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An ab Initio Investigation of the Reaction of Trifluoromethane with the Hydroxyl Radical

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The reactants, products, and the transition state for the reaction $CHF_3 + OH \rightarrow CF_3 + H_2O$ have been investigated using ab initio molecular orbital theory at the MP2 level. Geometry optimizations and vibrational frequency calculations have been performed on all reactants, products, and the transition state at both the MP2/3-21G** and MP2/6-311G** level. Single-point energy calculations at the MP2/6-311G** level using the MP2/3-21G** optimized geometries and at the QCISD/6-311G** level using the MP2/6-311G** optimized geometries have also been carried out on all species. Classical barriers corresponding to these different calculations have been determined and corrected for zero-point energy effects. Transition state theory including tunneling contributions has been used to determine a rate constant which was compared with available experimental data. The QCISD/6-311G**//MP2/6-311G** calculations lead to a classical barrier of 9.589 kcal mol^{-1} and a rate constant at 298 K (using a nonsymmetric Eckart barrier to compute the tunneling correction) of 1.034×10^{-16} cm^3 molecule^{-1} s^{-1}, in excellent agreement with the best experimental value of 2.1×10^{-16} cm^3 molecule^{-1} s^{-1}. This leads to an estimated lifetime for CHF_3, based on its reaction with OH radicals in the troposphere, of 65.5 yr.

Introduction

The importance of halocarbons, and especially of the radicals resulting from their decomposition, in atmospheric chemistry is well established. Chlorofluorocarbons and chlorofluorobromocarbons (halons) are known to have a deleterious effect on the ozone in the upper atmosphere and are being phased out. These compounds are being replaced by hydrofluorocarbons (HFC's). The HFC's contain no chlorine or bromine, and fluorine is believed to be relatively innocuous in its effect on the ozone layer. Among the HFC's under consideration for use is trifluoromethane, CHF_3. This compound is representative of many of the proposed HFC's in that it contains a CF_3 grouping which will be found as a radical or part of a radical if the HCF species decomposes and is thought to be possibly involved in fluorine-catalyzed ozone loss.[1] In this paper the focus will be on the reaction between CHF_3 and hydroxyl radicals which are abundant in the troposphere with the aim of predicting a classical barrier for the reaction and a structure for the transition state. This information will be used to determine a rate constant for the reaction which can then be compared with available experimental values.

The rate constant for the reaction of CHF_3 with the hydroxyl radical has been determined experimentally at 298 K by Howard and Evenson[2] and by Nip et al.[3] and at 387 K and 410 K by Jeong and Kaufman.[4] A NASA panel which evaluated chemical kinetic and photochemical data for use in atmospheric modeling[5] recommended use of the Howard and Evenson[2] value of 2.1×10^{-16} cm^3 molecule^{-1} s^{-1} as the best value for k_{298} but indicated that, because of the experimental difficulties involved in measuring rate constants around 10^{-16} cm^3 molecule^{-1} s^{-1}, this value should be considered as an upper limit. Jeong and Kaufman[6] also used their experimental data on CHF_3 and several

other chloro- and fluoro-substituted methanes to test various models of transition state geometries and transition state theory. Cohen and Benson[7] applied transition state theory to the reaction of the hydroxyl radical with a series of halomethanes and haloethanes to determine the enthalpy of activation which, along with the experimental value of k_{298}, was used to calculate k_T at higher temperatures.

While several ab initio calculations have been carried out on the reaction of methane with the hydroxyl radical,[8] the authors are aware of only one such study on the abstraction of hydrogen from CHF_3 by the hydroxyl radical.[9] In that study, which also looked at several other halomethanes, the geometries of the reactants and of the transition state were optimized at the Hartree–Fock level using a 3-21G* basis set. Single-point energy calculations using the HF/3-21G* optimized geometries were then carried out at the MP2 level using a 6-31G* basis set. Spin-projected MP2 energies were used for the transition state. Zero-point energies were determined at the Hartree–Fock level. The classical barrier at the Hartree–Fock level was found to be 32.23 kcal mol^{-1} and at the MP2/6-31G*//3-21G* level, 4.87 kcal mol^{-1}. No rate constants were evaluated.

