Hydrogen Abstraction from Methane and its Fluoro Derivatives by Methyl Radicals

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Hydrogen abstraction from methane and its fluoro derivatives by methyl radicals has been studied by theoretical calculations using the split-valence 3-21G basis set. Electron correlation has been introduced by use of Møller–Plesset perturbation theory up to the second order. The results obtained correctly reproduce the experimental irregular ordering of the energy barriers. The various factors which could be responsible for this ordering are analysed.

Hydrogen-abstraction reactions, in which a hydrogen atom is transferred from a substrate to a radical, are a particular case of free-radical substitution reactions. These processes play an important role in the propagation of many chain reactions of special interest.

In recent years, the relative importance of the various factors (bond strength, polarity, steric effects) which determine the reactivity of free-radical substitution reactions has been considered.[1] At first sight, one might expect that the introduction of polar substituents in the substrate would scarcely affect the reaction rate with neutral radicals. However, this is not confirmed by experimental results.

In the case of hydrogen abstraction from methane and its fluoro derivatives by methyl radicals, the experimental activation energy decreases when one goes from CH_4 to CH_2F_2, but suddenly increases when a third fluorine atom is introduced, the activation barrier for CHF_3 being still somewhat smaller than that corresponding to methane.[1] Rationalization of this irregular ordering is difficult.

Theoretical studies of hydrogen abstraction from methane by several free radicals have been carried out, both by semi-empirical[2-5] and by *ab initio*[3,6,7] methods. However, a complete study of the hydrogen abstraction from its fluoro derivatives has never been undertaken previously. This paper reports such a study, with CH_3 as the free radical, designed to interpret the irregular ordering of the experimental energy barriers.

Table 1. Geometrical parameters[a] of the transition states

	$CH_4 + CH_3$	$CH_3F +$ CH_3	$CH_2F_2 +$ CH_3	$CHF_3 +$ CH_3
R^1	1.356	1.354	1.358	1.381
R^2	1.356	1.359	1.347	1.316
C^1X^1	1.079	1.390	1.363	1.342
C^1X^2	1.079	1.077	1.363	1.342
C^1X^3	1.079	1.077	1.073	1.342
C^2H^1	1.079	1.079	1.079	1.079
C^2H^2	1.079	1.079	1.079	1.079
C^2H^3	1.079	1.079	1.078	1.079
X^1C^1H	105.0	108.2	108.1	109.9
X^2C^1H	105.0	105.6	108.1	109.9
X^3C^1H	105.0	105.6	108.5	109.9
H^1C^2H	105.0	105.4	104.8	104.7
H^2C^2H	105.0	104.4	104.8	104.7
H^3C^2H	105.0	104.4	104.2	104.7
θ	179.9	183.3	177.4	180.1

[a] Distances in Å; angles in degrees.

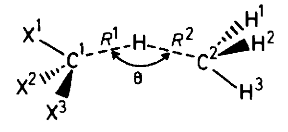

Figure. Approach of the methyl radical to the substrate

Method

Ab initio calculations were carried out with the Gaussian 82 system of programs,[8] using the minimal STO-3G and the split-valence 3-21G basis sets.[9] The restricted Hartree–Fock (RHF) method was employed for closed-shell systems, and the unrestricted Hartree–Fock (UHF) method for open shells.

The transition states were directly located in the complete potential-energy hypersurface by using the Schlegel algorithm[10] for gradient minimization at the Hartree–Fock level. The effect of electron correlation was estimated by use of Møller–Plesset perturbation theory[11] up to the second order (MP2).[12]

