Thermochemical Parameters of CHFO and CF_2O

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Thermochemical properties of CHFO and CF_2O and their derivatives were calculated by using coupled-cluster theory (U)CCSD(T) calculations with the aug-cc-pV*n*Z (n = D, T, Q, 5) basis sets extrapolated to the complete basis set limit with additional corrections. The predicted properties include the following. Enthalpies of formation (298 K, kcal/mol): $\Delta H_f(CF_2O) = -144.7$, $\Delta H_f(CHFO) = -91.1$, $\Delta H_f(CFO^\bullet) = -41.6$. Bond dissociation energy (0 K, kcal/mol): BDE(CFO−F) = 120.7, BDE(CHO−F) = 119.1, BDE(CFO−H) = 100.2. Ionization potential (eV): $IP_1(CF_2O) = 13.04$, $IP_2(CF_2O) = 14.09$, $IP_1(CHFO) = 12.41$, $IP_2(CHFO) = 13.99$, $IP_1(CFO^\bullet) = 9.34$. Proton affinity (298 K, kcal/mol), $PA_O(CF_2O) = 148.8$, $PA_O(CHFO) = 156.7$, $PA_F(CHFO) = 154.5$ kcal/mol. Electron affinity: $EA(CFO^\bullet) = 2.38$ eV. Triplet−singlet separation gap (eV): $\Delta E_{T1-S0}(CF_2O) = 4.47$, $\Delta E_{T1-S0}(CHFO) = 4.36$. Triplet−triplet transition energy (eV): $\Delta E_{T2-T1}(CF_2O) = 0.44$. The new calculated values contribute to solving some persistent discrepancies in the literature. The effects of F-atoms on thermochemical parameters are not linearly additive, and the changes are largely dominated by the first F-substitution. On the basis of the calculated proton affinities of CF_2O and CF_3OH, the nucleophilicities of the oxygen atoms are, within computational errors, the same in both compounds.

Introduction

The molecules CFHO and CF_2O have been implicated in a number of chemical processes relevant to atmospheric chemistry, in particular as products of the photo-oxidation of hydrofluorocarbons (HFC).[1] HFCs have low toxicity and do not deplete ozone, but may have an impact in terms of global warming.[2] In the atmosphere, oxidation of HFCs containing CF_3 groups (such as $CF_3CH_mF_n$) eventually produces the trifluoromethoxy $CF_3O^\bullet$ radical,[3] which can abstract H from H_2O or high concentration organic molecules such as CH_4 in the atmosphere leading to the formation of trifluoromethanol (CF_3OH).[4,5] This simplest perfluorinated primary alcohol is unstable[6–8] in various media and undergoes HF elimination at room temperature giving CF_2O.[8] The $CF_3O^\bullet$ radical also reacts with other oxygen-containing species such as NO or O_3, generating CF_2O.[9] Reactions of the excited oxygen atom $O(^1D)$ with HFCs[10–13] or of the OH radical with CF_3[14] can yield either CHFO or CF_2O and HF. The carbonyl fluorides formed under these conditions undergo further fragmentations giving rise to carbon monoxide.[10] CF_2O is the main product from the gradual decomposition of perfluoro polyalkyl ethers.[15] Recent experiments[16] demonstrated that CF_2O can be formed from reactions of CO_2 with F_2 under various conditions.

In an earlier theoretical study, we predicted the enthalpies of formation of FCO and CF_2O by using high level ab initio molecular orbital theory.[17] More recently, we carried out a theoretical study on the energetics and mechanism of the decomposition of CF_3OH in the gaseous phase.[18] Together with a detailed study on the potential energy surfaces, we re-evaluated the enthalpies of formation of CF_3OH and its derivatives using the electronic energies calculated at the coupled-cluster theory CCSD(T) with the aug-cc-pV*n*Z (n = D, T, Q) basis sets extrapolated to the complete basis set limit with additional smaller corrections including core-valence, scalar relativistic, and spin−orbit terms in addition to the zero point energy.[18] Our earlier work[17] resolved the issues[19–24] with the enthalpy of formation of CF_2O. There is still an issue with the proton affinity of CF_2O. For CHFO, the enthalpy of formation is given in the NIST-JANAF Tables[25] and the NASA compilation,[26] but relatively little else is known about the thermochemical properties of this monofluorinated formaldehyde. We have also previously reported the heat of formation of HCO on the basis of high level calculations.[27]

The present theoretical study provides a uniform set of basic thermochemical properties of CF_2O and CHFO by using high accuracy electronic structure computations following an approach developed by our laboratory in conjunction with work at the Pacific Northwest National Laboratory and Washington State University.[28] We have used this approach to calculate the fundamental thermochemical parameters for a number of organic compounds,[29–31] and found excellent agreement with the most recent experimental determinations, with accuracies of ±0.5 kcal/mol for molecules containing two heavy atoms, and ±0.8 kcal/mol for molecules with three heavy atoms. To evaluate the effects of F-substitution on properties of the carbonyl functional group, we have also evaluated the corresponding data for formaldehyde using the same methodologies.

Computational Methods

Electronic structure calculations were carried out by using the Gaussian 03[32] and MOLPRO[33] suites of programs. The enthalpy of formation of each molecule considered was determined from the corresponding total atomization energies (TAE). Geometry parameters of each structure were fully optimized using molecular orbital theory at the second-order perturbation MP2 and coupled-cluster theory CCSD(T) levels with the

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correlation-consistent aug-cc-pVTZ basis set. The fully unrestricted formalism MP2 was used for open-shell system calculations done with Gaussian03. The single-point electronic energies were calculated at the CCSD(T)/aug-cc-pVTZ geometries using the coupled-cluster CCSD(T) formalism[34–37] in conjunction with the correlation-consistent aug-cc-pV*n*Z (n = D, T, Q and 5) basis sets.[38] For simplicity, the basis sets are denoted hereafter as aV*n*Z. Only the spherical components (5-*d*, 7-*f*, 9-*g*, 11-*h*) of the Cartesian basis functions were used. The open-shell CCSD(T) calculations in MOLPRO were carried out at the R/UCCSD(T) level. In this approach, a restricted open shell Hartree-Fock (ROHF) calculation was initially performed and the spin constraint was relaxed in the coupled cluster calculation.[39–41] The CCSD(T) energies were extrapolated to the complete basis set (CBS) limit energies using the following expression:[42]

$$E(x) = A_{\mathrm{CBS}} + B\exp[-(x-1)] + C\exp[-(x-1)^2] \quad (1)$$

where x = 2, 3, and 4 for the aV*n*Z basis, n = D, T and Q, respectively; and[43]

$$E(x) = E_{\mathrm{CBS}} + \mathrm{B}/x^3 \quad (2)$$

where x = 4 and 5 for aVQZ and aV5Z, respectively.

