

diatoms and their ions are not continuous as a function of electron population, as required.⁵ The general trend in electronegativities follows chemical experience with high values for BeF, CC, CN, OF, and FF. These may be of use in understanding relationships among parts of larger molecules.

Extension of these methods to diatoms containing Na to Cl is merely an exercise. Finding more D_{0s} of good accuracy for XY and XY^+ will allow diatoms of elements beyond Ar to be dealt with thus.

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Structure of Fluoromethyl Radicals. Conjugative and Inductive Effects

Fernando Bernardi,*^{1a} William Cherry,^{1b} Sason Shaik,^{1b} and Nicolaos D. Epiotis*^{1b}

Contribution from the Laboratorio CNR Composti del Carbonio, Istituto di Chimica Organica, Università di Bologna, Bologna, Italy, and the Department of Chemistry, University of Washington, Seattle, Washington 98195. Received December 8, 1976

Abstract: Factors determining the geometry of CH_nX_{3-n} radicals are illuminated on the basis of one-electron MO (OEMO) theory. Inductive and conjugative effects are found to be operative in fluoromethyl radicals ($X = F$). The relative importance of these two effects is discussed. The qualitative conclusions are supported by ab initio calculations of the fluoromethyl radicals.

The geometry of the methyl radical has been probed by means of a variety of spectroscopic,² chemical,³ and theoretical⁴ methods. The consensus is now that this radical exists in a near-planar geometry, the deviation from planarity being small and much dependent on the experimental technique or the sophistication of the quantum-mechanical calculation. A much more pronounced trend which has been revealed by spectroscopic methods is the progressive increase in the pyramidalicity of the methyl radical as each hydrogen is successively replaced by a more electronegative first period atom such as F, O, etc.² The origin of this effect can be understood by focusing attention on the following two electronic factors: (a) the σ inductive effect of the electronegative atom⁵ and (b) the π conjugative effect of the electronegative atom. The mode of operation of the σ inductive effect in dictating the bond angles of molecules has been discussed recently, using a simple MO approach.⁶ It was argued that the bending of a linear AB_2 molecule or pyramidalization of a planar AB_3 molecule will tend to occur if such a geometric change allows substantial mixing of the highest occupied π MO (HOMO) with the lowest unoccupied σ MO (LUMO). Specifically, it was demonstrated that in cases where A is a second-row element or when B is an electronegative atom, such mixing becomes substantial owing to a decreasing HOMO-LUMO energy gap. The basic arguments can be easily applied to the problem at hand, as discussed below.

Consider the planar methyl radical whose MO's are shown in Figure 1. Upon pyramidalization, the symmetry of the molecule is relaxed from D_{3h} to C_{3v} . This allows Ψ_4 (i.e., the singly occupied MO) to mix with Ψ_1 and Ψ_5 . Now, the Ψ_1 - Ψ_4 interaction results in stabilization or destabilization, depending

on several factors (vide infra). However, this effect is small and may be neglected.⁷ The Ψ_4 - Ψ_5 interaction always results in stabilization and, consequently, favors the nonplanar geometry. As the electronegativity of the substituents is increased, the energy of Ψ_5 decreases. This effectively decreases the Ψ_5 - Ψ_4 energy gap and increases the strength of the interaction between these orbitals. Consequently, as the electronegativity of the substituents is increased, the preference for nonplanarity should increase.

On the basis of the above model which focuses exclusively on the substituent inductive effect, the following specific predictions can be made.

(a) The pyramidalicity of the radical center will increase in the order $\dot{C}X_3 > \dot{C}X_2H > \dot{C}XH_2$, where X is a σ inductively withdrawing group.

(b) Charge transfer from the radical center to the heteroatom X will occur upon pyramidalization, and its magnitude will vary in the order $\dot{C}X_3 > \dot{C}X_2H > \dot{C}XH_2$. Accordingly, the C-X bond in all three radicals will acquire greater ionic character as the planar form is transformed to a pyramidal form, the effect being greatest for $\dot{C}X_3$.

The π conjugative effect refers to the interaction of the " π " lone pair of X with the singly occupied carbon AO, and it can have important conformational consequences. We shall utilize a one-electron MO (OEMO) approach with inclusion of overlap to investigate the effect of conjugation in substituted methyl radicals, and our approach will be illustrated by reference to the model systems CH_2F , CHF_2 , and CF_3 .