Theory

All molecular orbital calculations were carried out using the Gaussian 92 package of programs (10) on a Vax 4000 Model 60 computer. Optimized geometries and corresponding vibrational frequencies were initially determined for the reactants (CHF_3 and OH), for the products (CF_3 and H_2O), and for the transition state (F_3CHOH) at the MP2/3-21G** level. Single-point energy calculations using these optimized geometries were then carried out at the MP2/6-311G** level. Following this, optimized geometries and corresponding vibrational frequencies were determined for all species at the MP2/6-311G** level. Finally, single-point energy calculations using these latter optimized geometries were determined at the QCISD/6-311G** level. (Optimized geometries for the reactants and products were determined at the QCISD/6-311G** level, but because of storage limitations we were unable to optimize the transition

TABLE 1: Optimized Geometries of CF₃H, OH, CF₃, and H₂O[a]

	MP2/3-21G**	MP2/6-311G**	QCISD/6-311G**
CF₃H			
R_{C-F}	1.3711	1.3354	1.3336
R_{C-H}	1.0742	1.0872	1.0894
∠HCF	110.3552	110.3050	110.3318
E_{MP2}	−335.40916620	−337.61518018	−337.62495054[b]
OH			
R_{O-H}	0.9629	0.9667	0.9693
E_{PMP2}	−75.07939964	−75.57438808	−75.58649326[b]
CF₃			
R_{C-F}	1.3567	1.318	1.3172
∠FCF	111.713	111.3293	111.3105
E_{PMP2}	−334.73990727	−336.94338821	−336.95035861[b]
H₂O			
R_{O-H}	0.9509	0.9578	0.9576
∠HOH	103.067	102.4492	102.7089
E_{MP2}	−75.75506765	−76.26397189	−76.27169911[b]

[a] Bond lengths are in angstroms, angles are in degrees, and energy is in hartrees. [b] QCISD energy.

TABLE 2: Vibrational Frequencies and Intensities of CF₃H, OH, CF₃, and H₂O[a]

	MP2/3-21G**	MP2/6-311G**	experimental[b]
CF₃H			
a₁ C−H str	3386.41 (62.2)	3224.04 (47.2)	3036 (s)
a₁ CF₃ (s) str	1131.39 (108.7)	1163.82 (118.3)	1117 (vs)
a₁ CF₃ (s) def	667.43 (22.1)	709.80 (15.7)	700 (m)
e CH bend	1487.26 (93.8)	1448.80 (77.2)	1372 (m)
e CF₃ deg str	1227.35 (171.9)	1203.30 (286.4)	1152 (vs)
e CF₃ deg def	486.69 (6.9)	516.27 (3.1)	507 (m)
OH			
σ₈ OH str	3824.93 (0.2)	3851.36 (10.6)	3735
CF₃			
a₁ CF₃ (s) str	1069.92 (49.0)	1121.97 (54.9)	1089
a₁ CF₃ (s) def	665.22 (23.2)	715.40 (16.1)	701
e CF₃ deg str	1321.78 (267.4)	1298.35 (385.2)	1260.2
e CF₃ deg def	482.99 (5.6)	518.69 (2.2)	508
H₂O			
a₁ OH (s) str	3891.71 (0.7)	3904.78 (6.2)	3657
a₁ HOH bend	1680.14 (43.4)	1667.36 (51.2)	1595
b₂ OH (a) str	4070.45 (2.3)	4012.64 (33.5)	3756

[a] Frequencies are in cm⁻¹, intensities are in km mol⁻¹. [b] CF₃H, ref 14; OH, ref 15; CF₃, ref 16; H₂O, ref 17.

