) and $\theta$, which were assumed to be the same as in the ethyl free-radical.[38] The $r(X$–H) values are those calculated by Pople.[39] The dihedral angle $H_1zH_2$ was kept constant at 120°.

The detailed geometrical structures[40] for the chosen conformation of the β-substituted ethyl free-radicals and their *ab initio* energies are given in Table 1. Except for
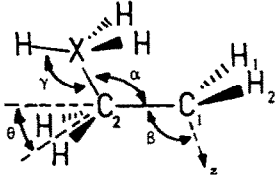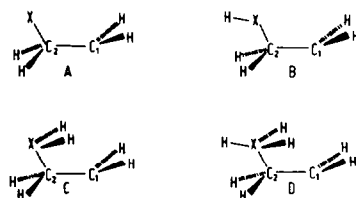
Fig. 1. The chosen configurations for the β $XH_n$ substituted ethyl free-radicals.

Fig. 2.

Table 1. Theoretical STO-3G RHF geometry and RHF/UHF energies for the $\beta$-substituted ethyl free-radicals[a,b]



| $XH_n$ [c) ] | $r_{(C_1C_2)}$ | $r_{(C_2X)}$ | $r_{(XH)}$ [d) ] | $\alpha$ | $\beta$ [e) ] | $\gamma$ | ENERGIES STO-3G RHF | STO-3G UHF |
|---|---|---|---|---|---|---|---|---|
| H [f) ] | 1.516 | 1.090 | | 111.2 | 101.5 | | -77.65916 | -77.66300 |
| $CH_3$ | 1.532 | 1.397 | 1.090 | 110.4 | 98.6 | 109.5 | -116.23286 | -116.24204 |
| $NH_2$ | 1.536 | 1.504 | 1.033 | 112.4 | 99.4 | 109.9 | -131.96238 | -131.97015 |
| $NH_3^+$ | 1.524 | 1.555 | 1.044 | 112.2 | 94.7 | 111.0 | -132.39598 | -132.40321 |
| OH | 1.522 | 1.452 | 0.990 | 107.8 | 98.3 | 103.7 | -151.48041 | -151.48768 |
| $OH_2^+$ | 1.509 | 1.512 | 0.990 | 110.9 | 90.8 | 112.5 | -151.86725 | -151.87468 |
| F | 1.528 | 1.397 | | 110.8 | 97.4 | | -175.10156 | -175.10882 |
| SH | 1.529 | 1.815 | 1.330 | 110.0 | 98.1 | 95.3 | -470.82042 | -470.83284 |
| Cl | 1.527 | 1.814 | | 112.1 | 97.0 | | -531.65388 | -531.66382 |

a) Bond lengths in angstroms, angles in degrees, energies in hartrees.

b) The following data, taken from ref. 38 for X = H, are assumed to be the same regardless of the identity of XHn : $r_{(C_1H)}$ = 1.083 Å, $r_{(C_2H)}$ = 1.087 Å, $\theta$ = 52.6°, $HC_2H$ = 108.3°, $\omega(C_2zH_1)$ = $\omega(C_2zH_2)$ = 120°.

c) Dihedral angle $\omega(HXC_1C_2)$ : when n = 1, $\omega$ = 180° ; when n = 2, $\omega$ = +60° and -60° ; when n = 3, $\omega$=180°, 60° and -60°.

d) Taken from the ref. 39 for the corresponding $XH_{n+1}$ molecule.

e) $\beta$ = $zC_1C_2$ = $zC_1H_1$ = $zC_1H_2$.

f) All the data for X = H are taken from ref. 35 and 38.

the protonated forms, in regard of the parent free-radical ($XH_n$ = H), there is a small lengthening of the $C_1-C_2$ bond of about 0.01 Å and a slight flattening of the radical centre (from 101.5° to 97 ± 1°). Moreover, we did not find any significant influence of X on $\alpha$ (all values are 111 ± 1°) which is not in agreement with the interpretations of the ESR results except when X = Cl and SH.[41] The protonation of OH and $NH_2$ leads to small shortening of the $C_1-C_2$ bond and, at the same time, a flattening of the radical centre.

(b) *$XH_n$ bridged ethyl free-radical.* Depending on the value of n in $XH_n$, the bridged structures are optimized in the configurations indicated in Fig. 3. All parameters, except the C-H bond length ( = 1.08 Å) and the dihedral angle (HCvH) ( = 120°) where Cv is an axis passing through C parallel to the z axis, were varied. The most important parameters which influence the energy are the distance (D) between X and the middle of the C-C bond and the r(C-C) bond length.

When only D is optimized keeping the r(C-C) bond equal to $r(C_1-C_2)$ bond length of the corresponding $\beta$-substituted ethyl free-radical, we find three kinds of situation: (1) For $XH_n$ = H, F, $CH_3$, OH, $NH_2$ this bridged structure has a very high energy relative to the initial structure (the energy difference being between 80 and 130 kcal/mol). (2) For $XH_n$ = Cl, $OH_2^+$, $NH_3^+$ the energy difference between BS and IS is around

50 kcal/mol. (3) In the case of $XH_n$ = SH it is not possible to locate an energy minimum before complete dissociation.