The π -type MO's of the planar substituted methyl radicals can be constructed by mixing the C p_z AO with the appropriate group MO's (GMO's) spanning the F p_z AO's. The fluorine

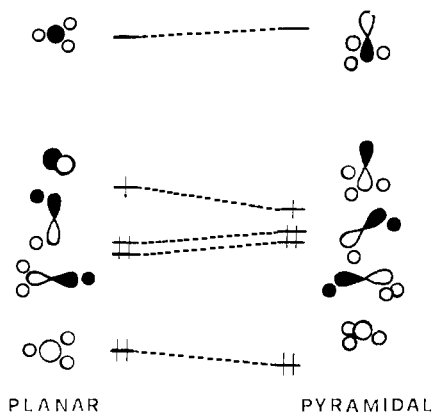


Figure 1. The correlation diagram of the CH_3 radical in the planar and pyramidal conformations.

GMO's in $\dot{\text{C}}\text{H}_2\text{F}$, $\dot{\text{C}}\text{HF}_2$, and $\dot{\text{C}}\text{F}_3$ are shown in Figure 2. Because of symmetry, the $\text{C } p_z$ AO can only interact with the lowest symmetric fluorine GMO in all three systems (Figure 3). A key point is that, as more fluorines are added to the methyl radicals, the lowest symmetric fluorine GMO decreases in energy.

We are now prepared to consider in some detail the interaction of a singly occupied $\text{C } p_z$ AO and the lowest symmetric GMO. In doing so, we shall make use of well-known results of OEMO theory. The stabilization energy (SE) resulting from the interaction of two nondegenerate MO's, ϕ_i and ϕ_j , is given by⁸ the equation

$$\text{SE} = \frac{m(H_{ij} - E_i S_{ij})^2 - n(H_{ij} - E_j S_{ij})^2}{\Delta E} \quad (1)$$

Here m and n are the number of electrons in ϕ_i and ϕ_j , respectively, H_{ij} is the off-diagonal matrix element, E_i and E_j are the unperturbed energies of ϕ_i and ϕ_j , respectively, S_{ij} is the overlap integral between ϕ_i and ϕ_j , and ΔE equals $E_i - E_j$. We now make the Wolfsberg-Helmholz approximation for the matrix element.⁹

$$H_{ij} = K S_{ij} \left[K = \frac{1.75}{2} (H_{ii} + H_{jj}) \right] \quad (2)$$

Thus, eq 1 reduces to

$$\text{SE} = \frac{[m(K - E_i)^2 - n(K - E_j)^2] S_{ij}^2}{\Delta E} \quad (3)$$

Returning to the case at hand, we find that three quantities must be determined if eq 3 is to be solved, i.e., S_{ij} , E_i , E_j . The overlap integral for the CH_2F radical is a simple overlap integral of two AOs.¹⁰ The overlap integral between the lowest symmetrical fluorine GMO in $\dot{\text{C}}\text{HF}_2$ (i.e., ψ_1') and the $\text{C } p_z$ AO is given by eq 4. Finally, the overlap integral between the lowest symmetric GMO in CF_3 (i.e., ψ_1'') and the $\text{C } p_z$ AO is given by eq 5.

$$\langle \text{C}_{p_z} | a_1 \text{F}_{p_z} + a_2 \text{F}_{p_z} \rangle = 2a_1 \langle \text{C}_{p_z} | \text{F}_{p_z} \rangle \quad (4)$$

$$\langle \text{C}_{p_z} | b_1 \text{F}_{p_z} + b_2 \text{F}_{p_z} + b_3 \text{F}_{p_z} \rangle = 3b_1 \langle \text{C}_{p_z} | \text{F}_{p_z} \rangle \quad (5)$$

The coefficients for the fluorine GMO's were determined from extended Hückel¹¹ (EH) calculations of the appropriate number of HF's in the appropriate geometry. The calculated overlap integrals are shown in Table I.