TABLE 3: Optimized Geometry of the CF₃HOH Transition State[a]

parameter	MP2/3-21G**	MP2/6-311G**
$R_{C-F}(1)$	1.3629	1.3244
$R_{C-F}(2)$	1.3713	1.3316
R_{C-H}	1.2551	1.2184
R_{H-O}	1.1629	1.2429
R_{O-H}	0.9616	0.9674
∠FCH(1)	110.0993	109.2754
∠FCH(2)	107.554	108.9068
∠FCF(1)	110.059	110.0884
∠FCF(1,2)	109.497	109.6368
∠CHO	160.037	166.417
∠HOH	99.931	97.9995
∠FCHF(1,2)	119.2436	119.7422
E_{PMP2}	−410.46735075	−413.17389208

[a] The transition state has a plane of symmetry containing the FCHOH grouping with the other two F's above and below this plane, respectively. (1) refers to the out-of-plane fluorines and (2) to the in-plane fluorine. Bond lengths are in angstroms, angles are in degrees, and energy is in hartrees.

state at this level or to obtain vibrational frequencies.) Following the recommendation of Sosa and Schlegel,[11] spin-projected MP2 energies were used for all open-shell species to eliminate spin contamination. This spin contamination is noticeably greater in the transition state (S^2 before annihilation = 0.7800) than in the hydroxyl radical (S^2 before annihilation = 0.7548). As a result, the barrier height using the spin-projected energies is lower than that found when spin contamination is not considered. Simple transition state theory was used to determine the rate constant over a range of temperatures.

Results and Discussion

The optimized geometries of the reactants and products are given in Table 1. Table 2 lists the calculated vibrational frequencies and intensities for these species as well as the experimental frequencies. The optimized geometry and vibrational frequencies and intensities of the transition state are shown in Tables 3 and 4, respectively. Table 5 summarizes the total energies for all species as determined at the different levels of theory. Table 6 lists the activation energies, reaction energies, and rate constants (with and without tunneling at 298 K) for the different levels of calculation. Finally, Table 7 lists the calculated rate constants (with and without tunneling) over the

temperature range 200−500 K and compares these results with experimentally derived rate constants. The calculations were carried out at four levels. First, the geometries of all species including the transition state were optimized and the vibrational frequencies determined at the MP2/3-21G** level. Second, these optimized geometries were used to determine single-point energies at the MP2/6-311G**. The assumption here is that the MP2/3-21G** optimized geometries will be a good approximation to the optimized geometries for the larger basis set and that the energies obtained will closely approximate the energies for the optimized structures using the 6-311G** basis set. This was checked by carrying out a full optimization of all the species at the MP2/6-311G** level. In the case of both OH and H₂O there is little change in geometry using the 3-21G** and 6-311G** basis sets, and there is close agreement between the single-point energy results at the 6-311G** basis set level using the 3-21G** optimized geometries and the energies obtained with full optimization at the 6-311G** basis set. There are significant differences however in the C−F bond lengths as optimized by the two basis sets for all fluorine-containing species and in the C−H and O···H distances in the transition state. The angles in all species are relatively insensitive to change in basis set. Finally, single-point energy calculations using the MP2/6-311G** optimized geometries were carried out at the QCISD/6-311G** level.

The overall reaction is exothermic by amounts ranging from 4.021 kcal mol⁻¹ at the MP2/3-21G** optimized level to 11.165 kcal mol⁻¹ at the MP2/6-311G** optimized level with the values for the single-point energy calculations falling between these limits. The values for the classical barrier show a reverse pattern though in a narrower range with the MP2/3-21G** classical barrier being 13.313 kcal mol⁻¹ and the value for the MP2/6-311G** optimized level being 9.837 kcal mol⁻¹.

