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# Dissociative Electron Transfer. Ab Initio Study of the Carbon-Halogen Bond Reductive Cleavage in Methyl and Perfluoromethyl Halides. Role of the Solvent

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**Abstract:** MP3 level calculations using pseudo-potentials for the halogens and semidiffuse functions for the heavy atoms indicate that in the series $CH_3X$ (X = F, Cl, Br, I), the reaction $CH_3X + e^- \rightarrow CH_3^{\bullet} + X^-$ is a concerted electron transfer-bond breaking process in accord with previous experimental findings (gas phase, solid matrixes, electrochemistry in polar solvents). The activation barriers and transition-state geometries thus found are in good agreement with the predictions of a recently developed empirical Morse curve based model leading to a quadratic activation-driving force relationship and an intrinsic barrier equal to one-fourth of the bond dissociation energy. The empirical model thus validated is of general applicability to the kinetic reactivity of the vast class of organic and inorganic molecules undergoing dissociative electron transfer upon reaction with homogeneous and heterogeneous outer-sphere electron donors. The comparison of the energy profiles obtained by means of full basis set calculations for $CH_3Cl$ and $CF_3Cl$ reveals the existence of an energy minimum in the anionic profile at large C–Cl distances with a much larger stabilization energy for $CF_3Cl^{\bullet -}$. Analysis of charge densities maps indicates that the bond between carbon and chlorine is of the electrostatic type and that the large stabilization in $CF_3Cl^{\bullet -}$ is due to strong polarization of $CF_3^{\bullet}$. Simulation of the effect of polar solvents shows the disappearance of the $CF_3Cl^{\bullet -}$ minimum. The reductive cleavage thus becomes a concerted electron transfer-bond breaking process in accord with previous conclusions derived from the electrochemistry of perfluoroalkyl halides in polar solvents. This result emphasizes and rationalizes the role of polar solvents among the parameter that govern the occurrence of concerted versus stepwise reductive cleavage mechanisms.

Alkyl and aryl halides constitute the most widely investigated ensemble among organic molecules containing a nucleofugal group. Their reactions with homogeneous and heterogeneous (electrodes) electron donors or with nucleophiles involve the breaking of the carbon–halogen bond. In the case where the homogeneous and heterogeneous electron donor, designated by $e^-$, is of the outer-sphere type,[2] the global reaction can be formulated as:

$$RX + e^- \rightarrow R^{\bullet} + X^- \quad (1)$$

An important mechanistic and practical issue[3] is whether the reaction is concerted (i.e., (1) is an elementary step) or stepwise, in which case, an anion radical, which will eventually dissociate, is formed as a first intermediate:

$$RX + e^- \rightleftarrows RX^{\bullet -} \quad (2)$$

$$RX^{\bullet -} \rightarrow R^{\bullet}X^- \quad (3)$$

In all cases investigated so far, aryl halides undergo a stepwise reaction in the gas phase,[4] in apolar or weakly polar matrixes,[5] and in polar solvents (direct or indirect electrochemistry).[6]

In the gas phase, alkali-metal reduction of simple aliphatic halides does not give rise to the anion radical, but yields directly the alkyl radical and the halide ion.[7,8] Dissociative electron transfer is also observed upon γ-ray irradiation in apolar or weakly solid polar matrixes.[5] The same is also true for the electrochemical reduction in polar solvents as deduced from the observed low values of the symmetry factor.[6d,9]

In the case of stepwise reactions, as with aryl halides, the electron transfer step is of the outer-sphere type, and therefore its dynamics can be approximately described by semiclassical models such as Marcus-Hush's.[10] The follow-up bond breaking step has been qualitatively described as an intramolecular concerted electron transfer–bond breaking process.[6d]

The Marcus-Hush model is not directly applicable to concerted electron transfer–bond breaking reactions since it is an inner-sphere process from the point of view of the acceptor even though an

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(2) (a) The outer-sphere/inner-sphere terminology was originally coined for electron transfer reactions involving coordination complexes.[2b,c] We use here the following generalization.[2d] In outer-sphere electron transfer reactions, either no bond is cleaved or formed within the time scale of the experiment or, in the opposite case, bond breaking and bond formation take place in separated steps, distinct from the electron transfer step. Conversely, if electron transfer is concerted with one or with the two other steps, one will deal with an inner-sphere electron transfer. An outer-sphere electron donor is thus a reagent that will not experience bond formation or bond breaking concerted with electron transfer during the rate-determining step. (b) Espenson, J. H. Homogeneous Inorganic Reactions. In *Investigation of Rates and Mechanisms of Reactions* (*Techniques of Chemistry*), Part 2; Bernasconi, C. F., Ed.; Wiley: New York, 1986; Vol. VI/4E, pp 487–563. (c) Taube, H. *Electron Transfer Reactions of Complex Ions in Solution*; Academic Press: New York, 1970. (d) Lexa, D.; Savéant, J.-M.; Su, K. B.; Wang, D. L. *J. Am. Chem. Soc.* **1988**, *110*, 7617.

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outer-sphere electron donor is involved. An approximate model of the dynamics of such reactions has recently been developed.[6d,11] It allows for the contribution of solvent reorganization and changes in length and angle of bonds that are not broken in the same manner as in the Marcus–Hush model. The contribution of the bond that breaks to the dynamics of the reaction is modelled by approximating the potential energy of the acceptor, RX, by a Morse curve and that of $R^{\bullet} + X^-$ by a purely dissociative curve taken as identical with the repulsive portion of the RX Morse curve. Under these conditions, the quadratic Marcus–Hush activation-driving force relationship:

$$\Delta E^{*} = \Delta E_0^{*}\left(1 + \frac{\Delta E}{4\Delta E_0^{*}}\right)^2 \qquad (4)$$

($\Delta E^{*}$, activation barrier, $\Delta E_0^{*}$, intrinsic barrier; $-\Delta E$, driving force) is maintained and the contribution of bond breaking to the *intrinsic barrier* is *one-fourth of the bond dissociation energy*. This model has been successfully applied to the electrochemical reduction of primary, secondary, and tertiary butyl and benzyl halides in polar solvents and to their homogeneous reduction by aromatic anion radicals.[11]

The first goal of the work reported in the following sections was to investigate the dynamics of concerted electron transfer–bond breaking reaction by means of ab initio techniques, taking as examples the methyl halides, $CH_3X$ (X = F, Cl, Br, I), and thus to evaluate the validity of the empirical model just described. The validation of the empirical model is an important task because the generality and simplicity of its predictions will allow one to rationalize the kinetic reactivity of an enormous number of organic and inorganic molecules, all those that undergo concerted rather than stepwise reductive cleavages.