The energy of the singly occupied p_z AO in the methyl radical has been determined experimentally as 0.360 au.² The energies of the fluorine GMO's were obtained from the EH calculations of the appropriate number of HF's. Subsequently, the energy of the lone-pair F p AO was adjusted to the experimental ionization potential of HF which is 0.580 au.¹² Next,

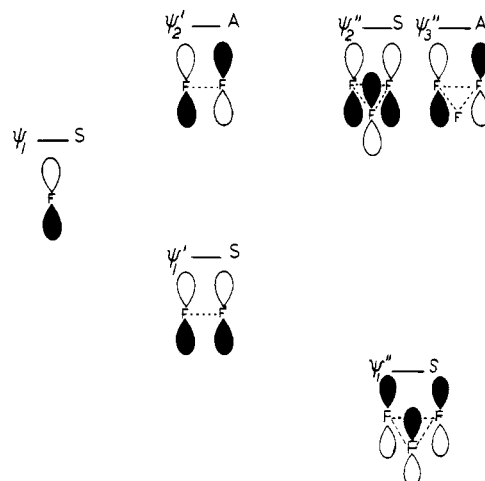


Figure 2. Group MO's for HF, 2(HF), and 3(HF) as the fluorines appear in planar CH_2F , CHF_2 , and CF_3 . Note the progressive lowering of the lowest symmetric group MO.

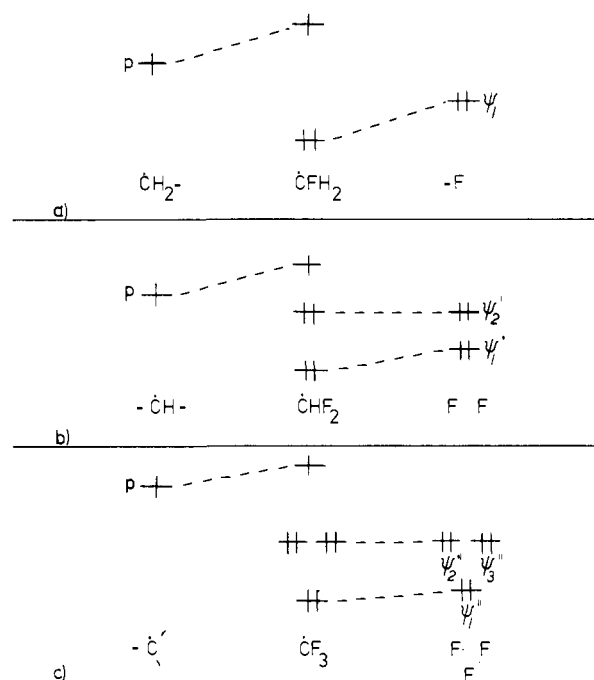


Figure 3. Interaction diagrams for (a) CH_2F , (b) CHF_2 , and (c) CF_3 . Note the widening energy gap between the carbon singly occupied p_z AO and the lowest symmetric fluorine group MO.

the fluorine GMO's for $\dot{\text{C}}\text{HF}_2$ and $\dot{\text{C}}\text{F}_3$ were adjusted by the same amount. These "experimentally adjusted" energies are shown in Table I.

Using these values, the stabilization energies can be calculated. These are shown in Table II.

The same calculations were repeated for the nonplanar radicals. All calculations were done assuming a tetrahedral geometry about the carbon with standard bond lengths and angles.¹³ The overlap integral in the CH_2F case is the overlap integral between and sp^3 AO and a p_z AO,¹⁴ given by eq 6.

$$\begin{aligned} \langle \text{C}_{\text{sp}^3} | \text{F}_{p_z} \rangle &= \left\langle \frac{1}{2} \left(\text{C}_s - \frac{1}{\sqrt{3}} \text{C}_{p_x} + \frac{2\sqrt{2}}{\sqrt{3}} \text{C}_{p_z} \right) \middle| \text{F}_{p_z} \right\rangle \\ &= \frac{\sqrt{2}}{\sqrt{3}} \langle \text{C}_{p_z} | \text{F}_{p_z} \rangle \quad (6) \end{aligned}$$

The energy of the singly occupied $\text{C } \text{sp}^3$ AO has been estimated in the following way. EH calculations were performed on both the planar and tetrahedral methyl radical. The eigenvalue for

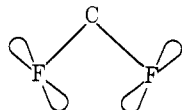
Table I. Unperturbed Energies and Overlap Integrals for $\dot{\text{C}}\text{H}_2\text{F}$, $\dot{\text{C}}\text{HF}_2$, and $\dot{\text{C}}\text{F}_3^a$

| Orbital energies, au ^b | Planar geometry | Tetrahedral geometry |
|---|-----------------|----------------------|
| C 2p _z | -0.360 | |
| C sp ³ | | -0.457 |
| F ₁ LOGMO | -0.580 | -0.580 |
| F ₂ LOGMO | -0.585 | -0.628 |
| F ₃ LOGMO | -0.591 | -0.662 |
| Overlap integrals | | |
| C 2p _z -F ₁ LOGMO | 0.1265 | |
| -F ₂ LOGMO | 0.1784 | |
| -F ₃ LOGMO | 0.2180 | |
| C sp ³ -F ₁ LOGMO | | 0.1032 |
| -F ₂ LOGMO | | 0.1422 |
| -F ₃ LOGMO | | 0.1742 |