For the calculation of the rate constants the classical barrier was corrected for zero-point energy, and the rate constant was determined at 298 K and over a range of temperatures from 200 to 500 K. Vibrational frequencies used were those determined at either the MP2/3-21G** or MP2/6-311G** optimized geometries and then scaled using a factor of 0.97. Rotational constants were those for the optimized geometries obtained with the two basis sets. The electronic partition function took into account the multiplicity of the states and, in the case of the OH radical, made use of the spin−orbit splitting constant of 138.88 cm⁻¹ determined by Dieke and Crosswhite.[12] We were not able to include a similar correction for the transition state, but any contribution from the spin−orbit coupling would

TABLE 4: Vibrational Frequencies and Intensities for the CF₃HOH Transition State[a]

MP2/3-21G**	MP2/6-311G**	MP2/3-21G**	MP2/6-311G**
a′ 3863.31 (7.3)	a′ 3842.97 (33.9)	a″ 1304.96(229.7)	a″ 1290.78 (298.7)
2855.14i	2466.01i	1059.07 (28.6)	1158.16 (62.1)
1671.50 (33.5)	1559.71 (3.8)	482.28 (12.3)	517.31 (5.1)
1288.03 (222.0)	1262.55 (333.1)	203.85 (122.7)	115.40 (94.3)
1139.88 (352.3)	1163.67 (388.8)	98.31 (2.9)	77.70 (25.3)
880.40 (78.4)	876.35 (159.2)		
703.32 (14.8)	754.43 (11.3)		
497.73 (7.2)	527.48 (5.7)		
398.68 (5.8)	446.96 (0.8)		
118.53 (9.3)	125.95 (7.9)		

[a] Frequencies are in cm⁻¹ and intensities are in km mol⁻¹.

TABLE 5: Total Energies of CF₃H, OH, CF₃, H₂O, and CF₃HOH[a]

	CF₃H	OH	CF₃	H₂O	CF₃HOH
E_{MP2}/3-21G** OPT	−335.409 166 20	−75.079 399 64	−334.739 907 27	−75.755 067 65	−410.467 350 75
E_{MP2}/6-311G**//3-21G**[b]	−337.611 722 91	−75.574 365 30	−336.939 110 23	−76.263 875 02	−413.171 528 91
E_{MP2}/6-311G** OPT	−337.615 180 18	−75.574 388 08	−336.943 388 21	−76.263 971 89	−413.173 892 08
E_{QCISD}/6-311G**//MP2/6-311G**[c]	−337.624 938 21	−75.586 486 60	−336.950 355 99	−76.271 697 36	−413.192 868 82
E_{QCISD}/6-311G** OPT	−337.624 950 54	−75.586 493 26	−336.950 358 61	−76.271 699 11	

[a] Energies are in hartrees. [b] Single-point MP2 calculation using 6-311G** basis and MP2/3-21G** optimized geometries. [c] Single-point QCISD calculation using 6-311G** basis and MP2/6-311G** optimized geometries.

TABLE 6: Classical Barrier, Reaction Energies, and Rate Constants for CHF₃ + OH → CF₃ + H₂O

calculation level	classical barrier,[a] kcal mol⁻¹	reaction energy,[a] kcal mol⁻¹	rate constant without tunneling,[b] cm³ molecule⁻¹ s⁻¹	rate constant with tunneling,[b] cm³ molecule⁻¹ s⁻¹
MP2/3-21G** OPT	13.313 (10.935)	4.021 (3.985)	8.251 × 10⁻²¹	2.880 × 10⁻¹⁷
MP2/6-311G**//3-21G**	9.136 (6.758)	10.603 (10.567)	9.546 × 10⁻¹⁸	2.924 × 10⁻¹⁵
MP2/6-311G** OPT	9.837 (7.782)	11.165 (10.707)	3.911 × 10⁻¹⁸	9.414 × 10⁻¹⁶
QCISD/6-311G**//MP2/6-311G**	11.644 (9.589)	6.670 (6.212)	1.850 × 10⁻¹⁹	1.034 × 10⁻¹⁶

[a] Values in parentheses are corrected for zero-point energies. [b] Rate constants determined at 298 K.

