Comparisons between Density Functional Theory and Conventional ab Initio Methods for 1,2-Elimination of HF from 1,1,1-Trifluoroethane: Test Case Study for HF Elimination from Fluoroalkanes[†]

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Density functional theory, DFT, and high-level conventional ab initio calculations, together with RRKM calculations, have been employed to study the nature of the transition state geometry for 1,2 elimination of HF from 1,1,1-trifluoroethane-d_0,-d_3; these serve as test cases for 1,2-HF elimination from fluorocarbons. Quantities calculated include structural parameters, bond indices, energies, atomic charges, vibrational frequencies, and moments of inertia for the reactant and the transition state geometry. The threshold energies for HF and DF elimination were computed and the vibrational frequencies and moments of inertia data were used with the RRKM theory to calculate the entropies of activation, preexponential factors for thermal activation, and also rate constants and the kinetic isotope effect for both thermally and chemically activated 1,1,1-trifluoroethane-d_0,-d_3. Of all the methods employed, the hybrid DFT methods incorporating either the three-parameter exchange functional of Becke with the correlation functional of Perdew and Wang or the correlation functional of Lee, Yang, and Parr were found to give results more consistent with the experimental studies. Both the 6-31G(d′,p′) and cc-PVDZ basis sets gave comparable agreement with experiment and suggest that basis sets of double-ζ quality in the valence region, which include polarization functions, appear to be adequately flexible to describe the systems studied here. There appears to be little to be gained in going from the computationally efficient DFT calculations to the computationally very expensive methods such as G2 or MP2.

I. Introduction

A. Overview. The unimolecular decomposition of an alkyl halide, RX, to form an alkene and HX has been extensively studied in the gas-phase.[1] Our group has been conducting experimental studies of these 1,2-elimination reactions in which a haloethane or halopropane is prepared by combination of alkyl and halocarbon radicals with an energy given by the enthalpy of reaction.[2] We often compare the experimental results to those computed using the RRKM theory. If the RRKM computations are to provide precise interpretations of kinetic data, accurate threshold energy barriers and the average energy of the energized reactant must be known, and also accurate vibrational frequencies and moments of inertia for both the reactant and the transition state structure (TS) are needed. Reliable energies of activation can be obtained from bond dissociation energies, but the threshold energy barrier (E_0), the vibrational frequencies, and moments of inertia are generally not available for the C3 and C4 haloalkanes, halo alcohols, and haloethers that we are currently investigating. Therefore, the E_0 and the frequencies and moments of inertia for the reactant and transition state structure will be computed with ab initio methods using the Gaussian suite of programs. Our initial investigations have shown that high-level ab initio methods, such as MP4 and G2, are computationally too expensive for C3 and C4 compounds containing multiple halogen substituents. The primary objective of this study is to ascertain whether density functional theory, DFT, can provide E_0 values, vibrational frequencies, and moments of inertia that will lead to reliable RRKM kinetic data for the 1,2-HF elimination reaction from chemically activated C3 and C4 compounds containing a CF_3 substituent. If density functional theory successfully models the 1,2-HF elimination process, then a second objective is to compare the transition state structure from DFT to previous ab initio computations.

As a test case for comparison of DFT and ab initio methods, we selected the 1,2-HF/DF elimination from 1,1,1-trifluoroethane-d_0,-d_3. This unimolecular dehydrohalogenation reaction has been thoroughly studied by thermal and chemical activation methods,[3] and because it contains three fluorines, it is similar to the trifluoroalkanes, trifluoro alcohols, and trifluoroethers we will be investigating and, also it should be a more stringent test of the computational methods than either fluoro- or difluoroethane.

B. Selection of the Best Experimental Data. Kinetic data is available for thermally activated CH_3CF_3 and for chemically activated CH_3CF_3 and CD_3CF_3. The experimental data for thermally activated CH_3CF_3 that will be compared with the computed results will be the threshold energy and the preexponential factor from thermal activation at 800 K. The experimental kinetic data available for CH_3CF_3 and CD_3CF_3 are the rate constants and the kinetic isotope effect following excitation by combination of CH_3 (CD_3) and CF_3 radicals.

Four experimental thermal activation studies[4−7] have appeared. The earliest shock-tube investigation[5] was shown to use temperatures that were in error by several hundred degrees, and

