

HYBRID DENSITY FUNCTIONAL THEORY INVESTIGATION OF THE HYDROGEN ABSTRACTION REACTION OF FLUOROMETHANE BY THE HYDROXYL RADICAL

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Abstract

A number of hybrid density functional theory methods have been used to calculate energetic and geometric parameters for the hydrogen abstraction reaction of fluoromethane by the hydroxyl radical, an important atmospheric reaction. The results show that some of the theoretical methods investigated here give calculated classical barrier heights for the abstraction reaction that are very small while other methods overestimate the recommended value. The determining factor is the contribution of the Hartree-Fock exchange. We propose three new hybrid density functional theory methods that give classical barrier heights in the range of the best estimate proposed in the literature of 2.8-3.1 kcal/mol.

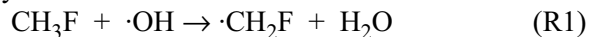
Keywords:

Hydrogen Abstraction, Fluoromethane, Barrier Height, Density Functional Theory, Hartree-Fock Exchange

Introduction

Chlorofluorocarbons, more generally called halocarbons, are chemical compounds containing chlorine, fluorine, and carbon and are predominantly responsible for the destruction of the ozone layer in the stratosphere (1). For this reason, many hydrogen-containing halocarbons are presently of interest as possible chlorofluorocarbon replacements for various industrial products. Hydrohalocarbon atmospheric lifetime, a fundamental factor of their potential environmental impact, is determined primarily by their rate of reaction with a variety of atmospheric radicals particularly hydroxyl radicals. However, a complete understanding of the degradation processes of hydrohalocarbons in atmosphere is still unknown at the present time, and computational studies can be used to advance our knowledge about these processes.

A prototypical reaction for the first step of degradation process of hydrofluorocarbons in atmosphere is the attack by the hydroxyl radical on the C-H bond in fluoromethane, which is the simplest hydrohalocarbon:



This reaction has been broadly studied both experimentally (2-7) and theoretically (8-12). In a

recent *ab initio* and theoretical kinetic study on the title reaction, based on fitting *ab initio* calculated rate constants to the experimental ones, Lien *et al.* (12) proposed an estimated barrier height of 2.8-3.1 kcal/mol for this reaction. This value was overestimated by *ab initio* methods used in that study. The rate constant calculations for reaction R1 by Lien *et al.* (12) as well as those of Schwartz *et al.* (10) and Espinosa-Garcia *et al.* (9) used dual-level dynamics calculations involving corrections to the energy, using higher level calculations, along the minimum energy path determined at a lower level of theory. These dual-level dynamics methods (13-15) are typically used because the dynamics calculations using high-level electronic structure theory calculations are computationally prohibited while those using low-level theories are generally inaccurate.

Density functional theory (DFT) and hybrid density functional theory (HDFT) calculations yield reasonable molecular properties like geometries, vibrational frequencies, and enthalpies of formation but most methods fail to perform well in the transition-state region where bond breaking and forming occur. However, by optimizing existing methods against kinetics data, new HDFT methods have been recently developed for use in kinetics studies (16-18), and these methods provide more

accurate barrier heights and a better description of the potential energy surface (PES) in the transition state region.

The purpose of this study is to investigate the energetics, with a special focus on the classical barrier height, for the title reaction using a large number of HDFT methods, and to determine which of these methods would be appropriate for accurately investigating the dynamics of the title reaction on a single-level PES. We determined three new HDFT methods that give classical barrier height in the range of the best estimate (2.8-3.1 kcal/mol) proposed by Lien *et al.* (12).

Computational Methodologies

The one-parameter hybrid Fock–Kohn–Sham operator can be written as:

$$F = F^H + (X/100)F^{HFE} + [1 - (X/100)](F^{SE} + F^{GCE}) + F^C \quad (1)$$

where F^H is the Hartree operator (i.e., the nonexchange part of the Hartree–Fock operator), F^{HFE} is the Hartree–Fock (HF) exchange operator, X is the fraction of Hartree–Fock exchange, F^{SE} is the Dirac–Slater local density functional for exchange, F^{GCE} is the gradient correction for the exchange functional, and F^C is the total correlation functional including both local and gradient-corrected parts.

