ELSEVIER

Journal of Fluorine Chemistry 79 (1996) 105–110

JOURNAL OF FLUORINE CHEMISTRY

Intervention of sulphur dioxide in the atmospheric degradation of HFC134a

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Received 16 July 1995; accepted 1 May 1996

Abstract

The possible involvement of sulphur dioxide in the tropospheric degradation of 1,1,1,2-tetrafluoroethane (HFC134a) was examined using semi-empirical calculations to assess the exothermicities of reactions. The formation of trifluoromethoxy sulphuric acid, from the trifluoromethoxy radical, in areas of highest sulphur dioxide pollution is indicated. From its energy of deprotonation, it is estimated to be as strong as sulphuric acid and stronger than the other predicted end-product acids (HCOOH, CF_3COOH and HF). Joining a perfluoroalkyl group to sulphur via an oxygen atom enhances stability compared with direct linkage to sulphur. Thus CF_3OSO is more stable than CF_3SO_2 and $CF_3OSO(OH)$ than CF_3SO_2OH. Trifluoromethanol, a degradation intermediary, is about as strong an acid as formic acid and there is a possibility that at least part can be stabilized as a salt $NH_4[OCF_3]$ at high altitudes where solvolysis is minimized.

Keywords: Sulphur dioxide; Atmospheric degradation; HFC134a; Semi-empirical calculations; Reaction exothermicities

1. Introduction

The replacement of ozone-depleting CFCs with HFCs or their ethers has commenced with the commercialization of HFC134a (CF_3CH_2F). This has prompted extensive studies on the possible environmental impact of HFC134a [1] which will depend on how long it survives, its decomposition products and their interactions. The consequences will only become measurable in the next century because of its long life as well as the interfering effects of remaining CFCs. A decomposition mechanism, or rather a sequence of possible reactions, has been proposed. The projected atmospheric concentrations of HFC134a will be in the ppt/v range [2] or of the order 10^7 molecules cm^{-3} in the units employed by most investigators, which is smaller than the concentrations [X] of many other reactive species in the troposphere.

Bimolecular reactions of the HFC are treated as pseudo-unimolecular with the average concentrations [X] remaining constant. Estimated 'life times' τ are then defined as $3.15 \times 10^7/k[X]$ years for decay to 37% (1/e)th of the original value. The rate constants k are quoted in cm^3 $molecule^{-1}$ s^{-1} units which are 6×10^{20} as small as the conventional mol^{-1} dm^3 s^{-1} units. Because there is a considerable temporal and spatial variation of [X], averaged values are taken. These give averaged lives which are more useful for inter-comparisons than for their absolute values. A high reactant concentration can compensate for a small rate constant. HFCs are not directly oxidized by di-oxygen but require the reactive hydroxy radical to abstract hydrogen in a slow rate-determining step. In practice, τ values are obtained by comparing them with that of methyl chloroform (mc) to avoid having to integrate the variable hydroxy concentrations through the atmosphere [3], i.e. $\tau\text{HFC} = \tau\text{mc} \cdot k\text{mc}/k\text{HFC}$ where $\tau\text{mc} = [\text{mc}]$ in atmosphere/production rate of mc. The production rate should include both man-made and natural production [4].

The purpose of this paper is to examine the possible participation of sulphur dioxide in the proposed mechanism which has not been considered previously. Semi-empirical methods are employed to assess the thermodynamic feasibility of reactions whose rate constants will need to be determined by experiment.

2. Calculation methods

Heats of formation and geometries were calculated with semi-empirical AM1 and PM3 parameterizations of MNDO available in the MOPAC program [5]. Charge distributions and spin densities were also obtained to follow charge movement and likely centres for addition to radicals. While errors in semi-empirical heats can be larger than in *ab initio* heats,

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PII S0022-1139(96)03481-1

Table 1
Comparison of formation heats (in kcal mol^{-1}) obtained semi-empirically with *ab initio* or experimental values

Molecule	AM1	PM3	*Ab initio* [a]	Experimental	Group additivity
CF_4	−225.7	−225.1		−223.3	
OCF_2	−146.3	−141.6	−145.3	−152.7 [b]	−156.7
CF_3OH	−227.0	−222.8	−217.7		−213.5
CF_3O	−160.1	−162.4	−150.4		−156.7
CF_3OF	−172.8	−187.3	−173.0	−182.8	
CF_3OO	−157.0 [c]	−157.0	−147.8		−161.4
HCOF	−93.0	−88.9	−91.6		
$CF_3O_2CF_3$	−349.9		−342.8, −346.9	−360.2 [d]	

[a] 6.31G*/MP3 or MP4 [8].