After the valence electronic energy, the largest contribution to the TAE is the zero-point energy (ZPE). Harmonic vibrational frequencies of each of the monomeric species were calculated at the equilibrium geometry using the (U)MP2/aVTZ method. We obtained an estimate of the anharmonic corrections which are largest for the OH and CH stretches. A scaling factor for the OH stretches of 0.9798 was obtained from CF_3OH by averaging the calculated MP2/aVTZ value (3829.8 cm^{-1}) with the experimental value[44,45] (3675 cm^{-1}) and dividing by the MP2 value. For the CH stretches, we obtained a scale factor of 0.9701 in a similar way from the experimental[44,46] (2844, 2962, and 2999 cm^{-1}) and theoretical (3055.1, 3126.6, and 3183.8 cm^{-1}) values of CH_3OH. The ZPEs for :CF_2 and :CFH were obtained from the average of the experimental[47] and calculated values (see Table S2 of the Supporting Information).

To evaluate the TAEs, smaller corrections are also required. Core-valence correlation corrections (ΔE_{CV}) were obtained at the CCSD(T)/cc-pwCVTZ level of theory.[48] Scalar relativistic corrections (ΔE_{SR}), which account for changes in the relativistic contributions to the total energies of the molecule and the constituent atoms, were included at the CI-SD (configuration interaction singles and doubles) level of theory using the cc-pVTZ basis set. ΔE_{SR} is taken as the sum of the mass-velocity and 1-electron Darwin (MVD) terms in the Breit−Pauli Hamiltonian.[49] Most calculations using available electronic structure computer codes do not correctly describe the lowest energy spin multiplet of an atomic state as spin−orbit in the atom is usually not included. Instead, the energy is a weighted average of the available multiplets. The spin−orbit corrections are 0.085 kcal/mol for C, 0.223 kcal/mol for O, and 0.380 kcal/mol for F, all of them from the excitation energies of Moore.[50] These corrections are summarized in Table 1. The core-valence correction terms are positive and on the order of 0 to 1.5 kcal/mol, and the scalar relativistic and spin−orbit terms terms are negative and range from 0 to −1.1 kcal/mol.

The total atomization energy ($\sum D_0$ or TAE) of a compound is given by the expression

$$\sum D_0 = \Delta E_{\mathrm{elec}}(\mathrm{CBS}) - \Delta E_{\mathrm{ZPE}} + \Delta E_{\mathrm{CV}} + \Delta E_{\mathrm{SR}} + \Delta E_{\mathrm{SO}} \quad (3)$$

By combining our computed $\sum D_0$ values with the known enthalpies of formation at 0 K for the elements ($\Delta H_{\mathrm{f}}°(\mathrm{H})$ = 51.63 ± 0.001 kcal/mol, $\Delta H_{\mathrm{f}}°(\mathrm{C})$ = 169.98 ± 0.1 kcal/mol, $\Delta H_{\mathrm{f}}°(\mathrm{O})$ = 58.99 ± 0.1 kcal/mol, and $\Delta H_{\mathrm{f}}°(\mathrm{F})$ = 18.47 ± 0.07 kcal/mol), we can derive $\Delta H_{\mathrm{f}}°$ values at 0 K for the molecules in the gas phase. We obtain enthalpies of formation at 298 K by following the procedures outlined by Curtiss et al.[51] For example, for the molecule $A_xB_yH_z$, the following expression is used:

$$\begin{aligned}\Delta H_f^0(\mathrm{A}_x\mathrm{B}_y\mathrm{H}_z, 298\ \mathrm{K}) &= \Delta H_f^0(\mathrm{A}_x\mathrm{B}_y\mathrm{H}_z, 0\ \mathrm{K}) + \\ &[H^0(\mathrm{A}_x\mathrm{B}_y\mathrm{H}_z, 298\ \mathrm{K}) - H^0(\mathrm{A}_x\mathrm{B}_y\mathrm{H}_z, 0\ \mathrm{K})] - \\ &x[H^0(\mathrm{A}, 298\ \mathrm{K}) - H^0(\mathrm{A}, 0\ \mathrm{K})]_{\mathrm{st}} - y[H^0(\mathrm{B}, 298\ \mathrm{K}) - \\ &H^0(\mathrm{B}, 0\mathrm{K})]_{\mathrm{st}} - z[H^0(\mathrm{H}, 298\ \mathrm{K}) - H^0(\mathrm{H}, 0\ \mathrm{K})]_{\mathrm{st}} \quad (4)\end{aligned}$$

The heat capacity corrections from 0 to 298 K are the terms in square brackets and the subscript "st" stands for the standard state of the elements. The heat capacity correction for the molecule is obtained from statistical mechanics expressions in the rigid rotor-harmonic oscillator approximation[52] using the calculated geometries and frequencies. For the atoms, the corrections for the elements in the JANAF Tables are used directly and have been given.[51]

Results and Discussion

Total energies of the molecules as a function of basis set are given in Table S1 of the Supporting Information, frequencies of vibrational modes and unscaled ZPEs are given in Table S2, and CCSD(T)/aVTZ optimized geometries are given in Table S3. The components used to predict the total atomization energies TAE ($\sum D_0$) are given in Table 1. The predicted enthalpies of formation at 0 K and 298 K are summarized in Table 2, as well as the average value from the two extrapolation procedures. In general, the two different extrapolation procedures lead to differences of 0.3–0.5 kcal/mol for the TAEs of the (CF_2O) system. These differences are reduced to ∼0.3 kcal/mol for (CHFO) and ∼0.1 kcal/mol for (CH_2O). The enthalpies of formation derived from the CBS(DTQ) electronic energies are consistently more negative than those using the CBS(Q5) (Table 2). We average the two extrapolated values to provide the best recommended value. A variety of thermochemical properties calculated in the present work from the averaged enthalpies of formation are shown in Tables 3, 4, and 5, and where possible, compared with experiment. The calculated results discussed below are taken from the average values.

Thermochemical Parameters of CF_2O and Derivatives. For CF_2O, we confirm our previous theoretical result and our calculated enthalpy of formation $\Delta H_{\mathrm{f}}(CF_2O)$ = −144.7 kcal/mol at 298 K is close to previous theoretical results[17–21] ranging from −144.6 to −145.6 kcal/mol, and different from the latest experimental value of $-149.1\ ^{+1.4}/_{-0.7}$ kcal/mol derived by Asher et al.[22] from a photoionization study. As discussed previously,[17] the results from the photoionization study are not correct.

