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ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY · OCTOBER 1985

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the measured atmospheric lifetime of $\text{NO}_3^{3,4,7}$ and that expected from the sequence of reactions 1 and 2 is not due to errors in the previous measurements of these parameters, and that the NO_3 is certainly scavenged. Neither does it seem that the scavenging is due to reaction with any of the other molecules studied here. Platt et al.³ estimate that a rate coefficient of the order of $1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ with CO would be required to reduce the NO_3 lifetime to that observed. The upper limits observed for the reaction of NO_3 with CO, H_2O_2 , and SO_2 are two slow for these reactions to explain the atmospheric scavenging of NO_3 and are also in accord with preliminary data reported by Noxon^{4,7} and Calvert.³⁴

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In conclusion we report here a study of the NO_3 spectrum and a direct study of some reactions of NO_3 using a new modulated photolysis apparatus designed to measure small optical density changes from 200 to 700 nm. F_2 has been used as a photolytic source of free radicals and the results obtained confirm the anticipated high reactivity of NO_3 with other free radicals.

Acknowledgment. The authors thank W. Schneider, who wrote the programs to control the signal averager and process the data, and G. Schuster, who provided valuable technical assistance. Thanks go also to D. W. T. Griffith and D. Perner for useful discussions during the course of the work. The work was supported in part by the Deutsche Forschungsgemeinschaft through the Middle Atmosphere Program and the Max Planck Gesellschaft.

Registry No. SO_2 , 7446-09-5; CO, 630-08-0; CH_4 , 74-82-8; H_2O_2 , 7722-84-1; CS_2 , 75-15-0; NO_2 , 10102-44-0; NO_3 , 12033-49-7; N_2O_5 , 10102-03-1; Cl_2 , 7782-50-5.

Theoretical Analysis of Radical Addition Reactions: On the Anomalous Behavior of CH_3 toward Fluoro-Substituted Olefins

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Although radicals usually attack the less substituted site of olefins, CH_3 adds to the more substituted end of $\text{CF}_2=\text{CFH}$. A theoretical study of this anomalous reaction as well as the addition of CH_3 to $\text{CH}_2=\text{CHF}$, which conforms to the normal orientation rule, has been done by means of UHF 3-21G calculations. In contrast with semiempirical results (MNDO), the ab initio calculations are found to account correctly for the experimental facts. The energy barriers have been analyzed by means of the energy partitioning proposed by Morokuma. From these results and a comparison with available data on fluoro-substituted ethanes the origin of the anomalous regioselectivity in the reaction of CH_3 with $\text{CF}_2=\text{CFH}$ is rationalized.

Simple as they seem to be, radical addition reactions have provided a seemingly endless series of surprising results.¹ Among them, those concerning the regioselectivity of the reaction are still not well understood. Several effects are apparently in competition along the reaction, and the final result is difficult to predict. Thus Tedder^{1c} and Giese^{1f} have independently proposed sets of five different rules to predict the outcome of these reactions. The picture remaining after these works, summarizing more than 20 years of experimental effort, is that bond strength, polarity, and steric effects compete in a rather complex way. It is not surprising that a simple rule could not be formulated. In passing, let us note that a similar situation has been found in the case of intramolecular addition reactions.^{1c} There, in addition, the entropic effects can also play a substantial role.

Although many theoretical studies on these reactions have been reported²⁻³⁵ the regioselectivity problem has not been frequently faced by theoreticians.²⁹⁻³⁵ Using a three-center three-electron valence bond approach Salem and co-workers³⁰ pointed out the importance of the relative electronegativity of the reaction partners in determining the orientation ratio of the reaction. More recently,^{32,33} application of the Morokuma energy decomposition analysis³⁶ to this problem led to the suggestion³² that the deformation energy of the reactants to attain the transition-state structure (DEF) is a good index for the regioselectivity. Nevertheless the generality of this proposal cannot be considered

conclusive as will be discussed later. Moreover, since the DEF term can only be obtained after determination of the transition-