Results and Discussion

We have found that hydrogen abstraction from methane and its fluoro-derivatives by methyl radicals proceeds in one step, the methyl radical approaching a hydrogen atom of the substrate in a staggered conformation as indicated in the Figure. Given that the 3-21G geometries of reactants and products are well established,[13] we present in Table 1 only the geometrical parameters corresponding to the transition states of the four reactions. The values of the angle θ indicate a linear C--- H --- C structure in the case of CH_4 and CHF_3, but a slight deviation from linearity (about 3°) in the other two cases. The transition state for hydrogen abstraction from CH_4 has D_{3d} symmetry, the abstracted hydrogen atom being exactly equidistant from the two carbon atoms ($R^1 = R^2$). In the case of CHF_3, the symmetry is reduced to C_{3v} and the H atom is clearly closer to the carbon atom of the methyl radical than to the carbon atom of the substrate. In the intermediate cases, with one or two fluorine atoms, R^1 and R^2 are similar, but whereas R^1 is smaller than R^2 for the reaction of CH_3F, the contrary applies to the reaction of CH_2F_2. The variation of these distances along the series shows that the transition state slightly advances towards the reactants when the first fluorine atom is introduced in methane, but that it is displaced towards the products when more fluorine atoms are introduced. With regard to the other bond lengths, the CH values are all very similar, and the CF bond lengths diminish when one goes from CH_3F to CHF_3, as occurs in the reactants.

Table 2 presents the energy barriers for the four reactions at different levels of calculation and the corresponding experimental activation energies. Several interesting features may be

Table 2. Energy barriers (kcal mol^{-1})[a]

	STO-3G//STO-3G	3-21G//3-21G	MP2/3-21G//3-21G	Experimental
CH_4	26.31	27.20	21.22	14.2
CH_3F	21.69	26.01	18.77	11.8
CH_2F_2	18.39	26.02	17.85	10.4
CHF_3	16.53	27.69	19.04	13.6

[a] 1 kcal = 4.184 kJ.

Table 3. C–H dissociation energies[a] in the substrates

	3-21G//3-21G	MP2/3-21G//3-21G
CH_3–H	86.64	101.01
CH_2F–H	83.57	95.23
CHF_2–H	83.84	93.91
CF_3–H	89.21	98.63

[a] In kcal mol^{-1}; 1 kcal = 4.184 kJ.

observed. First, the energy barriers increase when one goes from the STO-3G results to the 3-21G ones. This variation of the energy barrier as the size of the basis set is increased agrees with previous 6-31G calculations for hydrogen abstraction from methane, in which a value of 29.90 kcal mol^{-1} was found.[6] The same tendency was also observed by Dannenberg and co-workers.[3] for the same reaction using the STO-3G and 4-31G basis sets, although in these calculations some geometrical restrictions were imposed on optimization. In contrast the introduction of energy correlation by use of Møller–Plesset perturbation theory up to the second order, keeping the 3-21G geometries unchanged, leads to a drastic lowering of the energy barriers. In the case of CH_4, this diminution was previously observed by Sana *et al.*,[6] who obtained a value of 19.69 kcal mol^{-1} in a CI calculation using an extended basis set. In spite of this, the calculated energy barriers are still about 7 kcal mol^{-1} greater than the experimental activation energies. It is true that the calculated and experimental values do not represent the same physical property, since zero-point energy, tunnelling, and temperatures corrections have not been introduced. However, introduction of such corrections by Sana *et al.*[6] in the case of hydrogen abstraction from CH_4 leads to a theoretical activation energy of 18.30 kcal mol^{-1}, which is still greater than the experimental one. The reasons for this discrepancy are not clear.

Let us now consider the variation of the energy barriers as more fluorine atoms are introduced in methane. At the STO-3G level, the energy barrier decreases monotonically along the series, in contradiction with the irregular ordering of the experimental values. When the 3-21G basis set is used, the calculated energy barriers show an irregular ordering, but they still differ from the experimental ones in that the minimum value occurs for the reaction with CH_3F. Moreover the energy barrier for the last member of the series is greater than that corresponding to methane; this is just the opposite to the experimental results. Finally, the energy barriers obtained when energy correlation is introduced show a very good correlation with the experimental activation energies, the difference between the two values being almost constant along the series. Thus energy correlation is essential to reproduce theoretically the experimental facts in hydrogen abstraction by methyl radicals.