For the radical cation $CF_2O^{\bullet+}$, we considered the two lowest-lying $^2B_2$ and $^2B_1$ electronic states formed by electron removal from the in-plane n(σ) and out-of-the-plane π orbitals respectively. The σ-state $^2B_2$ of the cation is lower in energy than the π-state $^2B_1$, following the ordering of the orbitals. There is a substantial stabilization of 15.8 kcal/mol from the vertical ionization potential (vert-$^2B_2$, Table 3) to the adiabatic ionization potential (IP). As expected from the shape of the HOMO (Figure 1), geometrical changes on ionization to the $^2B_2$ state include elongation of the CO bond from 1.176 to 1.272 Å (CCSD(T)/aVTZ level) and shortening of the CF bonds from 1.316 to 1.244

TABLE 1: Components of Calculated Atomization Energies (in kcal/mol)

	CBS (DTQ)[a]	CBS (Q5)[b]	ΔE_{ZPE}[c]	ΔE_{CV}[d]	ΔE_{SR}[e]	ΔE_{SO}[f]	ΣD_0 (DTQ, 0 K)	ΣD_0 (Q5, 0 K)
O^+	−312.99	−313.57		−0.29	0.13	−0.223	−313.37	−313.96
F^+	−401.25	−401.74		−0.30	0.23	−0.380	−401.70	−402.19
CF_2O ($^1A_1$)	419.60	419.26	8.80	1.25	−0.97	−1.068	410.02	409.68
$CF_2O^{\bullet+}$ ($^2B_2$)	119.21	118.74	8.88	0.86	−0.77	−1.068	109.34	108.88
$CF_2O^{\bullet+}$ ($^2B_1$)	95.05	94.66	8.79	0.73	−0.76	−1.068	85.15	84.76
$CF_2O^{\bullet+}$ (vert-$^2B_2$)	103.38	102.87	g	0.85	−0.72	−1.068	93.57	93.05
CF_2O ($^3A''$)	315.30	315.03	7.33	0.91	−0.87	−1.068	306.94	306.67
CF_2O ($^3A'$)	305.26	305.03	7.52	0.85	−0.87	−1.068	296.66	296.43
CF_2O (vert-$^3B_2$)	207.95	207.58	g	0.92	−0.59	−1.068	198.40	198.03
CF_2OH^+ ($^1A'$)	261.72	261.16	16.85	1.16	−0.99	−1.068	243.98	243.42
$HF-CFO^+$ ($^1A'$)	237.50	236.90	13.60	1.22	−0.87	−1.068	223.18	222.58
CF_2 ($^1A_1$)	258.25	258.21	4.34	0.37	−0.50	−0.845	252.93	252.89
CF_2 ($^3B_1$)	201.46	201.23	4.31	0.81	−0.68	−0.845	196.44	196.21
CFH ($^1A'$)	212.40	212.46	7.73	0.37	−0.30	−0.465	204.27	204.33
CFH ($^3A''$)	197.59	197.55	7.82	0.76	−0.40	−0.465	189.66	189.62
$CFO^{\bullet}$ ($^2A'$)	294.81	294.64	5.23	0.98	−0.61	−0.688	289.26	289.09
CFO^+ ($^1\Sigma^+$)	80.99	80.68	6.82	1.06	−0.55	−0.688	73.99	73.69
CFO^- ($^1A'$)	348.29	348.12	3.61	0.77	−0.51	−0.688	344.25	344.08
CH_2O ($^1A_1$)	373.33	373.42	16.59	1.11	−0.43	−0.308	357.12	357.21
$CH_2O^{\bullet+}$ ($^2B_2$)	120.27	120.18	15.20	0.95	−0.29	−0.308	105.43	105.33
$CH_2O^{\bullet+}$ ($^2B_1$)	47.90	47.97	16.34	0.46	−0.28	−0.308	31.43	31.50
CH_2O ($^3A''$)	298.74	298.83	14.84	1.09	−0.38	−0.308	284.30	284.38
CH_2O ($^3A'$)	266.99	267.12	15.21	0.89	−0.37	−0.308	251.99	252.12
CH_2O (vert-$^3B_2$)	207.86	207.85	g	0.98	−0.28	−0.308	191.67	191.65
CH_2OH^+ ($^1A'$)	237.21	237.15	25.38	1.03	−0.47	−0.308	212.09	212.02
$CHFO$ ($^1A'$)	402.56	402.42	12.95	1.17	−0.67	−0.688	389.42	389.27
$CHFO^{\bullet+}$ ($^2A'$)	116.18	115.91	12.60	0.86	−0.52	−0.688	103.23	102.96
$CHFO^{\bullet+}$ ($^2A''$)	80.28	80.10	12.82	0.63	−0.50	−0.688	66.90	66.72
$CHFO^{\bullet+}$ (vert-$^2A'$)	108.28	107.97	g	0.90	−0.48	−0.688	95.42	95.11
$CHFO$ (^3A)	300.77	300.67	11.53	0.98	−0.62	−0.688	288.91	288.82
$CHFO$ (vert-$^3A''$)	193.23	193.06	g	1.05	−0.48	−0.688	180.16	179.99
trans-$CFHOH^+$ ($^1A'$)	252.65	252.33	21.20	1.10	−0.71	−0.688	231.14	230.82
cis-$CFHOH^+$ ($^1A'$)	253.65	253.35	21.12	1.08	−0.71	−0.688	232.21	231.91
$HF-HCO^+$ ($^1A'$)	248.34	247.80	16.72	1.16	−0.58	−0.688	231.51	230.96

[a] CCSD(T)/CBS energies extrapolated using eq 1, with aVnZ basis sets, for n = D, T and Q, at the CCSD(T)/aVTZ optimized geometries. Total energies in Table S1 (Supporting Information). [b] CCSD(T)/CBS energies extrapolated using eq 2, with aVnZ basis sets, where n = Q and 5, at the CCSD(T)/aVTZ optimized geometries. Total energies in Table S1 (Supporting Information). [c] Zero point energies. MP2/aVTZ vibrational modes in Table S2 (Supporting Information). Scaling factors of 0.9798 and 0.9701 were used for the OH and the CH stretches, respectively. See text. [d] Core/valence corrections at the CCSD(T)/cc-pwCVTZ level. [e] Scalar relativistic correction (MVD) from CISD/aVTZ calculations. [f] Atomic spin−orbit correction from Moore tables (ref 50). [g] Vertical process so no ZPE correction is used.

Å, accompanied by a closing of ∠FCO bond angles from 126.2° to 119.7°. For the $^2B_2$ ground state, the calculated $IP_1(CF_2O) = 13.04$ eV is in excellent agreement with the experimental results of 13.024 ± 0.004 eV, 13.035 ± 0.030 eV, and 13.04 eV obtained from photoionization[22,53] and photoelectron spectra.[54] The experimental value of $\Delta H_f(CF_2O^{\bullet+}) = 151.2\ ^{+1.4}/_{-0.7}$ kcal/mol at 298 K[22] is ~5 kcal/mol lower than our predicted value of 156.3 kcal/mol, consistent with the differences predicted for $\Delta H_f(CF_2O)$. The vertical IP for the $^2B_2$ state of $CF_2O^{\bullet+}$ (vert-$^2B_2$) is 13.73 eV, in good agreement with the value of 13.62 eV obtained from photoelectron spectra.[54] The good agreement for the IP suggests that there is a systematic error in the experimental value from the appearance potentials in the photoionization measurements.

