Molecular modelling studies on the reactions of fluoroalkenes with sulfur trioxide

John O. Morley,[a] **David W. Roberts**[b] **and Simon P. Watson**[a]

[a] *Department of Chemistry, University of Wales Swansea, Singleton Park, Swansea, UK SA2 8PP*
[b] *Unilever Research Port Sunlight Laboratory, Quarry Road East, Bebington, Wirral, UK L63 3JW*

Received (in Cambridge, UK) 1st April 1999, Accepted 13th July 1999

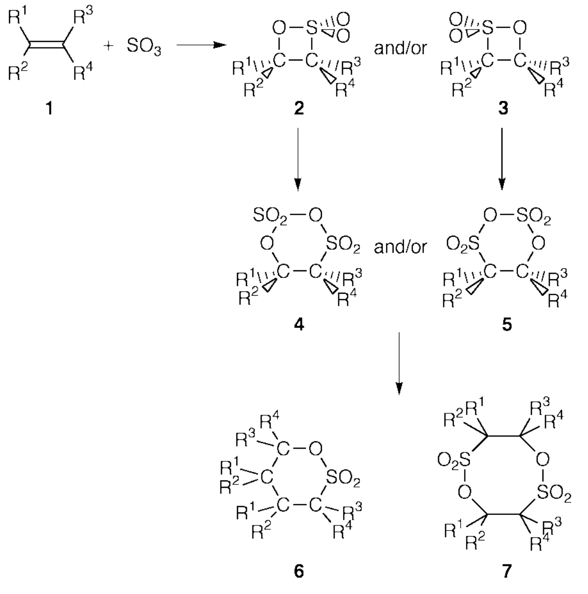
The structures, molecular energies and electronic properties of a series of substituted fluoroalkenes and the corresponding alkane sultones, derived from the addition of sulfur trioxide to the double bond, have been explored using a combination of molecular modelling and theoretical calculations. Both the calculated charge distributions at carbon and the calculated enthalpies of the addition process show a good correlation with the observed selectivity of electrophilic attack by the sulfur atom of sulfur trioxide, especially for unsymmetrical alkenes where there are two possible sites of addition. Mechanistically, the reactions of ethene and tetrafluoroethene with sulfur trioxide proceed *via* formation of stable π-complexes to give a transition state in the former case which is predicted to have a comparable energy to that found experimentally for the related reaction of octadec-1-ene.

Introduction

There have been a considerable number of experimental studies on the reaction of sulfur trioxide with alkenes, where the alkene **1** contains substituents such as alkyl, allyl, aryl, halogen, alkoxy and ester groups.[1–6] The initial products in all cases are the β-sultones **2** and/or **3**, which may subsequently react further either with sulfur trioxide to form the β-pyrosultones **4** and/or **5**, or with the alkene to form γ- or δ-sultones such as **6**, or dimerize to form the cyclic bis(β-sultones) such as **7**. The initial process is often reversible and fluoroalkane sultones readily dissociate back into the alkene and sulfur trioxide on heating (Scheme 1).

The specific products of the reaction depend upon the reactant : reagent ratio, the reaction temperature, the method of the product work-up, the degree of polymerization of the sulfur trioxide used, and the nature of the substituents on the alkene.[5] The reaction is thought to proceed *via* a concerted cycloaddition mechanism[1] but it is uncertain whether this occurs *via* the formation of an intermediate π-complex or by direct cycloaddition of the sulfur atom and oxygen atom to the two adjacent atoms of the double bond (Scheme 2).

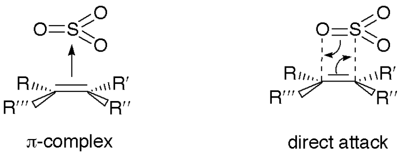
Unsymmetrical alkenes may form two different β-sultones with sulfur trioxide, designated **2** and **3**, resulting from the addition of the sulfur atom to each of the different carbon atoms at the 1- and 2-positions of the alkene.[5] Generally, the nature of the substituents has a marked effect on the rate and orientation of addition, with both electronic effects and steric effects contributing to the overall product composition. Fluoroalkenes react more readily than their chlorine analogues, but generally yield a single β-sultone as the major product, though under some conditions β-pyrosultones **5** are formed. 1,1-Difluoroethene **1b** and 1,1,2-trifluoroethene **1c** are attacked by sulfur trioxide to give the fluoroalkane sultones **2b** and **2c** respectively, where the sulfur atom is attached to the carbon containing the hydrogen atom(s).[2] 1,1-Dichloro-2,2-difluoroethene **1d** gives sultone **3d** where the sulfur atom is bonded to the carbon containing chlorine,[2,3,5] while 1-chloro-1,2,2-trifluoroethene **1e** gives a mixture of both possible sultones **2e** and **3e**.[3,5] In contrast, vinyl ethers such as **1g** and vinyl esters such as **1h** always give products which have the sulfur attached to the carbon atom which is not connected to the ether or ester group.[5] For example, *trans*-1-chloro-1,2-difluoro-2-methoxyethene **1g** gives sultone **3g**.[2]



a $R^1 = R^2 = R^3 = R^4 = H$
b $R^1 = R^2 = F, R^3 = R^4 = H$
c $R^1 = R^2 = R^3 = F, R^4 = H$
d $R^1 = R^2 = Cl, R^3 = R^4 = F$
e $R^1 = Cl, R^2 = R^3 = R^4 = F$
f $R^1 = R^2 = R^3 = R^4 = F$
g $R^1 = Cl, R^2 = R^3 = F, R^4 = OMe$
h $R^1 = OAc, R^2 = R^3 = R^4 = H$
i $R^1 = R^2 = R^3 = Cl, R^4 = CO_2H$
j $R^1 = F, R^2 = OMe, R^3 = R^4 = CF_3$

Scheme 1 Products of the reaction between sulfur trioxide and an alkene.