In order to determine the minimum energies of the bridged structures *in this given symmetry*, we optimized D and r(C-C) alternatively. When D increases, r(C-C) decreases but for $XH_n$ belonging to group 1 of the above classification, we did not discover an energy minimum before the dissociation state. More precisely for r(C-
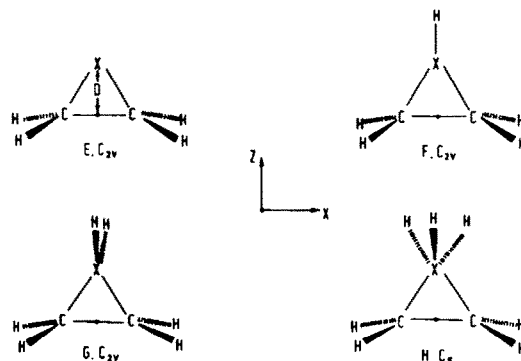


Fig. 3. The chosen configurations and their symmetry group for the different $XH_n$ bridged ethyl free-radicals. In all cases zy is a mirror plane (the middle of the C-C bond is the point of origin).

C) > 1.35 Å, we found an energy valley roughly parallel to the C–C axis. In other words in this region of the potential surface, the variation of D is not important, and the energy decreases very slowly. When the C–C bond length becomes close to that calculated for a C=C bond (1.306 Å[38]) $XH_n$ groups depart very rapidly with a rapid decrease of the energy without passing through a minimum value before the dissociation.

On the other hand, for the bridged structures of group 2 we can locate a real minimum with the parameters quoted in Fig. 4 (only the C–H and X–H bond lengths and the (HCvH) dihedral angle have not been optimized). Their corresponding energies and *the energy difference* $\Delta E$ between the bridged structures and the initial ones ($\Delta E = E_{BS} - E_{IS}$) are given in Table 2. The main features of the optimum structures are (i) a moving of the $XH_n$ groups away from the C–C bond, corresponding to a lengthening of 40% to 50% of the $\beta$-ethyl free-radical C–X bond; (ii) a shortening of the C–C bond, and (iii) an "in the plane" bending of the C–H bonds. Finally, when

$XH_n = S–H$, whatever the C–C bond length, the minimum energy point is the dissociation state.

Due to the absence of an optimum bridged structure for certain $XH_n$ groups, and in order to understand the factors which underlie such behaviour, we selected a C–C bond length of 1.5 Å and an $\alpha$ value of 10°. Thus we can locate for any $XH_n$ groups but S–H (*vide supra*) a minimum energy in regard to the D parameter. The results are collected in Table 3. In relation to the $\Delta E$
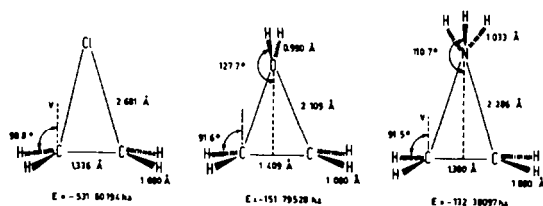


Fig. 4. Theoretical (STO-3G RHF) geometries and energies for $XH_n$ bridged ethyl free-radicals.

Table 2. Theoretical (STO-3G) energies for the $XH_n$ bridged ethyl free-radicals and the STO-3G energy differences between the bridged and open structures

| $XH_n$ | STO-3G RHF [a] | STO-3G UHF [a] | $\Delta E$ [b] STO-3G RHF | $\Delta E$ [b] STO-3G UHF |
|---|---|---|---|---|
| Cl | -531.60194 | -531.61080 | 33 | 33 |
| $OH_2^+$ | -151.79528 | -151.79823 | 45 | 48 |
| $NH_3^+$ | -132.30097 | -132.30286 | 60 | 63 |

a) *ab initio* energies in hartrees.  b) $\Delta E$ values in $kcal.mol^{-1}$.

Table 3. Optimization of D in the $XH_n$ bridged ethyl free-radicals[a]
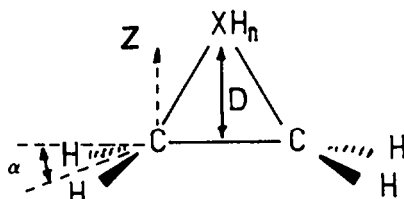


| $XH_n$ [b] | $D_{eq}$ | $r_{(CX)}/r^o_{(CX)}$ [g] | Energy STO-3G RHF | $\Delta E = E_{BS} - E_{IS}$ in kcal/mol |
|---|---|---|---|---|
| H | 1.038 | 1.17 | -77.52042 | 88 |
| $CH_3$ [c] | 1.658 | 1.17 | -116.06450 | 106 |
| $NH_2$ [d] | 1.734 | 1.26 | -131.76956 | 121 |
| $NH_3^+$ [e] | 2.220 | 1.51 | -132.27816 | 74 |
| OH | 1.523 | 1.17 | -151.27916 | 126 |
| $OH_2^+$ [f] | 2.003 | 1.41 | -151.77980 | 55 |
| F | 1.611 | 1.27 | -174.93145 | 107 |
| SH | 2.600 | 1.49 | -470.74776 | 46 |
| Cl | 2.396 | 1.39 | -531.57014 | 53 |

a) $r_{(CC)} = 1.500$ Å, $\alpha = 10°$, (HzH) = 120°, $r_{(CH)} = 1.08$ Å ; energies in hartree.