The first excited state of the radical cation corresponds to loss of an electron from the π orbital of CF_2O. The CO bond is further elongated to 1.322 Å, and CF bonds shorten to 1.238 Å. We obtain $IP_2(CF_2O) = 14.09$ eV in excellent agreement with the experimental value of 14.08 eV obtained from photoelectron spectra, but not in as good agreement with the other value of 14.26 eV reported for this state.[54] We predict an excitation energy of 1.05 eV (24.1 kcal/mol) for the $^2B_1 \leftarrow {}^2B_2$ transition of $CF_2O^{\bullet+}$, in good agreement with that found from photoelectron spectroscopy of 1.04 eV.[54]

We calculated the energy of two states in the triplet manifold of CF_2O. The lowest energy triplet state $^3B_2$ [...$(b_2)^1(a1)^1$] is 9.18 eV above the ground state in the vertical excitation process. It undergoes a large geometry change involving both CO bond lengthening and distortion at the carbon center on relaxation to the lowest energy structure and lowers its symmetry to C_s to give the $^3A''$ state. The first excited triplet has a pyramidal carbon, a long CO bond distance of 1.358 Å, and a CF bond distance of 1.328 Å. The adiabatic energy for the singlet to triplet transition is 4.47 eV as geometry relaxation brings about a substantial stabilization of 4.71 eV.

The second excited triplet T_2 state resulting from a $\pi^* \leftarrow \pi$ transition has $^3A'$ symmetry, and is located near the ground $^3A''$ state, with an adiabatic T_2-T_1 energy gap of only 10.2 kcal/mol (0.44 eV). The $^3A'$ state also has a pyramidal geometry with an even longer single CO bond length of 1.401 Å. Formation of a triplet CF_2O species has been postulated in the reaction of $H + CF_3O$.[55] Due to the energy content of the reactants, fluorine abstraction by H could take place, in competition with a radical recombination giving CF_3OH, either in the singlet or in the triplet state. On the triplet potential energy surface, F-abstraction can give rise to triplet CF_2O.

We have previously studied protonation of carbonyl difluoride.[18] We confirm our theoretical result for the proton affinity, $PA_O(CF_2O) = 148.8$ kcal/mol, which markedly differs from the experimental values of 159.9 kcal/mol reported by McMahon and co-workers,[56] 160.5 kcal/mol by Chyall and Squires,[23] and $\geq 132.4\ ^{+1.4}/_{-1.2}$ kcal/mol by Asher et al.[24] Dissociative F-

TABLE 2: CCSD(T)/CBS Enthalpies of Formation at 0 K and 298 K (kcal/mol) and MP2/aVTZ Entropies (S in cal/mol-K at 298 K)

molecule	ΔH_f (0 K) [DTQ]	ΔH_f (0 K) [Q5]	ΔH_f (0 K) [average]	ΔH_f (298 K) [DTQ]	ΔH_f (298 K) [Q5]	ΔH_f (298 K) [average]	S
O^+ [a]	372.4	372.9	372.7	372.8	373.4	373.1	37.04
F^+ [a]	420.2	420.7	420.4	420.7	421.2	421.0	38.65
CF_2O ($^1A_1$)	−144.1	−143.8	−143.9	−144.8	−144.5	−144.7	61.87
$CF_2O^{\bullet+}$ ($^2B_2$)	156.6	157.0	156.8	155.9	156.3	156.1	63.41
$CF_2O^{\bullet+}$ ($^2B_1$)	180.8	181.1	181.0	180.0	180.4	180.2	63.31
CF_2O ($^3A''$)	−41.0	−40.8	−40.9	−41.6	−41.3	−41.4	66.49
CF_2O ($^3A'$)	−30.7	−30.5	−30.6	−31.4	−31.2	−31.3	65.98
CF_2OH^+ ($^1A'$)	73.6	74.1	73.8	71.9	72.5	72.2	63.73
HF-CFO^+ ($^1A'$)	94.4	95.0	94.7	94.0	94.6	94.3	73.26
CF_2 ($^1A_1$)	−46.0	−46.0	−46.0	−45.9	−45.9	−45.9	57.52
CF_2 ($^3B_1$)	10.5	10.7	10.6	10.7	10.9	10.8	59.95
CFH ($^1A'$)	35.8	35.7	35.8	35.9	35.8	35.8	53.32
CFH ($^3A''$)	50.4	50.5	50.4	50.5	50.5	50.5	55.25
$CFO^{\bullet}$ ($^2A'$)	−41.8	−41.6	−41.7	−41.7	−41.5	−41.6	59.46
CFO^+ ($^1\Sigma^+$)	173.4	173.8	173.6	173.4	173.7	173.6	53.19
CFO^- ($^1A'$)	−96.8	−96.6	−96.7	−96.2	−96.0	−96.1	62.41
CH_2O ($^1A_1$)	−24.9	−25.0	−24.9	−25.8	−25.9	−25.8	52.24
$CH_2O^{\bullet+}$ ($^2B_2$)	226.8	226.9	226.9	225.9	226.0	226.0	53.80
$CH_2O^{\bullet+}$ ($^2B_1$)	300.8	300.7	300.8	299.9	299.8	299.9	54.01
CH_2O ($^3A''$)	47.9	47.8	47.9	47.1	47.0	47.1	56.46
CH_2O ($^3A'$)	80.2	80.1	80.2	79.4	79.3	79.4	56.89
CH_2OH^+ ($^1A'$)	171.8	171.8	171.8	169.9	169.9	169.9	54.46
CHFO ($^1A'$)	−90.4	−90.2	−90.3	−91.2	−91.1	−91.1	58.96
$CHFO^{\bullet+}$ ($^2A'$)	195.8	196.1	196.0	195.0	195.3	195.1	60.46
$CHFO^{\bullet+}$ ($^2A''$)	232.2	232.3	232.3	231.3	231.5	231.4	60.42
CHFO (^3A)	10.2	10.3	10.2	9.4	9.5	9.4	61.97
trans-$CFHOH^+$ ($^1A'$)	119.6	119.9	119.7	118.8	119.1	118.9	59.42
cis-$CFHOH^+$ ($^1A'$)	118.5	118.8	118.6	117.7	118.0	117.8	59.51
HF-CHO^+ ($^1A'$)	119.2	119.7	119.5	119.8	120.4	120.1	71.23

[a] Thermal correction and entropy from the JANAF Tables (ref 25) in the convention with the enthalpy of the electron set to 0.