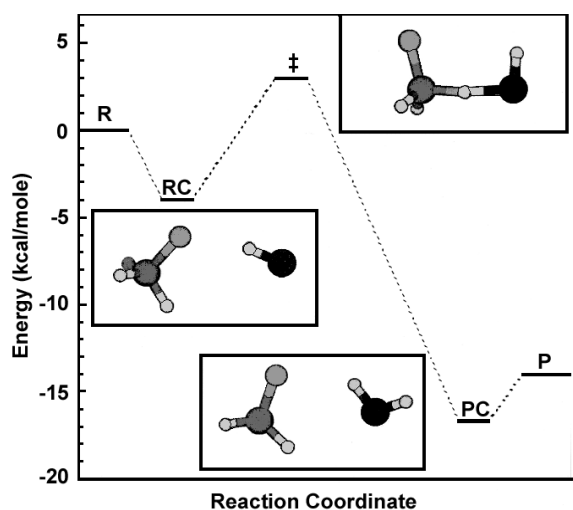


Figure 1. Energy profile for $\text{CH}_3\text{F} + \text{OH} \rightarrow \text{CH}_2\text{F} + \text{H}_2\text{O}$ reaction calculated at the mPW1PW91-33.0/6-31+G(d,p) level of theory. Saddle point, reactant complex, and product complex representations are shown inset. (R represents reactants, RC represents reactant complex, ‡ represents the saddle point or the conventional transition state, PC represents product complex, and P represents products.)

In this study we recommend new HDFT methods, with X values different than the ones currently presented in the literature. Their names are based on the original HDFT method from which they were derived but including the non-standard value of X . The HDFT methods obtained for non-standard values of X are labeled in this study by defining the gradient-correlated exchanged functional used, followed by 1 indicating a one-parameter method, followed by the correlation functional used, and finally by the value of X separated by dash. For example, mPW1PW91–33.0 represent a one-parameter hybrid density functional theory method based on the modified Perdew–Wang (mPW) gradient-corrected exchange functional (19) and PW91 gradient-corrected correlation functional (20), but with Hartree–Fock exchange contribution of 33.0% ($X = 33.0$).

The existing HDFT methods (i.e., HDFT methods present in the literature) used in this study are B3LYP (21-22), BH&HLYP, B3PW91 (22), PBE1PBE (23), mPW1PW91 (19), MPW1K (16), B1B95 (24), BB1K (17), mPW1B95 (18), MPWB1K (18) in conjunction with two different basis sets, 6-31G(d,p) and 6-31+G(d,p). Restricted wave functions were used for closed-shell systems and unrestricted wave functions for open-shell systems. We carried out the geometry optimizations using a tight convergence criteria and an ultrafine integration grid for numerical integrations. All electronic structure calculations were carried out using Gaussian 03 program (25).

Results and Discussion

The results of our calculations are presented in three tables and two figures. In Tables 1 and 2, we present the energetic parameters obtained with different HDFT methods, and in Table 3 we present selected geometric parameters of the saddle point and the van der Waals complexes between the reactants and the products. Figure 1 shows the energy profile for reaction R1 calculated using mPW1PW91-33.0/6-31+G(d,p) method, and Figure 2 shows the calculated barrier heights as a function of X , the contribution of HF exchange functional. In Tables 1 and 2, V_{RC} is the energy of the van der Waals complex between the reactants, OH and CH_3F , $V_{‡}^{\ddagger}$ is the classical (i.e., zero-point-exclusive) barrier height, V_{PC} is the energy of the van der Waals complex between the products, H_2O and CH_2F , ΔE

Table 1. Energetic parameters for $\text{CH}_3\text{F} + \text{OH} \rightarrow \text{CH}_2\text{F} + \text{H}_2\text{O}$ reaction calculated with 6-31G(d,p) basis set. All values are in kcal/mol except the imaginary frequency that is in cm^{-1} .