The orientation of the products obtained is highly dependent



Scheme 2 Attack of sulfur trioxide on an alkene double bond.

on the nature of the substituents present at the double bond though often the underlying reasons for the observed selectivity are little understood. The present molecular orbital studies have been carried out, therefore, to rationalize the observed selectivity both in terms of the structural features of the alkene and electronic effects of the substituents present at the double bond. While semi-empirical treatments such as the MNDO,[7] AM1[8] and PM3[9] methods appear to give a reasonable account of the geometry and electronic properties of the simple addition products derived from electrophilic addition of first row elements to the double bonds of alkenes, in sulfur containing systems they suffer from the disadvantage that the binding energy of the sulfur atom is represented by the valence 3s and 3p orbitals only. Although the sulfur parameterization[10] has been adapted to represent the vacant 3d orbitals, the absence of these functions would be expected to have a pronounced effect on the molecular geometry and energies of many organic sulfur containing systems as we have previously discussed.[11a]

Accordingly, we have used mainly *ab initio* methods to probe the structure, electronic properties, and enthalpies of the addition process which occurs in the gas phase (Scheme 1). No account has been taken of the entropy changes involved in the addition reaction which would be expected to be significantly negative for the formation of the sultones **2** and **3** and other cyclic products.

Methods of calculation

Initial calculations were carried out on representative structures for the sultone **2** using the MNDO,[7] AM1[8] and PM3[9] methods of the MOPAC package.[12] Because the results from these calculations were considered unsatisfactory (see later), the 4-31G basis set[13] of the GAMESS program[14] with polarization functions present for both sulfur and chlorine (subsequently referred to as 4-31G/S*) was used for all subsequent calculations. Although potentially more accurate basis sets are available, we do not believe that better results would have ensued because the reactions described here occur initially in the presence of an excess of reactants and end in the presence of an excess of product(s). Experimentally, the dielectric field experienced by the individual molecules during the course of the reaction will therefore vary and will have an influence on their geometry and properties, and the energetics of the reaction. For example, at the beginning of the reaction between ethene and sulfur trioxide, the reactants only experience a small dielectric field as the relative permittivities of both are small with values of 1.48 and 3.31, respectively.[15] However, as the reaction proceeds the dielectric field experienced by the reactants increases with increasing conversion to products, and near the end, the reactants will experience a very large dielectric field. Although there are no permittivity data available for the products described here, related compounds such as ethylene sulfite and dimethyl sulfone have large relative permittivities of 39.6 and 47.4, respectively.[15] The 4-31G/S* basis set was selected primarily because, in our recent studies on aryl sulfides,[11b] it gave identical C–S bond lengths and C–S–C angles to the 6-31G** basis set and showed a close fit with crystallographic data. Reaction coordinate calculations were carried out using the SADDLE directive and the transition states between sulfur trioxide and ethene or tetrafluoroethene were characterized by their single negative frequency using the FORCE directive in the program.[14] Energies were refined using single point calculations both at the gas phase Moller–Plesset MP2 level,[16,13] and in solvent using the PSSC directive of the Tomasi routine.[17] The π-complexes between sulfur trioxide and ethene or tetrafluoroethene gave all positive vibrational frequencies from FORCE calculations showing that they were genuine stationary points on the potential energy surface. All the structures were prepared and analysed before and after optimization using the SYBYL molecular modelling program,[18] and calculations were performed on a cluster of Silicon Graphics workstations.

Discussion

There have been a number of theoretical studies of electrophilic addition to the double bonds of alkenes both at the semi-empirical and *ab initio* levels. These include typical reactions such as the addition of hydrogen chloride[19] and alkyl radicals to ethene,[20] but there have been no previous reports on the addition of sulfur trioxide to alkenes to form alkane sultones although there has been one recent *ab initio* study on the decomposition of episulfones to form sulfur dioxide and either ethene or butene.[21] In the work described here, the structures and energies of the alkene and sultone were probed initially using semi-empirical methods and subsequently using the 4-31G basis set for all first row elements with additional d functions added to the sulfur and chlorine atoms only (subsequently referred to as the 4-31G/S* basis set). This approach is justified by our recent studies on the sulfonation of toluene where a marked improvement occurs in the key carbon–sulfur and sulfur–oxygen bond lengths when additional d orbitals are added to the sulfur atom in this way.[22]