Ab initio theoretical calculations on alkyl halides dissociative electron transfer have been limited to methyl fluoride and chloride.[12] C–X bond cleavage profiles obtained by means of multiconfigurational MCSCF calculations using the complete active space SCF (CAS SCF) method have been reported recently.[12d,f] In both studies, an avoided crossing is observed between the curves of the anion and that of the neutral molecule plus a free electron. However, whereas in the first of these studies,[12d] the $(RX)^{\bullet -}$ curve presents a minimum at short X–C distances, this minimum is not found in the second study,[12f] the $(RX)^{\bullet -}$ anionic curve being then purely repulsive. It has been recently suggested that this type of minima, which appear in the zone where the neutral species is more stable than the anionic species, originates in the use of very diffuse orbital functions that allows the electron to stand so far away from the molecule that, practically, the energy is that of the neutral ground-state system plus a free electron rather than that of a temporary anion radical.[13]

Electron attachment to perfluoromethyl halides, $CF_3X$, is quite different since it gives rise to the anion radical in the gas phase as well as in apolar or weakly polar solid matrixes.[7,14] There remains some uncertainty as to whether the anion radical is a "true" $\sigma^*$ radical as seems to be the case in solid matrixes and in the gas phase with $CF_3Br$ and $CF_3I$[7,14a,b] or a weakly bound $CF_3{}^{\bullet}X^-$ adduct as seems to be the case for $CF_3Cl$ in the gas phase.[14c]

On the other hand, the analysis of the kinetics of the electrochemical reduction of $CF_3Br$ and $CF_3I$ in aprotic polar solvents indicates that the reduction proceeds along a concerted electron transfer–bond breaking pathway rather than through the intermediacy of the anion radical.[15] It was suggested[15] that the change of behavior observed when passing from the gas phase to a polar solvent might be related to the acceleration of the cleavage, to the point of being concerted with electron transfer, thanks to strong solvation of the nucleofugal halide ion.

To our knowledge, no ab initio calculation study has been so far devoted to the reductive cleavage of perfluoromethyl halides. The second part of work described below is devoted to an ab initio analysis of the reductive cleavage of $CF_3Cl$, showing that it follows the stepwise mechanism in the gas phase in contrast with $CH_3Cl$ for which dissociative electron transfer takes place. The effect of polar solvents on the bond breaking profile will then be analyzed by means of a dielectric continuum applied directly within the quantum chemical calculations. The results show that the presence of the polar solvent completely changes the mechanism of the reductive cleavage of $CF_3Cl$ from stepwise to concerted, thus unravelling, with the example of this model reaction, the role of the solvent among the parameters that drive reactions of this type toward one or the other mechanisms.

## Methodology

All the calculations used for the analysis of the reductive cleavage of $CH_3X$ (X = F, Cl, Br, I) were done by using pseudo-potential techniques for chlorine, bromine, and iodine atoms in order to get rid of the core orbitals. A full basis treatment is possible for chlorine atom, but this calculation is beyond the present computer capabilities for bromine and iodine atoms. A full basis treatment was performed for the comparison between the reductive cleavage of $CF_3Cl$ and that of $CH_3Cl$. We employed a double-zeta ($\zeta$) basis set for all atoms including a set of d polarization functions on heavy atoms (C and X) and p polarization functions on hydrogens. Semidiffuse functions were included on carbon and halogen atoms. All the calculations were done within the unrestricted Hartree–Fock formalism.[16a] This treatment may raise some difficulties in the case of singlet molecules because of spin contamination from triplet and higher multiplicities. However, it was noted that this contamination is unimportant in the present case. Correlation energy was also introduced by using the Møller–Plesset perturbative treatment up to second (MP2) and third order (MP3).[16b] The result of a few configuration interaction calculations including all single and double excitations (CISD) will also be presented. We did not attempt to use multiconfigurational MCSCF techniques similar to those employed in the latest works on methyl fluoride and chloride,[12d,f] since they are not presently extendable to the case of methyl bromide and iodide. However, comparison of our results with the previous MCSCF results[12d,f] and with the experimental values will demonstrate that the present level of calculation produces satisfactory results. Geometry optimization with inclusion of the correlation energy is beyond the present computer capabilities. For this reason, all the results were obtained by using Hartree–Fock optimized geometries.

The basis parameters were the following.

**Carbon and Hydrogens.** Standard 4-31G basis set[17a] plus d polarization functions on C (exponent = 0.50) and p polarization functions on H (exponent = 0.50).

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**Table I.** Results of the ab Initio Calculations for the Neutral $CH_3X$ Molecules

| level | $r_{C-X}$[a] | $D$[b] | EA(X)[c] | $\Delta E$[d] |
|---|---|---|---|---|
| | | X = F | | |
| HF[e] | 1.36 | 69.4 | 24.4 | 45.0 |
| MP2[f] | | 111.7 | 73.4 | 38.2 |
| MP3[g] | | 105.1 | 62.6 | 42.6 |
| CISD[h] | | | 60.9 | |
| theor[i] | 1.40 | 104.1 | 62.4 | 41.7 |
| exp | 1.38[17a] | 108.1[17b] | 79.6[17c] | 28.5 |
| | | X = Cl | | |
| HF[e] | 1.80 | 53.2 | 57.7 | -4.5 |
| MP2[f] | | 83.8 | 76.0 | 7.8 |
| MP3[g] | | 79.4 | 73.8 | 5.6 |
| CISD[h] | | 78.4 | 72.4 | 6.0 |
| theor[i] | 1.79 | 78.9 | 72.7 | 6.2 |
| theor[j] | 1.82 | 68.9 | 50.6 | 18.3 |
| exp | 1.78[17d] | 83.5[17e] | 83.2[17c] | 0.3 |
| | | X = Br | | |
| HF[e] | 1.96 | 42.4 | 54.3 | -12.0 |
| MP2[f] | | 73.2 | 70.3 | 2.9 |
| MP3[g] | | 68.9 | 68.5 | 0.4 |
| CISD[h] | | | 67.1 | |
| exp | 1.93[17f] | 70.0[17g] | 77.6[17c] | -7.6 |
| | | X = I | | |
| HF[e] | 2.15 | 33.2 | 53.9 | -20.7 |
| MP2[f] | | 62.5 | 67.0 | -4.5 |
| MP3[g] | | 58.4 | 65.4 | -7.0 |
| CISD[h] | | | 64.3 | |
| exp | 2.14[17f] | 56.3[17b] | 70.6[17c] | -14.3 |

[a] Ground-state C–X distance in Å. [b] $H_3C–X$ bond dissociation energy in kcal/mol. [c] Electroaffinity of the halogen in kcal/mol. [d] Driving force of the reaction $CH_3X + e^-$ (zero energy) → $CH_3^{\cdot} + X^-$, $\Delta E = D - EA(X)$. [e] Hartree–Fock calculations. [f] Second-order Møller–Plesset perturbation calculations. [g] Third-order Møller–Plesset perturbation calculations. [h] Single and double excitation configuration interaction calculations. [i] Previous ab initio results from ref 12d. [j] Previous ab initio results from ref 12f.