b) Values for $r_{(XH)}$ are taken from ref. 39 and conformations are those of figure III. The following HXH angle values have been optimized : for $CH_3$ HCH = 112.6°, for $NH_2$ NHN = 104.2°, for $NH_3^+$ NHN = 110.7°, for $OH_2^+$ HOH = 113.9°.

g) $r^o_{(CX)}$ value obtained for the $XH_n$ ethyl free-radical (see table I).

values we find again the correlation noticed before. Moreover, it appears that the highest $\Delta E$ values correspond to the smallest lengthening of the C–X bond relative to the open structure (20–30%) and the lowest $\Delta E$ values to a more pronounced lengthening (up to 50%).

*Reaction II: Model for 1,5- and 1,6-migrations*

The STO-3G geometries and energies of the species of the initial state are summarized in Fig. 5. CH$_4$ and CH$_3$ values are found in the literature.[38] Data for CH$_3$Cl have been completely optimized in a D$_{3h}$ symmetry group, with the STO-3G RHF computation. The energy and the geometry values found here (see Table 4) are close to those determined by STO-3G UHF.[42] When X = Cl we only optimized the C–C length (other values are those obtained with X = H).

### DISCUSSION

*General remarks on the calculated $\Delta E$*

As a preliminary observation, we notice, for each XH$_n$ group a relationship between the calculated 1,2-migration energy $\Delta E$ and the place of the X atoms in the periodic classification. When X belongs to the first (H) and second row (C, N, O, F), it is not possible to discover a bridged structure for which the energy level is low enough to make the 1,2-migration feasible: the activation energy for the direct 1,2-migration of these XH$_n$ groups is too high compared to the other possible reactions such as coupling, transfer and so on. The 2 step elimination-addition

mechanism should not be much more favourable because the first step ($\beta$-elimination) is very endothermic (see Table 5), with, consequently, a still larger activation energy.[43] For the third row XH$_n$ groups, the calculations agree with the analysis of the experimental data: a 2-step mechanism for sulphur, but a direct 1,2-migration of Cl atom should be more favourable than the endothermic $\beta$-elimination. It is here very important to point out that the vacant d-orbitals are not included in our *ab initio* calculation, and consequently cannot be responsible for the special ability of the 3rd row XH$_n$ groups to achieve the 1,2-migration. As noticed before[33] the protonation of the OH group makes its direct 1,2-shift feasible; although being less important, this effect also should facilitate the direct 1,2-migration of NH$_2$.

In agreement with experiment,[10,14] our calculations show that if 1,2-shifts of H atoms are unexpected, 1,5- and 1,6-shifts should occur; in contrast, the reverse situation should occur for Cl atoms. Moreover, a preliminary calculation indicates, in agreement with experimental data,[14,15,45] that if an alkyl radical has a choice between intra- or inter-molecular transfer of either H of Cl atoms branched on the same carbon (eqn 11), transfer of the H atom is preferred.



$$(11)$$
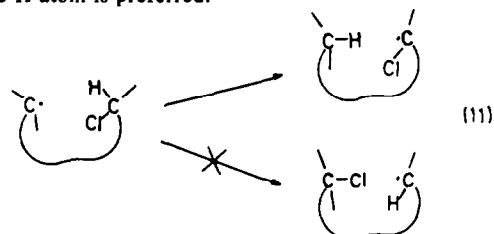
Most reactions can be analysed as being under charge control and/or orbital control.[21,46] This can indeed explain the differences in activation energy, i.e. the relative reactivity. As free-radicals are normally neutral species, the charge control cancels out, and their reactivity should be chiefly under orbital control. Among the MO's, the frontier orbital is thought to play the most important role. In free-radicals the frontier orbital is the singly occupied MO (SOMO), and, therefore, we have to investigate the variation of its energy level along the pathway.
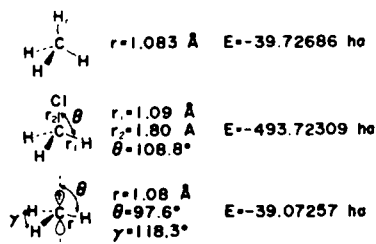


Fig. 5. Geometries and energies of the species involved in the linear X transfer. (Values for CH$_4$ are taken from Ref. 38; the STO-3G RHF energy of CH$_3$' has been obtained with parameters taken from Ref. 39).

