Thermochemistry of COF$_2$ and Related Compounds

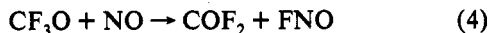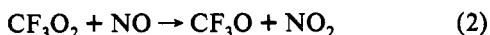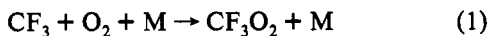## William F. Schneider* and Timothy J. Wallington

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Recent calculations by Montgomery and co-workers[1] suggest that the accepted value for the heat of formation of COF$_2$ is in error by more than 6 kcal mol^{-1}. Additional calculations reported here support this contention. The revised value for $\Delta_f H°_{298}$(COF$_2$) permits a reanalysis of available kinetic and thermodynamic data on the energies of a number of other small fluorine-containing molecules, including CF$_3$O radical, CF$_3$OF, and CF$_3$-OOCF$_3$, and resolves a number of discrepancies between previous calculated and experimental results. It also allows a reevaluation of the energetics of HF loss from CF$_3$OH, an important reaction in the atmospheric degradation of several HFCs.

Introduction

Because of their relevance to the atmospheric degradation of hydrofluorocarbons, the heats of formation of a variety of small fluorinated organics have been the topic of current interest and, in some cases, debate. A variety of HFCs, including HFC-23 (CF$_3$H),[2] HFC-125 (CF$_3$CF$_2$H),[3–5] HFC-134a (CF$_3$CFH$_2$),[6,7] and HFC-143a (CF$_3$CH$_3$),[8] produce CF$_3$ radicals in the course of their atmospheric degradation. The CF$_3$ radical further reacts according to the following scheme:

$$CF_3 + O_2 + M \rightarrow CF_3O_2 + M \qquad (1)$$

$$CF_3O_2 + NO \rightarrow CF_3O + NO_2 \qquad (2)$$

$$CF_3O + RH \rightarrow CF_3OH + R \qquad (3)$$

$$CF_3O + NO \rightarrow COF_2 + FNO \qquad (4)$$

$$CF_3OH \rightarrow COF_2 + HF \qquad (5)$$

An understanding of the relative importance of these reactions requires information about both their kinetics and thermodynamics. Reactions 3 and 5 are of particular interest because they bear most directly upon the fate of CF$_3$O radicals in the stratosphere. The atmospheric chemistry of the CF$_3$O radical is an important consideration in assessing the potential ozone-depleting potential of HFCs.[9]

The energetics of reactions 3 and 5 are dependent upon the heats of formation of CF$_3$O radical, CF$_3$OH, and COF$_2$. We have recently reported ab initio calculations of the energetics of reaction 3[10] and the heats of formation of CF$_3$O radical and CF$_3$OH.[11] Our results differed significantly from the previous heat of formation and CF$_3$O–H bond strength estimates of Batt and Walsh[12] and of Francisco.[13] In particular, we have predicted the CF$_3$O–H bond strength to be 119 ± 2 kcal mol^{-1}, implying that the bond is very robust in the stratosphere and that CF$_3$OH cannot serve as a reservoir for CF$_3$O radicals.[14] Benson[15] has questioned the credibility of our experimental and computational evidence for the CF$_3$O–H bond strength when compared with Batt and Walsh's work,[12] and we have given a brief analysis of the latter's data and methods.[16] Batt and Walsh's results for CF$_3$OH are based upon bond additivity arguments that may or may not be valid for polyfluorinated compounds, but their results for CF$_3$O radical are based upon a fairly extensive amount of

experimental results and are difficult to dispute. This discrepancy in the heat of formation of CF$_3$O radical is of some concern.

A possible explanation for this discrepancy has very recently presented itself. Montgomery and co-workers[1] calculated the heat of formation of COF$_2$ using two different methods and arrived at a value (-145.6 kcal mol^{-1} at 298 K) differing significantly from the previously accepted experimental result (-151.7 kcal mol^{-1} at 298 K).[17] We report herein additional calculations that support their results. Further, as we will show, when this revised value for $\Delta_f H°_{298}$(COF$_2$) is combined with the available kinetic and thermodynamic data used by Batt and Walsh to estimate $\Delta_f H°_{298}$(CF$_3$O), the disagreement between our and their estimates disappears. Thus, we believe that agreement is finally possible on the heats of formation of CF$_3$O radical, CF$_3$OH, and COF$_2$. In addition, these results allow a reevaluation of the energetics of reaction 5 as well as of the heats of formation of CF$_3$OOCF$_3$ and CF$_3$OF.