[b] This is an old value [7] and needs to be redetermined using alkaline hydrolysis in a closed system.

[c] MNDO value.

[d] A doubtful value [8].

derived via isodesmic reactions, the semi-empirical errors tend to compensate in reactions involving differences between related molecules. With small species such as OH, CF_3, NO and SO_2, there are large semi-empirical errors and experimental values are taken. With larger molecules, AM1 and PM3 values are in good agreement and an average can be used. Some semi-empirical heats are compared with recent *ab initio* and older experimental values in Table 1 to show the extent of the differences. In some instances the semi-empirical heats are closer than *ab initio* ones to the experimental values.

The reasonableness of some heats can also be roughly checked by equating F and OH 'isoelectronic heats' [6] or by simple group additivity where $\Delta H_f^\circ(XY)$ is derived as the mean of X_2 and Y_2 heats. As examples of the former, $\Delta H_f^\circ(CF_3F) \simeq \Delta H_f^\circ(CF_3OH)$ and $\Delta H_f^\circ(HCOF) \simeq \Delta H_f^\circ(HCOOH)$ and of the latter $\Delta H_f^\circ(CF_3OOH) \simeq \frac{1}{2}[\Delta H_f^\circ(CF_3OOCF_3) + \Delta H_f^\circ(HOOH)]$.

3. Sulphur dioxide concentrations and rate implications

Over 200 Mtonne of sulphur dioxide are generated annually, about one-quarter from the marine biosphere and volcanic activity with the remainder man-made. High localized concentrations occur over industrialized areas as evidenced by the averaged higher values of the northern over southern hemispheres. The significant facts that the concentrations of sulphur dioxide can exceed those of the reactive radicals NO, NO_2 and OH involved in HFC decompositions, and that SO_2 has quoted lifetimes ranging from days to weeks, show that the possibility of reaction with radicals derived from HFCs present at much lower concentrations should be considered. Some atmospheric concentrations, together with rate constants of their reactions with trifluoromethoxy radicals, are collected in Table 2.

Bimolecular reactions between radicals should have nearly zero activation energies (E_a) and rate constants (according to classical collision theory) of the order of 1.7×10^{-11} molecule^{-1} cm^3 s^{-1}, equal to the pre-exponential factor A in $k = Ae^{-E_a/RT}$. For simple radical–molecule reactions which are exothermic, activation energies up to 6 kcal mol^{-1} are expected [10], leading to rates of around 10^{-15} if the A factor is unaltered.

Table 2
Comparison of concentrations of reactant gases and rate constants for reactions with OCF_3

Gas	Conc. (molecules cm^{-3}) [a]	k_{298} (cm^3 $molecules^{-1}$ s^{-1})
OH	$6 \pm 2 \times 10^5$ [b]	
HO_2	$\sim 10^8$	
NO	10^8 to 2.5×10^{10}	2×10^{11}
NO_2	7.5×10^7–5×10^{10}	9×10^{-12}
SO_2	10^9–10^{12}	
CH_4	3.3×10^{13}	2.1×10^{-14}
H_2O	$\sim 10^{17}$	0.2–40×10^{-17}
O_2	$\sim 10^{18}$	

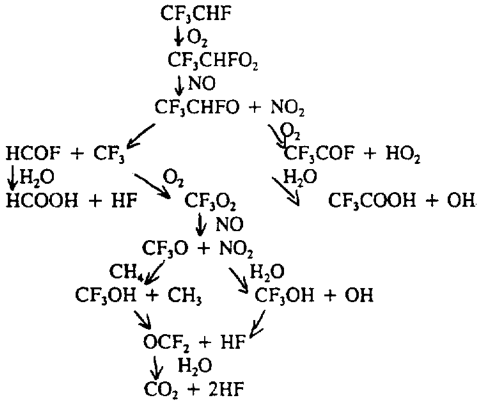
[a] Either global averages or limiting values between polluted and non-polluted areas are given.

[b] A height profile is shown in Ref. [9].