It is well known that the factors which control free radical substitution reactions with a series of substrates are mainly the relative strengths of the bonds being broken and formed and the polarity of the transition state. Given that the bond being formed is always the same (that between the methyl radical and a hydrogen atom), we have only to consider the other two factors.

Table 4. Energy[a] of frontier orbitals for methane and its fluoro derivatives

	CH_4	CH_3F	CH_2F_2	CHF_3
LUMO	0.297	0.279	0.276	0.284
HOMO	−0.545	−0.517	−0.528	−0.591

[a] In kcal mol^{-1}; 1 kcal = 4.184 kJ.

The strength of the bond being broken can be estimated from the C–H dissociation energy in the substrate. It can easily be calculated as the energy difference between reactants and products of the process $RH \longrightarrow R + H$, where $R = CH_3$, CH_2F, CHF_2, or CF_3. Table 3 presents the dissociation energies calculated in this way with 3-21G optimized geometries, both at the Hartree–Fock level and with inclusion of electron correlation. In the two cases, the values obtained show a good correlation with the corresponding energy barriers (Table 2). In fact, given that the bond being formed in our series of hydrogen-abstraction reactions is always the same, analogous correlations with no change in the slopes are obtained by taking the reaction energies instead of the dissociation energies. The existence of such Evans–Polanyi relationships seems to indicate that thermodynamic control (the faster reaction being the more exothermic) holds for hydrogen abstraction from methane and its fluoro derivatives by methyl radicals. Thus, the irregular ordering of the energy barriers could be interpreted as a direct consequence of the reaction energy. In comparison of Tables 2 and 3 it may seem surprising that the effect of electron correlation is to increase the binding energy in the substrate while decreasing the energy barrier of the hydrogen abstraction reaction. This does not appear strange if one takes into account that the inclusion of electron correlation will preferentially stabilize the structures where the electrons are more paired. Thus, in the dissociation process the inclusion of electron correlation will preferentially stabilize the reactant, leading to an increase in dissociation energy. On the other hand, it will stabilize the transition state of the hydrogen-abstraction reaction more than the reactants, the energy barrier being consequently diminished.

However, Evans–Polanyi relationships are usually found when polar effects are constant in a reaction series, a condition which does not hold in our case, where the number of fluorine atoms increases when one goes from methane to trifluoromethane. Several criteria have been used previously in order to estimate such polar effects in radical reactions. One of these is the more or less nucleophilic or electrophilic character of the radical. In the language of molecular orbitals, this amounts to the values attributable to SOMO–HOMO and SOMO–LUMO interactions.[14]

Table 4 presents the energies of the frontier orbitals of methane and its fluoro derivatives. Given that the UHF energies of the highest occupied α spin orbital and of the lowest unoccupied β spin orbital are, respectively, −0.386 and 0.163 a.u., it is seen that the methyl SOMO interacts about equally with both frontier orbitals of the substrate, although the interaction with the LUMO is expected to be somewhat greater, in good agreement with the nucleophilic character usually attributed to the methyl radical. The HOMO and LUMO energy values present an irregular ordering. The HOMO energy assumes its maximum value for CH_3F and the minimum value of the LUMO energy corresponds to CH_2F_2, although, in this latter case, the LUMO energies of fluoromethane and difluoromethane are very similar. Thus the SOMO–HOMO and SOMO–LUMO stabilizing interactions are expected to reach a maximum in the middle of the series, in such a way that polar effects contribute to the irregular ordering of the energy barriers.

In conclusion, theoretical calculations on hydrogen abstraction from methane and its fluoro derivatives by methyl radicals correctly reproduce the experimental irregular ordering of the energy barriers, when electron correlation is introduced. The results show that this ordering can be explained as a consequence of the strength of the bond being broken and of polar effects. The validity of this interpretation will be assessed by the study of hydrogen abstraction reactions by other radicals, now in progress in our laboratory.

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Received 11*th April* 1986; *Paper* 6/715