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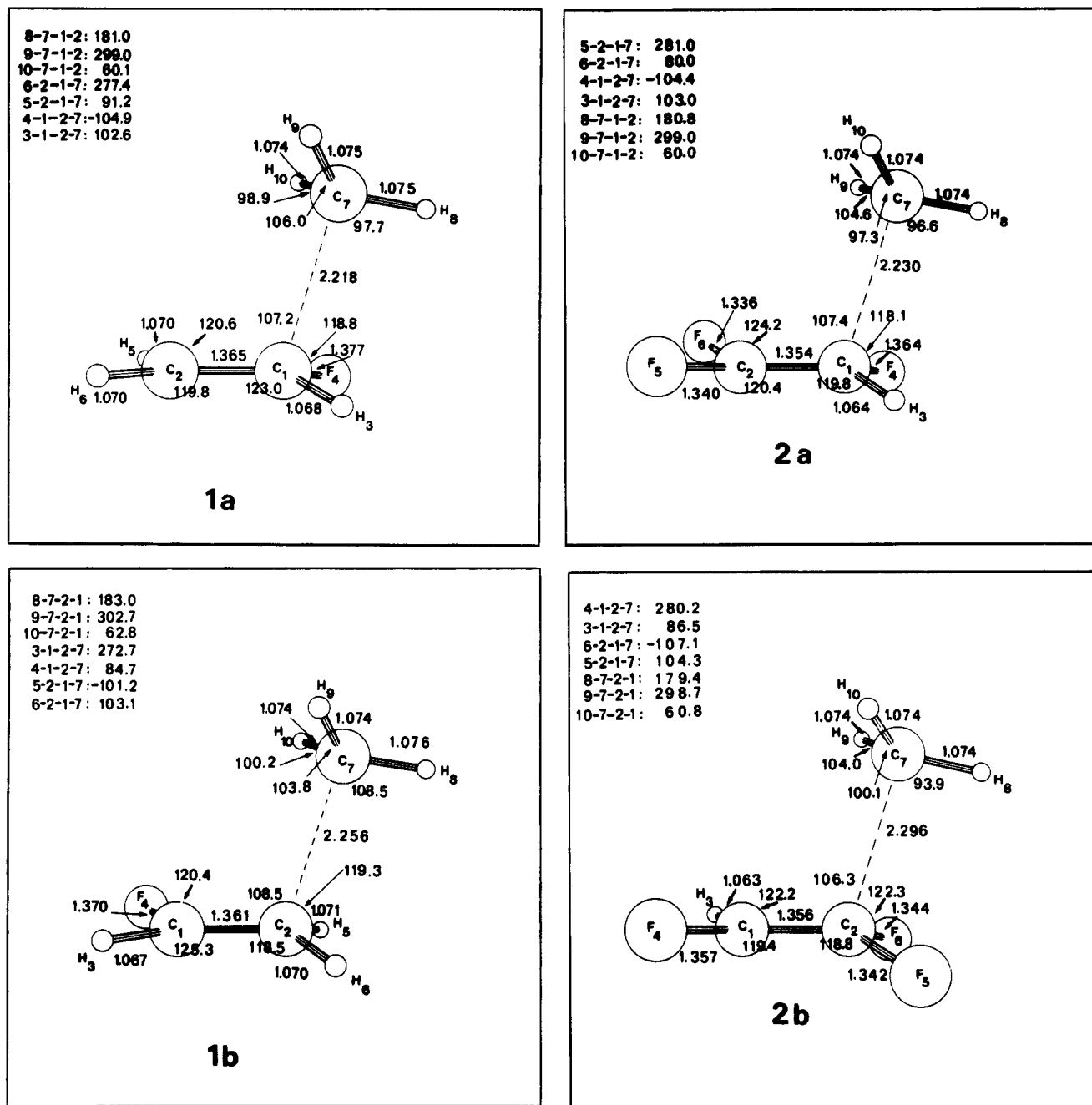


Figure 1. Transition-state structures for the additions of CH_3 to $\text{CH}_2=\text{CHF}$ and $\text{CF}_2=\text{CHF}$.

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We have been recently interested in different aspects of inter and intramolecular additions.^{27-29,35a} Contrary to early proposals² we suggested that the SOMO-HOMO interaction was the main orbital interaction on going from the reactants to the transition state.²⁹ As the transition states are found to be very early along the reaction coordinate, the three-electron interaction (which in principle could be attractive or repulsive³⁷) is attractive and the addition will happen at the carbon with the greater HOMO coefficient. It follows²⁹ that the addition will be preferentially done at the less substituted carbon of the olefin.