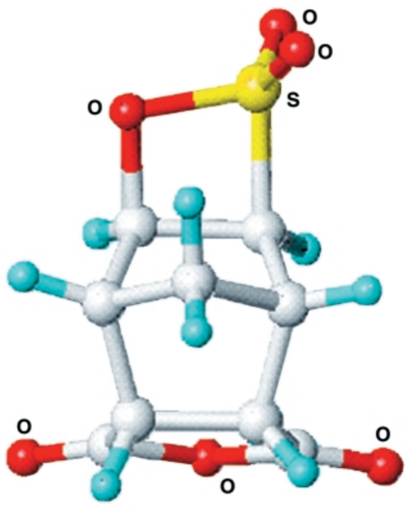
Structural effects

Initially, calculations were carried out on the sultone **2a** at the MNDO, AM1 and PM3 levels and the results compared with experimental data. Although sultones have been studied quite extensively, an examination of the Cambridge Structural Database (CSD)[23] shows only two examples of relevant structures, namely, *exo*-5,*exo*-6-norbornanesultone-*endo*-2,*endo*-3-dicarboxylic anhydride (**8**)[24] and 8-*exo*-9-*syn*-dichloro-3,3-dioxo-4,3-oxathiatricyclononane (**9**).[25] In the well-resolved structure of **8**[24] (*R*-factor = 4.7%),† there are two molecules in the unit cell which show average C–S, C–O, S–O, S=O and C–C bond lengths of 1.79, 1.49, 1.61, 1.42 and 1.56 Å respectively. However, in the latter structure (**9**),[25] which is less well-resolved (*R*-factor = 6.0%),† the C–S and C–O bond lengths are significantly different, with values of 1.74 and 1.46 Å, though the S–O, S=O and C–C bond lengths are comparable to **8** with values of 1.61, 1.43 and 1.54 Å respectively (Table 1).

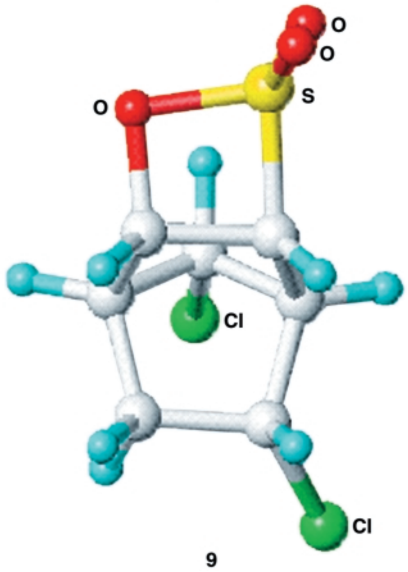
The calculated results obtained for **2a** using the MNDO method show that the C–S, S–O and S=O bond lengths at 1.86, 1.68 and 1.51 Å are clearly too long by comparison with expected results based on either set of experimental data, while the C–O bond is far too short (Table 1). In contrast, the AM1 parameterization gives better C–S and C–O bond lengths at 1.74 and 1.44 Å but the S–O bond is too long at 1.72 Å and the S=O bond is too short at 1.37 Å. The PM3 parameterization gives an improved S=O bond length at 1.42 Å but the C–S and S–O bonds are again too long at 1.82 and 1.73 Å (Table 1). Surprisingly, the bond angles predicted by all the semi-empirical methods appear to be more accurate with the smallest angle in the four membered ring (C–S–O) ranging from 77.9 (PM3) to 79.3° (AM1), and the largest (C–C–O) ranging from 95.5 (AM1) to 97.6° (MNDO) compared with experimental values of 83.0 to 84.0° for the former, and 95.8 to 96.5° in the latter (Table 1). Overall, the discrepancy between the experi-

---

† *R*-factor is a measure of the agreement between the structure as postulated relative to the diffractometer data as collected.



8



9

mental and calculated bond lengths at the semi-empirical level was considered to be too large for further consideration, and all subsequent calculations were carried out at the *ab initio* level.

At the *ab initio* level, the 4-31G results are poor, with the C–S, S–O and S=O bonds far too long at 1.90, 1.74 and 1.58 Å respectively, which reflect the absence of vacant d-orbitals on sulfur (Table 1). However, the 4-31G/S* basis set gives greatly improved results which are comparable to the experimental data, particularly for the well resolved structure of **8**, with C–S, C–O, S–O, S=O and C–C bond lengths of 1.79, 1.49, 1.60, 1.42 and 1.54 Å respectively (Table 1). The calculated bond angles are also close to the experimental data, with values in the four membered ring of 87.5 (C–C–S), 94.2 (C–C–O), 96.7 (C–O–S) and 81.6° (C–S–O) *versus* average crystallographic values of 85.6, 96.1, 93.9 and 83.5°, respectively (Table 1). Although the 4-31G/S* basis set gives good geometric results for molecules containing first row elements and sulfur, it has not been used previously to predict the structures of substituted sultones which contain chlorine. Unfortunately, there are no relevant experimental chloroalkane sultone structures available for comparative purposes, but the Cambridge Structural Database does contain a number of examples of chloroalkenes containing an additional electron attracting group which would be expected to have a roughly similar effect to the SO_2 group in the chloroalkane sultones. A good example is the well resolved structure of trichloroacrylic acid **1i**[26] (*R*-factor 3.4%),† which shows C–Cl1, C–Cl2, C–Cl3 and C=C bond lengths of 1.71, 1.70, 1.73 and 1.32 Å, respectively. Calculations on this structure at the 4-31G/S* level with d-orbitals on chlorine, however, show a good correlation with the experimental bond lengths with values of 1.72, 1.72, 1.73 and 1.33 Å for the same bonds, respectively, suggesting that this basis set is adequate to reproduce the trends in the structures of the chloroalkanes and chloroalkane sultones explored in this work.