Computational Details

All calculations were performed using the Gaussian 88 program suite.[18] Molecular structures were optimized using second-order Møller–Plesset (MP2) analytical gradients[19,20] with Pople's 6-31G(d,p) basis set.[21] Harmonic vibrational frequencies were evaluated numerically and were scaled by 0.95 to obtain zero-point energy corrections. Internal energy corrections to 298.15 K were calculated using standard statistical mechanical formulas.[22] Single-point energy evaluations were carried out at the MP2 geometries using Dunning's correlation-consistent polarized valence triple-zeta basis (cc-pVTZ)[23] in combination with the quadratic configuration interaction [QCISD(T)] electron correlation treatment.[24] The cc-pVTZ basis has dimension [4s3p2d1/3s2p1d] and is optimized for calculations that include electron correlation effects.

Diffuse basis functions are expected to have a large effect on the energetics of oxygen- and fluorine-containing compounds. To determine the energetic contributions of diffuse functions, calculations were also performed using the augmented cc-pVTZ basis (aug-cc-pVTZ).[25] Because of the large size of the basis set ([5s4p3d2f/4s3p2d] contractions) calculations were only possible at the MP2 level of theory for the larger molecules considered here. Approximate QCISD(T)/aug-cc-pVTZ energies were obtained using the following prescription:

$$E[\text{QCISD(T)}/\text{aug-cc-pVTZ}] \approx$$

$$E[\text{QCISD(T)}/\text{cc-pVTZ}] + \Delta \qquad (6)$$

$$\Delta = E[\text{MP2}/\text{aug-cc-pVTZ}] - E[\text{MP2}/\text{cc-pVTZ}] \qquad (7)$$

TABLE 1: Calculated Energies at the MP2/6-31G(d,p) Optimized Geometries (Energies in au)

	COF$_2$	HCOF	CH$_2$O	CO$_2$	H$_2$O	HF	H$_2$	CH$_4$	CH$_2$F$_2$
$\Delta_f H^\circ{}_{298}{}^a$	−151.7		−25.96	−94.05	−57.80	−65.32	0	−17.88	−108.3
HF/pVTZ	−311.73305	−212.82954	−113.91008	−187.70182	−76.05686	−100.05781	−1.13299	−40.21345	−237.99421
MP2/pVTZ	−312.61384	−213.47024	−114.30706	−188.30804	−76.31865	−100.32978	−1.16464	−40.41166	−238.66782
QCISD(T)/pVTZ	−312.64337	−213.49819	−114.33434	−188.32827	−76.33237	−100.33854	−1.17229	−40.43813	−238.70001
HF/aug-pVTZ	−311.73699	−212.83281	−113.91226	−187.70409	−76.06030	−100.06088	−1.13306	−40.21369	−237.99853
MP2/aug-pVTZ	−312.63697	−213.48704	−114.31630	−188.32138	−76.32899	−100.34089	−1.16501	−40.41445	−238.68858
QCISD(T)/aug-pVTZ			−114.34344		−76.34256	−100.34986	−1.17258	−40.44094	
QCISD(T)/pVTZ + Δ	−312.66650	−213.51500	−114.34358	−188.34161	−76.34271	−100.34965	−1.17266	−40.44091	−238.72077
ZPE^b	0.01348	0.02028	0.02605	0.01098	0.02080	0.00907	0.00998	0.04428	0.03232
ΔE^{298}	0.00330	0.00302	0.00286	0.00265	0.00284	0.00236	0.00236	0.00286	0.00311
total	−312.64972	−213.49169	−114.31466	−188.32798	−76.31907	−100.33822	−1.16032	−40.39377	−238.68534
G2 (298 K)^c	−312.68803^d		−114.33602	−188.35866	−76.32921	−100.34765	−1.16400	−40.40802	−238.71486

^{a} Experimental values from ref 31 in kcal mol^{-1}. ^{b} Based on scaled MP2/6-31G(d,p) frequencies. ^{c} From ref 27, corrected to 298 K with ΔE^{298}. ^{d} From ref 1.