This simple rule, which was based on the analysis of a series of potential energy surfaces, has an obvious limitation: the nature

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of the attacking radical is not explicitly considered. However, the experimental facts for the most part substantiate it suggesting that the main electronic events of the reaction have been captured by the rule. A careful analysis of its few exceptions should clarify its limitations and point toward a simple understanding of this problem.

The methyl radical shows an anomalous behavior in its additions to fluoro-substituted ethylenes.³⁸ The attack is at the less substituted carbon of fluoroethylene, as should be predicted from the simple rule, but at the more substituted one in trifluoroethylene. In contrast, other radicals like CF_3 ,³⁹ CCl_3 ,⁴⁰ or H^{41} attack the less substituted carbon in both cases, again in agreement with the rule.

It could be argued that the failure of the rule in the $\text{CH}_3 + \text{CF}_2=\text{CFH}$ reaction is due to an increase of the SOMO-LUMO interaction which overrides the effect of the SOMO-HOMO one. This interpretation cannot be correct because both experimental ionization potentials and theoretical calculations⁴² place the SOMO of CCl_3 higher than that of CH_3 so that the reversal of regioselectivity should be even higher in this case contrary to experiment. Steric effects cannot explain this result any better. What is then the reason for the anomalous behavior of CH_3 toward trifluoroethylene?

We initially studied this problem by using the MNDO semiempirical method⁴³ to determine the structure of reactants, products, and transition states of the reactions of CH_3 with $\text{CF}_2=\text{CFH}$ and $\text{CH}_2=\text{CFH}$. The geometries were optimized without any geometrical restriction. The use of a semiempirical method seemed justified by the excellent results we previously obtained using the MINDO/3 method.^{27,28,35a} Activation energies and kinetic isotope effects for intermolecular additions were very well reproduced showing that both the relative energies of reactants and transition states and the curvature of the potential surface at these points were well accounted for. Since the well-known problems in the MINDO/3 parameterization of halogen atoms have been claimed⁴⁴ to be overcome in the MNDO parameterization we initially chose this method. The disappointing result was that CH_3 is predicted to attack the less substituted carbon in both fluoro- and trifluoroethylene.

However the energetics of the reactions was reconsidered by using split valence-shell ab initio calculations on the MNDO optimized structures. The results were found to reproduce the experimental information. We concluded that a meaningful analysis could only be done from the ab initio potential energy surfaces for these processes. In this paper we present these ab initio calculations for the addition of CH_3 to $\text{CH}_2=\text{CHF}$ and $\text{CF}_2=\text{CHF}$ and comment on the origin of the exceptions to the SOMO-HOMO rule.

Method of Calculation

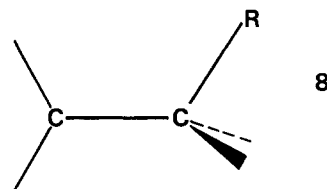
UHF ab initio calculations were carried out with the GAUSSIAN 80,⁴⁵ MONSTERGAUSS,^{46a} and HONDOS^{46b} series of programs using a split-valence 3-21G basis set.⁴⁷ Optimizations were carried out by a gradient procedure without any restriction unless otherwise stated. Single-point 6-31G* calculations⁴⁸ were done for

the stationary points of the 3-21G potential energy surfaces. Although use of a spin-unrestricted wave function suffers from the theoretical objection that it is not an eigenfunction of the total spin angular momentum operator S^2 , this problem did not raise any difficulties in the present calculations.

The UHF 3-21G activation energies (ΔE) were analyzed according to the Morokuma energy partitioning.³⁶ The activation energy is partitioned into energy deformation (DEF) and interaction (INT) terms. The DEF term is the energy difference of the reactants at the transition state and equilibrium geometries. The interaction term (INT) is partitioned into electrostatic (ES), exchange (EX), polarization (PL), and charge-transfer (CT) contributions. A mixing term (MIX) accounts for the coupling of the four previous contributions.