^a LOGMO = lowest occupied GMO (see Figure 2). ^b The adjustment of the computed orbital energies to the experimental ones was done by adding the difference between the negative value of the experimental ionization potential and the computed energy of the C 2p_z AO to the computed energy of the C sp³ AO. The same principle was applied to the adjustment of the fluorine LOGMO's energies, using the energy difference between the HF lone pair ionization potential and its computed energy as the adjustment factor.

the C p_z AO in the planar radical was adjusted to the experimental value. The same adjustment was then applied to the singly occupied sp³ AO in the tetrahedral radical.

The energies and coefficients of the fluorine GMO's in tetrahedral $\dot{\text{C}}\text{HF}_2$ and $\dot{\text{C}}\text{F}_3$ can be easily calculated realizing that the F p_z AO's in these radicals are no longer parallel but rather "lean" toward each other. However, by using known trigono-



metric relationships, one can calculate the overlap integral between nonparallel fluorine 2p AO's.¹⁵ This situation can then be simulated by a parallel F p_z AO's placed at a distance such that they produce the same overlap integral. This calculation yields the coefficients needed to calculate the overlap integral between the fluorine GMO's and the C sp³ AO and also the energies of the GMO's which are adjusted to experimental data as previously done for the planar cases. The calculated quantities are shown in Table I.

The calculated interaction energies, as well as the difference between the interaction energies due to π -type conjugation in the planar and tetrahedral systems, are shown in Table II. It can be seen that, in all cases, the tetrahedral forms are more stable and the preference increases as the number of fluorine atoms increases. These trends result from the fact that the interaction between a filled MO and a singly occupied MO is not always stabilizing as illustrated in Figure 4. Two important trends can be noted.

(a) For each value of the overlap integral, S_{ij} , between the interacting singly occupied and doubly occupied MO's, the interaction energy becomes less stabilizing and eventually destabilizing as the energy gap, ΔE , between the MO's increases.

(b) For a given value of ΔE the interaction energy becomes less stabilizing as the overlap integral, S_{ij} , increases. For $\Delta E > 0.1$ au, the system is increasingly destabilized as the overlap integral, S_{ij} , increases.

With these trends in mind, one can immediately understand why the three-electron π -conjugative interaction creates a preference for the tetrahedral form. Furthermore, by consulting Table I, we find that as we move along the series from $\dot{\text{C}}\text{H}_2\text{F}$ to $\dot{\text{C}}\text{F}_3$, $S_{ij}(\text{planar}) - S_{ij}(\text{pyramidal})$ increases and

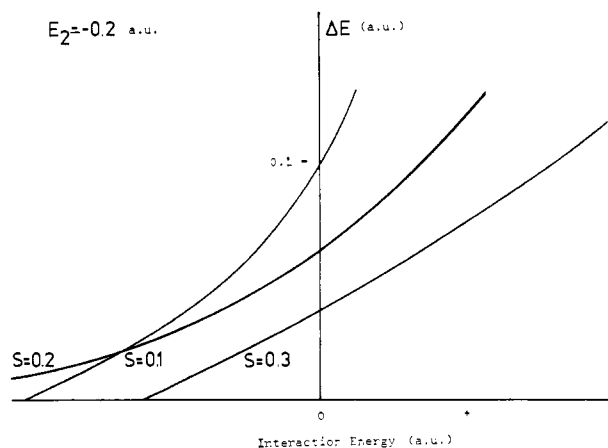


Figure 4. Plot of interaction energy vs. the energy gap (ΔE) between the interacting MO's. The orbital held constant at $E_2 = 0.2$ au is singly occupied while the other orbital which is varied in energy from -0.2 to -0.6 au is doubly occupied. A negative value of the interaction energy indicates a stabilizing interaction, whereas a positive value indicates a destabilizing interaction. The interaction energy is computed by solving the secular equations for the two-orbital interaction problem.

becomes responsible for the observed trend in the calculated interaction energies.