TABLE 3: Ionization Potentials, Electron Affinities, and Singlet−Triplet Splittings of CF_2O, CHFO, CH_2O and Derivatives Compared to Experiment in eV at 0 K

property	calculated (average)	experiment
$IP_1(CFO^{\bullet})$	9.34	9.3 ± 0.1[53] 9.25 ± 0.1[22]
$IP_1(CF_2O)$	13.04	13.035 ± 0.030[53] 13.04[54] 13.024 ± 0.004[22]
$IP_{1vert}(CF_2O)$	13.73	13.62[54]
$IP_1(CHFO)$	12.41	
$IP_{1vert}(CHFO)$	12.75	
$IP_1(CH_2O)$	10.92	10.88 ± 0.01[58]
$IP_1(O)$	13.60	13.62[57]
$IP_1(F)$	17.43	17.42[57]
$IP_2(CF_2O)$	14.09	14.08[54]
$IP_2(CHFO)$	13.99	
$IP_2(CH_2O)$	14.12	14.10[69]
$\Delta E(^2B_1-^2B_2)$ CF_2O^+	1.05	1.04[54]
$\Delta E(^2A''-^2A')$ $CHFO^+$	1.57	
$\Delta E(^2B_1-^2B_2)$ CH_2O^+	3.21	3.21[69]
$EA(CFO^{\bullet})$, eV	2.38	3.02 ± 0.16[59] 2.90 ± 0.24[60] 2.7[61]
$\Delta E_{T1-S0}(CF_2)$	2.45	
$\Delta E_{T1-S0}(CHF)$	0.64	
$\Delta E_{T1-S0}(CF_2O)$	4.47	
$\Delta E_{T1-S0}(CHFO)$	4.36	
$\Delta E_{T1-S0}(CH_2O)$	3.16	3.12[70]
$\Delta E_{T1-S0,vertical}(CF_2O)$	9.18	
$\Delta E_{T1-S0,vertical}(CHFO)$	9.07	
$\Delta E_{T1-S0,vertical}(CH_2O)$	7.18	
$\Delta E_{T2-T1}(CF_2O)$	0.44	
$\Delta E_{T2-T1}(CH_2O)$	1.40	

protonation of CF_2O is much less favored than O-protonation by 22.1 kcal/mol and it leads to a complex, in which the F-atom from HF interacts with a positively charged FCO^+.

TABLE 4: Proton Affinities of CF_2O, CHFO, CH_2O and Derivatives Compared to Experiment at 298 K in kcal/mol[a]

protonation site	calculated (average)	experiment
$PA_O(CF_2O)$	148.8	≥132.4 $^{+1.4}/_{-1.2}$ [20] 159.9[52] 160.5[23]
$PA_O(CHFO)$	156.7	
$PA_O(CFO)$	129.0	
$PA_O(CH_2O)$	169.9	170.4[52]
$PA_F(CF_2O)$	126.7	
$PA_F(CHFO)$	154.5	
$\Delta H_{acidity}(CHFO)$	360.7	

[a] $\Delta H_{f,298K}(H^+) = 365.7$ kcal/mol. Experimental value (ref 25).

For the $CFO^{\bullet}$ radical, the present value of $\Delta H_f(0\ K) = -41.7$ kcal/mol differs from our previous result of −44.1 kcal/mol.[17] This is due to the fact that some of the smaller corrections were not included in the earlier calculation. There are different experimental values for this parameter including −41 ± 15 kcal/mol tabulated in the JANAF Tables,[57] −43 ± 10 kcal/mol selected by Gurvich et al.,[58] and −36.2 ± 2.9 kcal/mol obtained from photoionization measurements.[53] The latter value is too high by ~5 kcal/mol.

For the electron affinity of $CFO^{\bullet}$, our predicted value of EA(CFO) = 2.38 eV is smaller than three early literature mass spectrometry estimates of 3.02 ± 0.16, 2.90 ± 0.24, and 2.7 eV.[59–61] The estimated value of 3.3 eV from ref 61 is clearly too high. In contrast, our calculated $\Delta H_f(CFO^+) = 173.6$ kcal/mol at 298 K is in good agreement with the experimental value of 173.5 $^{+1.4}/_{-0.7}$ kcal/mol.[22] Similarly, the calculated adiabatic ionization energy of $IP_1(CFO) = 9.34$ eV compares well with the experimental results of 9.25 ± 0.1 eV[22] and 9.3 ± 0.1 eV.[53] The earlier value of 8.76 ± 0.32 eV obtained from photoelectron

TABLE 5: Adiabatic Bond Dissociation Energies (BDE) in kcal/mol of CF_2O, CHFO, CH_2O, and Derivatives[a]

bond	BDE (0 K)	BDE (298 K)	BDE (298 K) expt[b]
CF_2-O	156.9	158.4	
CFO−F	120.7	122.1	122.0 127.9 ± 3 129.6 ± 3
CFO^+-F	35.3	36.5	
$CFO-F^+$	221.9	223.3	
CF_2-O^+	169.9	171.1	
CFH−O	185.0	186.6	
CHO−F	119.1	120.6	119.0 ± 2.5 ≤115.2
CFO−H	100.2	101.6	101.1 99.92 ± 0.06
$CHO-F^+$	234.8	236.3	
$CFH-O^+$	212.5	213.8	
$FCO-H^+$	127.5	129.0	
CH_2-O	177.3	178.9	
CHO−H	87.0	88.4	88.64 ± 0.1 88.15 ± 0.01 88.04 ± 0.1 88.0 88.8 ± 0.5
CO−F	33.0	34.2	
$CO-F^+$	219.6	221.0	

[a] Other enthalpies of formation (kcal/mol) used: experimental (ref 25), $\Delta H_{f,0K}(H) = 51.6$, $\Delta H_{f,298K}(H) = 52.1$, $\Delta H_{f,0K}(O) = 59.0$, $\Delta H_{f,298K}(O) = 59.6$, $\Delta H_{f,0K}(F) = 18.5$, $\Delta H_{f,298K}(F) = 19.0$, $\Delta H_{f,0K}(CO) = -27.2$, $\Delta H_{f,298K}(CO) = -26.4$, $\Delta H_{f,0K}(H^+) = 365.2$, $\Delta H_{f,298K}(H^+) = 365.7$; theoretical (ref 29), $\Delta H_{f,0K}(CH_2) = 93.4$, $\Delta H_{f,298K}(CH_2) = 93.5$; theoretical (ref 27), $\Delta H_{f,0K}(CHO) = 10.4$, $\Delta H_{f,298K}(CHO) = 10.5$. [b] Reference 65.

spectroscopic studies[62] is too small. We note that the radical $CFO^{\bullet}$ ($^2A'$) is strongly bent whereas the cation CFO^+ ($^1\Sigma^+$) is linear. Such a bent-to-linear geometrical change upon ionization results in a large Franck−Condon effect, manifested in a broad absorption band in the spectrum. This can lead to difficulties in assigning an accurate adiabatic value from the photoelectron spectrum.[62]

Thermochemical Parameters of CHFO and Derivatives. Apart from the estimated enthalpy of formation of ΔH_f(CHFO) = −90.0 kcal/mol at 298 K listed in the NIST-JANAF Tables,[25] and −91.6 ± 1.7 kcal/mol tabulated in the NASA compilation,[26] relatively little data are available for formyl fluoride. Our calculated value of −91.1 kcal/mol for ΔH_f(CHFO) at 298 K is in good agreement with these results.