Results and Discussion

The computed 3-21G transition-state geometries for the addition of CH_3 to $\text{CH}_2=\text{CHF}$ and $\text{CF}_2=\text{CHF}$ are shown in Figure 1. These geometries have been obtained without any geometrical restriction. The geometries of reactants and products for both reactions are shown in Figures 2 and 3. Some preliminary calculations for $\text{CFHCH}_2\text{CH}_3$ showed that the coupling of the CHF rotation and pyramidalization results in a fairly flat energy surface for these motions. This is not surprising in view of past experience.⁴⁹⁻⁵² It is well-known that the staggered conformation **8** is the most stable one for β -substituted ethyl radicals with



first-row substituents.⁵³⁻⁵⁵ As this conformation was found to be one of the minima on the $\text{CHFCH}_2\text{CH}_3$ surface we have optimized the product structures with the arbitrary assumption of a staggered conformation. Although lower minima can exist, the energy difference will be small and will have a minor effect on the comparison of the two possible products. Let us note that because of the presence of fluorines, the lowest energy structure will probably have a gauche type conformation.

The addition at the less substituted carbon of $\text{CH}_2=\text{CHF}$ was found to be preferred by 0.87 kcal/mol (3-21G level). The orientation is calculated to be reversed in the $\text{CF}_2=\text{CFH}$ attack where the more substituted side is preferred by 0.19 kcal/mol (Figure 4). These values not only account correctly for the orientation but are also in fairly good agreement with the actual orientation ratios, 5.00 and 0.52 for $\text{CH}_2=\text{CFH}$ and $\text{CF}_2=\text{CFH}$, respectively.^{1a} The difference in ΔH values is relatively small (1.3 kcal/mol) for the attack at $\text{CH}_2=\text{CHF}$ but quite sizeable in the case of $\text{CF}_2=\text{CFH}$ (10.4 kcal/mol). It is also noteworthy that while the route with the smaller energy barrier corresponds to the greater ΔH in the $\text{CF}_2=\text{CFH}$ attack, this is not the case in the $\text{CH}_2=\text{CHF}$ addition. This fact points toward an increased importance of the product stability control of the reaction in the first case.

Let us start our discussion by considering the transition-state structures. This will give some important clues for understanding the regioselectivity anomalies. Both transition states for the $\text{CH}_3 + \text{CH}_2=\text{CHF}$ additions (**1a**, **1b**) can be considered as early. The

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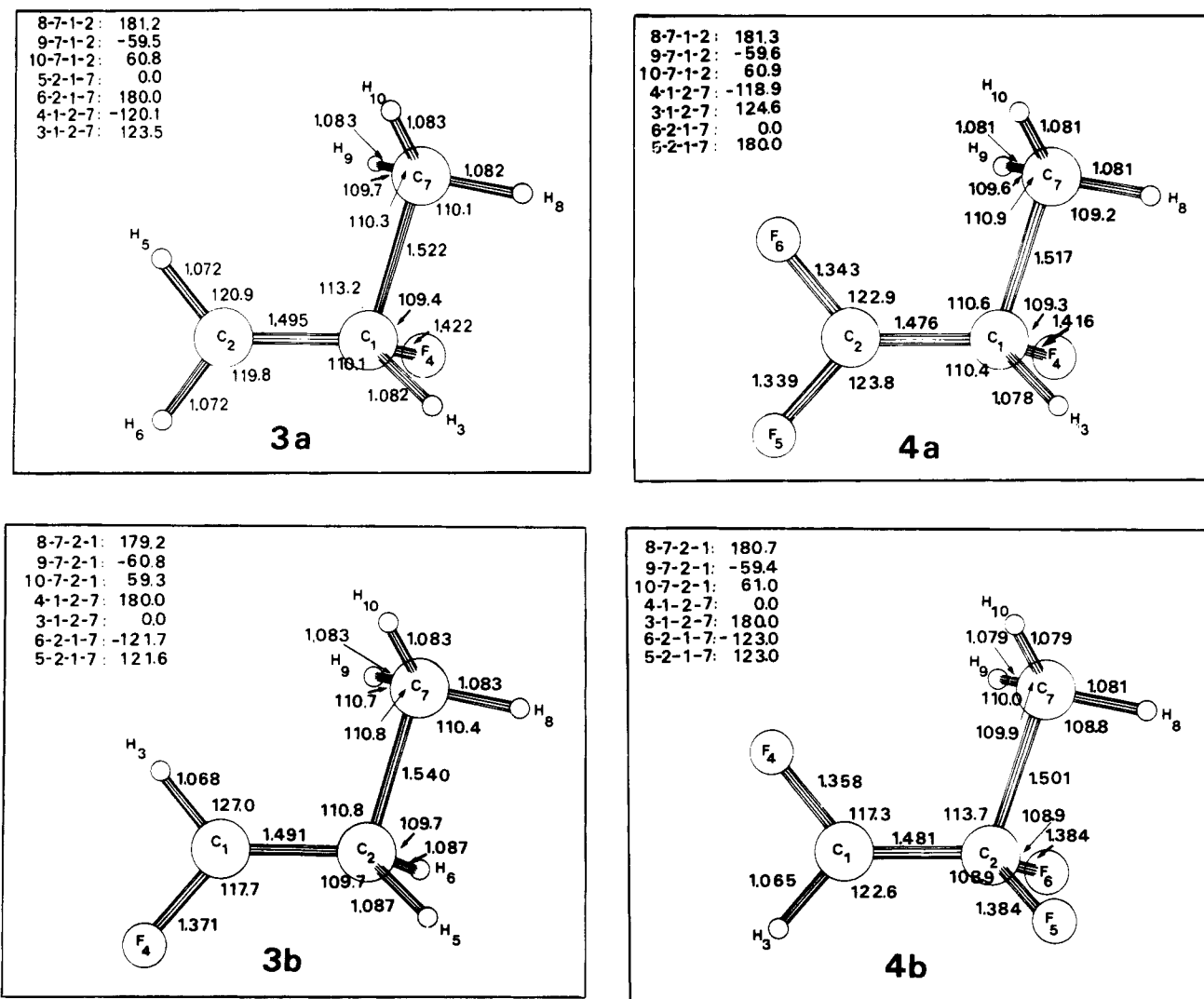