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a reanalysis by Tsang[8] favored an Arrhenius *A* factor of 8.0 10^{14} s^{-1} and an activation energy of 69.5 kcal/mol. This corresponds to a $k_\infty = 8.3$ 10^{-5} s^{-1} at $T = 800$ K. A later shock-tube study by Tschuikow-Roux and Quiring[7] reported an Arrhenius A factor of 1.0 10^{14} s^{-1} and an activation energy of 68.7 kcal/mol, giving a $k_\infty = 1.7$ 10^{-5} s^{-1} at $T = 800$ K. The first thermal activation study[4] used a heated flow tube and reported an Arrhenius *A* factor of 1.4 10^{12} s^{-1} and an activation energy of 61.4 kcal/mol that are obviously incorrect; however, the rate constant at 800 K is 2.4 10^{-5} s^{-1}, consistent with the two shock heating studies. All of these thermal activation reports were analyzed by Rodgers and Ford,[9] but they did not use the corrected Arrhenius parameters provided by Tsang.[8] Rodgers and Ford[9] recommend Arrhenius parameters (an *A* factor of 2.0 10^{14} s^{-1} and $E_a = 71.0$ kcal/mol) corresponding to $k_\infty = 0.80$ 10^{-5} s^{-1} at 800 K that was a factor of 2−10 smaller than the rate constant from the experimental studies. The most recent shock-tube investigation by Tsang and Lifshitz reports considerably higher thermal Arrhenius parameters (*A* factor = 7.0 10^{14} s^{-1} and $E_a = 74.0$ kcal/mol) giving a rate constant $k_\infty = 0.415$ 10^{-5} s^{-1} at $T =$ 800 K. Tsang and Lifshtz extracted the high-pressure rate expression using energy transfer stepsizes of 500−1000 cm^{-1}, and the Arrhenius parameters are very sensitive to the assumed stepsize. The *A* factor was about an order of magnitude larger than from the earlier experiments which according to Tsang and Lifshitz "suggests that the transition state for HF elimination is much looser than could be deduced from earlier results and indeed for all other known HX elimination processes". We will adopt $k_\infty = 1.4 \pm 1.0$ 10^{-5} s^{-1} at 800 K that is an average of the shock tube results of Tsang/Lifshitz and Tschuikow-Roux/Quiring and the early flow tube results. Using an average from the shock tubes gives $E_a = 71 \pm 3$ kcal/mol, and using the adopted k_∞, this provides an Arrhenius *A* factor of 3.5 10^{14} s^{-1} that is between the shock-tube values and has a sizable uncertainty. For a comparison to the ab initio computations, the threshold energy is needed, and based on a torsional model for the reactant, these Arrhenius parameters convert to a threshold energy $E_0 = 69.6 \pm 3$ kcal/mol and a preexponential factor, in partition function form, of 1.45 10^{14} s^{-1}. For a torsional model, which treats the motion of the CH_3 group with respect to the CF_3 group as a hindered torsion rather than a free rotation, the reaction path degeneracy is 6 so the preexponential factor[1] at 800 K is 2.4 ±1.0 10^{13} s^{-1} per reaction path. The adopted experimental data are summarized in Table 11.

Rodgers and Ford[9] also analyzed the experimental chemical activation data for HF loss from CH_3CF_3 prepared by the combination of CH_3 and CF_3 radicals and recommended a threshold energy of 69.2 kcal/mol. However, the early chemical activation studies using photolysis of acetone and hexafluoroactone mixtures were shown[10,11] to give rate constants that are too small because of the removal of CH_2CF_2 by reaction with the CF_3 radical. This complication lead Rodgers and Ford to suggest an E_0 that may be too large. Chemical activation studies[12] where addition of CF_3 radicals to the CH_2CF_2 was arrested gave experimental unimolecular rate constants between 3.2 and 3.8 10^{8} s^{-1} with efficient collision partners (SF_6, *n*-C_8F_{18}, and *n*-C_6F_{14}). These chemical activation studies favor a threshold energy barrier of 67−68 kcal/mol. We adopt a chemical activation rate constant of 3.5 ± 0.3 10^{8} s^{-1} for CH_3CF_3 and a $E_0 = 69 \pm 3$ kcal/mol that is consistent with the thermal and chemical activation results. For chemical activation by combination of methyl and trifluoromethyl radicals, the average excitation energy is 101.2 kcal/mol for CH_3CF_3 and 102.1 kcal/mol for CD_3CF_3. Two measurements of the chemical activation kinetic isotope effect have appeared. The earlier report[13] gave 3.1, but this was later questioned because the isotope effect was found to depend on the extent of conversion, presumably because of the addition of CF_3 radicals to CH_2CF_2 or CD_2CF_2. Data[11] extrapolated to zero conversion to correct for secondary reactions gave a kinetic isotope effect of 2.84 ± 0.07, which we adopt.

C. The 1,2-HF Transition State and Previous Theoretical Studies. Recent suggestions about the substituent effects for fluorine and chlorine and quantum chemical calculations[14] are at variance with the long-standing view[1,15] of the dehydrohalogenation reaction proceeding through a four-center transition state (TS) with an activation energy proportional to the carbon-halide bond strength. A common feature for all ab initio theoretical studies which have appeared on systems involving HF elimination from haloalkanes is a C−F bond that is substantially ruptured and a C−H bond length that is stretched only slightly (roughly 20% or less) from that in the molecule. It is not clear that these TSs would give kinetic isotope effects that agree with experiment.

The 1,2-elimination of HF from fluoroethane was first studied by Kato and Morokuma,[16] at the HF/4-31G level of theory. They found a syn elimination with a planar four-membered TS, with the C−F bond stretched to a greater extent than the C−H bond. They also predicted a H−F bond at the TS much longer than in the product, indicating a relatively early TS. Studies on the reverse reactions, i.e., HF additions to ethene,[17−19]arrive at the same conclusion regarding the TS geometry; that is, the C−H bond is more fully formed than the C−F bond.

More recently, Toto et al.[14] studied the 1,2-elimination of HX from $CH_{3-n}X_nCH_3$ (X = F and Cl for $n = 1-3$). In all cases, they found a strongly asymmetric TS (C−X bond stretched to a greater extent than C−H), with the degree of asymmetry increasing with increasing atomic number of X. As with previous studies, they assumed C_s symmetry for the TS. The levels of theory they used are modest by today's standards, and the agreement with experiment for threshold energies was good but not excellent. This study also suffered in other areas, such as bond orders, by only calculating TS values and, thus, not having a comparison of changes in going from reactant to TS (although formally a single bond would have a bond order of 1.0, calculated bond orders are usually at variance with this, as can be seen below). Clearly, there is a need for higher quality theoretical studies that are tested against experimental results.

The choice of which theoretical method to employ has always been a consideration of accuracy versus computational cost. In this regard, density functional theory (DFT) methods have become popular in recent years, because in many cases they provide similar, or even better, agreement with experiment than conventional ab initio methods, but at much less cost. For examples, see some of the books[20−22] that have recently appeared giving reviews of various applications of DFT.

A recent DFT study[23] of the addition of fluoromethyl radicals to fluoroethenes concluded that B3PW91 provides reasonable barrier heights for these reactions, with better results obtained when a fit to the Arrhenius equation was performed. Although four DFT methods were used, only one basis set, 6-31G(d,p), was employed, so basis set effects on these types of reactions remain to be seen. In the present paper, we present results calculated using a range of functionals and basis sets and include high-level conventional ab initio results for comparison.