TABLE 7: Rate Constants for the Reaction of CHF₃ with the Hydroxyl Radical as a Function of Temperature[a]

	200 K	250 K	300 K	350 K	400 K	450 K	500 K
MP2/3-21G** OPT	7.921 × 10⁻²⁵	2.114 × 10⁻²²	9.383 × 10⁻²¹	1.490 × 10⁻¹⁹	1.242 × 10⁻¹⁸	6.713 × 10⁻¹⁸	2.674 × 10⁻¹⁷
	(7.893 × 10⁻¹⁸)	(1.491 × 10⁻¹⁷)	(2.962 × 10⁻¹⁷)	(6.057 × 10⁻¹⁷)	(1.248 × 10⁻¹⁶)	(2.536 × 10⁻¹⁶)	(5.008 × 10⁻¹⁶)
MP2/6-311G**//3-21G**	2.905 × 10⁻²⁰	9.475 × 10⁻¹⁹	1.036 × 10⁻¹⁷	6.047 × 10⁻¹⁷	2.378 × 10⁻¹⁶	7.170 × 10⁻¹⁶	1.790 × 10⁻¹⁵
	(1.165 × 10⁻¹⁵)	(1.841 × 10⁻¹⁵)	(2.982 × 10⁻¹⁵)	(4.842 × 10⁻¹⁵)	(7.786 × 10⁻¹⁵)	(1.229 × 10⁻¹⁴)	(1.896 × 10⁻¹⁴)
MP2/6-311G** OPT	4.260 × 10⁻²¹	2.586 × 10⁻¹⁹	4.304 × 10⁻¹⁸	3.401 × 10⁻¹⁷	1.680 × 10⁻¹⁶	6.045 × 10⁻¹⁶	1.739 × 10⁻¹⁵
	(2.306 × 10⁻¹⁶)	(4.709 × 10⁻¹⁶)	(9.688 × 10⁻¹⁶)	(1.968 × 10⁻¹⁵)	(3.884 × 10⁻¹⁵)	(7.363 × 10⁻¹⁵)	(1.333 × 10⁻¹⁴)
QCISD/6-311G**//MP2/6-311G**	4.517 × 10⁻²³	6.807 × 10⁻²¹	2.077 × 10⁻¹⁹	2.531 × 10⁻¹⁸	1.730 × 10⁻¹⁷	8.014 × 10⁻¹⁷	2.821 × 10⁻¹⁶
	(2.044 × 10⁻¹⁷)	(4.614 × 10⁻¹⁷)	(1.069 × 10⁻¹⁶)	(2.486 × 10⁻¹⁶)	(5.657 × 10⁻¹⁶)	(1.233 × 10⁻¹⁵)	(2.549 × 10⁻¹⁵)
experimental	2.641 × 10⁻¹⁸	3.737 × 10⁻¹⁷	2.187 × 10⁻¹⁶	7.724 × 10⁻¹⁶	1.990 × 10⁻¹⁵	4.155 × 10⁻¹⁵	7.487 × 10⁻¹⁵

[a] Rate constants are in units of cm³ molecule⁻¹ s⁻¹. Values in parentheses include tunneling correction. Experimental rate constants are obtained using $k = 1.5 \times 10^{-12} \exp(-2650/T)$. See ref 5.

cause a small increase in the rate constant. The computed rate constants are corrected for quantum mechanical tunneling by using a one-dimensional nonsymmetrical Eckart barrier approach.[13]

There is a significant reduction in the activation energy in changing from the 3-21G** basis set to the 6-311G** basis set even without reoptimizing the geometry. In fact, the classical barrier determined using the MP2/3-21G** optimized geometry but with a 6-311G** basis set and that determined with the MP2/6-311G** optimized geometry are in close agreement despite significant differences in the two sets of optimized geometries. Most noticeably there is a greater stabilization of the CF₃H than the CF₃HOH when comparing the single-point calculation versus the optimized geometry result at the MP2/6-311G** level. This would indicate that the shorter C—F bond lengths which lend greater stability to the CF₃H also produce a shorter C—H bond in the transition state leading to a weaker complex between the CF₃H and the OH, so there is a cancellation effect present which leads to less stabilization of the complex than would have been expected. The QCISD single-point energy calculation shows an increase in the classical