As in $CF_2O^{\bullet+}$, the radical cation $CHFO^{\bullet+}$ is characterized by an n(σ) ground state followed by a π excited state. Following the behavior of $CF_2O^{\bullet+}$, the CO distance is stretched from the neutral 1.184 Å to 1.246 Å in the ground $^2A'$ state of the cation, and further to 1.322 Å in the excited $^2A''$ state of the cation. The CF bond distance shortens from 1.346 Å ($^1A'$) in the neutral to 1.254 Å ($^2A'$) and 1.239 Å ($^2A''$) in the cation. Geometry relaxation of the $^2A'$ state of the cation from the vertical geometry to the minimum energy structure results in an energy stabilization of 0.34 eV (7.8 kcal/mol). The $^2A'' \leftarrow {}^2A'$ excitation energy is 1.57 eV.

Due to the C_1 point group symmetry in the excited state, only the lowest-lying triplet state of CHFO can be calculated using CCSD(T). As in CF_2O, the planar vertical triplet structure (vert-$^3A''$) is 9.07 eV above the ground state. A large amount of relaxation occurs leading to the ground T_1 state with an energy gain of 4.71 eV (108.6 kcal/mol), and a triplet−singlet (T_1-S_0) gap of CHFO of 4.36 eV (105.5 kcal/mol). Thus the excitation of CHFO is very similar to that of CF_2O.

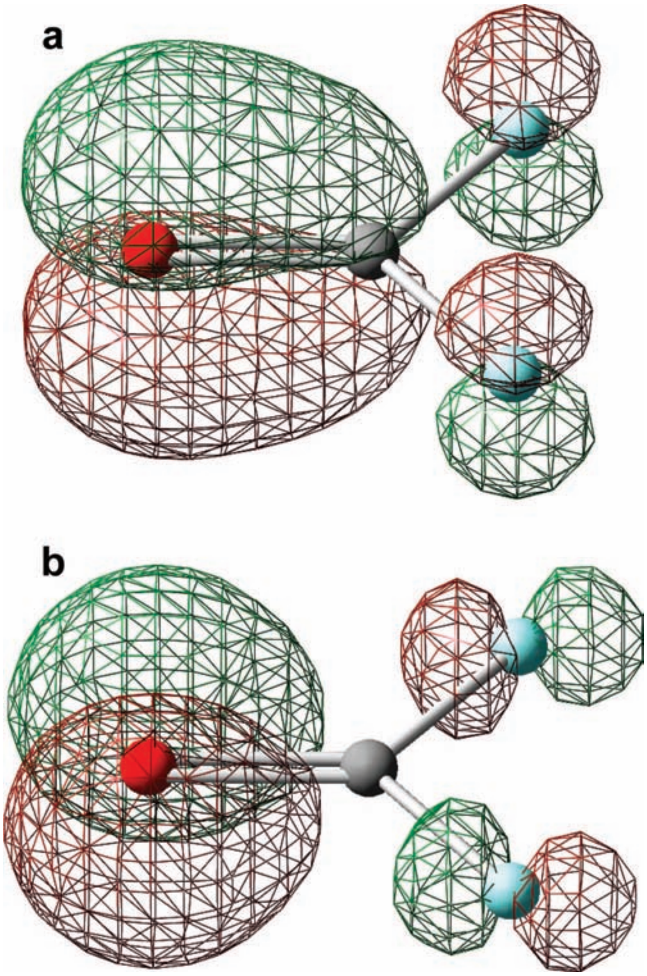

Figure 1. CF_2O highest occupied molecular orbitals: (a) σ HOMO; and (b) π HOMO−1. Isosurface: 0.075 au. Atom colors: red = O; gray = C; blue = F.

We found three distinct protonated forms of CHFO. O-protonation gives rise to $CHFOH^+$ in both *cis* and *trans* configurations, whereas F-protonation is dissociative yielding a $HF-HCO^+$ complex (see Figure 2). The *cis* configuration, in which both F and H(O) atoms are on the same side with respect to the CO bond, is the more stable isomer,[63] 1.1 kcal/mol below the *trans* isomer (Table 2). The higher stability of the *cis*-isomer is due to a *cis*-effect originating from a stabilizing interaction between n(F) electrons with the σ^*(OH) orbitals. $HF-HCO^+$ is ~1 kcal/mol above the *trans*-protonated form. Thus all three protonated species could be present in mass spectrometric experiments. We predict a proton affinity of PA_O(CHFO) = 156.7 kcal/mol at 298 K, where the cation is the *cis* isomer. Experimentally, it was found that the gas phase oxygen-PA of acetyl fluoride (CH_3CFO) is ~8 kcal/mol smaller than that of acetaldehyde (CH_3CHO).[64] Assuming an additivity of the F-effect on PAs, McMahon and co-workers[56] suggested a value of 167 kcal/mol for PA(CHFO). This value is thus ~9 kcal/mol too large as compared with our predicted value.

The gas phase acidity for CHFO is calculated as the enthalpy change for the reaction CHFO → CFO^- + H^+. The $\Delta H_{acidity}$(CHFO) = 360.7 kcal/mol at 298 K is consistent with the low stability of the conjugate anion.

Bond Dissociation Energies. We report important calculated bond dissociation energies (BDEs) at 0 K in Table 5. We define the diabatic BDE to be dissociation to the configurations most closely representing the bonding configuration in the reactant,

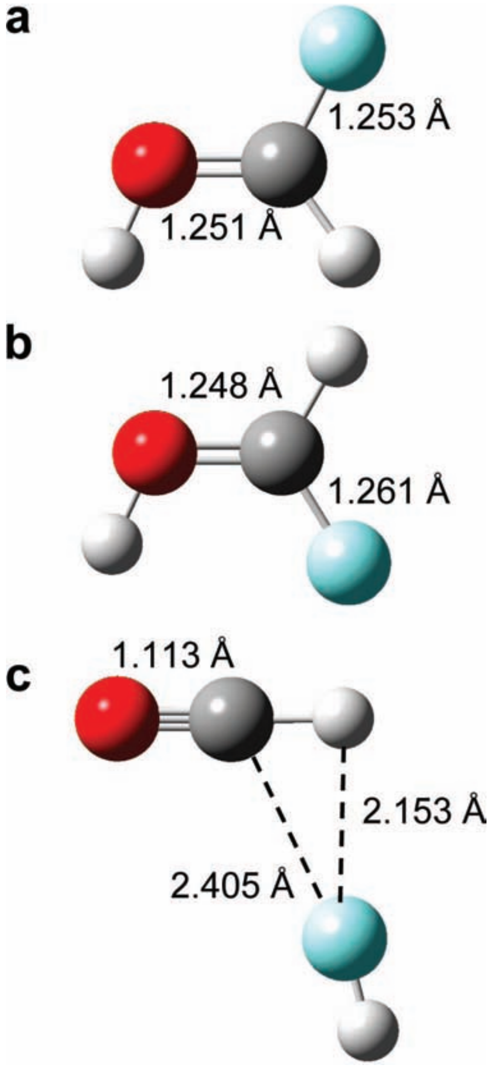

Figure 2. Optimized CCSD(T)/aVTZ structures for (a) *trans*-$CFHOH^+$; (b) *cis*-$CFHOH^+$; and (c) HF−CHO^+. Atom colors: red = O; gray = C; blue = F; white = H.

and the adiabatic BDE is defined as dissociation to the ground state of the separated species. For the diabatic BDE, we require that the spin be conserved, whereas in the adiabatic BDE, the process may not occur on the same spin surface. The adiabatic BDE will always be equal to or less than the diabatic BDE.