Accordingly, a series of calculations was carried out on the substituted sultones at this level of theory and the results are shown in Tables 2 and 3. Generally, the calculated bond lengths and angles are similar to those found for **2a**, though there are in all other cases except **2f**, two possible isomers **2** and **3** which in principle could lead to significant variations. For example, the substitution of hydrogen at one or both alkyl carbons by either halogen and/or oxygen has a marked effect on the geometry of the four-membered ring. Thus fluorine has an unexpected but pronounced effect on the C–S bond length, which increases from 1.79 Å in ethane sultone **2a** to 1.83 Å in both 1,1-difluoroethane sultone **3b** and 1,1,2,2-tetrafluoroethane sultone **2f** (Table 2). Chlorine appears to exert a similar effect to fluorine, with C–S bond lengths of 1.83 Å in both the 1,1-dichloro-2,2-difluoroethane sultones **3d** and **2d**, though a stronger effect is produced by the CF_3 group which increases the same bond length to 1.86 Å in **2j**. Surprisingly, a similar effect is detected also when the OCH_3 group replaces hydrogen at carbon, resulting in a C–S bond length of 1.85 Å in both **2g** and **3j**.

In contrast, the substitution of hydrogen at the carbon of the C–O bond by fluorine produces the opposite effect, with a reduction in its length from 1.49 Å in the parent **2a** to 1.41 Å in both **2b** and **3e**. This change is accompanied by an increase in the length of the connected O–S bond from 1.60 Å in **2a** to 1.64 Å in both **2b** and **3e**. While chlorine exerts a similar effect to fluorine at the C–S bond, it has a much weaker influence at the

Table 1 A comparison of calculated geometries in sultone **2a** *versus* experimental data for sultones **8** and **9**[a]

	2a						
Variable	MNDO	AM1	PM3	4-31G	4-31G*/S	**8**[b]	**9**[c]
C–S	1.856	1.737	1.821	1.900	1.794	1.791	1.741
C–O	1.409	1.436	1.43	1.475	1.494	1.489	1.464
S–O	1.680	1.720	1.727	1.739	1.601	1.614	1.609
S=O	1.511	1.370	1.419	1.579	1.418	1.424	1.431
C–C	1.554	1.543	1.540	1.537	1.542	1.557	1.543
C–C–S	86.23	90.45	88.65	88.45	87.50	85.57	85.66
C–C–O	97.57	95.46	97.31	97.69	94.18	95.79	96.47
C–O–S	98.13	94.83	96.14	96.86	96.72	94.48	93.35
C–S–O	78.07	79.27	77.89	77.01	81.60	83.01	83.97
O=S=O	118.3	121.3	120.3	120.9	120.3	118.8	116.9

[a] Bond lengths in Å, angles in degrees. [b] Ref. 24. Average values for the two molecules in the asymmetric cell; CSD refcode: pebcoo (*R*-factor = 4.7%). [c] Ref. 25. CSD refcode: vecsol (*R*-factor = 6.0%).

Table 2 Calculated bond lengths for alkene **1** and sultones **2** and **3** obtained at the 4-31G/S* level[a]

Bond	Alkene/sultone	**a**	**b**	**c**	**d**	**e**	**f**	**g**	**i**	**j**
C–C	**1**	1.315	1.298	1.299	1.305	1.305	1.297	1.307	1.327	1.328
	2	1.542	1.525	1.535	1.563	1.553	1.543	1.556		1.563
	3		1.522	1.533	1.561	1.551		1.551		1.556
C–S	**2**	1.794	1.796	1.815	1.828	1.835	1.835	1.851		1.854
	3		1.832	1.836	1.851	1.842		1.839		1.850
C–O	**2**	1.494	1.414	1.411	1.459	1.431	1.405	1.431		1.442
	3		1.486	1.438	1.405	1.405		1.452		1.456
S–O	**2**	1.602	1.641	1.638	1.613	1.626	1.639	1.626		1.635
	3		1.600	1.620	1.631	1.636		1.614		1.604
S=O[b]	**2**	1.418	1.411	1.407	1.407	1.405	1.404	1.412		1.409
	3		1.410	1.407	1.408	1.406		1.410		1.407
C–R^1	**1**	1.073	1.342	1.333	1.717	1.697	1.334	1.703	1.723	1.352
	2	1.072	1.349	1.339	1.741	1.724	1.339	1.729		1.369
	3		1.354	1.343	1.746	1.724		1.729		1.365
C–R^2	**1**	1.073	1.342	1.339	1.717	1.354	1.334	1.359	1.720	1.300
	2	1.072	1.349	1.348	1.741	1.355	1.339	1.353		1.333
	3		1.354	1.350	1.746	1.362		1.362		1.326
C–R^3	**1**	1.073	1.067	1.361	1.333	1.334	1.334	1.357	1.732	1.488
	2	1.076	1.076	1.367	1.345	1.343	1.342	1.370		1.522
	3		1.071	1.350	1.342	1.340		1.365		1.532
C–R^4	**1**	1.073	1.067	1.063	1.333	1.333	1.334	1.331	1.480	1.483
	2	1.076	1.076	1.073	1.345	1.344	1.342	1.322		1.523
	3		1.071	1.068	1.342	1.339		1.326		1.531

[a] Bond lengths in Å. [b] Average values for the two exocyclic oxygens.