TABLE 1: Structural Parameters for 1,1,1-Trifluoroethane, from Experiment and Various Levels of Theory

level	C−F	C−H	C−C	∠FCF	∠HCH	∠FCC	∠HCC
experiment[a]	1.335	1.085	1.530	107.87[b]	110.60[b]	111.03	108.32
BLYP/6-31G(d′,p′)	1.369	1.100	1.518	107.24	109.32	111.63	109.62
BLYP/cc-pVDZ	1.372	1.106	1.516	107.08	109.38	111.78	109.55
B3LYP/6-31G(d′,p′)	1.350	1.093	1.506	107.23	109.39	111.64	109.55
B3LYP/cc-pVDZ	1.353	1.099	1.504	107.08	109.46	111.77	109.48
B3PW91/6-31G(d)	1.353	1.090	1.495	107.22	109.72	111.64	109.22
B3PW91/6-31G(d′,p′)	1.346	1.093	1.503	107.23	109.37	111.64	109.57
B3PW91/cc-pVDZ	1.349	1.098	1.500	107.08	109.44	111.77	109.50
B3PW91/6-31++G(d′,p′)	1.351	1.093	1.502	106.87	109.58	111.97	109.36
B3PW91/aug-cc-pVDZ	1.355	1.095	1.500	106.85	109.72	111.99	109.22
CBS-4 [c]	1.352	1.079	1.490	107.23	109.49	111.63	109.45
CBS-Q[d]	1.346	1.094	1.504	107.35	109.55	111.52	109.39
G2[e]	1.325	1.082	1.500	107.21	109.53	111.65	109.41
MP2/6-31G(d′,p′)	1.345	1.090	1.501	107.42	109.55	111.45	109.39

[a] Reference 38. [b] Calculated value. [c] From HF/3-21G* calculation. [d] From HF/6-31G(d′) calculation. [e] From HF/6-31G(d) calculation.

II. Computational Methods

Ab initio computations were conducted on a DEC 500au workstation using the Gaussian suite of programs,[24] with visualization provided by GaussView. The NBO program[25] was used to calculate natural population analysis (NPA) atomic charges and Wiberg bond indices.[26] Computer animations referenced herein were produced with AVS5[27] and the GIMP (GNU Image Manipulation Program).[28]

Density functional theory (DFT) calculations were performed using the hybrid three-parameter exchange functional of Becke,[29] (B3) in combination with the gradient-corrected correlation functionals of Lee, Yang, and Parr[30] (LYP) and Perdew et al.[31] (PW91). These are designated as B3LYP and B3PW91, respectively. We also employed one “pure DFT” method, using Becke 1988 exchange[32] in conjunction with LYP correlation, designated as the BLYP method. For geometry optimizations and vibrational frequencies the basis sets employed were the 6-31G(d′,p′)[33] set of Petersson and co-workers (defined as part of the complete basis set methods[34]), and Dunning et al.’s correlation-consistent polarized basis cc-pVDZ.[35] We also tested the effect of adding full sets of diffuse functions to all these basis sets.

To compare the DFT results with conventional ab initio methods, we also employed Møller−Plesset perturbation theory, the complete basis set methods CBS-4[36] and CBS-Q,[36] and Gaussian-2 (G2)[37] theory.

The calculated vibrational frequencies, moments of inertia, and threshold energies were used as input for RRKM calculations[1] of rate constants for 1,2-HF/DF elimination from CF_3CH_3 and CF_3CD_3. The Haarhoff method for sums and densities of states was employed, and the energy distribution for CF_3CH_3 was assumed to be the same for CF_3CD_3. Selection of the optimum DFT method and basis set will be based upon comparison of experimental and calculated results for the preexponential factor, the E_0 and the k_∞ at $T = 800$ K from thermal activation and for chemical activation the rate constant, k_E, and the kinetic isotope effect.

III. Results and Discussion

A. Structural Parameters, Vibrational Frequencies, and Moments of Inertia. Structural parameters for CF_3CH_3, from experiment[38] and various levels of theory, are presented in Table 1. Although every method employed here overestimates the FCC and HCC bond angles, and the C−H and C−F bonds lengths (except for HF/6-31G(d) on the latter), and underestimates the C−C bond length and FCF and HCH angles, in general, the agreement with experiment is quite satisfactory (within 1.3° and 0.04 Å in most cases). Despite its well-known deficiencies, HF performs quite well, especially with the 6-31G(d′) basis set. The MP2/6-31G(d′,p′) level of theory gives very good agreement with experiment. The DFT methods, particularly with B3 exchange, all yield about the same results, which are in good agreement with the experimental structure.

In Table 2, we present the changes in key structural parameters (the interatomic distances in the four-center TS) between CF_3CH_3 and the HF elimination TS. As noted as in previous studies, at the TS there is greater rupture in the C−F than the C−H bond. The percent change in the C−C bond is small, but the bond length is about halfway between normal single- and double-bond lengths. For all of these parameters, the percent changes vary little from method to method, except that the addition of diffuse functions (see B3PW91/6-31++G(d′,p′) and B3PW91/aug-cc-pVDZ) yields the largest change in the C−F distance and the smallest changes in the C−H and H−F distances. The reverse is true for HF/3-21G*, the lowest level of theory employed.

The normal mode vibrational frequencies for CF_3CH_3, from experiment[38] and various levels of theory, are presented in Table 3, (Supporting Information) and Table 6 (Supporting Information) shows the CF_3CD_3 frequencies. The frequencies are not systematically overestimated by DFT, and no single method consistently outperforms the others. It is common practice to scale calculated frequencies (and derived quantities such as zero-point energy). For DFT methods, the scaling factors are very close to 1.0, and in any case, we are comparing differences between the reactant molecule and the TS (as in the quantities discussed below), so scaled or unscaled frequencies give the same result.