TABLE 2: Calculated and Experimental Heats of Reaction and Heats of Formation at 298 K (All Energies in kcal mol^{-1})

|	G2	QCISD(T)/cc-pVTZ	QCISD(T)/aug-cc-pVTZ	exptl
CH$_2$O + 2H$_2$ → CH$_4$ + H$_2$O	−46.54	−47.28	−49.25	−49.74
$\Delta_f H^\circ{}_{298}$(CH$_2$O)	−29.16	−28.41	−26.44	−25.96
CH$_2$F$_2$ + 2H$_2$ → CH$_4$ + 2HF	−37.94	−38.09	−40.30	−40.24
$\Delta_f H^\circ{}_{298}$(CH$_2$F$_2$)	−110.59	−110.44	−108.23	−108.30
COF$_2$ + 2H$_2$ → CH$_2$O + 2HF	−9.59	−8.24	−13.01	−4.9
$\Delta_f H^\circ{}_{298}$(COF$_2$)	−147.00	−148.36	−143.59	−151.7
COF$_2$ + H$_2$O → CO$_2$ + 2HF	−22.45	−20.44	−21.75	−15.2
$\Delta_f H^\circ{}_{298}$(COF$_2$)	−144.44	−146.45	−145.14	−151.7
COF$_2$ + CH$_4$ → CH$_2$O + CH$_2$F$_2$	28.35	29.86	27.29	35.3
$\Delta_f H^\circ{}_{298}$(COF$_2$)	−144.71	−146.22	−143.65	−151.7
2HCOF → CH$_2$O + COF$_2$		−11.15	−11.93	
$\Delta_f H^\circ{}_{298}$(HCOF)		−91.05	−91.44	

Similar basis function additivity assumptions have been exploited quite successfully in the G1[26] and G2[27] methods developed by Pople and co-workers. The approach used here most closely resembles their modified G2(MP2) method.[28] In this work the approximation is found to be accurate to within 0.15 kcal mol^{-1} for the small molecules CH$_4$, HF, H$_2$O, H$_2$, and CH$_2$O, for which full QCISD(T)/aug-cc-pVTZ calculations are possible. It seems reasonable to assume comparable accuracy for the larger molecules considered here. The energetic results for all molecules considered are included in Table 1.

Results

Montgomery and co-workers[1] estimated $\Delta_f H^\circ{}_{298}$(COF$_2$) from the heat of the isodesmic reaction

$$COF_2 + CH_4 \rightarrow CH_2O + CH_2F_2 \qquad (8)$$
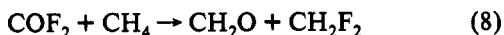
in combination with the experimental heats of formation of CH$_4$, CH$_2$O, and CH$_2$F$_2$. High levels of theory, including G2[27] and CBS-QCI/APNO[29] calculations, were employed. Because of the large discrepancy with the experimental heat of formation of COF$_2$, we thought independent analysis of this result warranted. To this end, we have recalculated the energetics of reaction 8, along with two other reactions of COF$_2$:

$$COF_2 + 2H_2 \rightarrow CH_2O + 2HF \qquad (9)$$

$$COF_2 + H_2O \rightarrow CO_2 + 2HF \qquad (10)$$
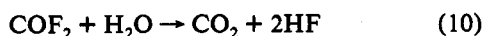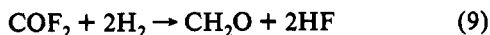
The hydrogenation energies of CH$_2$O and CH$_2$F$_2$ have also been calculated to calibrate the methods used:

$$CH_2O + 2H_2 \rightarrow CH_4 + H_2O \qquad (11)$$

$$CH_2F_2 + 2H_2 \rightarrow CH_4 + 2HF \qquad (12)$$
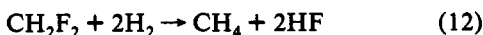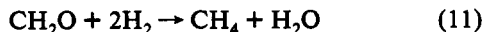
Reactions 9–12 are isogyric reactions[30] that involve species (save

COF$_2$) with well-known heats of formation. Reaction 8 is an isodesmic reaction that should lead to greater cancellation of computational errors, but which involves a species (CH$_2$F$_2$) with a potentially greater uncertainty in its heat of formation. We have employed basis sets optimized for correlated calculations along with a high-level treatment of electron correlation. Such an approach is mandatory for the reactions considered here. The energetic results for all five reactions are presented in Table 2.