Table 3 Calculated bond angles for alkene **1** and sultones **2** and **3** obtained at the 4-31G/S* level[a]

Angle	Alkene/sultone	**a**	**b**	**c**	**d**	**e**	**f**	**g**	**i**	**j**
C–C–S	**2**	87.50	87.00	86.86	87.84	87.48	87.18	86.69		86.51
	3		88.26	87.89	85.65	86.37		86.97		86.42
C–C–O	**2**	94.18	96.65	96.12	92.99	94.08	95.22	94.89		95.13
	3		93.66	94.13	96.06	95.75		94.44		94.49
C–O–S	**2**	96.72	97.06	98.35	100.3	100.39	100.1	100.2		99.60
	3		98.91	100.2	99.87	99.85		99.50		99.76
C–S–O	**2**	81.60	79.29	8.64	78.92	78.04	77.4	78.27		78.67
	3		79.17	77.81	78.42	78.00		79.08		79.33
O=S=O[b]	**2**	120.3	122.0	123.4	123.5	123.7	124.2	122.2		122.5
	3		122.8	123.4	122.6	123.6		122.5		121.7
C–C–R^1	**1**	121.7	125.3	125.8	121.0	125.1	123.5	125.3	112.1	118.1
	2	115.6	114.9	115.0	114.2	116.8	133.9	116.7		113.5
	3		112.1	114.8	114.2	116.0		116.8		114.6
C–C–R^2	**1**	121.7	125.3	122.5	121.0	119.6	123.5	119.5	120.8	128.9
	2	115.6	114.9	113.8	114.2	110.8	133.9	111.9		115.3
	3		115.1	113.6	114.2	111.4		112.2		113.1
C–C–R^3	**1**	121.7	120.1	120.1	124.4	123.6	123.5	119.9	120.6	118.0
	2	115.5	114.1	112.0	115.2	115.3	114.3	113.2		114.5
	3		114.2	113.7	114.9	115.0		112.9		114.6
C–C–R^4	**1**	121.7	120.1	124.0	124.4	124.4	123.5	125.3	123.4	123.9
	2	115.5	114.1	115.1	115.2	113.8	114.3	113.7		115.2
	3		114.2	116.4	114.9	113.7		114.1		114.2

[a] Bond angles in degrees. [b] Average values for the two exocyclic oxygens.

C–O bond, which contracts to 1.46 Å in **2d**. None of the substituents appear to have a large effect on the two exocyclic S=O bond lengths, which reduce slightly from 1.42 Å in sultone **2a** to around 1.41 Å in the substituted derivatives, probably because the electron-attracting groups are too far away to exert an influence (Table 2).

Surprisingly, the bond angles in the four-membered ring of the sultones show a smaller variation with substitution than that found for the bond lengths. Thus all substituents appear to reduce the C–S–O angle from 81.6° in the parent **2a** to around 78 to 79° in all other cases, with a concomitant increase in the S–O–C angle from 96.7° to around 97 to 100° (Table 3). However, there is a significant variation found at the C–C–O angle in moving from **2a** to the 1,1-difluoroethane sultone **2b**, with the value increasing from 94.2° in the former to 96.7° in the latter presumably reflecting the presence of two fluorine atoms at the central carbon.

Electronic effects

It is well-established, at many levels of theory, that ethene **1a** is polarized in such a way that two carbons are negatively charged and the four hydrogens positively charged.[13] However, the substitution of hydrogen by fluorine in ethene is known to result in substantial changes to the electron distribution so that, in 1,1-difluoroethene **1b**, the first carbon, C1, remains positive while the second, C2, becomes negative, with the relative magnitude of the effect dependent on the basis set employed.[13,27] At the 4-31G/S* level, we have found similar results for ethene **1a** with atomic charges (obtained by a Mulliken population analysis) of −0.326 at each carbon, changing in 1,1-difluoroethene **1b** to 0.801 at C1 and −0.410 at C2 (Table 4). In tetrafluoroethene **1f**, both carbons are positive,[13,27] because fluorine is more electronegative than carbon, resulting in calculated atomic charges here of 0.766 (Table 4). However, the predicted electron-

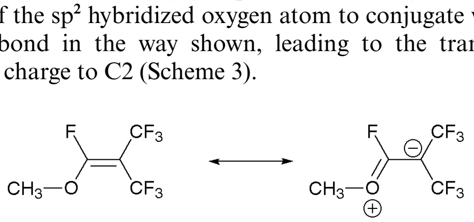
Table 4 Calculated atomic charges for the alkene **1** and sultones **2** and **3** obtained at the 4-31G/S* level