**Halogens.** Standard 4-31G basis set[17a] for fluorine and chlorine when no pseudo-potentials are used. Pseudo-potential parameters are taken from ref 17b for chlorine, bromine, and iodine. The basis set is also of double-ζ quality (similar to the 4-31G) and was also taken from ref 17b. A set of standard d polarization functions was also added for the halogens in all the calculations (exponents: F, 0.80; Cl, 0.50; Br, 0.36; I, 0.27).

**Semidiffuse Functions.** At the best level of calculation, standard semidiffuse sp functions on C (exp 0.0438) and semidiffuse p functions on halogens (exp: F, 0.055; Cl, 0.049; Br, 0.044; I, 0.040) were introduced.

All calculations were done by means of the GAUSSIAN 82 and 86 series of programs.[18a] The effect of solvent was treated by means of a dielectric continuum method, namely, the ellipsoidal cavity method,[18b] introduced directly within the quantum chemical calculations.

## Results and Discussion

**Methyl Halides.** The results of the ab initio calculations on the neutral $CH_3X$ molecules are listed in Table I together with previous theoretical and experimental data. They include the carbon–halogen bond distance ($r_{C-X}$), the dissociation energy of the alkyl halide ($D$), the electron affinity of the halogen (EA(X)), and the total driving force of the process, $\Delta E$, calculated at the Hartree–Fock level (HF) and at the MP2, MP3, and CISD (when available) levels, keeping, however, the HF geometries unchanged.

The importance of polarization functions is readily seen when comparing the equilibrium geometries of the minima. For instance, the optimized C–halogen distances are, for Cl, Br, I, 1.90/2.05/2.20 Å without polarization functions and 1.80/1.96/2.15 Å with the full basis set. The experimental values are 1.78/1.93/2.14 Å, respectively. The importance of the correlation energy is also clearly seen. When one compares the dissociation energy of $CH_3X$ and the electroaffinity of the halogen at different levels of calculation, Hartree–Fock results are always a poorer approximation to the experimental data than the MP2, MP3, and CISD results. Previous theoretical data are also available from literature[12] for $CH_3F$ and $CH_3Cl$. No previous ab initio work has been devoted to methyl bromide and iodide. The results of the latest ab initio results on $CH_3F$ and $CH_3Cl$ systems[12d,f] are also included in Table I for comparative purposes.

Before examining the results obtained at the different ab initio levels, it should be noted that the experimental values of the dissociation energies, $D$, and of the electron affinities derive from different experiments. Thus, in the ensuing estimation of the values of the thermodynamic driving forces, obtained from difference between these two quantities, errors can accumulate giving rise to poorly reliable data. It is clear from Table I that the Hartree–Fock (HF) energies do not reproduce satisfactorily the experimental data, whereas the Møller–Plesset perturbation theory up to second (MP2) and third order (MP3) and the configuration interaction method, including all single and double excitations (CISD), lead to more reliable results. The EA of the halogens is, however, clearly underestimated in all cases. The difficulty for ab initio methods to quantitatively reproduce EA values has been noted previously.[19a] It also appears in the previous theoretical results reported in Table I[12d,f] where results similar to ours were obtained even though more powerful methods were used.

The driving force data are equally affected by the EA errors. It is, however, worth noting that the relative experimental values along the series are very well reproduced by the theoretical results in spite of the absolute error. This is an important observation since our main purpose is to compare the theoretical prediction experiments, particularly, electrochemical experiments, where, for each halide molecule, the driving force can be varied at will by adjusting the electrode potential in the electrochemical case and by selecting the reducing power of the electron donor in the homogeneous case.

In this framework, MP2 and MP3 results compare equally well to the experimental data and produce similar bond breaking profiles. The reason that we prefer the MP3 level to analyze the reaction further is that it gives results that are very close to the CISD results, when available, and that MP2 results are known to overestimate the effect of correlation.[19b,c]

After this preliminary check of the methods, we investigated the electron transfer and bond breaking processes by calculating the energy of $CH_3X$, on the one hand, and of $CH_3X^{\cdot -}$, on the other, as a function of the distance C–X taken as reaction coordinate. For the neutral $CH_3X$ molecule, a free electron that does not contribute to the total energy of the system is assumed to be also present. Emphasis was laid on the calculation of the points of each curve that are located in the vicinity of the crossing point. The resulting energy profiles are depicted in Figure 1.

It appears that, in all cases, the $CH_3X^{\cdot -}$ anion radical is not stable with respect to the breaking of the C–X bond. In other words, the $CH_3^{\cdot} + X^-$ profile is repulsive. It was noted, in this connection, that no minimum is found in the anion radical structure at large distance. This point was investigated in more details in the case of $CH_3Cl$ showing that no such minima, which could result from a weak charge-induced dipole interaction, appear at this level of calculation.

The crossing point between the two profiles thus corresponds to the transition state of what should be viewed as a concerted electron transfer–bond breaking reaction in agreement with the gas-phase, solid matrix, and electrochemical experimental results.

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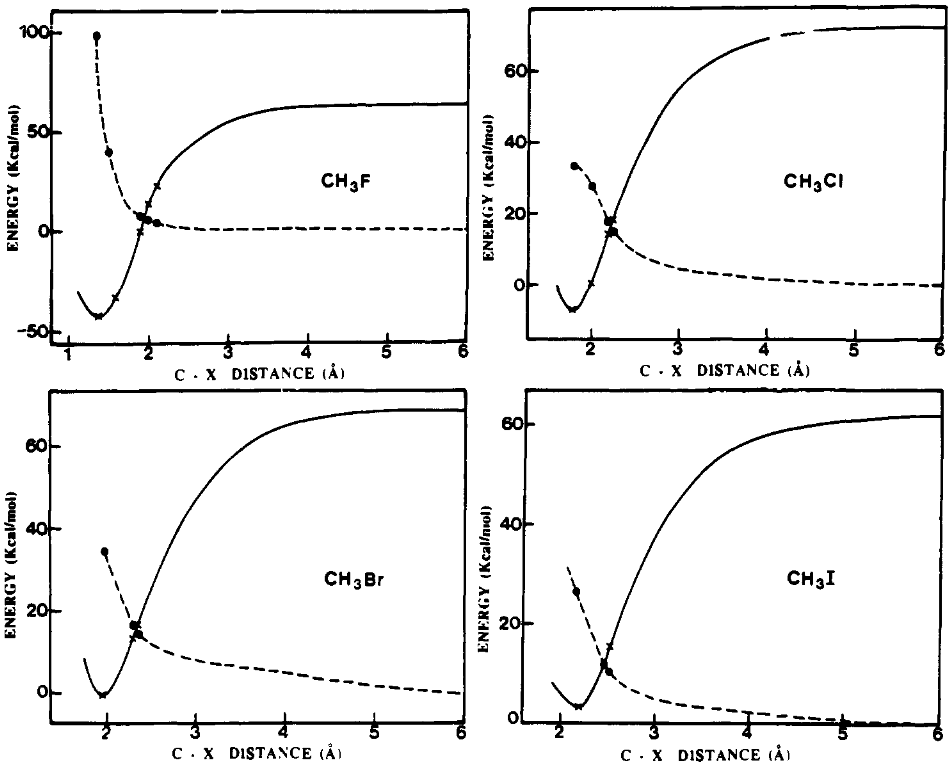