In CF_2O, the CO adiabatic BDE of 156.9 kcal/mol forming $^1CF_2 + O(^3P)$ is 36.2 kcal/mol higher than the CF adiabatic BDE forming $F(^2P) + {}^2FCO$. For comparison, the CO adiabatic BDE in CH_2O is 177.3 kcal/mol to form $^3CH_2 + O(^3P)$. The diabatic and adiabatic CO BDEs in CH_2O are the same. The dissociation channel in CH_2O to form $^1CH_2 + O(^3P)$ is 186.3 kcal/mol.[26] Thus, perfluorination lowers the CO BDE by almost 30 kcal/mol if we form the singlet carbene in both cases. If we form the triplet carbene on the diabatic surface for CF_2O ($^3CF_2 + O(^3P)$), the CO BDE in CF_2O is 213.5 kcal/mol, 36 kcal/mol greater than the CO BDE in CH_2O to form $^3CH_2 + O(^3P)$. If we form $^1CF_2 + O(^1D)$,[50] the diabatic BDE in CF_2O is 202.2 kcal/mol, somewhat less than the diabatic CO BDE on the triplet surface. The diabatic CO BDEs of CH_2O and CF_2O are consistent with the CO bond lengths, stretching frequencies and force constants. For example, the calculated CO stretch in CF_2O is 1951 cm^{-1} as compared to the calculated value of 1753 cm^{-1} for CH_2O, consistent with the diabatic BDE in CF_2O being larger than that in CH_2O. The difference in the adiabatic BDEs of the CO bonds in CH_2O and CF_2O is due to the different asymptotes and the stabilities of the corresponding carbenes. The calculated singlet−triplet splitting in CF_2 is 56.5 kcal/mol with the singlet being the ground state whereas in CH_2 the triplet is lower than the singlet by 9.0 kcal/mol.[26]

The CO adiabatic BDE in CHFO ($^1CHF + O(^3P)$) is 185.0 kcal/mol, 28.1 higher than that in CF_2O and essentially the same as the CO BDE in CH_2O on the surface yielding $^1CH_2 + O(^3P)$ (Table 5). The diabatic CO BDE ($^3CHF + O(^3P)$) is 199.7 kcal/mol, about 14 kcal/mol less than the diabatic CO BDE in CF_2O on the triplet surface and 22.4 kcal/mol above the adiabatic (diabatic) CO BDE in CH_2O. The reduction in the diabatic BDE in CHFO is consistent with the smaller calculated singlet−triplet splitting in CHF of 14.6 kcal/mol with the singlet being the ground state.

The CF BDE in CF_2O is 120.7 kcal/mol at 0 K and 122.1 kcal/mol at 298 K. This value can be compared to the 298 K values reported by Luo[65] of 127.9 ± 3, 129.6 ± 3, and 122.0 kcal/mol, where the latter value is in excellent agreement with our value. The CF BDE in CHFO (119.1 kcal/mol at 0 K) is slightly lower (by 1.6 kcal/mol) than that in CF_2O. Our calculated value at 298 K, 120.6 kcal/mol, is in very good agreement with the CF BDE of 119.0 ± 2.5 kcal/mol reported by Luo but not with the value of ≤115.2 kcal/mol reported by him.[65] The CH BDE in CHFO is 100.2 kcal/mol, 13.3 kcal/mol higher than that in CH_2O. The calculated value of 101.6 kcal/mol at 298 K is in good agreement with the two values of 99.92 ± 0.06 and 101.1 kcal/mol reported by Luo.[65] Once one of the F-atoms has been removed from CF_2O, the energy required to remove the second F is considerably lower, only 33.0 kcal/mol ($^2CFO \rightarrow {}^2F + {}^1CO$) due to the formation of the very stable closed shell CO from the high energy FCO radical. This value is in good agreement with the one given by Luo of 31.1 ± 3 kcal/mol.[65] The CH BDE in HCO is even weaker, 14.1 kcal/mol at 0 K.

Because of the low BDE in F_2, reaction 5 is substantially endothermic (ΔH_f,0K(CO) = −27.2 ± 0.04 kcal/mol and ΔH_f,0K(HF) = −65.1 ± 0.2 kcal/mol)[25]

$$CF_2O \rightarrow F_2 + CO \qquad \Delta H_{0K} = 117.5\,\text{kcal/mol} \qquad (5)$$

and will not be important. In contrast, UV photolysis of CHFO has been reported to lead to three different channels:[66]

$$\begin{aligned} CHFO &\rightarrow HF + CO & \Delta H_{0K} &= -1.2\ \text{kcal/mol} \quad (6a)\\ &\rightarrow H + FCO & \Delta H_{0K} &= 100.2\ \text{kcal/mol} \quad (6b)\\ &\rightarrow F + HCO & \Delta H_{0K} &= 119.1\ \text{kcal/mol} \quad (6c) \end{aligned}$$

The experiments found that that channel 6b is only accessible through the excited states of CHFO with reaction 6c being the dominant channel.[66] The dissociation process 6a was also observed, but is not the dominant channel. Comparison of 6a with its CH_2O analogue shows that the reaction energetics are very similar.

$$CH_2 \rightarrow H_2 + CO \qquad \Delta H_{0K} = -1.4\ \text{kcal/mol} \qquad (7)$$

Townsend et al.[67] found two competitive dissociation pathways for reaction 7 leading to H_2 and CO for excitation energies above 86.6 kcal/mol. The first pathway proceeds through the traditional transition state with an energy barrier of 81.8 kcal/mol. The second path with an energy barrier of 86.6 kcal/mol proceeds by loss of H which can orbit the HCO and abstract the hydrogen leading to formation of H_2 and CO. It is interesting to speculate whether such a process plays a role in reaction 6.

The CF BDE in CF_2O^+ to form FCO^+ is only 35.3 kcal/mol, again due to the formation of the more stable closed shell FCO^+ from the free radical CF_2O^+. In contrast, the energy required to remove an F^+ ion from CF_2O^+ (the F^+ affinity) is very high ($^2CF_2O^+ \rightarrow F^+(^3P) + {}^2FCO$, = 221.9 kcal/mol) due to the very high first ionization potential of F and the instability of ^2FCO. The same logic holds for the removal of F^+ from CFO^+ ($CFO^+ \rightarrow F^+ + CO$ = 219.6 kcal/mol), showing that CO has a very high F^+ affinity.