Angle	Alkene/sultone	**a**	**b**	**c**	**d**	**e**	**f**	**g**	**i**	**j**
C1	**1**	−0.326	0.801	0.759	−0.170	0.320	0.766	0.288	−0.022	1.005
	2	0.005	1.087	1.089	0.126	0.634	1.112	0.682		1.162
	3		0.574	0.566	−0.451	0.067		0.119		0.634
C2	**1**	−0.326	−0.410	0.197	0.893	0.810	0.766	0.824	−0.077	−0.425
	2	−0.559	−0.567	0.032	0.661	0.615	0.576	0.512		−0.743
	3		0.004	0.587	1.186	1.150		1.041		−0.116
S	**2**	1.378	1.366	1.368	1.391	1.390	1.387	1.402		1.497
	3		1.383	1.386	1.437	1.414		1.421		1.408
O	**2**	−0.675	−0.661	−0.662	−0.627	−0.650	−0.666	−0.657		−0.665
	3		−0.674	−0.677	−0.662	−0.666		−0.675		−0.623
O[a]	**2**	−0.571	−0.531	−0.504	−0.506	−0.498	−0.488	−0.525		−0.500
	3		−0.523	−0.506	−0.504	−0.497		−0.517		−0.512
R^1	**1**	0.163	−0.413	−0.396	0.025	0.032	−0.383	−0.002	0.027	−0.403
	2	0.233	−0.382	−0.359	0.100	0.095	−0.362	0.074		−0.382
	3		−0.390	−0.368	0.111	0.107		0.084		−0.389
R^2	**1**	0.163	−0.413	−0.402	0.025	−0.391	−0.383	−0.405	0.058	−0.744
	2	0.233	−0.382	−0.375	0.100	−0.355	−0.362	−0.359		−0.698
	3		−0.390	−0.383	0.111	−0.362		−0.367		−0.712
R^3	**1**	0.163	0.218	−0.414	−0.387	−0.388	−0.383	−0.424	0.030	1.218
	2	0.259	0.301	−0.381	−0.370	−0.368	−0.354	−0.397		1.280
	3		0.269		−0.362	−0.361		−0.390		1.275
R^4	**1**	0.163	0.218	0.249	−0.387	−0.383	−0.383	−0.744	0.814	1.220
	2	0.259	0.301	0.304	−0.370	−0.364	−0.354	−0.684		1.291
	3		0.269	0.280	−0.362	−0.356		−0.680		1.290
μ[b]	**1**	0.000	2.293	2.049	0.895	1.212	0.000	3.363	0.929	6.743
	2	6.591	4.436	3.197	3.285	2.668	1.450	4.175		5.158
	3	6.591	4.888	3.417	3.093	2.659	1.450	4.513		4.782

[a] Average values for the two exocyclic oxygens. [b] Dipole moment in D.

attracting effect of chlorine in 1,1-dichloro-2,2-difluoroethene **1d** is much less pronounced than fluorine at the 4-31G/S* level, with C1 negative and C2 positive, with values of −0.170 and 0.893, respectively. While fluorine is generally strongly negatively charged in all the structures described here, chlorine is predicted to be slightly positive. For example, in 1-chloro-1,2,2-trifluoroethene **1e**, the three fluorine atoms are all negative, with values of −0.391 at C1 and −0.388 and −0.383 at C2, while the chlorine atom has a small residual positive charge of 0.032 (Table 4).

While many of the trends in the atomic charges can be rationalized on the basis of simple electronegativities, it is not possible to deduce those in the more complex alkenes such as *trans*-1-chloro-1,2-difluoro-2-methoxyethene **1g** and 1-fluoro-1-methoxy-2,2-di(trifluoromethyl)ethene **1j**. In these systems, the carbon containing the methoxy group is strongly positively charged, with values of 0.824 at C2 in the former (**1g**) and 1.005 at C1 in the latter (**1j**). Interestingly, the carbon at C2 of **1j** is predicted to be negatively charged, with a value of −0.425, despite the presence of the two electron-attracting trifluoromethyl groups which are more powerful attractors than the combination of the fluorine atom and methoxy group at carbon C1 (Table 4). The explanation for this apparent anomalous behaviour of the methoxy group almost certainly lies with the ability of the sp^2 hybridized oxygen atom to conjugate with the double bond in the way shown, leading to the transfer of negative charge to C2 (Scheme 3).



Scheme 3 Canonical forms of 1-fluoro-1-methoxy-2,2-di(trifluoromethyl)ethene **1j**.

In the sultones, the sulfur atom is predicted to be strongly positive, and the cyclic and exocyclic oxygens are negative in all the derivatives explored here. However, the presence of sulfur has a large effect on the charge distributions at the two carbons. Thus in ethane sultone **2a**, the carbon attached to sulfur, C2, is negatively charged while that attached to oxygen, C1, is slightly positive, with values of −0.559 and 0.005, respectively (Table 4). The introduction of two fluorine atoms at C1 to give **2b** produces large changes in the charge distribution at C1, which now becomes strongly positive with a value of 1.087, though C2, which is joined to the sulfur atom, remains negative with a value of −0.567. However, in the isomer **3b**, the positive charge at C1 found in **2b** is much reduced to 0.574 while that at C2 is essentially zero (Table 4).