Figure 2. Computed structures for the products of the reactions $\text{CH}_3 + \text{CFH}=\text{CH}_2$ and $\text{CH}_3 + \text{CF}_2=\text{CFH}$.

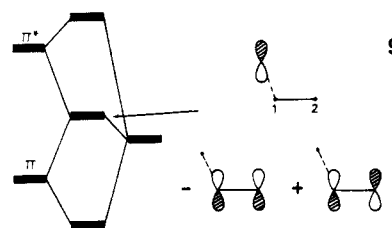
elongation of the olefinic C_1C_2 bond is $\approx 32\%$, and the pyramidalization at the attacked carbon is small with respect to the products in both cases. The nonattacked side remains planar in **1a** and slightly pyramidalizes and rotates in **1b**.

Close examination of the electronic characteristics of the transition states shows a very strong spin polarization of the olefinic bond (0.893 (C_1), -0.818 (C_2) in **1b**; 0.988 (C_2), -0.756 (C_1) in **1a**). Although spin polarization cannot always be equated with bond rupture, these values are suggestive of a considerable weakening of the olefinic $\text{C}-\text{C}$ bond. If the overlap populations are taken as a measure of the bond strength, the C_1-C_2 bond is half broken in both transition states. As we remarked previously^{35a} in our study of intramolecular additions, the disruption of the olefinic bond in the transition state is more important than what is suggested by its geometric structure.

The newly formed $\text{C}-\text{C}$ bond is longer for the addition at the less substituted side (2.256 vs. 2.218 Å). This fact was also observed by Arnaud et al.³³ on the system $\text{H} + \text{CH}_2=\text{CF}_2$, by Delbecq et al.³² on $\text{H} + \text{CH}_2=\text{CHNH}_2$, and by Schlegel and Sosa²¹ on $\text{H} + \text{CH}_2=\text{CHCl}$. By contrast this distance is longer for the hydrogen attack at the more substituted side of $\text{CH}_2=\text{CHBH}_2$.³² These results fit well with the consequences of the HOMO-SOMO interaction rule which, as we have verified from the structure of the transition-state orbitals, is again operative in the $\text{CH}_2=\text{CHF} + \text{CH}_3$ reaction.

The main electronic events of the addition reactions can be appropriately described by considering the interaction of π and π^* of the olefin and the radical orbital. In the initial stage of the reaction, the transfer of radical character from the incoming radical to the nonattacked side of the olefin is described by the

mixing of the α radical orbital with the HOMO (α) and LUMO (α) of the olefin as shown schematically in **9**. This results with



an accumulation of α electron density on carbon 2. In an UHF view this is supplemented with a shift of β electron density in the opposite direction. Only when the accumulation of β electron density in carbon 1 is greater enough the new bond establishes. Obviously, these changes occur gradually along the reaction coordinate.