Table 4. Theoretical (STO-3G RHF) geometry and energy data for the linear transition state optimized in a D$_{3h}$ symmetry group[a]



| X | r(CX) | r(CH) | r(CX)/r$^0$(CX) | $\delta$ | energy (ha) | $\Delta E$ (kcal/mol) |
|---|---|---|---|---|---|---|
| H | 1.295 | 1.083 | 1.19 | 107.1 | −78.74917 | 32 |
| Cl[b] | 2.021 | 1.083 | 1.12 | 107.1 | −532.71990 | 48 |

a) bond lengths in angstroms, angles in degrees
b) values of r(CH) and $\delta$ are those obtained for X = H

## 1,2-Free-radical migrations

All the data concerning the 1,2-migrations are collected in Table 6. Note that these data correspond to the results given in Table 3, for the bridged structure with r(C–C) = 1.5 Å.

(a) *XH$_n$ β-ethyl free-radicals.* In the β-substituted radicals, except for the protonated ones, the SOMO energy levels are roughly equal: actually, the *ab initio* calculation shows that the SOMO's are mainly $C_{2p}$ AO's (Fig. 6). This indicates a weak interaction between this AO and the rest of the molecule. Protonation of XH$_n$ lowers all the MO's of the molecule and among them the SOMO is lowered by more than 0.2 Hartree.

(b) *Bridged structures (BS).* The SOMO energy levels are roughly equal in the XH$_n$ β-substituted free-radicals

(except for the protonated ones) but they strongly depend on the nature of XH$_n$ in the bridged structures (see Table 6). Moreover, we notice a lowering of the SOMO energy level in the bridged structure relative to the corresponding open structure ($\Delta\epsilon_{SOMO} = \epsilon_{SOMO}^{BS} - \epsilon_{SOMO}^{IS} < 0$) only in the case of Cl, OH$_2^+$ and NH$_3^+$, the



Fig. 6.

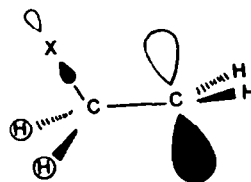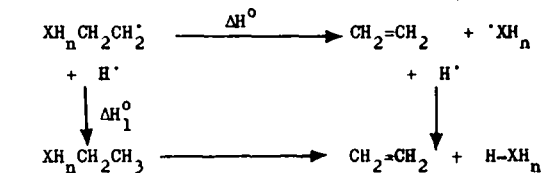Table 5. Activation energies (E$_a$) and enthalpies ($\Delta H^0$) for the β-elimination of XH$_n$

$$XH_nCH_2CH_2^{\cdot} \xrightarrow{\Delta H^0} CH_2{=}CH_2 + {}^{\cdot}XH_n$$

$$+ \; H^{\cdot} \qquad\qquad\qquad + \; H^{\cdot}$$

$$\downarrow \Delta H_1^0 \qquad\qquad\qquad\qquad \downarrow$$

$$XH_nCH_2CH_3 \longrightarrow CH_2{=}CH_2 + H{-}XH_n$$

| XH$_n$ | $\Delta H^{0\,a)}$ | E$_a$$^{b)}$ |
|---|---|---|
| H | 38.7 | 40.9 |
| CH$_3$ | 25.2 | 31.4 |
| NH$_2$ | 19.4 | |
| OH | 31.9 | |
| F | 46.3 | |
| SH | 11.4 | |
| Cl | 22.0 | 23.9 |
| Br | 7.9 | |

a) $\Delta H^0 = \Delta H_1^0 + \Delta H_f^0(CH_2{=}CH_2) - \Delta H_f^0(XCH_2CH_3) + \Delta H_f^0(H) + \Delta H_f^0(XH_n)$
where $\Delta H_1^0 = 98$ kcal.mol$^{-1}$ whatever XH$_n$ is, and $\Delta H_f^0$ are taken in ref. 44a.
b) in kcal.mol$^{-1}$, from ref 44b.

Table 6. Theoretical data for the 1,2-free-radical migrations

| XH$_n$ | D$_{eq}$$^{a)}$ | r(CX)/r$^0$(CX)$^{a)}$ | $\Delta E$$^{a)}$ | $\epsilon_{SOMO}^{IS}$$^{b)}$ | $\epsilon_{SOMO}^{BS}$$^{c)}$ | $\Delta\epsilon$$^{d)}$ | $\langle np_z^X|2p_z^C\rangle$$^{e)}$ | $\langle np_x^X|2p_z^C\rangle$$^{e)}$ | q$^{XH_n}$$^{f)}$ |
|---|---|---|---|---|---|---|---|---|---|
| H | 1.038 | 1.17 | 90 | −0.002 | +0.059 | +0.061 | | | +0.15 |
| CH$_3$ | 1.658 | 1.17 | 106 | −0.001 | +0.102 | +0.103 | 0.198 | 0.131 | +0.11 |
| NH$_2$ | 1.734 | 1.26 | 121 | −0.015 | +0.172 | +0.187 | 0.165 | 0.099 | 0 |
| NH$_3^+$ | 2.220 | 1.51 | 74 | −0.235 | −0.315 | −0.080 | 0.093 | 0.039 | +0.30 |
| OH | 1.523 | 1.17 | 126 | −0.019 | +0.208 | +0.227 | 0.160 | 0.114 | −0.11 |
| OH$_2^+$ | 2.003 | 1.41 | 55 | −0.268 | −0.330 | −0.062 | 0.093 | 0.045 | +0.22 |
| F | 1.611 | 1.27 | 107 | −0.029 | +0.135 | +0.164 | 0.123 | 0.079 | 0 |
| Cl | 2.396 | 1.39 | 53 | −0.042 | −0.068 | −0.026 | 0.106 | 0.040 | −0.36 |