Tables 5 and 8 (Supporting Information) have the moments of inertia for the reactant and TS for CF_3CH_3 and for CF_3CD_3, respectively. Also shown are the ratio of the product of the moments of inertia for the TS versus the reactant, that is used in the rate constant calculations. All DFT methods and basis sets give very similar results; the ratio of the product of the moments of inertia are 1.33 ± 0.04 for CF_3CH_3 and 1.26 ± 0.04 for CF_3CD_3. Greater variation in the ratio is found among the ab initio methods and the model chemistries of CBS-4 and CBS-Q. The square root of the ratio of the product of the moments for the TS versus the product for the reactant is used to calculate the rotational contribution to the rate constant. Because all DFT methods give nearly identical results, the rotational contribution to the computed rate constants will be independent of the DFT method and the basis set. There will be a very small contribution from rotations to the kinetic isotope effect, $k^H/k^D = (1.33)^{1/2}/(1.26)^{1/2} = 1.027$.

TABLE 2: Changes to Key Structural Parameters, at Various Levels of Theory

level of theory	molecule	TS	% change
		C...F	
BLYP/6-31G(d′,p′)	1.369	1.971	44.0
BLYP/cc-pVDZ	1.372	1.958	42.7
B3LYP/6-31G(d′,p′)	1.350	1.933	43.2
B3LYP/cc-pVDZ	1.353	1.927	42.4
B3PW91/6-31G(d)	1.353	1.906	40.9
B3PW91/6-31G(d′,p′)	1.346	1.915	42.3
B3PW91/cc-pVDZ	1.349	1.914	41.9
B3PW91/6-31++G(d′,p′)	1.351	1.995	47.7
B3PW91/aug-cc-pVDZ	1.355	1.986	46.6
CBS-4[a]	1.352	1.844	36.4
CBS-Q[b]	1.346	1.939	44.1
G2[c]	1.325	1.986	49.9
MP2/6-31G(d′,p′)	1.345	1.878	39.6
		C...H	
BLYP/6-31G(d′,p′)	1.100	1.365	24.1
BLYP/cc-pVDZ	1.106	1.369	23.8
B3LYP/6-31G(d′,p′)	1.093	1.356	24.1
B3LYP/cc-pVDZ	1.099	1.359	23.7
B3PW91/6-31G(d)	1.090	1.367	25.4
B3PW91/6-31G(d′,p′)	1.093	1.358	24.2
B3PW91/cc-pVDZ	1.098	1.358	23.7
B3PW91/6-31++G(d′,p′)	1.093	1.309	19.8
B3PW91/aug-cc-pVDZ	1.095	1.313	19.9
CBS-4[a]	1.079	1.428	32.3
CBS-Q[b]	1.094	1.360	24.3
G2[c]	1.082	1.313	21.3
MP2/6-31G(d′,p′)	1.090	1.354	24.2
		H...F	
BLYP/6-31G(d′,p′)	2.663	1.253	−52.9
BLYP/cc-pVDZ	2.668	1.256	−52.9
B3LYP/6-31G(d′,p′)	2.638	1.235	−53.2
B3LYP/cc-pVDZ	2.642	1.239	−53.1
B3PW91/6-31G(d)	2.623	1.220	−53.5
B3PW91/6-31G(d′,p′)	2.633	1.225	−53.5
B3PW91/cc-pVDZ	2.635	1.230	−53.3
B3PW91/6-31++G(d′,p′)	2.638	1.286	−51.3
B3PW91/aug-cc-pVDZ	2.638	1.284	−51.3
CBS-4[a]	2.617	1.182	−54.8
CBS-Q[b]	2.629	1.235	−53.0
G2[c]	2.611	1.244	−52.4
MP2/6-31G(d′,p′)	2.624	1.213	−53.8
		C−C	
BLYP/6-31G(d′,p′)	1.518	1.418	−6.59
BLYP/cc-pVDZ	1.516	1.419	−6.40
B3LYP/6-31G(d′,p′)	1.506	1.407	−6.57
B3LYP/cc-pVDZ	1.504	1.407	−6.45
B3PW91/6-31G(d)	1.495	1.395	−6.69
B3PW91/6-31G(d′,p′)	1.503	1.404	−6.59
B3PW91/cc-pVDZ	1.500	1.404	−6.40
B3PW91/6-31++G(d′,p′)	1.502	1.404	−6.52
B3PW91/aug-cc-pVDZ	1.500	1.403	−6.47
CBS-4[a]	1.490	1.392	−6.58
CBS-Q[b]	1.504	1.402	−6.78
G2[c]	1.500	1.400	−6.67
MP2/6-31G(d′,p′)	1.501	1.406	−6.63

[a] From HF/3-21G*calculation. [b] From HF/6-31G(d′) calculation. [c] From HF/6-31G(d) calculation.