The sooner the orbital mixing becomes effective, sooner the polarization and accumulation of β electron density at the attacked carbon will start to play its role and the transition state will be reached earlier. Because of the proximity of the levels the SOMO-HOMO interaction is dominating at this stage of the reaction²⁹ and the whole process will be more effective when the radical approaches the carbon with the greater HOMO coefficient. This is why the approach is less costly in energy and the transition state earlier for the attack at the less substituted site of the olefin in the $\text{CH}_3 + \text{CH}_2=\text{CHF}$, $\text{H} + \text{CH}_2=\text{CHCl}$,²¹ $\text{H} + \text{CH}_2=\text{CF}_2$,³³ and $\text{H} + \text{CH}_2=\text{CHNH}_2$ ³² reactions but at the more substituted one in $\text{H} + \text{CH}_2=\text{CHBH}_2$.³²

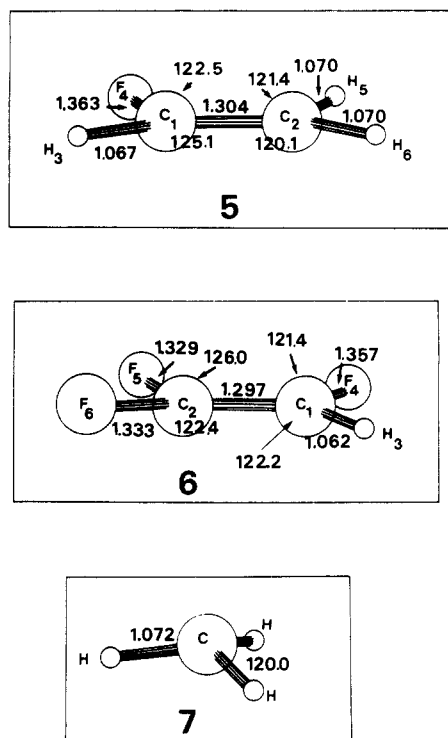


Figure 3. Computed structures for $\text{CF}_2=\text{CFH}$, $\text{CFH}=\text{CH}_2$, and CH_3 .

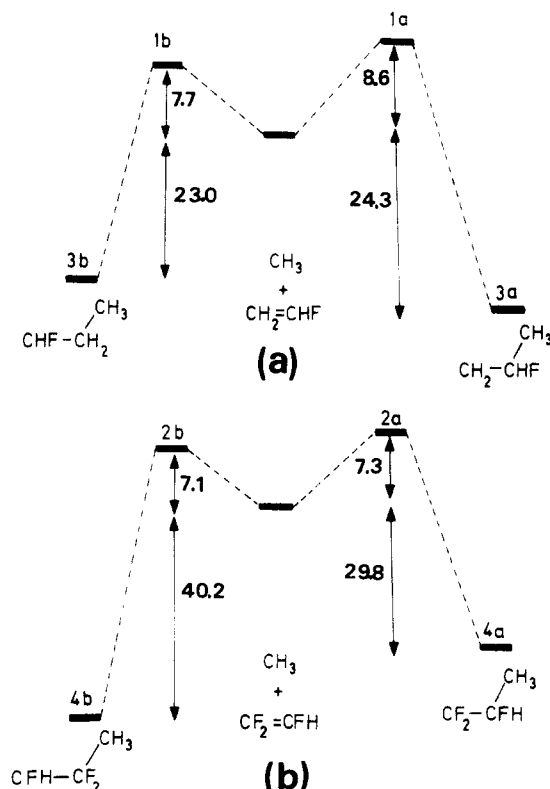


Figure 4. 3-21G energy profiles (kcal/mol) for the methyl radical addition to (a) $\text{CH}_2=\text{CHF}$ and (b) $\text{CF}_2=\text{CFH}$.

The olefinic C-C bond in the $\text{CH}_3 + \text{CF}_2=\text{CFH}$ transition states (2a and 2b) is again 32% broken according to the geometric modifications. From the electronic viewpoint, i.e., changes in the overlap populations, the bonds are 62 and 59% broken for the additions at the less and more substituted sites, respectively. The difference between the geometric and electronic description of the bond breaking is even stronger here. The pyramidalization of the nonattacked center is small but slightly greater for the attack at the less substituted site. The pyramidalization at the attacked carbon is again small with respect to the products.