Reactions 11 and 12 were studied to examine the level of computational sophistication necessary to obtain reliable results for carbonyl-containing compounds and to serve as a benchmark for the COF$_2$ calculations. The accepted value of $\Delta_{11}H^\circ{}_{298}$ is −49.74 kcal mol^{-1}, based on the heats of formation compiled by Atkinson et al.[31] The enthalpy of this reaction has been reported to be well reproduced at the Hartree–Fock level.[30] Such agreement is apparently fortuitous, because we find that only with the largest basis set and correlation treatment employed here does the energy converge to the experimental result. In fact, even the G2 method,[27] which has an impressive record for calculating reaction enthalpies, underestimates $\Delta_{11}H^\circ{}_{298}$ by greater than 3 kcal mol^{-1}. The QCISD(T)/aug-cc-pVTZ calculations agree to within 0.5 kcal mol^{-1} with the experimental value for $\Delta_{11}H^\circ{}_{298}$. The same result (to within 0.1 kcal mol^{-1}) is obtained whether the QCISD(T)/aug-cc-pVTZ energies are evaluated directly or using the approximate formulation in eqs 6 and 7.

Similar results are obtained for reaction 12. The G2 and QCISD(T)/cc-pVTZ energies are very close, but both differ by about 2 kcal mol^{-1} from the experimentally accepted value for $\Delta_{12}H^\circ{}_{298}$. Including the effects of diffuse functions through the use of the approximate QCISD(T)/aug-cc-pVTZ energies greatly improves the agreement with experimental results. However, $\Delta_f H^\circ{}_{298}$(CH$_2$F$_2$) may not be known with sufficient accuracy to distinguish between these two sets of results. From the results for reactions 11 and 12, the QCISD(T)/aug-cc-pVTZ energies would appear to be sufficiently accurate to treat the COF$_2$

hydrogenation and hydrolysis reactions and presumably more than adequate to treat COF_2 isodesmic reactions.

The isodesmic reaction 8 has previously been reported to have an energy of 29.34 kcal mol^{-1} (corrected to 298.15 K) using the CBS-QCI/APNO method.[1] The QCISD(T)/aug-cc-pVTZ calculations (Table 2) differ by 2 kcal mol^{-1} from this value. Using our calculated $\Delta_8 H°_{298}$ in combination with the experimental heats of formation of CH_4, CH_2O, and CH_2F_2,[31] we obtain a value of -143.6 kcal mol^{-1} for $\Delta_f H°_{298}(COF_2)$, compared to the value of -145.6 kcal mol^{-1} previously reported.[1] While not in as close an agreement as one might hope, these calculated values are consistent with one another, and both differ substantially from the accepted value of -151.7 kcal mol^{-1}.[17]

A potential concern in applying reaction 8 to determine $\Delta_f H°_{298}$-(COF_2) is the accuracy of the experimental value for $\Delta_f H°_{298}$-(CH_2F_2). Use of the hydrogenation reaction 8 or hydrolysis reaction 10 circumvents this possible difficulty. $\Delta_{10} H°_{298}$ is calculated to be -21.75 kcal mol^{-1}, corresponding to a derived value for $\Delta_f H°_{298}(COF_2)$ of -145.1 kcal mol^{-1}. This result is intermediate between those obtained above by the two different computational methods. The result varies by only 1.3 kcal mol^{-1} between the cc-pVTZ and aug-cc-pVTZ basis sets used here and is in equally good agreement with G2 results for reaction 8. The good agreement between methods for this reaction provides further support for the revised $\Delta_f H°_{298}(COF_2)$.

As with reaction 11, the energy of hydrogenation reaction 9 is slow to converge with increasing basis set size and correlation treatment. The QCISD(T)/aug-cc-pVTZ energy $\Delta_{11} H°_{298}$ is -13.01 kcal mol^{-1}, which correponds to a value of -143.6 kcal mol^{-1} for $\Delta_f H°_{298}(COF_2)$, the same as that obtained from reaction 8. Both the G2 and CBS-QCI/APNO[32,33] methods yield results for $\Delta_{11} H°_{298}$ larger by up to 3.5 kcal mol^{-1} and thus values for $\Delta_f H°_{298}(COF_2)$ smaller by the same amount. This relatively large range of results obtained for reaction 11 is surprising and reflects the difficulty in modeling hydrogenation reactions, just as was observed for reaction 9. It is difficult to recommend one calculated value over another, although the range gives some indication of the potential error in these calculations.