B. Imaginary Frequencies, Bond Orders, and Atomic Charges. For the TS for elimination of HF/DF from CF_3CH_3/CF_3CD_3, the imaginary frequency (corresponding to the reaction coordinate) and the other vibrational frequencies, calculated at various levels of theory, are presented in Table 4 (Supporting Information) for CF_3CH_3 and Table 6 (Supporting Information) for CF_3CD_3. As visualized with GaussView, the main motion for the imaginary frequency is the movement of the H from the carbon to which it is attached toward the fluorine of the HF fragment being eliminated, with the proviso that in fact this mode is an unbound oscillation, rather than an oscillation as shown. Also, the C−C bond oscillates as the π bond is forming, and the CH_2 and CF_2 groups oscillate between pyramidal and planar geometries. All of these motions are as we expect for a 1,2-HF elimination and help to confirm that the proper TS has been located. An animated GIF of the normal mode for the imaginary frequency, at the B3PW91/6-31G(d′,p′) level of theory, has been produced (using AVS5 and the GIMP) and is available for viewing as Supporting Information. As a final confirmation that we located the proper TS, we performed an intrinsic reaction coordinated (IRC) calculation, again at the B3PW91/6-31G(d′,p′) level of theory, using the method of Gonzalez and Schlegel.[39] Using the default step size, we calculated as many points as needed (96 from TS to reactant and 86 from TS to products) to follow the reaction path from reactant through the TS to products. An MPEG movie of this path has been produced (using AVS5) and is available for viewing as Supporting Information. This animation shows that the H and F atoms to be eliminated first become coplanar with the carbon atoms. In the next stage, the H and F atoms move away from the carbons and toward each other, with movement of the F leading that of the H. Near the TS the main motion is movement of the H toward the F in a planar geometry. For all DFT methods, the TS geometry had a torsional angle of zero to three decimal places. After the H−F bond forms, this fragment moves away, while the C−C bond shortens and the CF_2 and CH_2 groups flatten, forming $CF_2{=}CH_2$.

To further explore changes in bond order, we calculated Wiberg bond indices at several levels of theory, for both starting material and the TS, and these are presented in Table 9. We should caution that for DFT methods the first-order density matrix does not have any physical meaning, so the resulting Wiberg bond indices and atomic charges must be viewed with care. However, reasonable results, including for TSs, have been obtained in the past.[40] In general, our results confirm that at the TS the C−F bond has been broken to a greater extent than the C−H bond, but these bond orders, see Table 9, are closer together than those of previous studies.[3,14] The H−F bond has been formed to an extent of 0.3 or less, depending on the level of theory. The double C═C bond has formed by about one-third. The DFT methods, both pure and hybrid, all give results in fair agreement with one another, especially for the C−C bond. By comparison, the conventional ab initio methods yield bond indices which suggest that at the TS the C═C and H−F bonds have not formed to as great an extent as with the DFT methods. All methods employed here give a C−H reactant molecule−TS bond index difference of about 0.50, whereas the bond index difference for C−F varies from 0.526 with BLYP/cc-pVDZ to 0.618 with G2.

NPA atomic charges for CF_3CH_3, the TS, and the change from reactant to TS, are presented in Table 10. Toto et al.[14] employed the Mulliken population analysis (MPA) method, in which overlap populations are divided equally between bonded atoms, irrespective of their relative electronegativities. Thus, MPA tends to underestimate electron populations on electronegative atoms. It also has some basis set dependency. NPA charges calculated with DFT methods (in particular, B3LYP) are known to be in excellent agreement with high-level post-HF ab initio treatments.[41] Comparing our NPA charges for the TS to their MP2/6-31G(d,p)//HF/4-31G charges (see their Table 15), ours have consistently higher magnitudes, indicating a greater charge separation in the TS. However, we cannot make a valid comparison for the hydrogenic carbon, because they sum the charges on the hydrogens not being eliminated into the carbon. They report changes in charge, but use the eclipsed

TABLE 9: Wiberg Bond Indices for Bonds Being Broken or Formed in TS

theory	state	C—C	C—F	C—H	H—F
BLYP/6-31G(d′,p′)	CF_3CH_3	1.021	0.875	0.928	0.002
	TS	1.335	0.295	0.433	0.295
	change	+0.314	−0.580	−0.495	+0.293
BLYP/cc-pVDZ	CF_3CH_3	1.029	0.876	0.917	0.002
	TS	1.341	0.350	0.418	0.312
	change	+0.312	−0.526	−0.499	+0.310
B3PW91/6-31G(d′,p′)	CF_3CH_3	1.020	0.880	0.905	0.001
	TS	1.332	0.328	0.405	0.303
	change	+0.312	−0.552	−0.500	+0.302
B3PW91/cc-pVDZ	CF_3CH_3	1.029	0.864	0.916	0.002
	TS	1.345	0.325	0.406	0.296
	change	+0.316	−0.539	−0.510	+0.296
G2	CF_3CH_3	1.013	0.829	0.926	0.001
	TS	1.296	0.211	0.432	0.246
	change	+0.283	−0.618	−0.494	+0.245
MP2/6-31G(d′,p′)	CF_3CH_3	0.966	0.819	0.877	0.001
	TS	1.241	0.272	0.396	0.264
	change	+0.275	−0.547	−0.481	+0.263
Hassler and Setser[a,b]	TS	1.8	0.8	0.2	0.2
	change	+0.8	−0.2	−0.8	+0.2
O′Neal and Benson[a,c]	TS	1.5	0.5	0.5	0.5
	change	+0.5	−0.5	−0.5	+0.5
Tschuikow-Roux and Maltman[d]	TS	1.5	0.26 ± 0.07	0.26 ± 0.07	0.5
	change	+0.5	−0.73 ± 0.07	−0.73 ± 0.07	+0.5
Toto et al.[a,e]	TS	1.595	0.119	0.369	0.282
	change	+0.595	−0.881	−0.631	+0.282

[a] Bond orders for the reactant were assumed to be 1.00. [b] Reference 44. [c] Reference 45. [d] Reference 46. [e] Table 14 for CF_3CH_3 from ref 14.