a) See Table 3.  b) Energetic value of the SOMO in the XH$_n$ ethyl free-radical.
c) Energetic value of the SOMO in the XH$_n$ bridged ethyl free-radical.  d) $\Delta\epsilon = \epsilon_{SOMO}^{BS} - \epsilon_{SOMO}^{IS}$.
e) Overlap between the quoted atomic orbitals.  f) Total charge on the XH$_n$ group.

species for which the 1,2-shift is found feasible. For all other $XH_n$ groups the SOMO in the bridged structure is higher in energy than in the corresponding open one ($\Delta\epsilon_{SOMO} > 0$). This analysis gives rise to a nearly linear relationship between $\Delta E$ and $\Delta\epsilon_{SOMO}$ as illustrated in Fig. 7. Since, furthermore, the $\epsilon_{SOMO}$'s in the open structures have roughly the same value regardless of the identity of $XH_n$, the $\Delta\epsilon_{SOMO}$ values are chiefly dependent on the $\epsilon_{SOMO}$ values in the bridged structures.

It is therefore important to understand, first of all, why the SOMO energies are strongly dependent on the nature of the $XH_n$ group in the bridged structure whilst weakly so in the open one and then how $\Delta E$ is related to $\Delta\epsilon_{SOMO}$.

It can be easily shown that the SOMO energy decreases for all $XH_n$ groups (except $XH_n = H^{47}$) as the $XH_n$ group is moved away from the equilibrium distance, $D_{eq}$, quoted in Table 6. However, concurrently, the total energy ($E_t$) of the bridged structure increases as illustrated in Fig. 8 for $XH_n = F$. It means that when D changes there is no relationship between $E_t$ and $\epsilon_{SOMO}$. To understand this effect other MO's should be taken into account.
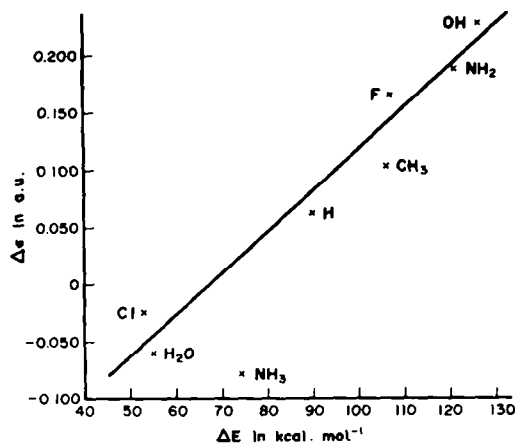
The MO's of the bridged structure can be schematically built by mixing the $\pi$ and $\pi^*$ group MO's (GMO) of the $C_2H_4$ group with the GMO's of the $XH_n$ group. Three situations are met as illustrated on Chart 1. When $XH_n = H$, we have the three MO's quoted on Chart 1(a), the SOMO being a $b_2$ type orbital. When $XH_n \neq H$, the $p_z$ and $p_x$ GMO's of the $XH_n$ group can be mixed with the $\pi$ and $\pi^*$ GMO's giving 4 MO's. The sequence of the MO's and, consequently the type of the SOMO, are nevertheless dependent on the nature of $XH_n$: when $XH_n = CH_3$, $NH_2$, OH or F, the SOMO is a $b_2$ type orbital (Chart 1(b)) whereas when $XH_n = Cl$, $NH_3^+$ or $OH_2^+$ the SOMO is a a $a_1$ type MO (Chart 1(c)).[48]