TABLE I: Energy Partitioning Analysis of the Barrier Heights $\Delta H(3\text{-}21\text{G})^a$ for the Addition of CH_3 to $\text{CH}_2=\text{CHF}$ and $\text{CF}_2=\text{CFH}$

	$\text{CH}_3 + \text{CH}_2=\text{CHF}$		$\text{CH}_3 + \text{CF}_2=\text{CFH}$	
	$\text{CHF}-\text{CH}_2\cdots\text{CH}_3$	$\text{CH}_2-\text{CHF}\cdots\text{CH}_3$	$\text{CFH}-\text{CF}_2\cdots\text{CH}_3$	$\text{CF}_2-\text{CFH}\cdots\text{CH}_3$
ΔE	7.71	8.58	7.08	7.27
DEF	6.74	8.80	10.62	9.05
CH ₃	1.22	1.28	0.84	0.88
olefin	5.52	7.52	9.78	8.17
INT	0.97	-0.22	-3.54	-1.78
ES	-18.15	-20.15	-16.39	-16.68
EX	42.32	46.10	35.30	36.42
PL	-1.00	-1.51	-1.28	-0.97
CT	-11.51	-13.56	-11.10	-10.81
MIX	-10.68	-11.09	-10.05	-9.73

^a Energies in kcal/mol.

The new C---C bond is relatively long. The one corresponding to the attack at the less substituted site is similar to that found in the $\text{CH}_2=\text{CHF}\cdots\text{CH}_3$ transition state. The difference between the two C---C distances (2.230 vs. 2.296 Å) is now nearly twice that found in the $\text{CH}_3 + \text{CH}_2=\text{CHF}$ reactions. In addition, the distance corresponding to the more favorable attack at $\text{CF}_2=\text{CFH}$ is 0.04 Å longer than in the $\text{CH}_2=\text{CHF}$ case indicating an even earlier transition state.

The analysis of the transition states orbitals shows that the SOMO-HOMO interaction continues to be more important than the SOMO-LUMO one. All these facts are clearly telling us that the reversal of the regioselectivity does not find its origin in a violation of the SOMO-HOMO predominant role but in some additional effect strongly stabilizing the incipient C---C bond at the more substituted site.

Before discussing the origin of this extra stabilization it is useful to look at the results of the Morokuma energy partitioning. It is also interesting to note that, judging from the ratio of the distances corresponding to the newly formed bond in the transition state and products, the transition states for the CH_3 additions are later (ratio: 1.45–1.50) than those of the atomic hydrogen (1.72–2.00^{19,32,33}) and earlier than those of halogen atoms (1.31–1.36^{19,21}).

The results for the transition-state energy partitioning for the CH_3 attacks at $\text{CH}_2=\text{CHF}$ and $\text{CF}_2=\text{CFH}$ are shown in Table I. If we bear in mind the previously reported partitioning analyses,^{32,33} some remarks can be immediately made. Firstly, the DEF term is always the more important one. The analysis of this term shows that the CH_3 contribution does not discriminate between the two modes of attack and that the olefin contribution is by far the most important (73–92%). Since in the addition of atoms the DEF term comes exclusively from the olefin, this observation provides some justification for the use of the SOMO-HOMO rule. Essentially the SOMO-HOMO rule indicates which is the best way to prepare (i.e., polarize and accumulate β density at the attacked carbon) the favorable interactions in the transition state, while the DEF term is a quantitative measure of the energetic cost of this preparation. It should be remarked that implicit in the use of the SOMO-HOMO rule is the assumption that the route with the best reactants interaction corresponds also to the easiest reactants preparation. The use of the smallest DEF term as regioselectivity index is a quantitative version of the same assumption. It is to be expected that both approaches will succeed and fail in the same type of situations. Secondly, the DEF term follows the ΔE difference for the $\text{CH}_2=\text{CHF}$ attack but not for the $\text{CF}_2=\text{CFH}$ one! This shows that the DEF term is not better than the SOMO-HOMO rule to rationalize the regioselectivity and confirms the previous comment. Thirdly, in all previously reported analyses^{32,33} the INT term was found to be destabilizing as it is in the $\text{CHF}-\text{CH}_2\cdots\text{CH}_3$ transition state. This can be traced back to the dominance of the exchange repulsion. It is only when one carbon in the incipient C---C bond contains fluorine substituents that the INT term becomes stabilizing. The effect seems to increase with the number of fluorines.