TABLE 10: NPA Atomic Charges for CF_3CH_3, TS, and Change in Charge

theory	state	C_F	C_H	H_F[a]	H_C	F_H[a]	F_C
BLYP/6-31G(d′,p′)	CF_3CH_3	1.053	−0.657	0.227	0.227	−0.359	−0.359
	TS	1.004	−0.795	0.436	0.248	−0.570	−0.285
	change	*−0.049*	*−0.138*	*0.209*	*0.020*	*−0.211*	*0.074*
BLYP/cc-pVDZ	CF_3CH_3	1.101	−0.738	0.243	0.243	−0.364	−0.364
	TS	0.979	−0.850	0.446	0.256	−0.515	−0.286
	change	*−0.122*	*−0.112*	*0.202*	*0.013*	*−0.151*	*0.078*
B3PW91/6-31G(d′,p′)	CF_3CH_3	1.088	−0.819	0.270	0.270	−0.360	−0.360
	TS	0.999	−0.919	0.465	0.282	−0.546	−0.282
	change	*−0.090*	*−0.100*	*0.194*	*0.012*	*−0.186*	*0.078*
B3PW91/cc-pVDZ	CF_3CH_3	1.153	−0.756	0.249	0.249	−0.381	−0.381
	TS	1.047	−0.884	0.472	0.264	−0.556	−0.304
	change	*−0.106*	*−0.127*	*0.223*	*0.014*	*−0.175*	*0.077*
G2	CF_3CH_3	1.284	−0.735	0.241	0.241	−0.424	−0.424
	TS	1.290	−0.936	0.504	0.2638	−0.696	−0.345
	change	*0.006*	*−0.201*	*0.263*	*0.0224*	*−0.272*	*0.079*
MP2/6-31G(d′,p′)	CF_3CH_3	1.102	−0.783	0.255	0.2550	−0.361	−0.361
	TS	1.052	−0.831	0.448	0.2456	−0.570	−0.295
	change	*−0.050*	*−0.048*	*0.193*	*−0.0094*	*−0.209*	*0.066*

[a] Refers to atom being eliminated.

conformation of CF_3CH_3 as the starting point, so a direct comparison with our results is not possible. For what it’s worth, there is fair agreement.

In the majority of cases, the calculated charges have greater magnitudes with B3PW91 vs BLYP and cc-pVDZ vs 6-31G(d′,p′). HF/6-31G(d) gives anomalously large magnitudes for both carbon and fluorine atoms in the CF_3 group. Of more interest than the raw charges is how they change in going from reactant to TS. The DFT methods are at least semiquantitatively consistent in their predictions. HF/6-31G(d) is again anomalous in predicting a slight positive change in charge for the CF_3 carbon and larger magnitudes of change for other atoms. MP2/6-31G(d′,p′) tends to give smaller magnitudes and is the only method predicting a negative change for the CH_2 hydrogens. The general picture is that the carbons become more negative (the hydrogenic carbon more so); the leaving hydrogen becomes more positive, whereas the leaving fluorine becomes more negative; the remaining hydrogens and fluorines become slightly more positive. As the HF fragment breaks off from CF_3CH_3 to leave CF_2CH_2, the carbon atoms become more electronegative in going from sp^3 to sp^2 hybridization; the effect is enhanced when the substituents are relatively electropositive hydrogens. This change in charge must be balanced by the remaining substituents. In the forming HF fragment, the atoms are experiencing a greater electronegativity difference than when they were bonded to carbons, thus increasing the magnitude of their charges. Holmes and Paisley[2a] suggested that in terms of electron flow the C—H bonding electron pair shifts to become the π bond of the C═C, the C—F electron pair becomes a lone pair on the fluorine, and a lone pair on the fluorine becomes the H—F bond. Whereas “lone pair” is more useful as a concept than a statement of reality, the present results do show a shift in electron density from the hydrogen, through the carbons, and to the fluorine.

C. Comparison of Experimental and Theoretical Results. Threshold energies are compared in Table 11, with the calculated

TABLE 11: Threshold Energy Barriers, Thermal and Chemical Activation Rate Constants, and Kinetic-Isotope Effects for 1,1,1-Trifluoroethane

level[a]	threshold energies (kcal mol^{-1}) [DF]	preexponential factor for HF (10^{13} s^{-1})[b]	$\Delta S^\dagger_{vib}$(cal K^{-1})[c]	$(\{I^\dagger\}/\{I\})^{1/2}$	k_∞^{HF}, 800 K (10^{-5} s^{-1})	$k_\infty^{HF/DFT}$ $T = 800$ K	k_a^{HF} (10^8 s^{-1})[d]	$k_a^{HF/DF}$
BLYP/6-31G(d′,p′)	62.2 [63.5]	2.56	0.812	1.16	156	2.42	46.1	2.45
BLYP/cc-pVDZ	59.6 [60.9]	2.31	0.493	1.12	723	3.65	75.3	2.38
B3LYP/6-31G(d′,p′)	69.1 [70.5]	2.19	0.410	1.15	1.85	2.58	6.28	3.08
B3LYP/cc-pVDZ	66.6 [67.9]	2.17	0.390	1.15	8.27	2.43	11.0	2.64
B3PW91/6-31G(d)	71.9 [72.9]	2.51	0.704	1.15	0.318	1.83	2.05	2.27
B3PW91/6-31G(d′,p′)	68.8 [70.1]	2.34	0.482	1.14	2.09	2.40	6.20	2.79
B3PW91/cc-pVDZ	66.4 [67.7]	2.06	0.276	1.14	8.46	2.41	11.5	2.67
B3PW91/6-31++G(d′,p′)	65.8 [67.1]	2.54	0.739	1.17	16.2	2.63	17.2	2.81
B3PW91/aug-cc-pVDZ	64.1 [65.4]	2.28	0.408	1.17	42.0	2.47	23.4	2.62
MP2/6-31G(d′,p′)	74.6 [75.9]	2.05	0.320	1.13	0.051	2.43	1.03	3.60
CBS-4	76.8 [78.1]	1.98	0.341	1.15	0.0000699	1.51	0.00304	3.80
CBS-Q	72.6 [73.9]	3.08	1.29	1.16	0.27	2.74	3.82	3.32
G2[e]	72.2 [73.5]	2.93	1.18	1.14	0.33	2.70	4.18	3.19
experiment	69 ± 3.0[d]	2.4 ± 1.0[d]			1.4 ± 1[d]		3.5 ± 0.3[d]	2.84 ± 0.07[d]