Typical examples of rate lowering on replacing a radical by an electron-paired molecule are the reactions of OH with NO and SO_2 for which the k values are 3×10^{-13} and 8.7×10^{-16}, respectively, i.e. a 3000-fold diminution [10]. Changes in activation energies (E_a in kcal mol^{-1} units) will soon outweigh any variation in the A factor as shown by the expression:

$$pk = 0.73E_a + pA$$

where pk and pA are $-\log k$ and $-\log A$, respectively, and the pA variability is unlikely to exceed a few units. Hence sulphur dioxide in bimolecular reactions with radicals should be competitive with nitrogen oxides (or even methane reactions) when present near its highest concentrations, but it would be uncompetitive with reactions involving oxygen or water molecules present at least at 10^6-fold higher concentrations.



Scheme 1. Main steps in the proposed oxidation of HFC134a.

4. Intervention of sulphur dioxide in the oxidation of HFC134a

The principal reactions proposed after the initial hydrogen abstraction are outlined in Scheme 1 [1]. They lead to three acids as products, one strong (HCOOH), one weak (HF) and one of intermediate strength (CF_3COOH) in aqueous solution. There is a bifurcation in arriving at CF_3CHFO which can either suffer hydrogen abstraction with di-oxygen, or fission to trifluoromethyl and formyl fluoride. Experimental work shows that about two-thirds of the CF_3CHFO molecules will undergo fission although there is a considerable height variation, ranging from 80% fission at ground level to 25% at the top of the troposphere [12]. The most likely intermediates for reaction with sulphur dioxide are the CF_3 and CF_3O radicals. The CF_3–SO_2 reaction is uncompetitive with the CF_3–O_2 reaction because of the much higher oxygen concentration as pointed out previously. However, the former reaction is of interest in illustrating the ambidentate nature of sulphur dioxide which can link via the S or O atom [13]. The latter is by far the more favourable; the former is endoergic when allowance is made for the entropy decrease.

$$CF_3+SO_2 \longrightarrow CF_3SO_2 \quad \Delta H=-0.3$$
$$\searrow CF_3OSO \quad \Delta H=-48.9$$

(enthalpies in kcal mol^{-1} not in the text are collected in an appendix).

In CF_3SO_2, the SO_2 precursor acts as a base with an average charge transfer of 0.36*e* from SO_2 to CF_3, whereas in CF_3OSO the SO_2 is acidic with a charge transfer of 0.12*e* away from CF_3. Electronegativity values tabulated by Pearson [14] for CF_3 and SO_2 also indicate initial electron transfer to SO_2.

At the next step (oxygen abstraction from CF_2O_2), sulphur dioxide could compete with nitric oxide if SO_2 concentrations were about 1000×NO concentrations. (Compare the rate ratios of OH with NO and SO_2 [11].)

$$CF_3OO+NO \longrightarrow CF_3O+NO_2 \quad \Delta H=-17.7$$

$$CF_3OO+SO_2 \longrightarrow CF_3O+SO_3 \quad \Delta H=-27.6$$

Free energies would be little different as entropy changes are small (CF_3O is more stable by 5.4 kcal mol^{-1} than CF_3OO from PM3 values and by 2.6 kcal mol^{-1} from *ab initio* calculations: a mean stabilization of 4.0 kcal mol^{-1} is used). The CF_3O radical can then react with methane ($k=2\times 10^{-14}$) and to some extent with nitric oxide [15].

$$CF_3O+CH_4 \longrightarrow CF_3OH+CH_3 \quad \Delta H=-14.6$$

$$CF_3O+NO \longrightarrow ONF+OCF_2 \quad \Delta H=-32.2\ [16]$$

$$CF_3O+NO \longrightarrow CF_3+NO_2 \quad \Delta H=+21.7$$

The second reaction may proceed via a CF_3ONO intermediate which has a weak O–N bond of length 1.59 Å (cf. 1.46 Å in HO–N=O)

$$CF_3O+NO \longrightarrow CF_3ONO \quad \Delta H=-41.4$$

The other suggested reaction with water [15] is just about thermoneutral.

$$CF_3O+H_2O \longrightarrow CF_3OH+OH \quad \Delta H=-0.1$$

Sulphur dioxide should react competitively with nitric oxide towards CF_3O since the reaction is just as exothermic.

$$CF_3O+SO_2 \longrightarrow CF_3OSO_2 \quad \Delta H=-32.5$$

$$CF_3O+SO_2 \longrightarrow CF_3+SO_3 \quad \Delta H=+14.4$$

There is little information on the kinetics of SO_2 reactions with methoxy radicals and none on reactions with the fluorinated equivalents. The reaction of excess CH_3O_2 with SO_2 under pseudo first-order conditions yielded a *k* value of 8.2×10^{-15} and reacted at least 10^4-times more slowly with CH_3O_3, although the products were not identified [17]. In a later paper the first *k* value was given as 1.6×10^{-14}, with the presence of NO enhancing this rate [18]. An upper limit for $k(CF_3O\text{–}SO_2)$ is probably about 10^{-14} cm^3 $molecule^{-1}$ s^{-1}.