Reactivity and thermodynamics of sultone formation

Thermodynamically, the formation of ethane sultone **2a**, from the reaction between ethene **1a** and sulfur trioxide, occurs readily as shown by the substantial energy difference predicted between the reactants and the product, which is calculated at -14.3 kcal mol^{-1} (Table 5). Unfortunately, there is no experimental data for this process because ethane sultone **2a** is highly reactive and is converted immediately to other products such as the pyrosultone (Scheme 1). The substitution of hydrogen by fluorine appears to facilitate the thermodynamics of the addition process so that the driving force for the formation of tetrafluoroethane sultone **2f** from tetrafluoroethene **1f** is now around -19.1 kcal mol^{-1} (Table 5). However, for the partially fluorinated alkenes, there are two possible alkane sultone isomers that can be formed in most cases and these reactions are generally energetically dissimilar. For example, both possible isomers of difluoroethane sultone can result from the addition of sulfur trioxide to 1,1-difluoroethene **1b**, but the addition of the sulfur atom to C2 to give sultone **2b** is energetically much more favoured than the addition to C1 to give **3b**, by margins of -20.9 and -4.79 kcal mol^{-1}, respectively (Table 5). Furthermore, in terms of the reactivity of the alkene **1b**, the calculated charge distribution of 0.801 and −0.410 at C1 and C2 (Tables 4 and 5) suggests that the latter would be expected to preferentially react with the electrophilic sulfur atom of sulfur trioxide, which shows a charge distribution at sulfur and oxygen of 1.467 and −0.489 respectively at this level of theory. Both of these results from energy and charge calculations are in accord with

Table 5 Molecular energies (E) of the alkenes **1** and sultones **2** and **3** and calculated energies of their formation (ΔE) *versus* experimental results[a]

	Alkene **1**							
		Atom charge		Sultones				
Alkene	E	C1	C2	E (**2**)	E (**3**)	ΔE (**2**)	ΔE (**3**)	Experimental product
a	−77.922138	−0.326	−0.326	−699.213173	−699.213173	−14.26	−14.26	**4a**/**5a**
b	−275.381301	0.801	−0.410	−896.674569	−896.649763	−20.87	−4.79	**4b**
c	−374.089818	0.759	0.197	−995.377091	−995.368848	−12.83	−7.66	**2c** (68%) **3c** (32%)
d	−1192.233655	−0.170	0.893	−1813.439879	−1813.513529	−1.09	−11.29	**3d**
e	−832.516898	0.320	0.810	−1453.793600	−1453.801648	−35.93	−40.98	**2e** (34%) **3e** (66%)
f	−472.803453	0.766	0.766	−1094.094746	−1094.094746	−19.11	−19.11	**2f**/**3f**
g	−847.511518	0.288	0.824	−1468.795916	−1468.802776	−14.56	−18.87	**3g**
j	−960.731208	1.005	−0.425	−1581.995009	−1581.98406	−1.86	5.05	**4j**

[a] E is given in hartrees; ΔE is given in kcal mol^{-1} and is derived from the difference in energy between the sultone and the sum of the energies of the alkene and sulfur trioxide (−621.260830 hartrees).

available experimental data where the only reported product is the β-pyrosultone **4b**, which is formed by attack of a second sulfur trioxide molecule on sultone **2b**. Similar trends are observed for 1,1-dichloro-2,2-difluoroethene **1d** but here alkane sultone **3d** is favoured over **2d** by 10.2 kcal mol^{-1}, and the charge distribution in the alkene shows that C1 is negatively charged and C2 positively charged. Both sets of data are fully consistent, therefore, with the experimental addition reaction which gives **3d** only (Table 5).

In 1,1,2-trifluoroethene (**1c**), the position is more complicated as the calculated energy differences between the reactants and two possible sultone products are much closer, with **2c** favoured over **3c** by a smaller margin of 5.17 kcal mol^{-1}. The calculated charge distribution in this alkene shows both C1 and C2 to be positive, with values of 0.759 and 0.197 respectively, suggesting that the reaction of this alkene (**1c**) with sulfur trioxide will be more difficult to achieve than the previous two examples. Both sets of evidence indicate that two products are likely to be formed and this is indeed observed experimentally, where **2c** and **3c** are produced in yields of 68 and 32%, respectively (Table 5). However, there is no guarantee that the kinetics of product formation will necessarily reflect the thermodynamics of the process.

A similar complex picture emerges for 1-chloro-1,2,2-trifluoroethene **1e**, where the energy differences between the reactants and two possible sultone products are again fairly close together, but here **3e** is favoured over **2e** by a margin of 5.05 kcal mol^{-1}. The calculated charge distribution shows both C1 and C2 to be positive, with values of 0.320 and 0.810 respectively, again suggesting that the reaction of alkene **1e** with sulfur trioxide will be difficult to accomplish. These results suggest that two products are likely to be formed, in line with the experimental yields of 66 and 34% for **3e** and **2e** respectively (Table 5).