**Figure 1.** MP3 calculated energy profiles of $CH_3X$ (●, solid lines) and of $CH_3^{\bullet} + X^-$ (×, dashed lines).

**Table II.** Transition-State Characteristics of the Dissociative Electron Transfer

$CH_3X + e^- \rightarrow CH_3^{\bullet} + X^-$

| | $\Delta E^{*}$ [a] | | | $\Delta r^{*}$ [b] | | |
|---|---|---|---|---|---|---|
| | | empirical model | | | empirical model | |
| X | MP3 calculations | *c* | *d* | MP3 calculations | *c* | *d* |
| F | 49.1 | 51.9 | 43.2 | 0.59 | 0.67 | 0.56 |
| Cl | 23.5 | 22.7 | 19.3 | 0.42 | 0.48 | 0.42 |
| Br | 15.9 | 17.5 | 12.5 | 0.37 | 0.45 | 0.36 |
| I | 9.5 | 14.6 | 7.8 | 0.33 | 0.41 | 0.30 |

[a] Activation energy in kcal/mol. In the empirical model, $\Delta E^*$ is calculated from eq 4. [b] Increase of the C–X distance from the ground state, in Å. In the empirical model $\Delta r^*$ is calculated from eq 5 and $\beta$ is obtained from the following stretching frequencies: 1048.2 ($CH_3F$), 732.1 ($CH_3Cl$), 611 ($CH_3Br$), 532.8 ($CH_3I$) cm$^{-1}$ (Herzberg, G. *Infrared and Raman Spectra*; Van Nostrand: New York, 1945; p 314). [c] $D$ and $\Delta E$ from the MP3 calculations. [d] From the experimental $D$ and $\Delta E$ values.

**Table III.** Negative Charge on the Halogen Atom[a]

| | reactant | crossing point | | product |
|---|---|---|---|---|
| X | $CH_3X$ | $CH_3X$ | $CH_3X^{\bullet -}$ | $CH_3^{\bullet} + X^-$ |
| F | 0.503 | 0.584 | 0.827 | 1.000 |
| Cl | 0.162 | 0.373 | 0.784 | 1.000 |
| Br | 0.114 | 0.269 | 0.769 | 1.000 |
| I | 0.027 | 0.189 | 0.765 | 1.000 |

[a] In atomic units.

The energies and geometries of the transition state are summarized in Table II.

Qualitatively we see that the results accord with the Evans–Polanyi principle[20a] and the Hammond postulate.[20b] From a quantitative viewpoint, it is interesting to compare the results of the ab initio results to the predictions of the empirical model evoked in the introduction. For this, we have computed the values of $\Delta E^*$ from eq 1, taking for $\Delta E$ and $D$ either the MP3 calculated values or the experimental values. The same was done for the geometry of the transition state, calculating, in the same manner, the increase of the C–X distance from the ground state to the transition state, $\Delta r^*$, according to[11]

$$\Delta r^* = \frac{1}{\beta}\left[\ln 2 - \ln\left(1 - \frac{\Delta E}{D}\right)\right] \qquad (5)$$

($b = \nu_0(2\pi^2\mu/D)^{1/2}$, $\nu_0$ = stretching frequency, $\mu$ = reduced mass). The resulting values are listed in Table II. We see that there is a quite satisfactory agreement between the results of the ab initio calculations and the predictions of the empirical model both concerning the activation energies and the transition-state geometries.

Further insights into the nature of the dissociative electron transfer reaction can be gained by inspecting the variation of the charge borne by the halogen atom along the bond breaking process (Table III). As expected, in the neutral molecule, the halogen charge diminishes along with the electronegativity in the series F–Cl–Br–I. When the C–X bond distance increases, the charge on the halogen also increases so that it is bigger at the crossing point where electron transfer takes place. A comparison of the charge distributions in the neutral and anionic species at the crossing point shows that only a fraction of the additional charge is initially located on the halogen atom. It may seem surprising, at first sight, that the halogen charge increment at the crossing point increases from fluorine to chlorine, bromine, and iodine. However, it must be taken into account that the more electronegative fluorine and chlorine atoms already possess a large electronic charge at the neutral crossing point structure so that a further increase is more difficult to achieve. During the electron transfer reaction, we observe that the charge difference between the four halogens, which is 0.5 au (atomic units) in the ground state, gently decreases, reaching 0.4 au at the neutral side of the crossing point, whereas in the anionic state at the crossing point, it decreases abruptly to 0.06 au. Thus, electronic differences between the four halogens show up principally in the zone where the neutral molecule is more stable than the anionic state, i.e., before the electron transfer takes place. After this has occurred, the C–X bond progressively breaks, being accompanied by a small and smooth increase of the negative charge on the halogen atom.

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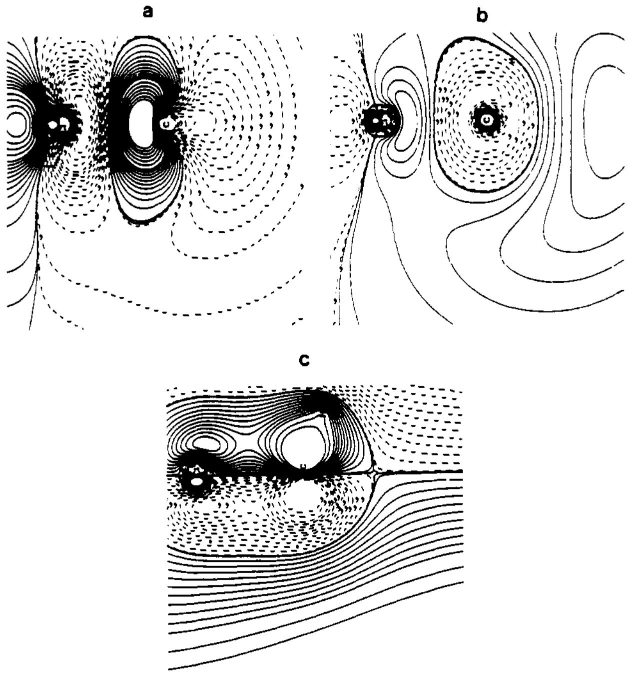

**Figure 2.** Contour plots of the last occupied $\alpha$ molecular orbital for the methyl chloride anion at the geometry of the ground-state minimum using a basis set, without semidiffuse functions (a), with the standard semidiffuse functions on carbon and chlorine (b), and with the diffuse function exponents multiplied by 1/10 (c). The solid lines stand for positive values of the wave function, whereas the dashed lines refer to the negative values. The positions of the atoms used to define the drawing plane are also indicated.