When D increases, the overlap decreases and, due to the out-of-phase overlap between $XH_n$ and $C_2H_4$ GMO's, the SOMO energy decreases, but concurrently the Highest Doubly Occupied MO (HOMO), an in-phase combination between the $XH_n$ and $C_2H_4$ appropriate GMO's (see Chart 1), is destabilized (see Fig. 8). If we plot the sum $\epsilon_{SOMO} + 2\epsilon_{HOMO}$ (where $\epsilon$ is the SCF energy of the orbital considered) vs D, we find, for each $XH_n$ an optimum value (see Fig. 9 and Table 7) which matches the value obtained from the equilibrium geometry. Thus it seems, according to these observations, that the total energy change is mainly determined by this two orbital energy change. This type of situation is close to the simplified model of the so-called "2-orbital 3-electron interaction" leading to a "subjacent control" described by Hudson,[49] Muller,[50] Salem,[51] and Bernardi et al.[52,53] According to Bernardi et al.[52] the most favourable situation for a "2-orbital 3-electron interaction" occurs at lower overlap when the energy gap between the two orbitals decreases. If we compare the situations when $XH_n = F$ or Cl, the energy gap at $D_{eq}$ between $\epsilon_{SOMO}$ and $\epsilon_{HOMO}$ is more important for F than for Cl (respectively 0.5345 ha and 0.3032 ha), this being chiefly due to the electronegative character of F. Consequently the balance between the stabilisation of the SOMO and the destabilisation of the HOMO occurs at more lengthening for Cl than for F (values of $\langle np_z^{XH_n}/2p_z^C \rangle$ are respectively 0.123 and 0.106, see Table 6).



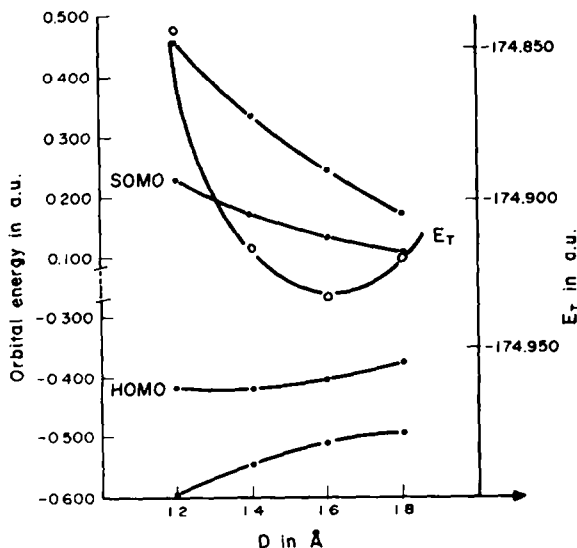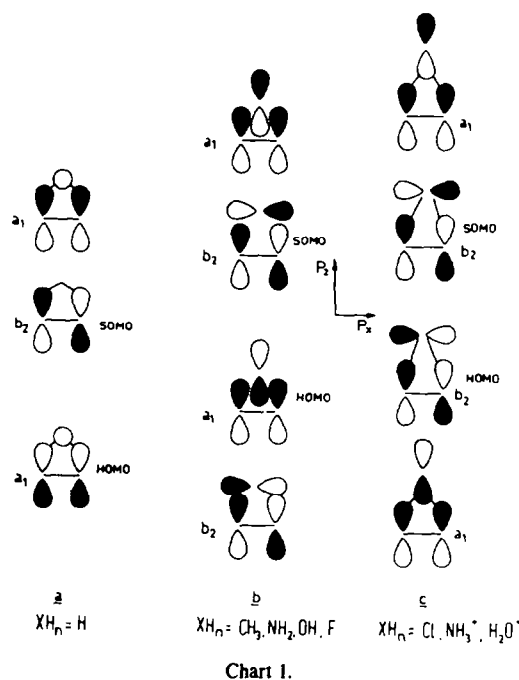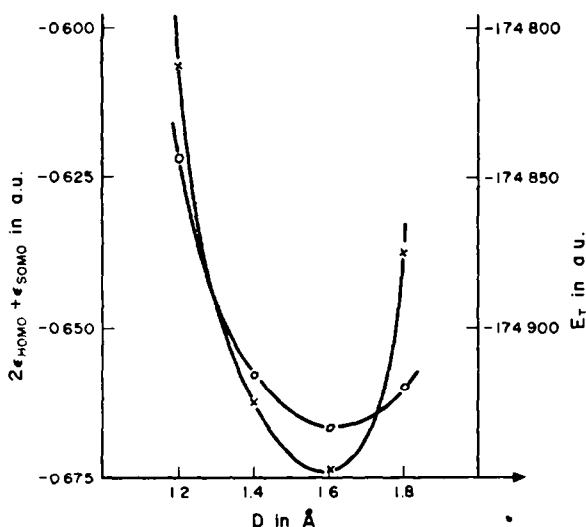Fig. 7. Relationship between $\Delta E = E_{BS} - E_{IS}$ and $\Delta\epsilon = \epsilon_{SOMO}^{BS} - \epsilon_{SOMO}^{IS}$



Fig. 8. Variation vs D of the MO's energy (.) and of the total energy $E_T$ (O) of the F bridged ethyl free radical.



Chart 1.

Fig. 9. Variation vs D of the total energy $E_T$ (●) and of the sum $2\epsilon_{HOMO} + \epsilon_{SOMO}$ (×) for the F bridged ethyl free radical.