[a] Ab initio data used as input for RRKM calculations. [b] Partition function form for unit reaction path degeneracy at 800 K. [c] Thermal $\Delta S^\dagger$ at $T = 800$ K. [d] Chemical activation energy of 101.2 kcal mol^{-1} for CF_3CH_3. See text. [e] From HF/6-31G(d) calculation.

values being simply the total energy difference with unscaled zero-point energy included. The DFT methods, especially B3PW91, followed closely by B3LYP, perform as well as high-level conventional ab initio methods which are much more computationally expensive. Many basis sets give E_0s within the experimental error with either the B3PW91 or the B3LYP method, but the larger basis sets give threshold energies too low by several kcal/mol. This gives us some confidence that we can use DFT to obtain accurate results in our studies, although it appears that the DFT methods systemically underestimate the E_0s. Although the G2 method has had a large degree of success in computing energies within thermochemical accuracy (1 kcal/mol), here it appears to slightly overestimate the threshold energy by 1 kcal/mol. In a recent study by Sendt et al.,[42] G2 calculated energies were found to be too high (by as much as 36 kcal/mol) to successfully model the decomposition of acrylonitrile. The G2 scheme was developed for the calculation of equilibrium energy differences rather than transition states and, thus, should not be expected to have the same degree of accuracy for threshold energies. We point out that the differences in threshold energies for HF and DF elimination are almost constant for all entries in Table 11; the $E_0(DF) - E_0(HF) = 1.3$ kcal/mol.

Theoretical rate constants from DFT-RRKM theory, see Table 11, are compared with the best experimental results selected in the Introduction section B. Because the calculated frequencies are input data for the RRKM calculations, it may be argued that the frequencies should be scaled. We tested this hypothesis with the HF/6-31G(d) frequencies, for which the scaling factor is generally well accepted,[43] and the scaling factor is greater than those for the MPn and especially DFT methods. The unscaled and scaled (by a factor of 0.89) vibrational frequencies gave computed thermal activation rate constants (not shown in the Table) that are essentially the same, and the kinetic isotope effects are nearly identical. This close accord gives us confidence in simply using unscaled frequencies.

For thermal rate constants, k_∞, at 800 K, most of the hybrid DFT results and G2 and CBS-Q are of the correct order of magnitude because these have threshold energies close to the experimental value. The CBS-4 method in particular is off by several orders of magnitude, because it severely overestimates the threshold energy. Both B3LYP and B3PW91 with the 6-31G(d′,p′) basis give excellent agreement within experimental uncertainity, whereas results with the cc-PVDZ basis set, which are a factor of 4 too large, are slightly outside the experimental error. Agreement is generally poorer for the chemical activation rate constants, except for the G2 and CBS-Q methods. Here again, the 6-31G(d′,p′) basis set gives superior results for the DFT methods. Although the G2 and CBS-Q methods underestimate the thermal rate constant, they give good agreement with the chemical activation results. The high E_0 for G2 and CBS-Q caused the thermal rate constant to be low, but the “loose” TS, $\Delta S^\dagger_{vib}$, nearly a factor of 2 larger than many DFT methods, accidentally gives a chemical activation rate constant in agreement with experiment.

Agreement between experimental and computed rate constants for both thermal and chemical activation is a stringent test of the theory because both the threshold energy and the energy dependence of the rate constant must be accurate. The thermal preexponential factor and $\Delta S^\dagger$ relate to the proper energy dependence of the rate constant, see Table 11. The large experimental uncertainty in the Arrhenius *A* factor and activation energy allows many computational methods to “agree” with the experiment; clearly, additional thermal activation studies of CH_3-CF_3 and CF_3CD_3 are warranted.

Transition state structures for unimolecular decompositions have been characterized as “loose” or “tight” structures based upon the value of $\Delta S^\dagger$. For all computational methods, the change in rotational entropy is 3.90 ± 0.10 cal/K, but 3.6 cal/K of this arises from the reaction path degeneracy, which is 6 for the torsional model employed here. A constant $\Delta S^\dagger_{rot}$ arises from relatively constant moments of inertia [see Tables 5 and 8 (Supporting Information)]; the square root of the ratio of the product of the moments of inertia for the TS versus the product of the moments of inertia for the reactant ranged between 1.13 and 1.17, see Table 11. The constancy of $\Delta S^\dagger_{rot}$ for all methods is also consistent with the close similarity of all molecular and TS bond lengths in Table 2. The $\Delta S^\dagger_{vib}$ values in Table 11 range from 0.27 to 1.29 cal/K. The greater variation seen for $\Delta S^\dagger_{vib}$ is to be expected based upon the variability of bond orders seen in Table 9. The $\Delta S^\dagger$ values for vibrations are between 0.3 and 0.7 for all DFT computational methods, but the last two entries in Table 11 have a somewhat looser TS with the $\Delta S^\dagger_{vib} = 1.18-1.29$ cal/K. The tighter transition states yielded by hybrid DFT methods result in an energy dependence of the rate constant more consistent with the experiment. For example, the B3LYP and B3PW91 methods using either the 6-31G(d′,p′) or the cc-PVDZ basis set overestimate both the experimental thermal and the chemical activation rate constants by a factor of 2−4, Table 11. This illustrates that the energy dependence of the rate constant is correct and a slightly higher threshold energy would give excellent agreement between computed and experimental results for both the thermal and chemical activation rate constants. The ab initio methods (G2 and CBS-Q) are not as successful as the DFT in matching the experimental energy dependence of the rate constant. These give thermal rates a factor of 5 too low, but a looser TS than for the best DFT method gives a chemical activation rate constant within 20% of experiment. Using the energy dependence of the rate constant as the basis for comparison, the hybrid DFT methods seem to out perform ab initio methods with the best agreement for either the B3PW91 or B3LYP method and either the 6-31G(d′,p′) or the cc-PVDZ basis set. Basis sets larger than either the 6-31G(d′,p′) or the cc-PVDZ are not an improvement and are computationally more demanding.