The use of semidiffuse functions is worth some additional comments. The necessity of including semidiffuse functions in the basis set in order to have a good description of the expanded electronic density of anionic systems has long been recognized.[21] However, when the radical anion lies energetically above the neutral ground-state system, the more stable position of the electon is to go away as far as possible from the molecule so that the same energy as that of the neutral molecule plus a free electron is obtained. The use of basis set with very diffuse functions tends to reproduce the latter situation. Evidence of this behavior can be found in literature for $CH_3F$, $CH_3Cl$, and related systems.[12d,13,22]

It follows that the lowering in energy is not a reliable criterion to justify the use of a given basis set but rather is its ability to reproduce the temporary anion state. In other words, we must find evidence that the anionic profiles presented in Figure 1 provide satisfactory representations of the diabatic profiles for the C–X bond cleavage process. In order to assess this point, additional calculations were carried out for the chloromethane anion at the fixed geometry of the ground-state minimum. Figure 2 depicts the wave-function contour plots of the last occupied $\alpha$-molecular orbital in the anion for three different basis sets. This orbital can be viewed as a picture of the region of space where the additional electron is located.

The antibonding $\sigma^*$ character of the orbital can be clearly seen in Figure 2a which shows the contour plot obtained without semidiffuse functions. It is, however, likely that this basis set does not provide a completely adequate description of the electronic density in the antibonding orbital[23a] resulting in a vertical electron affinity, 115,7 kcal/mol, that is most probably too high.[23b] The incorporation of standard semidiffuse functions on the heavy atoms as described in the methodology section leads to a molecular orbital that has the shape depicted in Figure 2b. The electronic density is significantly decreased as compared with the previous results (Figure 2a). However, the antibonding $\sigma^*$ character in the region between carbon and chlorine is still clearly apparent, indicating that this basis set provides an adequate representation of the anion radical state. The vertical electron affinity drops down to 44.5 kcal/mol at the SCF level.[23c] In the case where the diffuse character of the semidiffuse functions is largely increased as in Figure 2c where their exponents were multiplied by 0.1, the energy of the anion radical state drops dramatically, being only 7.8 kcal/mol above the ground state. As seen in Figure 2c, where the contour plots values have been divided by 100 with respect to the two previous cases, the additional electron does not fall into a $\sigma^*$ antibonding orbital but rather into a very diffuse $\pi$-type orbital that possesses only a very slight bonding character. It follows that this basis set does not lead to a correct representation of the diabatic bond cleavage at the anion radical state.

**Table IV.** $CH_3Cl$ and $CF_3Cl$: Characteristics of the Neutral Molecule and of the Transition State of the Reaction $RCl + e^-$ (zero energy) → $R^\cdot + Cl^-$

| | $r_{C-X}$[a] | $D$[b] | EA(Cl)[c] | $\Delta E$[d] | $\Delta E^{\ddagger}$[e] | $\Delta r^{\ddagger}$[f] |
|---|---|---|---|---|---|---|
| | | $CH_3Cl$ | | | | |
| pseudo-potentials (MP2) | 1.80 | 83.8 | 76.0 | 7.8 | 23.3 | 0.42 |
| full basis (MP2) | 1.80 | 81.3 | 77.9 | 5.6 | 24.2 | 0.40 |
| experimental | 1.78[17d] | 83.5[17e] | 83.2[17c] | –0.3 | | |
| | | $CF_3Cl$ | | | | |
| full basis (MP2) | 1.75 | 812 | 76.0 | 5.2 | 16.3 | 0.38 |
| experimental | 1.75[17h] | 86.1[17i] | 83.2[17c] | 2.9 | | |
| previous calculations[12e] | 1.75 | 83.0 | 62.5 | 20.5 | | |

[a] Ground-state C–X distance in Å. [b] C–Cl bond dissociation energy in kcal/mol. [c] Electroaffinity of chlorine in kcal/mol. [d] Driving force of the reaction $RCl + e^-$ (zero energy) → $R^\cdot + Cl^-$, $\Delta E = D - EA(Cl)$. [e] Activation energy in kcal/mol. [f] Increase of the C–X distance from the ground state, in Å.

The fact that the anion curves in Figure 1 provide a correct representation of the diabatic bond breaking is further confirmed by the analysis of the evolution of the last occupied $\alpha$-molecular orbital with the C–X distance. We have found that, whereas, initially, the main contribution to this orbital comes from the carbon s and p semidiffuse orbitals, the contribution of the chlorine semidiffuse and valence p orbitals smoothly increases with the C–X distance. At the distance corresponding to the crossing point, the orbital density is thus mainly located on the chlorine side. A quite different picture arises when largely diffuse functions are used. At short C–X distances, the orbital is $\pi$ bonding. As the C–X distance increases, an orbital crossing occurs and the $\pi$ bonding orbital suddenly changes to a $\sigma^*$ antibonding orbital.

The fact that the energy of the anion at short C–Cl distances drops near the energy of the neutral molecule when the diffuse character of the basis set is increased indicates that, in the reactant zone, the use of very diffuse orbital functions leads to the concept that the anion is then equivalent to the neutral molecule plus a free electron. We thus have a means of describing the adiabatic profile of the reductive cleavage reaction and to locate precisely the transition state. This aspect of the problem was investigated on the example of $CH_3Cl^{\cdot-}$ by adding to the standard basis previously employed a set of very diffuse sp functions (exponent, 0.001) on the carbon atom. We thus found a minimum located at a C–Cl distance of 1.8 Å with an energy close to that of the neutral molecule (0.65 kcal/mol), the additional electron being mostly located in the most diffuse s function of the carbon atom. As the C–Cl distance increases, the energy increases, reaches a maximum, and then decreases along the profile of the diabatic curve of the anion radical as the additional electron density tends to concentrate on the chlorine atom.