HDFT Method	X	V_{RC}	V^\ddagger	V_{PC}	ΔE	ΔH_0^\ddagger	ΔH	ΔG_{298}^\ddagger	ω^\ddagger
B3PW91	20	-5.6	-0.6	-18.1	-14.1	-1.2	-15.1	5.3	366.8 <i>i</i>
B3LYP	20	-6.9	-1.0	-18.1	-12.9	-2.2	-13.9	4.4	639.1 <i>i</i>
BH&HLYP	50	-6.8	7.8	-14.1	- 8.8	6.1	-9.8	12.8	1894.2 <i>i</i>
PBE1PBE	25	-6.8	-0.8	-18.9	-13.7	-1.7	-14.6	4.9	561.8 <i>i</i>
mPW1PW91	25	-6.3	0.1	-18.1	-13.5	-0.9	-14.4	5.7	618.6 <i>i</i>
MPW1K	42.8	-6.0	4.9	-16.0	-11.5	3.3	-12.4	10.0	1446.7 <i>i</i>
B1B95	28	-5.7	-0.3	-18.1	-13.9	-1.1	-14.8	5.4	489.8 <i>i</i>
BB1K	42	-5.7	4.2	-16.1	-11.8	2.6	-12.8	9.3	1310.0 <i>i</i>
mPW1B95	31	-6.6	0.3	-18.4	-13.3	-1.0	-14.2	5.6	784.2 <i>i</i>
MPWB1K	44	-6.4	3.8	-16.7	-11.7	2.2	-12.6	8.9	1375.7 <i>i</i>

is the classical energy of reaction, ΔH is the zero-point-inclusive energy of reaction, ΔH_0^\ddagger is the zero-point-inclusive barrier height, ΔG_{298}^\ddagger is the free energy of activation at 298 K, and ω^\ddagger is the imaginary frequency at the saddle point. (All reported energies are relative to the zero-point-exclusive energy of the reactants, which is considered the zero of energy.) The zero-point-inclusive barrier height, ΔH_0^\ddagger , is calculated as:

$$\Delta H_0^\ddagger = V^\ddagger + \sum_{m=1}^{14} \frac{\hbar \omega_m^\ddagger}{2} - \sum_{n=1}^9 \frac{\hbar \omega_n^{\text{CH}_3\text{F}}}{2} - \frac{\hbar \omega^{\text{OH}}}{2} \quad (2)$$

where ω_m^\ddagger are the frequency of the normal mode m for the saddle point, $\omega_n^{\text{CH}_3\text{F}}$ is the frequency of the normal mode n of CH_3F , and ω^{OH} is the hydroxyl normal mode frequency.

The results in Tables 1 and 2 as well as Figure 2 show that the barrier heights (both V^\ddagger and ΔH_0^\ddagger)

obtained with the smaller 6-31G(d,p) basis set are consistently smaller than the ones obtained with larger 6-31+G(d,p) basis set for the same HDFT method. The 6-31+G(d,p) basis set is the recommended basis sets for use in kinetics studies using HDFT (26-27), and it is the only basis set used in developing the new HDFT methods with good energetics for $\text{OH} + \text{CH}_3\text{F}$ reaction.

The fact that some HDFT methods give very low calculated barrier heights is somewhat surprising. Some values are even calculated to be slightly negative! An overestimated van der Waals interaction between the hydroxyl radical and fluoromethane (consistent with a shorter C...O distance in the complex) and an underestimated barrier height relative to this van der Waals complex are responsible for this apparent contradiction. These results demonstrate the need for a cautionary use of several existing HDFT methods in kinetic studies especially

Table 2. Energetic parameters for $\text{CH}_3\text{F} + \text{OH} \rightarrow \text{CH}_2\text{F} + \text{H}_2\text{O}$ reaction calculated with 6-31+G(d,p) basis set. All values are in kcal/mol except the imaginary frequency that is in cm^{-1} .