Thus, across three different reactions and a variety of computational approaches, the calculated heat of formation of COF_2 is consistently found to deviate from the accepted experimental value. We arrive at the same conclusion that Montgomery and co-workers have already reported: the experimental value for $\Delta_f H°_{298}(COF_2)$ is likely in error by more than 6 kcal mol^{-1}. On the basis of our and their work, we suggest adopting a value of -145.3 ± 1.7 kcal mol^{-1} for $\Delta_f H°_{298}(COF_2)$. This value is chosen as a compromise between the G2, CBS-QCI/APNO, and approximate QCISD(T)/aug-cc-pVTZ results for reactions 8 and 10, and the error range is chosen to reflect the span of results obtained by the variety of methods and reactions studied. The results from the more established G2 and CBS-QCI/APNO methods are weighted more heavily in this recommendation, although the calculations reported here support a slightly less negative value for $\Delta_f H°_{298}(COF_2)$.

Finally, another species of some importance to HFC chemistry is HCOF. Francisco has previously estimated $\Delta_f H°_0(HCOF)$ to be -93.8 ± 1.5 kcal mol^{-1}. As part of this work we have examined the isodesmic reaction

$$2HCOF \rightarrow CH_2O + COF_2 \qquad (13)$$
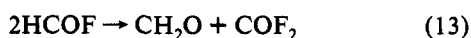
by the same computational approach as described above. Reaction 13 is calculated to be exothermic by 11.9 kcal mol^{-1}. Using our suggested value for $\Delta_f H°_{298}(COF_2)$ along with the experimental $\Delta_f H°_{298}(CH_2O)$ yields $\Delta_f H°_{298}(HCOF)$ of -91.6 ± 1.7 kcal mol^{-1}, in good agreement with Francisco's results.

Discussion

The experimental heat for formation of COF_2 was derived from the heat of hydrolysis to $CO_2(g)$ and aqueous HF.[34] The
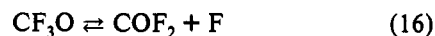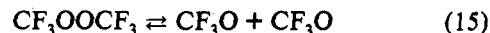
computational evidence is very strong that the accepted value is in error by better than 6 kcal mol^{-1}. This result has implications for the experimental heats of formation of a number of other species, which we now consider.

As was previously discussed,[16] Batt and Walsh made the first detailed study of the experimental data for the heats of formation of CF_3-containing species.[12] We later obtained results based on calculations that in some cases differed significantly from their work.[11] Batt and Walsh estimated $\Delta_f H°_{298}(CF_3O)$ from the enthalpy of the reaction

$$CF_3OOCF_3 \rightleftharpoons CF_3OF + COF_2 \qquad (14)$$
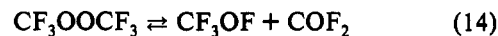
in combination with $DH°_{298}(CF_3O-OCF_3)$ and $\Delta_f H°_{298}(CF_3-OF)$ and $\Delta_f H°_{298}(COF_2)$. Clearly, any discrepancy in $\Delta_f H°_{298}$-(COF_2) results will propagate throughout these calculations. Because $\Delta_f H°_{298}(CF_3OF)$ is not known with great certainty, we have previously adopted a slightly different approach than Batt and Walsh in analyzing the experimental data,[16] which we revisit here.

The equilibrium constants for reaction 14 has been studied as a function of temperature and $\Delta_{14} H°_{298}$ determined to be 24.5 ± 0.7 kcal mol.[35] The kinetics of reaction 1 have been interpreted in terms of the following reaction mechanism:[36,37]

$$CF_3OOCF_3 \rightleftharpoons CF_3O + CF_3O \qquad (15)$$

$$CF_3O \rightleftharpoons COF_2 + F \qquad (16)$$

$$CF_3O + F \rightleftharpoons CF_3OF \qquad (17)$$

Arrhenius parameters for reaction 15 have been obtained by a number of groups.[36,38,39] If the activation energy for reaction 15 can be equated with the CF_3O-OCF_3 bond energy, as is usually assumed for homolytic cleavage reactions, then $\Delta_{15} H°_{298} = 46.8 \pm 0.5$ kcal mol^{-1}.[12] Similarly, Arrhenius parameters for the reverse of reaction 17[36,40] have been used to determine $\Delta_{17} H°_{298} = -44.0 \pm 0.5$ kcal mol^{-1}.[12] The enthalpies of reactions 14, 15, and 17 can be combined with the newly derived heat of formation of COF_2 along with $\Delta_f H°_{298}(F) = 18.97 \pm 0.07$ kcal mol^{-1},[31] to determine revised values for the heats of formation of CF_3O radical, CF_3OOCF_3, and CF_3OF. Following this approach yields $\Delta_f H°_{298}(CF_3O) = -148.0 \pm 1.9$ kcal mol^{-1}, $\Delta_f H°_{298}(CF_3OOCF_3) = -342.8 \pm 2.7$ kcal mol^{-1}, and $\Delta_f H°_{298}(CF_3OF) = -173.0 \pm 2.0$ kcal mol^{-1}, where the errors are propagated assuming normal error distributions.