barrier over the MP2/6-311G** optimized value due to the apparent differential stabilization of the reactants and transition state. It should be noted that the optimized geometries and energies determined for the reactants and products at the QCISD/6-311G** level are in very close agreement with the MP2/6-311G** optimized geometries and with the QCISD/6-311G** single-point energies calculated using these latter geometries. This would tend to confirm the overall validity of the QCISD/6-311G**//MP2/6-311G** results. It would seem reasonable to assume therefore that the most reliable value for the classical barrier for this reaction must be 9.589 kcal mol⁻¹ (including the zero-point correction) obtained by optimizing all structures at the MP2/6-311G** level and then doing a single-point QCISD/6-311G** calculation using these geometries, giving a rate constant (including tunneling) of 1.034 × 10⁻¹⁶ cm³ molecule⁻¹ s⁻¹ at 298 K. This compares quite well with the best experimental value of 2.1 × 10⁻¹⁶,[2,5] which is considered as an upper limit. The experimentally derived activation energy is 5.266 ± 0.994 kcal mol⁻¹, and the experimentally derived A factor of 1.5 × 10⁻¹² cm³ s⁻¹ compares well with our calculated value of 2.042 × 10⁻¹² cm³ s⁻¹.

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The tunneling corrections used utilize a nonsymmetric Eckart barrier. The reaction is quite exothermic, and a nonsymmetric Eckart barrier leading to substantially larger tunneling correction is more appropriate than the more commonly used symmetric Eckart barrier. The ratio of the quantum mechanical barrier crossing rate to the classical mechanical barrier crossing rate for a nonsymmetric Eckart barrier, Γ^*, is given by an integral which is not readily integrated analytically. It is, however, possible to compute Γ^* numerically as a function of the parameters α_1 ($=2\pi V_1/hv^*$), α_2 ($=2\pi V_2/hv^*$), and u^* ($=hv^*/kT$) were V_1 ($=9.589$ kcal mol^{-1}) and V_2 ($=15.801$ kcal mol^{-1}) are the forward and reverse classical barriers, respectively, and v^* ($=2466.01$ cm^{-1}) is the imaginary frequency for the transition state. This leads to values for α_1, α_2, and u^* of 8.545, 14.081, and 11.906, respectively, and results in a value for Γ^* of 558.7 at 298 K. When this correction is applied to the rate constant without tunneling for the QCISD/6-311G**//MP2/6-311G** result (Table 6), a value for the rate constant with tunneling of 1.034×10^{-16} cm^3 molecule^{-1} s^{-1} in very good agreement with the experimental value of 2.1×10^{-16} cm^3 molecule^{-1} s^{-1} [2,5] is obtained. This strongly suggests that the classical barrier obtained using the QCISD/6-311G**//MP2/6-311G** calculation is realistic and that a nonsymmetric Eckart barrier is the appropriate model to use for the tunneling correction in this case.

The above results for CF$_3$H indicate that its reaction with hydroxyl radicals is about 2 orders of magnitude slower than that of CH$_4$ ($k_{297} = 0.789 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}, $A = 5.59 \times 10^{-12}$ cm^3 s^{-1}, $E_a = 3.92 \pm 0.20$ kcal mol^{-1}).[4] Using the relationship lifetime(HCFC) $= 6.3$ yr $\times$ k(CH$_3$CCl$_3$ at 277 K)/k(HCFC at 277 K) as given by Derwent et al.,[18] the estimate for the lifetime of methylchloroform of 6.3 yr,[19] the rate constant at 277 K for methylchloroform of 7.531×10^{-15} cm^3 molecule^{-1} s^{-1},[20] and the rate constant for CHF$_3$ at 277 K as determined from our calculations of 7.247×10^{-16} cm^3 molecule^{-1} s^{-1} gives a lifetime for CHF$_3$, based on its reaction with OH radicals in the troposphere, of 65.5 yr. This is less than the 310 yr based on k_{277}(CHF$_3$) $= 1.530 \times 10^{-16}$ using the accepted experimental data,[5] but both values for the lifetime of CHF$_3$ indicate that it is among the longest lived of the HFC's in terms of its reaction with OH radicals.

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