The CF^+ BDE (the F^+ affinity of HCO) in $CHFO^+$ is very high, 234.8 kcal/mol; thus the F^+ affinity of HCO is higher than the F^+ affinities of FCO and CO by 12.9 and 15.2 kcal/mol, respectively. This is consistent with the low CH BDE in HCO which makes it quite unstable. The CO^+ BDE in $CHFO^+$ is 22.3 kcal/mol lower than the CF^+ BDE in the same molecule, but higher than the CO^+ BDE in CF_2O^+ by 42.6 kcal/mol. The proton affinity of FCO at 298 K can readily be obtained using ΔH_f,298K(H^+) = 365.7 kcal/mol and is 129.0 kcal/mol.

Effects of Fluorine Substitution on Thermochemical Properties of Carbonyl Compounds. Having determined the parameters for both carbonyl fluorides, we now consider the modifications due to the presence of fluorine atoms with respect to the corresponding values in the parent formaldehyde. From the values listed in Tables 3–5, some interesting trends emerge. Successive fluorination of formaldehyde tends to increase the first adiabatic ionization energy. However, the effect due to the first F-substitution in IP_1 (1.49 eV) is larger than that due to the second (0.63 eV). The σ electrons in the neutrals are more stabilized by F-atoms making their removal more difficult. In contrast, the F-atoms do not have a significant effect on the second ionization energy. The IP_2 value remains almost unchanged at ~14 eV, indicating a small perturbation of the π systems by the F-atoms. A direct consequence of such differential effects is that the excitation energy from ground σ state to excited π state of the radical cation is reduced substantially from 3.20 eV in CH_2O to 1.57 eV in CHFO to 1.05 eV in CF_2O.

Fluorine is the most electronegative element and exerts a strong inductive electron withdrawing effect taking negative charge away from the carbonyl oxygen, and reducing the basicity of the oxygen. This effect is manifested in the PAs at oxygen. Again, the effect is not additive as often assumed,[56] as the first F-atom provides a much larger reduction of the PA (13.2 kcal/mol) than the second F-atom (7.9 kcal/mol). The basicity of the F-atom is larger in the monofluoride than in the difluoride carbonyl derivative. A difference of 27.8 kcal/mol on the PA_F values points out the large extent of electron redistribution between the two F-atoms in CF_2O.

As in ionization, stabilization of electrons located in frontier orbitals upon F-substitution invariably disfavors electronic excitation either vertically or adiabatically. Increments of 27.7 and 2.5 kcal/mol are predicted for the changes in the adiabatic singlet−triplet (T_1-S_0) gap by one and two F-atoms, respectively. The T_2-T_1 excitation energy is also decreased, but to a lesser extent, upon replacement of H by F.

The adiabatic CO BDEs do not show any regular patterns with changes in fluorine substitution. As discussed above, this is due to the differences in the stability of the product carbenes and their respective electronic states as well as to any stabilization effects in the carbonyl compounds. The diabatic CO BDEs to form $^3CRR' + O(^3P)$ do exhibit an expected pattern with an increase of 22.4 kcal/mol from R = R′ = H to R = H, R′ = F and a smaller increase of 13.8 kcal/mol from R = H, R′ = F to R = R′ = F. Again, the effect of the first fluorine substitution is larger than the second. The strengths of the CF and CH bonds are also modified in a nonuniform manner. Compared with formaldehyde, the CH BDE in CHFO increases by 13.3 kcal/mol. This is consistent with the fact that the CF BDE in FCO (33.0 kcal/mol, 0 K) is greater than the CH BDE in HCO (14.1 kcal/mol, 0 K). Surprisingly, the CF BDE in CF_2O is only marginally increased by 1.6 kcal/mol over the CF BDE in CHFO even though we might have expected the same result due to the differences in the stability of the respective products FCO and HCO. This suggests that there is an additional stability in the reactant CHFO as compared to CF_2O for the CF bond.

Relative Nucleophilicities of COF_2 and CF_3OH. Recently it has been shown that COF_2 and HF are in equilibrium with CF_3OH (eq 8).[6]

$$COF_2 + HF \rightleftarrows CF_3OH \qquad (8)$$

When, in the presence of catalytic amounts of SbF_5, CH_3F was added to these solutions, CF_3OCH_3 was formed in very high yield (eq 9). These results were interpreted in terms of an intermediately formed $CH_3^+SbF_6^-$ methylating the oxygen atom of CF_3OH (eq 9).

$$CH_3OH + CH_3^+SbF_6^- \rightarrow CF_3OCH_3 + HF + SbF_5 \qquad (9)$$

The question has been raised whether the CF_3OCH_3 could equally well have been formed by direct methylation of COF_2 (eq 10).[68]

$$COF_2 + CH_3^+SbF_6^- \rightarrow CF_3OCH_3 + SbF_5 \qquad (10)$$

The question is thus whether the relative basicities or nucleophilicities of the oxygen atoms in COF_2 and CF_3OH differ significantly. Since the relative affinities for CH_3^+ and H^+ of COF_2 and CF_3OH should be the same and we now have accurate proton affinities, calculated by the same methods at the same level of theory, for both compounds,[16] it is interesting to compare these proton affinities. Our calculated proton affinities of oxygen in COF_2 and CF_3OH are 148.8 and 147.5 kcal/mol, respectively. Thus, from thermodynamic considerations, the protonation or methylation of COF_2 and CF_3OH are equally likely and, therefore, the reaction kinetics are likely to determine the mechanism of this reaction.

Concluding Remarks. We have predicted a uniform set of thermochemical properties for CHFO and CF_2O and their derivatives from high accuracy electronic structure calculations. From our recent extensive studies on similar organic compounds, these calculated results are expected to be accurate to ±1.0 kcal/mol. Our calculated results clearly demonstrate that the effects of the stepwise replacement of hydrogen by fluorine atoms on the thermochemical properties of carbonyl compounds are not linearly additive, with the changes being dominated by the first F-substitution. The results show that a comparison of adiabatic and diabatic bond dissociation energies can provide insights into the bonding in the equilibrium region. The comparison of CO adiabatic and diabatic BDEs reinforces the concept that the adiabatic BDEs of polyatomic molecules are not necessarily a direct measure of the bond strength in the region of the minimum of the molecule. The nucleophilicities of the oxygen atoms in COF_2 and CF_3OH are within computational error identical and, based on thermodynamic considerations, do not allow us to choose a preferred mechanism for the SbF_5 catalyzed ether formation reaction in the COF_2/HF/CH_3F system.

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Supporting Information Available: Total CCSD(T) energies (E_h) as a function of basis set extrapolated to the complete basis set limit. MP2/aug-cc-pVTZ harmonic frequencies (cm^{-1}). Symmetry and Cartesian coordinates of CCSD(T)/aug-cc-pVTZ geometries. This material is available free of charge via the Internet at http://pubs.acs.org.

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