HDFT Method	X	V_{RC}	V^\ddagger	V_{PC}	ΔE	ΔH_0^\ddagger	ΔH	ΔG_{298}^\ddagger	ω^\ddagger
B3PW91	20	- 3.4	0.2	-17.4	-15.5	-0.2	-16.6	6.2	289.1 <i>i</i>
B3LYP	20	- 4.1	0.0	-17.2	-14.5	-1.1	-15.6	5.4	491.1 <i>i</i>
BH&HLYP	50	- 4.6	8.4	-13.8	-10.3	6.6	-11.4	13.3	1857.7 <i>i</i>
PBE1PBE	25	- 4.4	0.1	-18.3	-15.1	-0.7	-16.2	5.8	430.7 <i>i</i>
mPW1PW91	25	- 3.9	0.9	-17.5	-14.9	0.0	-15.9	6.5	493.7 <i>i</i>
MPW1K	42.8	- 4.1	5.5	-15.7	-12.9	3.8	-13.9	10.4	1362.5 <i>i</i>
B1B95	28	- 3.3	0.6	-17.4	-15.2	-0.1	-16.3	6.4	384.8 <i>i</i>
BB1K	42	- 3.6	4.9	-15.8	-13.2	3.2	-14.2	9.8	1206.8 <i>i</i>
mPW1B95	31	- 4.1	1.2	-17.8	-14.7	0.0	-15.8	6.5	620.1 <i>i</i>
MPWB1K	44	- 4.2	4.5	-16.4	-13.2	2.9	-14.2	9.5	1265.3 <i>i</i>
mPW1PW91-33.0	33	- 4.0	3.0	-16.7	-14.0	1.5	-15.0	8.1	902.7 <i>i</i>
B1B95-34.3	34.3	- 3.5	3.0	-16.5	-14.1	1.6	-15.1	8.1	832.9 <i>i</i>
mPW1B95-38.0	38	- 4.1	3.0	-17.0	-13.9	1.5	-14.9	8.0	984.5 <i>i</i>

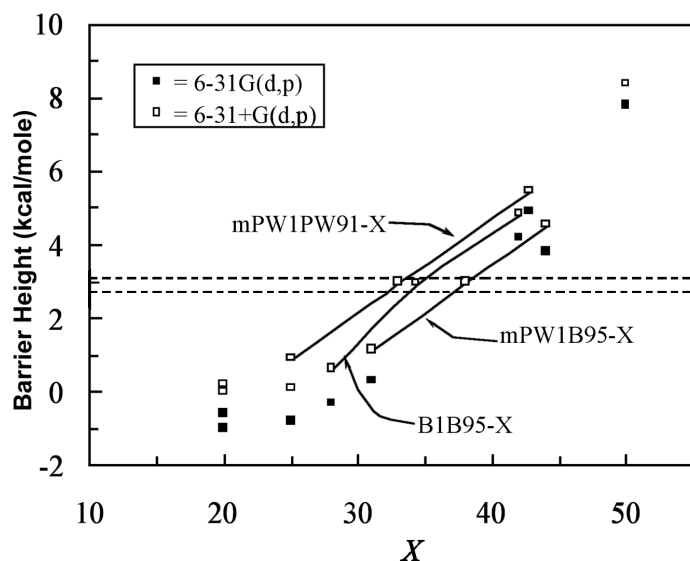


Figure 2. Classical barrier heights calculated with various HDFT methods function of the Hartree-Fock exchange contribution X in the exchange-correlation energy. Horizontal dotted lines represent the limits of the best estimate range of the classical barrier height (2.8-3.1 kcal/mol).

for reactions with small barrier heights and strong attractive interactions between reactants. It is known that some DFT methods, especially used in conjunction with a basis set without diffuse functions, overestimate the non-bonding interactions between molecules.

The results in Tables 1 and 2 as well as Figure 2 also show consistently that the calculated barrier heights increase as the HF exchange contribution (i.e., the value of X) is increased. This is a property of HDFT methods that make them extremely attractive for use in dynamics studies because one can choose the HF exchange contribution that provide more accurate energetics for the reaction of interest.

By inspecting the calculated classical barrier heights, one can classify the HDFT methods investigated here into two categories based on the HF exchange contribution to the exchange energy. The first category contains HDFT methods with $X=20-31$ (namely B3LYP, B3PW91, PBE1PBE, mPW1PW91, B1B95, mPW1B95), while the second category contains HDFT methods with $X > 40$ (MPW1K, BB1K, MPWB1K, BH&HLYP). The results in Tables 1 and 2 and in Figure 2 show that HDFT methods with $X < 31$ give calculated classical barrier heights for the abstraction reaction that are

very small, smaller than the best estimate, especially for calculations with the smaller 6-31G(d,p) basis set. The methods with higher X values (> 40) systematically overestimate the best estimate of the classical barrier height. It is clear that HDFT methods with HF exchange contributions between those two categories (around 35%) should provide more accurate energetics for this reaction. We therefore investigated more carefully what HF exchange contribution will give barrier heights in the range of 2.8-3.1 kcal/mol proposed by Lien *et al.* (12). We focus on only mPW1PW91, B1B95, and mPW1B95 hybrid functionals because these are the most promising ones, and because these are also the functionals for which methods designed for kinetics (i.e., the K methods: MPW1K, BB1K, and MPWB1K) are already proposed in the literature (16-18).