Accurate localization of the transition on the adiabatic curve reveals that the corresponding C–Cl distance is practically the same as that of the crossing of the two diabatic curves. The transition-state energy thus calculated is only 1 kcal/mol below that of the diabatic crossing point. This value is a measure of the resonance energy between the two diabatic states. Its smallness falls in line with the outer-sphere character of the electron donor.

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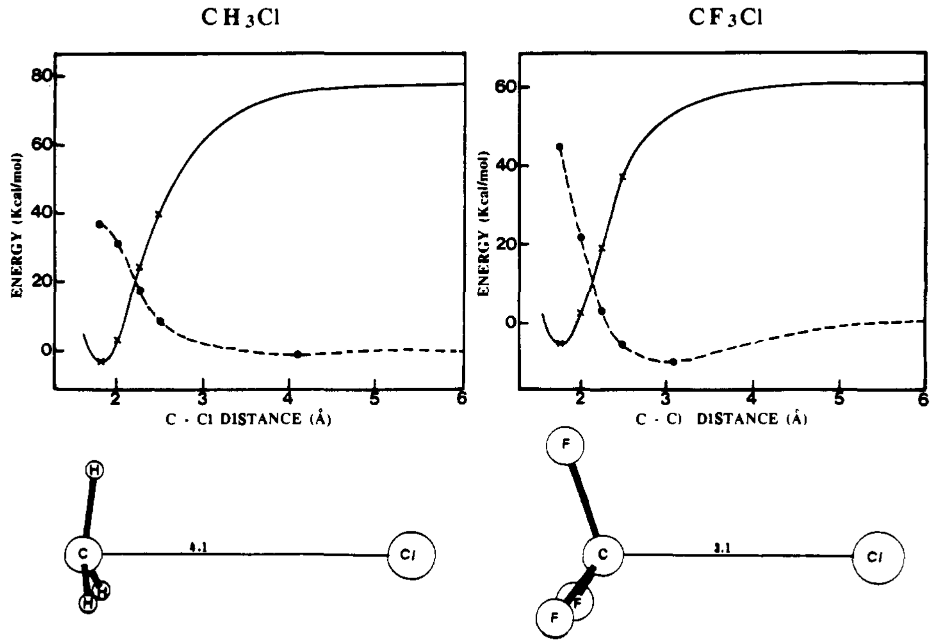

Figure 3. Comparison of the neutral (solid lines) and anion (dashed lines) energy profiles of $CH_3Cl$ and $CF_3Cl$ obtained by using full basis sets and of the anion geometries at the large distance energy minimum.

These results validate the strategy based on diabatic curve crossing employed for the comparison with the empirical model, one important interest of which is the possibility to predict variations in the activation barrier triggered by an external change of the driving force.

**Perfluoromethyl Chloride.** The comparison between methyl- and perfluoromethyl chlorides does not require the use of pseudo-potentials. We have thus re-examined the case of $CH_3Cl$ using a full basis set. Table IV compares, at the MP2 level of calculation, the results obtained with the latter method to those previously gained using a pseudo-potential. We note that the use of this more powerful methodology improves only slightly the results that are, in both cases, in close agreement with the experimental data. This applies to the characteristics of the neutral molecules and to the energy and geometry of the transition states, thus justifying the use of pseudo-potentials for obtaining the results described in the preceding section. The energy profiles obtained with the full basis set calculations are depicted in Figure 3. In the range of small and medium C–Cl distances, the profiles are very similar to those previously obtained with the use of a pseudo-potential (Figure 1). There is, however, a slight but noticeable difference between the anion profiles at large distances. We indeed noted the presence, in the anion curve, of a very shallow energy minimum (0.8 kcal/mol below the final products, $CH_3^{\bullet}$ + $Cl^-$) at a C–Cl distance of 4.1 Å.[24a] The full geometry of this state is depicted in Figure 3. At first sight, the presence of this minimum may give the impression that the stepwise mechanism is followed in that case. However, at the level of free energies, this very small minimum will be wiped out by the counteracting entropy term. In addition to this, long-range interactions are usually overestimated in standard ab initio calculations due to the neglect of the basis set superposition error (BSSE).[25a] This error originates in the fact that the size of the basis used for describing the radical anion minimum is greater than that of the basis used for each of the two separate fragments, $CH_3^{\bullet}$ and $Cl^-$. A simple method to deal with the BSSE is the counterpoise method.[25b] The energies of the product are then calculated in the full minimal basis set of the two fragments and substracted from the total energy of the minimum. Using this approach we found that the minimum practically disappears since it falls only 0.03 kcal/mol below products.

The full basis set results concerning $CF_3Cl$ are given in Table IV. Correlation energy has been included only up to the second perturbation level (MP2) since the third level is not reachable at present time and since, as noted before in the case of $CH_3Cl$, MP2 and MP3 levels lead to similar results. The energy profiles for $CF_3Cl$ are shown in Figure 3. Comparison with $CH_3Cl$ (Table IV, Figure 3) shows that the C–Cl distance is slightly smaller with $CF_3Cl$ than with $CH_3Cl$ and that the activation barrier is significantly smaller in the first case than in the second. This latter finding falls in line with previous electrochemical data showing that, for the same leaving halogen ion, perfluoroalkyl halides are easier to reduce than alkyl halides.[9a,15]

The $CF_3Cl$ anion energy profile also exhibits a minimum at large C–Cl distances (Figure 3),[26] but the energy decrease vis-à-vis the final products is much larger (−9.8 kcal/mol) than in the case of $CH_3Cl$ and the C–Cl distance significantly shorter (3.1 Å versus 4.1 Å). In this case the BSSE calculated by means of the counterpoise method has no practical effect on the stabilization energy of the minimum which decreases very slightly down to −8.9 kcal/mol. The full geometry of this state is depicted in Figure 3. The existence of this clearly marked minimum in the anion profile is in agreement with gas-phase and solid matrix experimental data.[7,14]

Besides the change in the C-Cl length, the geometries of $(CF_3Cl)^{\bullet -}$ and $(CH_3Cl)^{\bullet -}$ at the long distance energy minimum also exhibits significant differences in the bond angles. Whereas the hydrogens of the methyl fragment bend toward the chloride, the fluorines of the $CF_3$ fragment point in the opposite direction. A Mulliken population analysis of the atomic charges reveals that in both case the $Cl^-$ anion has been already formed (−0.99 au on Cl in the case of $CH_3Cl$ and −0.93 au in the case of $CF_3Cl$). The computation of the atomic charges in the radical fragments shows

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(24) (a) Energy minimization procedures by means of the Standard Schlegel Modified Conjugate Gradient Algorithm was used to exactly determine the position and energy of the minimum.[24b] (b) Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214. (c) When attempting to use a pseudo-potential for chlorine, we found no minimum in the anion profile indicating, as in the case of $CH_3Cl$, that effective core potential methods are unable to find intermediates in the bond breaking process at large C–X distances. It is worth noting in this connection that a recent high level ab initio calculation for hydrogen chloride anion indicates the existence of a minimum at large H–Cl distances.[24d] (d) Astrand, P. O.; Karlstrom, G. *Chem. Phys. Lett.* **1990**, *175*, 624.