A final test of the theory with experiment is comparison to the chemical activation kinetic isotope effect comparing CH_3-CF_3 with CF_3CD_3. Satisfactory agreement with experiment is achieved for several methods, with B3PW91 using either 6-31G-(d′,p′) or 6-31++G(d′,p′) being within experimental error. All of the hybrid DFT methods are close to the experimental range and outperform the more expensive CBS and G2 methods. As with the threshold energies, pure DFT methods underestimate the isotope effect, conventional ab initio methods overestimate it, and the hybrid methods yield values between those.

In summary, the DFT calculation with B3PW91/6-31G(d′,p′) provides the best overall agreement with experiment; it gives a threshold energy, a thermal preexponential factor, a thermal rate constant at 800 K, and the chemical activation kinetic-isotope effect all within acceptable error of experimental values. The B3PW91/6-31G(d′,p′) rate contants were less than a factor of 2 too large, but a slightly larger threshold energy would allow the DFT results to match both the thermal and chemical activation experimental rate constants. The B3PW91/6-31G-(d′,p′) is one of only two methods, with B3PW91/6-31++G-(d′,p′) being the other, within experimental error of the kinetic isotope effect. The cc-pVDZ basis set with either B3PW91 or B3LYP was slightly less successful than the B3PW91/6-31G-(d′,p′). All ab initio methods performed less well than the best DFT method.

D. Comparison of Transition State Models. One method of modeling the transition state is from assigned bond orders for the bonds that are ruptured or formed as the reaction progresses. For 1,2-dehydrohalogenation, the initial models conserved bond orders and were estimated for the C−H, C−X, H−X, and C−C bonds to be 0.2, 0.8, 0.2, and 1.8 by Hassler and Setser.[44] Benson's group[45] used one-, two- or three-electron bonds, corresponding to a bond order of 0.5 for C−H, C−X, and H−X and 1.5 for C−C bonds, respectively, to estimate Arrhenius *A* factors. More recent models[46] incorporated a partial formal charge in the TS that so that the sum of the TS's bond orders plus the partial formal charge separations equals the bond order in the activated molecule. For this model, the bond orders for C−C and H−X were adopted from O'Neal and Benson,[45] and the C−H and C−X bond orders were assumed to be identical but were varied to conserve the overall bond order. Typical values for the C−H and C−X bond orders were 0.26 ± 0.07. This approach was consistent with ionic/polar character for the TS proposed by MacColl[15] to account for the effect of substituents on the E_as. Common features of all of the TSs were relatively weak C−H and H−X bonds which were necessary for calculated RRKM data to agree with the experimental kinetic H/D isotope effect. In the past, the C−X bond was believed to be only moderately lengthened in the TS in order to agree with heavy atom isotope effect[47] for elimination of $H^{35}Cl/H^{37}Cl$ of 1.001. Table 9 summarizes the bond orders for previous models and the results for some DFT and ab initio methods. The changes in bond orders are also listed. Our TS bond orders for B3PW91/6-31G(d′,p′), Table 9, show a weaker C−C bond order (1.33) than any of the previous models, the changes in the C−X bond order = −0.55 is similar to the value recommended by O'Neal and Benson[45] and by Tschuikow-Roux and Maltman,[46] and the change in C−H bond order, −0.50, is also close to the value recommended by Benson, whereas the change in the H−X bond order, +0.30, is close to the Setser[44] models and to the value calculate by Toto et al. Our results, for the change in bond order for C−C, C−H, and C−F, are significantly differently than those obtained by Toto et al.[14] utilizing the Pauling relation. Finally, we note that the relatively strong C−H and C−X bonds suggests that considerable energy has yet to be released to the products, and this energy release will occur as the HX and alkene moieties separate from each other. A similar picture for the energy disposal has been proposed.[48]

IV. Conclusions

The transition state for 1,2-HF/DF elimination from CF_3CH_3 and CF_3CD_3 is asymmetric, with the C−F bond stretched from its equilibrium position to a much greater extent than the C−H bond. However, Wiberg bond indices suggest that the bond order changes, while still asymmetric, are quite close. NPA atomic charges suggest significant charge separation in the transition states, and that in progressing from reactant to transition state, the carbons and leaving fluorine become more negative, with the other atoms becoming more positive. The transition state geometry, bond orders, imaginary vibrational frequencies, and the IRC all indicate that the fluorine atom begins leaving prior to the hydrogen atom.

DFT input parameters to RRKM provide close agreement with the experimental results, and the DFT methods are especially viable compared with other more costly ab initio methods. All of the DFT methods give comparable performance for structures and vibrational frequencies. For threshold energies and the thermal and chemical activation rate constants, the hybrid methods are superior. B3PW91 or B3LYP with either 6-31G(d′,p′) or cc-pVDZ gives the best overall performance and appear to be superior to methods such as G2, which are much more computationally expensive. The most gratifying result is the close accord between the B3PW91/6-31G(d′,p′) DFT method and the experimental thermal and chemical activation rate constants and the chemical activation kinetic-isotope effect. The close accord arises because DFT methods give threshold energies close to experiment and they yield tighter transition state structures than conventional ab initio methods. However, the threshold energy barriers are very sensitive to the DFT method and to the basis set; thus, extrapolation from the best method for CF_3CH_3 to a suitable method for fluoropropanes should be done with caution.

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Supporting Information Available: Tables 3−8 are available as Supporting Information. An animated GIF of the normal mode for the imaginary frequency, at the B3PW91/6-31G(d′,p′) level of theory, and an MPEG movie of the reaction path from reactant through the TS to products are also available as Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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