Ab Initio Results

In this section, we report the results of an initio investigation of the radicals $\dot{\text{C}}\text{H}_2\text{F}$, $\dot{\text{C}}\text{HF}_2$, and $\dot{\text{C}}\text{F}_3$, where computations have been performed with the purpose of testing the previous OEMO analysis. The ab initio results have been obtained using an unrestricted Hartree-Fock procedure and all computations have been carried out at the 4-31G¹⁶ level using the Gaussian 70 series of programs.¹⁷ The results are given in Table III. In the case of $\dot{\text{C}}\text{HF}_2$, we have first fully optimized the geometry for the planar conformation. In the subsequent computations, we have kept constant the C-H bond length at the computed value and we have reoptimized $r(\text{C-F})$ and $\angle\text{FCF}$ for various values of the angle α (in particular, $\alpha = 35, 40,$ and 45°). The angle $(180 - \alpha)$ is the angle between the C-H bond axis and the bisector of the FCF angle. Interpolation with respect to α of the energy values leads to an optimum α value at 42° . We have also interpolated the values of $r(\text{C-F})$ and $\angle\text{FCF}$ corresponding to $\alpha = 42^\circ$ and, using these geometric parameters, we have recomputed the energy. For $\dot{\text{C}}\text{F}_3$, we have first optimized the planar structure and then the pyramidal one. The final results clearly show that, when hydrogens are successively replaced by fluorines, the radical becomes more pyramidal and the inversion barrier increases very significantly. These results are in agreement with the experimental ESR evidence¹⁸ and also with a previous CNDO investigation.¹⁹ The excellent agreement between the experimental and computed values of α and $\angle\text{FCF}$ in $\dot{\text{C}}\text{F}_3$ (see Table III) should also be noted.

Table IV lists the overlap populations of the C-F bond for the various radicals in the planar and pyramidal conformations. The following points are of interest: (a) The π overlap population of the C-F bond is negative; i.e., the π component of the C-F bond in all three radicals has antibonding character.²⁰ (b) The C-F π antibonding character is reduced through pyramidalization. Therefore, the ab initio results suggest that a π conjugative effect is operative; i.e., the interaction between the fluorine GMO's and the singly occupied MO is destabilizing in these radicals and pyramidalization reduces destabilization.

In addition, the ab initio results suggest that the inductive effects play an important role acting in the same direction of the conjugative effects. As we have already discussed, there is an increase of positive charge on carbon and negative charge

Table II. Interaction Energies (in au) for Planar and Tetrahedral $\dot{\text{C}}\text{H}_2\text{F}$, $\dot{\text{C}}\text{HF}_2$, and $\dot{\text{C}}\text{F}_3$ ^a

| $\dot{\text{C}}\text{H}_2\text{F}$ | | | $\dot{\text{C}}\text{HF}_2$ | | | $\dot{\text{C}}\text{F}_3$ | | |
|------------------------------------|---------|------------------|-----------------------------|---------|------------------|----------------------------|---------|------------------|
| p | t | p-t ^b | p | t | p-t ^b | p | t | p-t ^b |
| +0.0070 | -0.0010 | +0.0080 | +0.0143 | +0.0055 | +0.0088 | +0.0219 | +0.0122 | +0.0097 |

^a Interaction energy is negative if the interaction results in stabilization of the system. t = tetrahedral, p = planar. ^b p-t denotes the interaction energy difference between the planar and the tetrahedral forms.

Table III. Computed Energies (*E*) and Geometric Parameters^a for the Planar and Optimum Conformations of $\dot{\text{C}}\text{H}_2\text{F}$, $\dot{\text{C}}\text{HF}_2$, and $\dot{\text{C}}\text{F}_3$

| Radicals | α | <i>E</i> | <i>r</i> (C-F) | <i>r</i> (C-H) | $\angle\text{HCH}$ | $\angle\text{FCF}$ | Rel energy |
|--------------------------------------|-------------------------|------------|-------------------------------|--------------------|-------------------------------|-------------------------------|------------|
| $\dot{\text{C}}\text{H}_2\text{F}^b$ | 0.0 | -138.22558 | 1.370 | 1.070 ^d | 127.5 | | 0.00 |
| | 29.0 | -138.22639 | 1.374 (1.318) ^e | 1.070 ^d | 123.0 (113.1) ^e | | -0.51 |
| $\dot{\text{C}}\text{HF}_2$ | 0.0 | -236.94839 | 1.345 | 1.059 | | 114.9 | 0.00 |
| | 42.0 | -236.95924 | 1.351 (1.284) ^e | 1.059 ^c | | 111.7 (138.7) ^e | -6.81 |
| $\dot{\text{C}}\text{F}_3$ | 0.0 | -335.65451 | 1.332 | | | 120.0 | 0.00 |
| | 49.0, 49.5 ^d | -335.69452 | 1.336 (1.288) ^e | | | 111.7 | -25.11 |
| | (0.0) ^e | | | | 01111.1 ^d | (120) ^e | |