These HDFT methods designed for kinetics overestimate the best estimate of the classical barrier height, with calculated values of 5.5, 4.9, and 4.5 kcal/mol for MPW1K, BB1K, and MPWB1K, respectively. Based on these K methods and the original methods (mPW1PW91, B1B95, and mPW1B95) that underestimate the best estimate of the barrier height, we proposed three new density functional methods with calculated classical barrier heights in the range of the best estimate. These new methods, mPW1PW91-33.0, B1B95-34.3, and mPW1B95-38.0 give classical barrier heights of 2.98, 2.96, and 2.99 kcal/mol, respectively.

More precisely, there should be a range of values of X that provides classical barrier heights in the range of the best estimate and we decided to determine this range for the same three pairs of exchange-correlation functionals from above. For each of these three functionals, we fit quadratically the three calculated barrier heights vs. X and found, based on the fit, the limits of X that give barrier heights in the best estimate range. These limits are 32.3 to 33.5 for mPW1PW91- X , 33.8 to 34.8 for B1B95- X , and 37.3 to 38.4 for mPW1B95- X . These methods should provide barrier height for the title reaction in the best estimate range of 2.8-3.1 kcal/mol. This methodology for creating HDFT with specific reaction parameters (SRP) that provide accurate energetics is quite general, and it can be used for other reactions.

Table 3. Selected geometric parameters for the saddle point (\ddagger), the van der Waals complex between CH_3F and OH (RC), and the van der Waals complex between CH_2F and H_2O (PC). All values are in Å.

HDFT Method	$r_{\text{C}\cdots\text{H}}^{\ddagger}$	$r_{\text{H}\cdots\text{O}}^{\ddagger}$	$r_{\text{C}\cdots\text{O}}^{\ddagger}$	$r_{\text{C}\cdots\text{O}}^{\text{RC}}$	$r_{\text{C}\cdots\text{O}}^{\text{PC}}$
B3PW91/6-31G(d,p)	1.172	1.420	2.570	3.263	3.159
B3LYP/6-31G(d,p)	1.200	1.354	2.535	3.235	3.136
BH&HLYP/6-31G(d,p)	1.245	1.244	2.471	3.237	3.115
PBE1PBE/6-31G(d,p)	1.184	1.375	2.530	3.212	3.107
mPW1PW91/6-31G(d,p)	1.188	1.364	2.530	3.239	3.132
MPW1K/6-31G(d,p)	1.218	1.281	2.479	3.246	3.123
B1B95/6-31G(d,p)	1.182	1.385	2.545	3.236	3.139
BB1K/6-31G(d,p)	1.214	1.291	2.486	3.230	3.121
mPW1B95/6-31G(d,p)	1.195	1.339	2.509	3.207	3.105
MPWB1K/6-31G(d,p)	1.216	1.284	2.475	3.207	3.096
B3PW91/6-31+G(d,p)	1.161	1.457	2.614	3.804	3.287
B3LYP/6-31+G(d,p)	1.188	1.385	2.570	3.732	3.207
BH&HLYP/6-31+G(d,p)	1.235	1.260	2.490	3.679	3.124
PBE1PBE/6-31+G(d,p)	1.172	1.411	2.575	3.618	3.146
mPW1PW91/6-31+G(d,p)	1.177	1.394	2.566	3.739	3.205
MPW1K/6-31+G(d,p)	1.208	1.299	2.501	3.728	3.151
B1B95/6-31+G(d,p)	1.172	1.417	2.585	3.817	3.194
BB1K/6-31+G(d,p)	1.205	1.310	2.509	3.784	3.155
mPW1B95/6-31+G(d,p)	1.184	1.369	2.547	3.636	3.145
MPWB1K/6-31+G(d,p)	1.206	1.304	2.503	3.615	3.089
mPW1PW91–33.0/6-31+G(d,p)	1.195	1.339	2.501	3.735	3.180
B1B95–34.3/6-31+G(d,p)	1.194	1.344	2.533	3.801	3.172
mPW1B95–38.0/6-31+G(d,p)	1.197	1.328	2.519	3.625	3.124