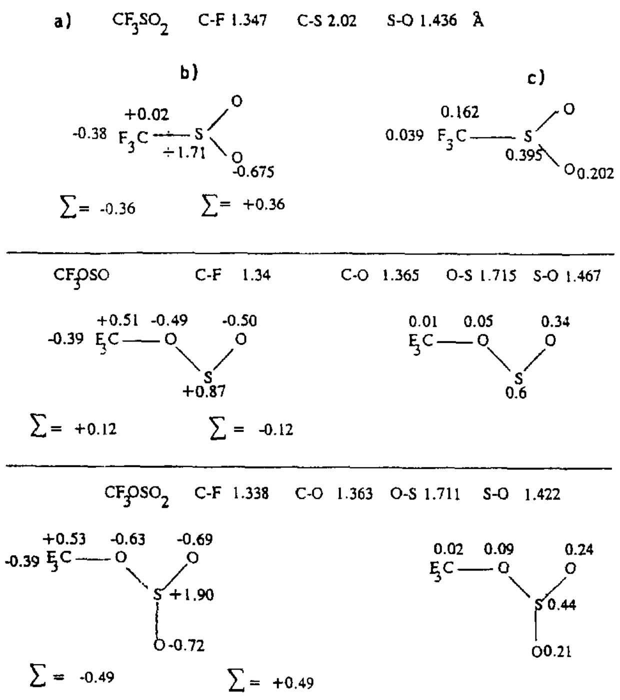
5. Properties of CF_3OSO_2

Bond lengths, charge distribution and spin densities calculated with PM3 are shown in Scheme 2. There is a 0.49*e* transfer from SO_2 to OCF_3 on formation, i.e. SO_2 acts as a base. The odd electron resides mainly on the sulphur, the atom to which other radicals would attach. In CF_3O the odd electron is almost completely on the oxygen. The CF_3OSO_2 radical could then react with OH or NO radicals with nearly zero activation.

$$CF_3OSO_2+OH \relbar\relbar (CF_3O)SO_2OH \quad \Delta H=-86.4$$

$$CF_3OSO_2+NO \longrightarrow CF_3OSO_2NO \quad \Delta H=-16.3$$

(Reactions of CF_3OSO_2 with water or methane, which yield the sulphuric or sulphinic acids CF_3OSO_2OH or CF_3OSO_2H, are endothermic by 12.5 and 32.9 kcal mol^{-1}, respectively.) Alternatively, the former could be formed via



Scheme 2. Comparison of (a) bond lengths, (b) charge and (c) spin density distribution in CF_3SO_2, CF_3OSO and CF_3OSO_2.

$$CF_3O + SO_2OH \longrightarrow CF_3OSO_2OH \quad \Delta H = -76$$

although SO_2OH – the radical involved in SO_2 oxidation – would be present at much lower concentrations than SO_2.

The acid strength of trifluoromethoxy sulphuric acid can be derived from the free energy of deprotonation in the gas phase. (In aqueous solution the strongest acids are levelled to equal strengths, but generally the order of strengths for the weaker acids is preserved.) The relative acidities can be estimated from the difference between the heats of formation of an acid and its anion since the $\Delta H_f^\circ(H^+)$ term is constant and provided entropy changes are not too variable. Calculated values are collected in Table 3 with some experimental values for comparison.

The strongest sulphuric acids with the easiest deprotonations have enthalpies around 300 kcal mol^{-1}, the weakest acids around 350 kcal mol^{-1} and intermediate strengths between 320 and 330 kcal mol^{-1}. Replacing CF_3 by CH_3 on average increases deprotonation energies by 21 kcal mol^{-1}. Viggiano et al. [19] measured rates of proton transfer between fluoro, trifluoromethyl and sulphuric acids and various anions to obtain the order of acidity $CF_3SO_3H > HSO_3F > H_2SO_4$ and correlated this order with the free energies or enthalpies of deprotonation which differed by only 7 kcal mol^{-1}. Kebarle et al. also measured proton transfers mass spectrometrically to compare the acidities of CF_3COOH and CH_3COOH [20], and derived the acidity order from $\Delta H_d^\circ = D(A\text{–}H) - IE(H) - EA(A)$.