^a Bond lengths in Å, bond angles in deg, energies in au, and relative energies in kcal/mol. ^b Taken from ref 7. ^c Not reoptimized. ^d Experimental values (from ref 17). ^e MINDO/3 calculations (from ref 25).

Table IV. Total and π Overlap Population (OP) of the C-F Bond in the Planar and Optimum Conformations of $\dot{\text{C}}\text{H}_2\text{F}$, $\dot{\text{C}}\text{HF}_2$, and $\dot{\text{C}}\text{F}_3$

| | α , deg | Total OP ^a | π OP ^a |
|------------------------------------|----------------|-----------------------|-----------------------|
| $\dot{\text{C}}\text{H}_2\text{F}$ | 0.0 | 0.2857 | -0.0409 |
| | 29.0 | 0.2745 | -0.0289 |
| $\dot{\text{C}}\text{HF}_2$ | 0.0 | 0.3201 | -0.0484 |
| | 42.0 | 0.2846 | -0.0008 |
| $\dot{\text{C}}\text{F}_3$ | 0.0 | 0.3509 | -0.0446 |
| | 49.0 | 0.2974 | +0.0391 |

^a Per C-F bond.

on fluorine as pyramidalization occurs as a result of charge transfer from the carbon singly occupied AO to the $\sigma^*\text{CF}$ MO. Hence, a decrease in the covalent character of the C-F bond is expected. The latter effect is reflected in the decrease of the total overlap populations of the C-F bond (see Table IV) while the predicted charge variation is confirmed by the ab initio values listed in Table V.

The relative importance of the inductive and conjugative effects can also be assessed from the ab initio computational data. Thus, if the conjugative effect dominated, the direction of charge transfer would be from fluorine to the central carbon and, since the π -conjugative interaction is destabilizing, the C-F bond total overlap population would increase upon pyramidalization. The opposite trends are predicted for the case of dominance of the inductive effect as a result of $\text{C } p_z \rightarrow \sigma^*\text{CF}$ charge transfer. On the basis of the ab initio computations, we suggest that this latter effect is primarily responsible for the conformational trends observed in the $\dot{\text{C}}\text{X}_3$, $\dot{\text{C}}\text{X}_2\text{H}$, and $\dot{\text{C}}\text{XH}_2$ series, where X is an inductively electron-withdrawing group containing a first period heteroatom.

The conclusions reached in this work, namely, that the increase in pyramidalization along the series $\dot{\text{C}}\text{H}_2\text{F}$, $\dot{\text{C}}\text{HF}_2$, and $\dot{\text{C}}\text{F}_3$ is due to a combination of inductive and conjugative effects involving a two-orbital three-electron interaction, are in contrast to recent proposals by Dewar and Bingham.^{21,22} In their analysis, the π MO's of $\dot{\text{C}}\text{HXY}$, where X and Y are substituents with lone pairs (or σ bonds) are constructed in steps by successive union of $\text{H}-\dot{\text{C}}<$ with X and Y.²² On the basis of the MO interactions it is argued that four-electron conjugative

Table V. Gross Atomic Charges in the Planar and Optimum Conformations of $\dot{\text{C}}\text{H}_2\text{F}$, $\dot{\text{C}}\text{HF}_2$, and $\dot{\text{C}}\text{F}_3$

| | α , deg | C | F | H |
|------------------------------------|----------------|---------|---------|---------|
| $\dot{\text{C}}\text{H}_2\text{F}$ | 0.0 | +0.0774 | -0.4282 | +0.1754 |
| | 29.0 | +0.1022 | -0.4345 | +0.1661 |
| $\dot{\text{C}}\text{HF}_2$ | 0.0 | +0.5765 | -0.4018 | +0.2271 |
| | 42.0 | +0.6366 | -0.4143 | +0.1919 |
| $\dot{\text{C}}\text{F}_3$ | 0.0 | +1.0877 | -0.3626 | |
| | 49.0 | +1.1545 | -0.3848 | |

destabilization leads to "antagonism" between the substituents and enforces pyramidalization of the system. However, the discussion of the conjugative destabilization is based on two incorrect assumptions.