For the three new HDFT methods that give classical barrier heights of same value, there is also a good correlation between the imaginary frequency at the saddle point (Table 2) and the barrier height with respect to the reactant complex. The imaginary frequency at the saddle point can be seen as a measure of the thickness of the barrier. The mPW1B95–38.0 method provides a larger imaginary frequency (a narrower barrier) due to a deeper $\text{CH}_3\text{F}\cdots\text{OH}$ complex while the B1B95–34.3 provides a wider barrier due to a shallower $\text{CH}_3\text{F}\cdots\text{OH}$ complex.

The results in Table 3 show that the HDFT methods with smaller X values give early transition states characterized by relatively short $\text{C}\cdots\text{H}$ distances and relatively long $\text{H}\cdots\text{O}$ distances, while HDFT methods with bigger X values give late (or later) transition states. Within the same HDFT method, the larger basis set gives an earlier transition state compared to the smaller basis set.

We also investigated the geometry of the transition state obtained with various HDFT methods, particularly the sum of the making ($r_{\text{H}\cdots\text{O}}^{\ddagger}$) and breaking ($r_{\text{C}\cdots\text{H}}^{\ddagger}$) bond distances. This sum, called perpendicular looseness (26), is a measure of the looseness of the structure in a direction perpendicular to the reaction coordinate. We observe that the transition state gets looser as the HF exchange contribution decreases. Also, within the same HDFT method, the transition state gets looser using a larger basis set. Comparing only the three methods that give calculated barrier height values in the range of the best estimate, the mPW1B95–38.0 method also gives a tighter transition state ($r_{\text{C}\cdots\text{H}}^{\ddagger} + r_{\text{H}\cdots\text{O}}^{\ddagger} = 2.526 \text{ Å}$) while B1B95–34.3 method gives a looser transition state ($r_{\text{C}\cdots\text{H}}^{\ddagger} + r_{\text{H}\cdots\text{O}}^{\ddagger} = 2.538 \text{ Å}$). This difference is mainly due to a longer $\text{H}\cdots\text{O}$ distance at the transition state. Note also that the $\text{C}\cdots\text{H}\cdots\text{O}$ angle is less than 180 degrees so $r_{\text{C}\cdots\text{O}}^{\ddagger} < r_{\text{C}\cdots\text{H}}^{\ddagger} + r_{\text{H}\cdots\text{O}}^{\ddagger}$. For the methods used in this study, $\text{C}\cdots\text{H}\cdots\text{O}$ angle is around 165 degrees for 6-31G(d,p) basis set and around 173 degrees for 6-31+G(d,p) basis set.

Conclusions

HDFT methods are quite flexible in the choice of exchange and correlation functional that one uses, and this property makes them very attractive methods for use in reaction dynamics studies. Our interest is in obtaining HDFT methods that can be used for accurately investigating chemical dynamics of important environmental and atmospheric processes. This paper introduces a simple procedure for obtaining hybrid density functional theory methods with specific reaction parameters (HDFT-SRP) providing superior reaction energetics by optimizing the HF exchange contribution. We used this procedure to develop three new HDFT methods with good energetics for the hydrogen abstraction reaction of fluoromethane by the hydroxyl radical. These new methods can be used in calculating dynamic properties on an accurate PES surface without the use of dual-level dynamics.

The keywords to carry out mPW1PW91–33.0 calculations in Gaussian03 are mPWPW91/6-31+G(d,p) and IOp(3/76=0670003300). The keywords to carry out B1B95-34.3 calculations in Gaussian 03 are BB95/6-31+G(d,p) and IOp(3/76=0657003430). The keywords to carry out mPW1B95–38.0 calculations in Gaussian 03 are mPWB95/6-31+G(d,p) and IOp(3/76=0620003800).

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