Table 7. $D_{eq}$ vs energy total $E_T$ and the frontier orbital energy sum $2\epsilon_{HOMO} + \epsilon_{SOMO}$

| $XH_n$ | $D_{eq}$ versus $E_T$ | $D_{eq}$ versus $2\epsilon_{HOMO} + \epsilon_{SOMO}$ |
|---|---|---|
| H | 1.038 | – |
| $CH_3$ | 1.658 | – |
| $NH_2$ | 1.734 | 1.6 |
| $^+NH_3$ | 2.220 | 2.1 |
| OH | 1.523 | 1.4 |
| $^+OH_2$ | 2.003 | 1.9 |
| F | 1.611 | 1.6 |
| Cl | 2.396 | 2.4 |

Although an F atom is clearly acting as a strong withdrawing group, the total charge on F is nevertheless zero (see Table 6). In fact, F is also acting as a donor through the overlap between $2p_x^F$ and $C_2H_4\pi^*$ leading to the bonding and antibonding $b_2$ type MO's (Chart 1(b)). Thus, in addition to the 2 orbital-3 electron interaction, this stabilising 2 orbital-2 electron interaction tends to keep the F atom close to the C–C bond in the bridged structure. This interaction exists also for Cl but is smaller (due to a small overlap value, the charge transfer through the $3p_x^{Cl}/2p_z^C$ overlap is only 0.04 and the total charge on Cl is $-0.36$). Furthermore this interaction is found less sensitive to D variation around the equilibrium. This analysis in terms of subjacent control is readily generalized to all the second row groups.
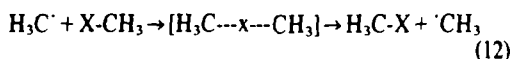
As noted earlier, the protonation lowers all the MO's, this effect being, however, more pronounced on the doubly occupied MO's than on the SOMO's. Due to this more important energy gap, the balance between the stabilisation of the SOMO and the destabilisation of the HOMO is reached at a more important lengthening for the protonated groups than for the unprotonated ones. Furthermore the back-donation effect through the $2p_x^{XH_n}/C_2H_4\pi^*$ interaction is no longer possible.

According to this study, the $\Delta E$-$\Delta\epsilon_{SOMO}$ (or $\Delta E$-$\epsilon_{SOMO}$) relationship, can be used as a criterion for predicting feasibility of 1,2-free-radical migrations, the relation being well understood if one takes into account the subjacent doubly occupied MO control. Our results are in agreement with the work of Salem[54] and Yamaguchi and Fueno,[55] who show that a triangular approach, for a free-radical reaction, is spin-forbidden and that, nevertheless, when the overlap is weak enough the reaction becomes feasible as in the case of Cl, $H_2O^+$ and $\overset{+}{N}H_3$.

### 1,5- and 1,6-Free-radical migrations

If the relationship $\Delta E$-$\Delta\epsilon$ proves to have a general validity it will be useful to apply it to other types of reactions. For example one of the most important reactions in the field of the free radical chemistry is the H or Cl bimolecular atom transfer.

This reaction can be taken, as justified above, as a model for the 1,5 (or 1,6)-intramolecular atom transfer.

$$H_3C^\cdot + X\text{-}CH_3 \rightarrow [H_3C\text{---}x\text{---}CH_3] \rightarrow H_3C\text{-}X + {}^\cdot CH_3$$
$$(12)$$

For such a reaction, $\Delta H = 0$ and the transition state is assumed to be symmetrical.[42] Furthermore, since the initial free-radical is the same, the $\Delta E$-$\Delta\epsilon_{SOMO}$ relationship is reduced to the $\Delta E$-$\epsilon_{SOMO}$ relationship.

It is therefore relevant to compare the SOMO energies in the transition state when X = H and X = Cl. For this purpose MO's of the transition state may be built using the following GMO's: (a) the $\sigma_{C...C}$ and $\sigma^*_{C...C}$ for the $CH_3...CH_3$ group. These two GMO's are surely quasi degenerate because the C–C bond length is presumably much higher than 2.2 Å, i.e. longer than twice a normal C–H bond length. (b) the X GMO's: 1s for H and 3s and 3p AO's for Cl.

Using the classical rules for orbital mixing, we obtain Chart 2.

From this it is obvious that the SOMO energy for X = H is roughly the same as the $\sigma^*_{C-C}$ GMO energy. Furthermore for X = Cl, the two out-of-phase MO's, the lowest one being the SOMO, have to be higher than the SOMO of the X = H transition state. As a 3s AO is lower than a 3p one, the MO sequence should be as indicated in Chart 2, at least if the overlap integrals are comparable.

Therefore, if the relationship $\Delta E$-$\Delta\epsilon$ is operative

$$\epsilon_{SOMO}^{Cl} > \epsilon_{SOMO}^H \Rightarrow E_a^{Cl} > E_a^H \quad (E_a = \text{activation energy})$$

that should indicate that a linear Cl transfer is more difficult than that of a H atom.