(1) The interaction between a singly occupied and a filled orbital results in stabilization, the magnitude of which increases as the overlap between the interacting orbitals increases. By contrast, we have shown that firstly, three-electron two-orbital interaction may be either stabilizing or destabilizing, and, secondly, the interaction becomes more destabilizing (or less stabilizing) as the overlap between the interacting MO's increases (see Table II and Figure 4).

(2) The destabilizing interaction of two filled orbitals increases as their energy separation decreases.²² This is at variance with the well-known equation²³ according to which overlap repulsion does not depend on the energy separation of the two interacting MO's, but rather on the average of their energies. Thus, situation A is more destabilizing than B although the energy separation of the latter is smaller.



In summary, the Dewar-Bingham's model^{21,22} is not theoretically sound and, thus, cannot serve as a reliable model for interpretation of experimental data.²⁴ From the computational standpoint, a comparison of the ab initio and MINDO/3 results²⁵ regarding the structure of the three radicals $\dot{\text{C}}\text{H}_2\text{F}$, $\dot{\text{C}}\text{HF}_2$, and $\dot{\text{C}}\text{F}_3$ is interesting. The predicted bond lengths and bond angles are shown in Table III. It is clear that the

MINDO/3 method predicts abnormally short C-F bonds and planar geometries for radicals known to be pyramidal. The latter trend may be an indirect consequence of the former. We conclude that the ab initio methods used in this work are more reliable for studying open-shell systems such as organic radicals.

It should be pointed out that ZDO methods may be inappropriate for studying problems where overlap repulsion plays a key role.^{26,27}

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Correlation between Exothermicity, Rate, and Negative Temperature Dependence in Slow Ion-Molecule Reactions

M. Meot-Ner (Mautner)* and F. H. Field*

Contribution from The Rockefeller University, New York, New York 10021.

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Abstract: The rate constants (k_{450}) of 22 H^- transfer reactions between C_2 - C_7 carbonium ions and C_3 - C_{10} cyclic and acyclic hydrocarbons were measured. The values of k_{450} range between 2.2×10^{-9} and $3 \times 10^{-13} \text{ cm}^3/\text{mol}\cdot\text{s}$, corresponding to collision efficiencies of approximately 1 to 10^{-4} . The rate constants exhibit large negative temperature coefficients of the form $k = AT^{-n}$, $n = 1.5$ -6.8. A direct relation between k_{450} and exothermicity is observed. An inverse linear correlation between $\ln k_{450}$ and the magnitude of the negative temperature coefficient (n) is also noted.

Introduction

The kinetics of slow hydride ion transfer reactions between carbonium ions and hydrocarbons were investigated in our laboratory in the past 3 years.^{1,2} In the course of our studies we observed that exothermic H^- transfer reactions exhibit unusually large negative temperature coefficients of the functional form $k = CT^{-n}$, $n = 1.5$ -5.4. It was demonstrated that activation energy is absent in one of the reactions, and it is plausibly absent in the remainder of these exothermic ion-molecule processes. In the present paper we shall discuss new observations concerning a correlation between the rate constants and the exothermicities of the transfer reactions. Another correlation of interest which we observed in H^- transfer reactions is the relation between the rate constants and their temperature coefficients. The present correlations are based on the kinetic data concerning 22 H^- transfer reactions. These data were obtained in part in previous work² and in part as the

result of new measurements which were executed in order to enlarge the data set which is the basis for the present correlations.

Experimental Section

The present work was carried out by pulsed, high-pressure mass spectrometry on The Rockefeller University Chemical Physics Mass Spectrometer. The experimental techniques used were identical with those described in previous publications.^{1,2} The hydrocarbons used were obtained from Chemical Samples Co., were of purity >98%, and were used without further purification.

Results

In this paper we present relations between rates, temperature coefficients, exothermicities, and structure for reactions between $C_2H_5^+$, *sec*- $C_3H_7^+$, and *t*- $C_4H_9^+$ and C_2 - C_7 hydrocarbons, for which kinetic data were obtained in the course of previous studies.⁷ In addition, we performed measurements