The careful reader will have noticed the close parallelism between this observation and what is known about the C-C bond strength in fluorosubstituted ethanes:⁵⁶ fluorine substituents stabilize the adjacent C-C bond if fluorines accumulate on the same carbon (i.e., 1,1-difluoroethane is stabilized with respect to 1,2-difluoroethane). Thus, judging from the C-C distances, successive replacement of hydrogens by fluorines at one carbon progressively strengthens the C-C bond while progressive substitution at both sides increasingly destabilizes the C-C bond. The rationale for this fact has been discussed by Epiotis, Shaik, and co-workers⁵⁷ from the viewpoint of the linear combination of fragment configurations and can be traced back to the increased role of a charge-transfer configuration with the difference of electron affinities between the two CR_3 fragments.

That this effect is also operative in our case can be inferred from the results of Figure 4. **3a** is found more stable than **3b** and in the same manner **4b** is more stable than **4a** but the difference in the last case is substantially greater. Although to a lesser extent, the same type of stabilizing interactions will affect the transition states **1a-2b** as shown by the results of Table I. In other words, the product stability is not strong enough to reverse the SOMO-HOMO control in the monosubstituted case but finally imposes the orientation ratio in the 1,1 disubstituted one. It should be pointed out that even if other electronegative substituents have the same effect on the ethane stability, the effect is smaller. This fact and the small difference in the activation energies calculated for $CH_3 + CF_2=CFH$ suggest that such regioselectivity reversals will not be commonly found.

In order to test whether our interpretation is basis set dependent we have carried out 6-31G*|| 3-21G calculations for **1-7**. The addition to the less substituted site of $CH_2=CHF$ was found to be preferred by 1.1 kcal/mol (10.5 kcal/mol for **1b** vs. 11.6 kcal/mol for **1a**) and the ΔH values are 24.1 (**3b**) and 27.4 kcal/mol (**3a**). The activation energies for the addition to $CHF=CF_2$ are 9.9 (**2b**) and 9.8 kcal/mol (**2a**) while the ΔH values are 41.1 (**4b**) and 29.9 kcal/mol (**4a**). Except for the reversal of the activation energies in the last case—but in our opinion this is not significant considering the very small energy differences involved and the fact that the transition states have not been reoptimized—the essential features of the 3-21G calculations are all verified.

As we mentioned in the Introduction, the regioselectivity is "normal" for the addition of other radicals like CF_3 , CCl_3 , or H to $CF_2=CFH$. That this has to be this way in the first two cases

is obvious from the previous explanation. The product control outweighs the SOMO-HOMO one in the case of maximum dissymmetry in the substitution. When this dissymmetry is decreased by putting halogens on the attacking radical the region of the HOMO-SOMO control is again reached (and, in fact, the C-C bond in CF_3-CF_3 seems to be less stable than in CH_3-CH_3). From the experimental C-H bond distances⁵⁸ and stretching force constants⁵⁹ for fluoro-substituted methanes, a similar bond-strengthening effect in the H additions will not be operative and consequently, only the HOMO-SOMO control remains. This explains the "normal" orientation in these cases.

In summary, as the result of this and our previous contributions, we suggest that the SOMO-HOMO interaction does control the regioselectivity of the radical additions to substituted olefins. This control can be violated in two cases: (a) when there are geometrical constraints to the interaction as in some intramolecular cases (i.e., the hex-5-enyl radical cyclizations³⁵) and (b) when the substituents can appreciably stabilize the bond to be formed (i.e., in $CH_3 + CF_2=CHF$). Available thermochemical data should allow the prediction of the last ones.^{60,61}

Acknowledgment. We are grateful to Drs. S. Shaik for very fruitful discussions, J. M. Lefour for making available the energy partitioning program, and J. P. Flament for his help in the use of his version of HONDOS. We thank Drs. Nguyen Trong Anh and J. M. Lefour for their comments and for a preprint of their work. We are indebted with Dr. S. Olivella who kindly informed us of their independent work on this problem. We are grateful to the Centre de Calcul Vectoriel pour la Recherche (C.N.R.S.) for a generous allocation of the CRAY computer time.

Registry No. CH_3 , 2229-07-4; $CF_2=CFH$, 359-11-5; $CH_2=CFH$, 75-02-5.

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