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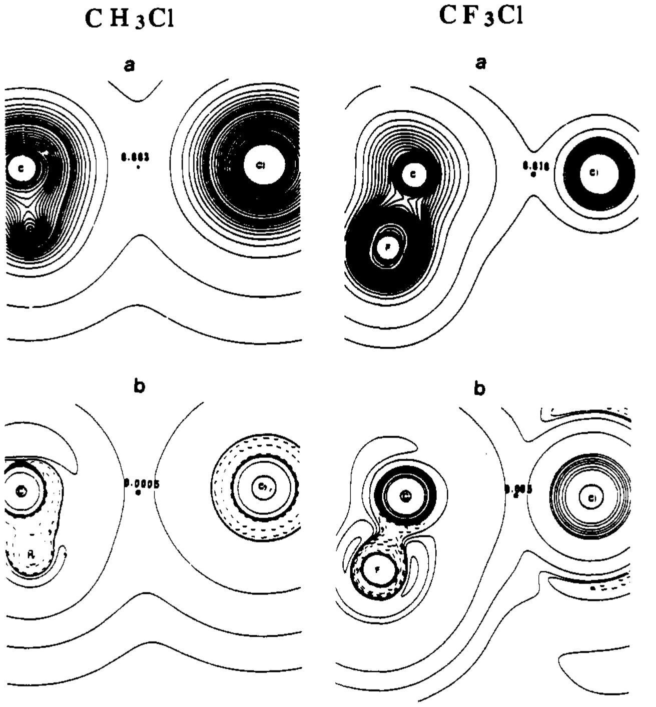

**Figure 4.** (a) Isodensity contour plots of the electronic density, $\rho(r)$, for the minima of the anionic states. The numbers indicate the value of $\rho(r)$ at the bond critical point between carbon and chlorine. (b) Isodensity contour plots to the Laplacian of the electronic density, $\nabla^2\rho(r)$, for the minima of the anionic states. Solid lines, $\nabla^2\rho > 0$, dashed lines, $\nabla^2\rho < 0$. The numbers indicate the values of $\nabla^2\rho(r)$ at the critical point between carbon and chlorine.

that, whereas, in the case of $CH_3Cl$, a slight positive charge lies on the hydrogens (+0.07 au), the carbon bearing a small negative charge (−0.2 au), in the case of $CF_3Cl$, the fluorines are negatively charged (−0.40 au) owing to their strong electronegativity and the carbon bears a large positive charge (+1.13 au).

This simple analysis of the atomic charges provides an explanation of the differences between the stabilization energies and geometries of the two energy minima. In the case of $CF_3Cl$, the stabilization arises essentially from a $C^+$–$Cl^-$ electrostatic interaction and is therefore much stronger than in the case of $CH_3Cl$, where $Cl^-$ interacts mainly with the inverted and slightly positively charged hydrogens.

What the nature of the "bond" between the chlorine and carbon atoms is in each case is a question that we have investigated by means of a topological analysis of the charge density. Figure 4a depicts the isodensity contour plots of the charge density, $\rho(r)$, in the plane containing the chlorine, the carbon, and one hydrogen (or fluorine). In both cases, a bond critical point appears between carbon and chlorine. The value of $\rho(r)$ at the critical point is a measure of the bond order.[26a] It is clearly larger in the case of $CF_3Cl$ than in the case of $CH_3Cl$, indicating, as expected, that the bond is stronger in the first case than in the second. In both cases, this bond is considerably weaker than in the ground state of the neutral molecules ($\rho(r) = 0.13$ and 0.17 for $CH_3Cl$ and $CF_3Cl$, respectively).

The simple analysis of the charge density maps does not, however, uncover the exact nature of the bond. To investigate this point, we have computed the maps of the Laplacian of the charge density, $\nabla^2\rho(r)$. As previously discussed,[26b] a negative value of $\nabla^2\rho(r)$ in the internuclear region indicates that the interactions arise from the sharing of charge density resulting in a contraction of the electronic charge and therefore that a covalent or polar bond is present. On the opposite, $\nabla^2\rho(r) > 0$ indicates that the electronic charge is depleted in the interatomic region pointing to the presence of an ionic or a van der Waals bond.[26b] The $\nabla^2\rho(r)$ contour plots for the two minima, in the same molecular plane as in Figure 4a, are depicted in Figure 4b. It is seen that the two plots are very similar. In both cases, $\nabla^2\rho(r) > 0$ in the bond critical point region indicating that the bond between the radical and the chloride ion is of the electrostatic type.

Confirmation of the latter conclusion was obtained by means of an estimation of the interaction energy, $\Delta E_{INT}$, between the radical and the chloride ion fragments at the two minima. The global stabilization energy, $\Delta E_S$, can be expressed as:

$$\Delta E_S = \Delta E_{DEF} + \Delta E_{INT}$$

where $\Delta E_{DEF}$ is the intramolecular deformation energy. The interaction energy, $\Delta E_{INT}$ can then be shared in an ionic (electrostatic with polarization) and a covalent (charge transfer) contribution.[26c] We found, as expected, that the deformation energy is small in both cases and therefore that the interaction energies are close to the total stabilization energies. In order to assess the ionic or covalent character of the bond, the anionic fragment was replaced by a point charge. The interaction energy is then an approximate measure of the ionic stabilization. In both cases, energies very close to the total interaction energies were obtained, the charge transfer interaction energies being below 1 kcal/mol. These results show that no covalent interactions are present in both systems. It follows that the larger stabilization of $CF_3Cl^{\bullet-}$ as compared to $CH_3Cl^{\bullet-}$ derives essentially from the larger polarization of $CF_3^{\bullet}$ as compared to $CH_3^{\bullet}$.