More recently Koppel has obtained free energies of ionization of super acids, defined as those with $\Delta G < 300$ kcal mol^{-1}, by ion cyclotron resonance stepped relative to $\Delta G(HBr)$ of 318.1 kcal mol^{-1} [21]. Errors tend to accumulate with the number of steps. They showed that large basis sets were needed to reproduce experimental values within 3 kcal mol^{-1} since accurate entropies and zero point energies also required calculation. With smaller basis sets, experimental and calculation free energies can be linearly correlated in spite of large errors in calculated values. Their experimental ΔG values for CF_3SO_3H, HSO_3F and H_2SO_4 of 299.5, 299.8 and 302.2 kcal mol^{-1}, respectively, are in line with the above acidity order. However, CF_3OH ($\Delta G = 340.7$ kcal mol^{-1}) appears a much weaker acid than CH_3SO_2OH ($\Delta G = 315$ kcal mol^{-1}) but approaches the strength of formic acid ($\Delta G = 338.4$ kcal mol^{-1}) within 1.7 pK_a units.

Table 3
Heats of deprotonation of acids (HA) (kcal mol^{-1})

HA	$-\Delta H_f^\circ(HA)$ [a]	$-\Delta H_f^\circ(A^-)$	ΔH_d [b]	
$HOSO_2OH$	177(4)	241.9(4) [e]	302(4)	309 [19]
FSO_2OH	182.3(4) [c]	244.7(4) [d]	303(4)	307 [19]
CF_3SO_2OH	259.1(1)	323.6(1)	301(1)	306 [19]
CH_3SO_2OH	131.8(1)	166.6(1)	331(1)	
CF_3COOH	244(3)	290.5(3)	319(3)	320 [20]
CH_3COOH	103.3(4)	122.5(4)	346(4)	345 [20]
$(CF_3O)SO_2OH$	343.0(1,3)	406.7(1,3)	302(1,3)	
$(CH_3O)SO_2OH$	180.3(1,3)	225.6(1,3)	320(1,3)	
$(CF_3O)SOOH$	304.8(1,3)	343.7(1,3)	327(1,3)	
$(CH_3O)SOOH$	91.6(1,3)	103.7(1,3)	353(1,3)	
CF_3OH	222.8(3)	256.4(3)	332(3)	
CH_3OH	360(4)	48.1(4)	353(4)	

[a] (1) AM1; (3) PM3; (1,3) mean of (1) and (3); (2) *ab initio*; (4) experimental values.

[b] $\Delta H_d = \Sigma\Delta H_f^\circ$ $(H^+ + A^- \rightarrow HA)$ where $\Delta H_f^\circ(H^+) = 365.4$ kcal mol^{-1}).

[c] Value in Ref. [27] updated with newer $\Delta H_f^\circ(HF)$ value.

[d] From $\Delta H_f^\circ(SO_3F)$ and its electron affinity.

[e] From a lattice energy calculation.

Trifluoroacetic acid, one of the end-products of HFC134a oxidation, is only moderately strong in aqueous solution with quoted K_a values from 0.6–9 mol l^{-1} [22]. The discrepant values are due to the difficulty in separating ionization from dissociation as is found with another end-product HF of the HFC134a decomposition. It is a very weak acid in aqueous solution although fully ionized [23]. In contrast, the conjectured product, trifluoromethoxy sulphuric acid, would be as strong as sulphuric acid in aqueous solution. The acidity of CF_3OH has a bearing on its fate in the atmosphere. It is almost as strong an acid as formic acid. The strengthening of acidity, or conversely the weakening of basicity, on replacing methyl by trifluoromethyl groups is well known. For example, $N(CF_3)_3$ remains unprotonated in hot mineral acids. Hence the increase in acidity of CF_3OH over CH_3OH is expected. Indeed, Kloeter and Seppelt observed salt formation on reaction with trimethylamine [24].