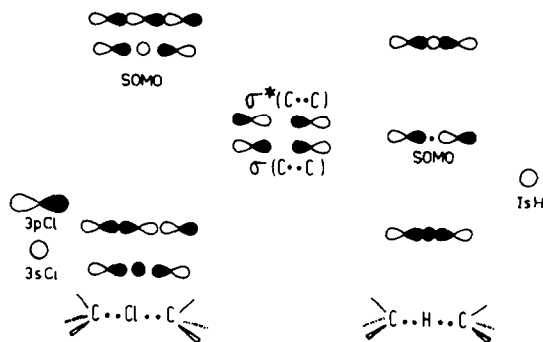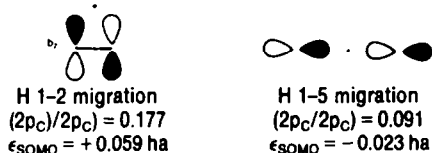Chart 2.

The *ab initio* calculations performed for the transition state with X = H and X = Cl (see Table 4) are in complete agreement with these predictions: $\epsilon^{Cl}_{SOMO} > \epsilon^{H}_{SOMO}$ and $\Delta E^{Cl} > \Delta E^{H}$.

The assumption that the $\sigma_{C-C}$ and $\sigma^{*}_{C-C}$ GMO's were quasi-degenerate can be checked by *ab initio* calculation. The X = H SOMO in the transition state is actually the $\sigma^{*}_{C-C}$ GMO and its energy level is roughly the same as that of the $CH_3^{\cdot}$ SOMO. Therefore it shows that, at the transition state calculated C...C length, the out-of-phase and in-phase combinations have comparable energies.
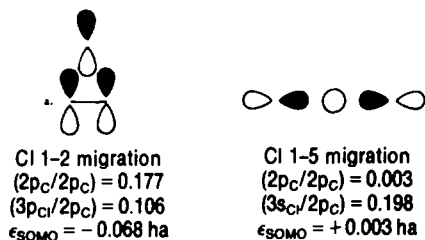
*1,2- or 1,5-Migration?*

The reverse order of the SOMO energy levels found when comparing 1,2- and 1,5-free radical migrations can be easily understood in terms of the structure of these SOMO's.

When X = H the $\langle 2p^C/2p^C \rangle$ destabilizing out-of-phase overlap in the SOMO decreases strongly from the 1,2- to the 1,5-migration, and consequently its energy level decreases too.



H 1-2 migration
$(2p_C/2p_C) = 0.177$
$\epsilon_{SOMO} = +0.059$ ha

H 1-5 migration
$(2p_C/2p_C) = 0.091$
$\epsilon_{SOMO} = -0.023$ ha

On the other hand, when X = Cl the $\langle 2p^C/2p^C \rangle$ stabilizing in-phase overlap for the 1,2-migration vanishes for 1,5-migration and furthermore the destabilizing out-of-phase overlap between the $2p^{C'}$s and one of the Cl GMO's increases.



Cl 1-2 migration
$(2p_C/2p_C) = 0.177$
$(3p_{Cl}/2p_C) = 0.106$
$\epsilon_{SOMO} = -0.068$ ha

Cl 1-5 migration
$(2p_C/2p_C) = 0.003$
$(3s_{Cl}/2p_C) = 0.198$
$\epsilon_{SOMO} = +0.003$ ha

This study reveals that the H migration requires a linear transition state in order to minimize a destabilizing overlap in the SOMO. This effect explains the failure of 1,2-H migration but also the relatively high activation energies observed for 1,3- and 1,4-H migration,[6] since ring strain precludes a linear transition state in the latter instances. 1,n H migration for n > 5 is possible from this point of view, but the activation entropy becomes more and more unfavourable.[10] It also becomes obvious that a bimolecular H transfer has to pass through a linear transition state.

By contrast, for Cl migrations, the overlap factor is less favorable in the linear transition state than in the triangular one. This explains the failure of the 1,5-migration; considering the series of possible 1,n (n = 5 to 2) migrations, the Cl atom migration should become more favoured as n decreases. We then can question why 1,3- and 1,4-Cl migrations have never been observed.

## CONCLUSION

1,2-Migrations are often observed in cations but rarely in free-radicals. In fact, the extra electron plays a determining role since the approximate energy, $\Delta E$, be-

tween the open structure and the bridged one is related to the variation of energy, $\Delta \epsilon$, of the singly occupied molecular orbital. The known examples of 1,2-phenyl or vinyl migrations *via* cyclisation-ring opening mechanism are well understood by the fact that the SOMO is not destabilized in the cyclic intermediate: the single electron is either well delocalised on the phenyl ring or, for vinyl migrations, at the same or nearly the same energy level as in the initial state.

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[48]The reverse sequence of MO's between (b) and (c) on Chart 1 is in fact related to the equilibrium distance, $D_{eq}$ (Table 6), between $XH_n$ and the middle of the C–C bond. When D increases, the energy of the two bonding MO's increases and the energy of the two antibonding MO's decreases; at long distance, for lengthening $r(C - X)/r(C_0 - X)$ higher than 40%, the MO sequence for F, $CH_3$, $NH_2$ or OH is found to be the same as for Cl (Chart 1(c)).

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