The next question we wish to discuss is the effect of a polar solvent on the energy profiles in the case of $CF_3Cl$ and, in particular, to see whether or not the $CF_3Cl^{\bullet-}$ energy minimum found in the gas phase is maintained. In this purpose we used a continuum ellipsoidal cavity model[18b] introduced directly into the quantum chemical calculations. The dielectric constant was taken as equal to 37, a value suited to solvents, such as acetonitrile, dimethyl sulfoxide, and *N,N'*-dimethylformamide, currently used in the electrochemistry of alkyl halides. From the results depicted in Figure 5, it is seen that the energy profile of the neutral molecule is not significantly affected, whereas the anionic state is considerably stabilized. The stabilization increases along with the C–Cl distance, leading to an energy profile that decreases monotonically

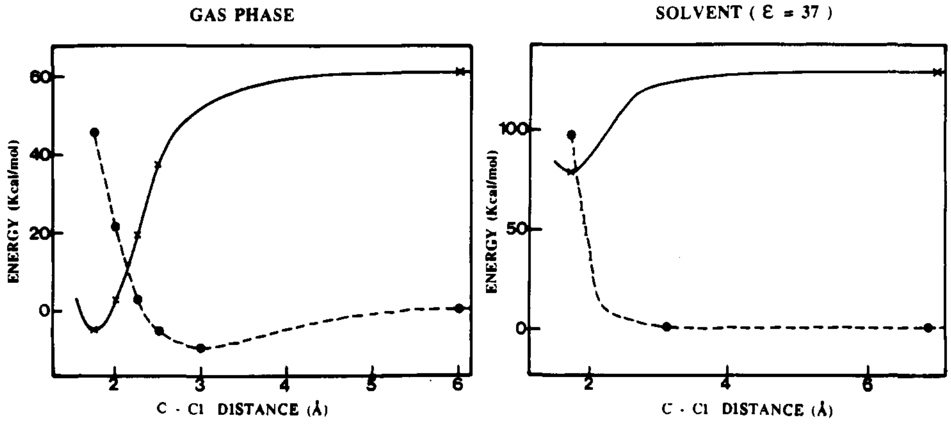

**Figure 5.** Comparison between the energy profiles of $CF_3Cl$ (solid lines) and $CF_3Cl^{\bullet-}$ (dashed lines) in the gas phase and in a polar solvent.

along this reaction coordinate. The $CF_3Cl + e^- \rightarrow CF_3^{\bullet} + Cl^-$ reaction therefore appears, in polar solvents, as a concerted electron transfer-bond breaking process in agreement with what was previously suggested from the analysis of the kinetics of the electrochemical reduction of the perfluoroalkyl halides.[15]

## Conclusions

The following conclusions emerge from the results described in the preceding sections. MP3 calculations using pseudo-potentials for the halogens and semidiffuse functions in the carbon orbital set indicate that in the series $CH_3F$, $CH_3Cl$, $CH_3Br$, $CH_3I$, the reaction $CH_3X + e^- \rightarrow CH_3^{\bullet} + X^-$ is a concerted electron transfer-bond breaking process in accord with previous experimental observations pertaining to the reductive cleavage of alkyl halides in the gas phase, in apolar or weakly polar solid matrixes and in their electrochemical reduction in polar solvents. The magnitudes of the activation barrier and the geometries of the transition state thus found are in good agreement with the application of a previously developed empirical model based on Morse curves approximation, in which the activation barrier is quadratically related to the driving force and the intrinsic activation barrier is equal to one-fourth of the $CH_3$–X bond dissociation energy. This validation of the empirical model reinforces the confidence in its general applicability to a vast class of organic and inorganic reductive cleavage reactions.

The comparison of the energy profiles obtained by means of full basis set calculations for $CH_3Cl$ and $CF_3Cl$ reveals that a shallow minimum appears on the anion profiles at large C–Cl distances in both cases. The stabilization energy vis-â-vis $R^{\bullet} + Cl^-$ is, however, much larger with $CF_3Cl$ than with $CH_3Cl$. Analysis of the charge density maps of these states shows that the bond between carbon and chlorine is of the electrostatic type and that the larger stabilization found with $CF_3Cl^{\bullet -}$ essentially derives from the polarization of the $CF_3^{\bullet}$ fragment as compared to the $CH_3^{\bullet}$ fragment.

Simulation of the effect of polar solvents on the energy profiles of $CF_3Cl$ and $CF_3Cl^{\bullet -}$ shows that the energy minimum on the $CF_3Cl^{\bullet -}$ disappears. The $CF_3Cl + e \rightarrow CF_3^{\bullet} + Cl^-$ thus appears as a concerted electron transfer-bond breaking process in agreement with the conclusions previously derived from the kinetics of the electrochemical reduction of perfluoroalkyl halides in polar solvents. These results emphasize and rationalize the role of the solvent among the parameters that drive reductive cleavage reactions toward either the concerted or the stepwise mechanism.

**Acknowledgment.** We thank Prof. M. Duran for fruitful discussions on the nature of unstable radical anions. Thanks are also due to Dr. R. Rodriguez Pappalardo from the Universidad de Sevilla for kindly performing the cavity solvation calculations with a so far unreleased program. Financial support by the "Science" EEC program is also gratefully acknowledged.

**Registry No.** $CH_3F$, 593-53-3; $CH_3Cl$, 74-87-3; $CH_3Br$, 74-83-9; $CH_3I$, 74-88-4; $CF_3Cl$, 75-72-9; $CF_3Cl^{\cdot -}$, 58194-41-5; $CH_3Cl^{\cdot -}$, 69685-01-4.

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# Bond Alternation in Triannelated Benzenes: Dissection of Cyclic π from "Mills-Nixon" Effects

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**Abstract:** The structures of a number of triannelated benzenes are calculated at the ab initio 6-31G(D) and local density functional levels of theory. Their structures are discussed in terms of ring strain and cyclic π effects. The results offer no evidence for the "Mills-Nixon" postulate in simple annelated benzenes. A new motif in bond-alternating benzenes is proposed.

Classic examples of bond alternation in benzenoid structures are seen experimentally in the central ring of triphenylene (**1**)[2] and starphenylene (**2**) (Figure 1).[3,4] Speculation has been made that similar bond alternation exists in simple triannelated benzenes like tricyclobutabenzene.[5] Computations at the ab initio 3-21G level and below support these notions,[6] although the low-temperature X-ray analysis of perfluorotricyclobutabenzene (**3**) reveals no such alternation (Figure 2).[7] Ab initio 6-31G(D) computations provide a structural data base consistent with experiment. Dissecting this set into cyclic π and "Mills-Nixon" components dispels some notions and generates new speculations. From this vantage point, the present investigation begins.

## Methods

The molecular structures of all stationary points have been determined with both the semiempirical AM1 method[8] and the split valence 6-31G(D) basis set at the restricted Hartree-Fock (RHF) self-consistent field (SCF) level of theory.[9] This basis set includes a set of six d polarization functions on all heavy atoms. For illustration purposes, several calculations were also performed using the 3-21G basis set[10] in order to supplement available literature calculations and, at the ab initio level, using the local density functional (LDF) approach.[11] Geometry optimizations

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