These results are based entirely on experimental data, save the use of the calculated heat of formation of COF_2. $\Delta_f H°_{298}(CF_3O)$ obtained in this fashion agrees very well with the previously calculated value of -150.4 ± 2 kcal mol^{-1}.[11] A reasonable compromise between these two, and the value we recommend, is $\Delta_f H°_{298}(CF_3O) = -149.2 \pm 2.0$ kcal mol^{-1}. Similarly, $\Delta_f H°_{298}(CF_3OOCF_3)$ calculated here compares favorably with the previous estimate of -346.9 kcal mol^{-1}.[11] Thus, we believe that the discrepancy between the calculations and the experimental data for these molecules is resolved by incorporation of the new value for $\Delta_f H°_{298}(COF_2)$. A discrepancy still remains between the calculated $DH°_{298}(CF_3O-H)$ and that derived by the group additivity method.[12] The group additivity calculation essentially assumes that the bond energy difference between a peroxy RO-OR and a hydroxyl RO-H linkage is constant regardless of the R group. Such an approximation is likely not justified when R $= CF_3$ because of the unique electronic properties of this group.[41] Thus, we recommend use of the calculated values of $DH°_{298}$-(CF_3O-H) = 119.4 kcal mol^{-1} [10,11,32,42] and $\Delta_f H°_{298}(CF_3OH) = -217.7 \pm 2$ kcal mol^{-1}.[1,11] All the recommended heats of formation obtained here are summarized in Table 3.

TABLE 3: Recommended Heats of Formation in kcal mol⁻¹

	$\Delta_f H°$(298 K)		$\Delta_f H°$(298 K)
COF_2	-145.3 ± 1.7	CF_3OF	-173.0 ± 2.0
CF_3O	-149.2 ± 2.0	CF_3OOCF_3	-342.8 ± 2.7
CF_3OH^a	-217.7 ± 2.0	HCOF	-91.6 ± 1.7

^{a} Reference 11.

Atmospheric Implications

Reactions 3 and 5 are of some atmospheric importance, and their energetics have been open to dispute. The heats of formation obtained here should help to resolve these differences. The energy of reaction 3 and of the hydrogen abstraction reaction

$$CF_3OH + OH \rightarrow CF_3O + H_2O \qquad (18)$$
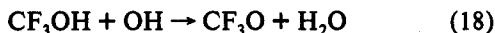
are determined by $DH°_{298}(CF_3O-H)$. The computational data[10,11,32,42] support a value of about 119 kcal mol⁻¹ for $DH°_{298}$-(CF_3O-H). Available kinetic results for reaction 3 with a variety of alkanes[43–48] are also consistent with this result. Based on this bond energy, CF_3OH will form readily in the atmosphere from CF_3O radicals, and back-reaction to re-form CF_3O radicals by reaction 18 will not be possible.[14] CF_3OH is a permanent sink and not a reservoir for CF_3O radicals in the atmosphere.

CF_3OH formed in the atmosphere may decompose either heterogeneously or in the gas phase by reaction 5,[49] the energy of which has been the subject of some debate.[11,13,49,50] Using the heats of formation recommended here, we obtain $\Delta_5 H°_{298} = 6.9$ kcal mol⁻¹, in excellent agreement with the most recent direct calculations.[49,50] The entropy contribution makes reaction 5 thermodynamically spontaneous down to about 200 K, so reaction 5 is thermodynamically feasible under typical atmospheric conditions up to and throughout the stratosphere. The atmospheric fate of CF_3OH is either decomposition by reaction 5 to yield COF_2 and HF or incorporation into cloud–rain–sea water where hydrolysis will occur to yield CO_2 and HF. The partitioning between these two processes is presently unknown but is unimportant with respect to the environmental impact of HFCs, because COF_2 formed by the former process will ultimately be hydrolyzed by atmospheric or sea water to yield CO_2 and HF.[51]

References and Notes

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