It has been assumed that HF and CO_2 are the sole products of CF_3OH decomposition. In the gas phase CF_3OH slowly decomposes to COF_2 and HF, with reported half-lives varying from minutes to hours [1]. The unimolecular decomposition has been described as orbitally forbidden and indeed an *ab initio* calculation predicts a very high activation energy of 47.9 kcal mol^{-1} [25]. In the gas phase, proton transfers from acids have rate constants of the order of 10^{-9} cm^3 $molecule^{-1}$ s^{-1} [19] and hence salt formation with NH_3 is both kinetically and thermodynamically favourable, the endothermic ion formation being compensated by the large lattice energy (U) as the solid forms.

$$CF_3OH + NH_3 \longrightarrow CF_3O^- + NH_4^+$$

$$\Delta H = +130 \text{ (gas phase)}$$

The values of $U(NH_4^+OCF_3^-)$ must be > 153 kcal mol^{-1}, the value for the isoelectronic NH_4HSO_4, since the radius of the OCF_3^- anion must be smaller than that of the hydrogen sulphate anion (S–O = 1.53 Å as against C–F = 1.37 Å). Alkali metal salts (K–Cs) have been made by reacting COF_2 with metal fluorides in methyl cyanide [26].

$$OCF_2 + F^- \longrightarrow OCF_3^- \quad \Delta H = -49 \text{ (in the gas phase)}$$

Although the reaction can be reversed on heating, the stabilities seem to be between those of fluorosulphites (SO_2F^- with $\Delta H = -37$ kcal mol^{-1}) and the isoelectronic fluorosulphate (SO_3F^- with $\Delta H = -78$ kcal mol^{-1}) also made by addition to metal fluorides. However the trifluoromethoxides are unstable in moist atmospheres, presumably because of solvolysis by water protons.

$$OCF_3^- + H^+ \longrightarrow CF_3O^-H^+ \rightleftarrows$$

$$CF_3OH \longrightarrow COF_2 + HF$$

The equilibrium is displaced to the right as the very volatile COF_2 (b.p. −83 °C) is dispersed. (Both HF and CF_3OH boil at around 20 °C.) Near the top of the troposphere with temperatures as low as −55 °C to −60 °C the salt could persist because of a slow heterogeneous reaction in the solid state with ice particles, although proton mobility in ice is little different from that in water. Aerosols of ammonium sulphate are known to persist as high altitudes.

A final possible intervention by SO_2 could be by insertion into the C–F bonds of formyl and acetyl fluorides. These reactions, although exothermic by 46 kcal mol^{-1}, are unlikely to occur under atmospheric conditions in preference to the less exothermic and slow hydrolyses to acids [27], if only because of the relative atmospheric concentrations of SO_2 and H_2O.

Conclusions

Rate constants of CF_3O–SO_2, and the subsequent reaction with hydroxy, are required to check if trifluoromethoxy sulphuric acid could form during oxidation of HFC134a. The stability of $NH_4^+OCF_3^-$ as a possible product from hydrogen trifluoromethoxide should also be investigated.

Appendix: Additional auxiliary enthalpies used in deriving heats of reaction (kcal mol^{-1})

Species	ΔH_f°(gas) [a]	Species	ΔH_f°(gas)
OH	9.4(4)	SO_2OH	−102.5(1)
NO	21.6(4)		−104.2(3)
NO_2	7.9(4)	SO_2F	−110.6(1)
SO_2	−71.0(4)		−102.2(3)
SO_3	−94.6(4)	HCOF	−93.0(1)
F^-	−61.0(4)		−88.9(3)
CF_3	−112.4(4)		−91.6(2)
NH_3	−11.0(4)	$HCOSO_2F$	−134.2(1)
NH_4^+	149(4)		−139.2(3)
		CF_3COF	−237.7(1)
CF_3SO_2	−182.5(1)		−239.3(3)
	−184.9(3)	CF_3OOSO_2F	−282.4(1)
CF_3OSO	−232.6(1)		−286.5(3)
	−231.9(3)	CH_3OSO	−66.1(1)
CF_3OSO_2	−266.8(1)		−67.7(3)
	−263.7(3)	CH_3OSO_2	−98.9(1)
CF_3ONO	−176.8(3)		−97.1(3)
CF_3OSO_2NO	−257.4(1)	CH_3O	−1.4(1)
			−0.5(4)
		CH_3SO_2	−50.8(1)
			−52.1(3)

[a] (1) AM1; (3) PM3; (4) experimental value.

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