The calculated results for the two methoxyalkenes **1g** and **1j** also appear to follow the experimental trends (Table 5). However, in *trans*-1-chloro-1,2-difluoro-2-methoxyethene **1g**, both carbons are positively charged but C1 is most likely to attack the sulfur atom of sulfur trioxide because of its much smaller charge, leading to the formation of sultone **3g**. Energetically, **3g** is favoured over **2g** by 4.31 kcal mol^{-1}, suggesting that both products are likely to be formed, but experimentally only **3g** has been reported. In 1-fluoro-1-methoxy-2,2-di(trifluoromethyl)ethene (**1j**), carbon C2 is negatively charged and would be expected to attack the sulfur atom of sulfur trioxide, leading to the formation of sultone **2j** which is calculated to be more stable than **3j** by 6.91 kcal mol^{-1}. Experimentally, the β-pyrosultone **4j** is the only reported product, which is thought to arise from the attack of a second sulfur trioxide molecule on sultone **2j**.

Mechanism of the addition reaction

The possibility that the sultones are formed *via* the intermediacy of π-complexes, rather than by direct cycloaddition of the sulfur atom and oxygen atom to the two adjacent atoms of the double bond (Scheme 2), has been investigated using ethene **1a** and tetrafluoroethene **1f** as the model alkenes. We have previously shown that sulfur trioxide forms a stable π-complex with toluene at the 4-position of the ring with the sulfur atom positioned 2.96 Å above the ring plane.[22] An investigation of the reaction of sulfur trioxide with ethene **1a** shows that a stable π-complex is formed also in this case where the sulfur atom lies 2.89 Å perpendicularly above the first carbon, C1, with one bonded oxygen lying over the second carbon, C2, at a distance of 3.09 Å and the remaining two oxygen atoms of sulfur trioxide lying in an eclipsed fashion over the two hydrogens at C2. The C1–C2 bond length at 1.324 Å is slightly longer than in ethene itself at 1.315 Å; there is net transfer of electrons from the alkene to sulfur trioxide, which has a negative charge of −0.062, and the structure is calculated to be 5.53 kcal mol^{-1} more stable than the reactants (Table 6).

The corresponding reaction with tetrafluoroethene **1f** produces a less tightly bound π-complex where the C1–S and C2–O bonding distances are now 3.47 and 3.42 Å, respectively, with a C1–C2 bond length unchanged from that found in **1f** at 1.30 Å. There is a smaller transfer of charge from the alkene to sulfur trioxide of −0.014 electrons, and the structure is only 2.86 kcal mol^{-1} more stable than the reactants (Table 6).

Saddle calculations on starting structures, which were based on the ethene and tetrafluoroethene π-complexes, gave transition states which are calculated to be 17.03 and 34.47 kcal mol^{-1} above the isolated reactants respectively (Table 6). Electronically, there are net transfers of charge of −0.422 and −0.309 from ethene and tetrafluoroethene, respectively, to sulfur trioxide in these transition states, which were characterized by their unique single negative frequencies of −553.8 and −507.5 cm^{-1} obtained from separate force calculations on each structure respectively. Geometrically, the transition state from the reaction of ethene with sulfur trioxide shows the sulfur atom and one oxygen atom of sulfur trioxide to be located perpendicularly over carbons C1 and C2 of the alkene, with C–C, C–S and C–O bond lengths of 1.408, 2.027 and 2.203 Å respectively *versus* 1.542, 1.794 and 1.494 Å in the product of the reaction, ethane sultone **2a**, and 1.315 Å for the double bond in ethene **1a** (Table 2).

The corresponding transition state from the reaction of tetrafluoroethene with sulfur trioxide shows the sulfur atom and one oxygen atom of sulfur trioxide again located perpendicularly over carbons C1 and C2 of the alkene with C–C,

Table 6 Molecular energies of the reactants, π-complexes (π) and transition states (TS) formed from the reaction of ethene or tetrafluoroethene with sulfur trioxide[a]

			4-31G/S*-PSSC	
	4-31G/S*	4-31G/S*-MP2	$\varepsilon = 1.48$	$\varepsilon = 3.11$
E_{SO_3}	−621.260830	−621.803919	−621.273386	−621.292514
$E_{C_2H_4}$	−77.922138	−78.104702	−77.924076	−77.926611
E_π	−699.191781	−699.919066	−699.203897	−699.221286
ΔE_π	−5.53	−6.55	−4.04	−1.36
E_{TS}	−699.155831	−699.870463	−699.179488	−699.213824
ΔE_{TS}	+17.03	+23.94	+11.28	+3.33
μ_{TS}	7.79	7.79	8.33	9.11
$E_{C_2F_4}$	−472.803453	−473.473666	−472.806865	−472.811757
E_π	−1094.059723	−1095.276788	−1094.069711	−1094.084232
ΔE_π	+2.86	+0.50	+6.61	+12.57
E_{TS}	−1094.009347	−1095.302951	−1094.028563	−1094.057194
ΔE	+34.47	+30.35	+32.43	+29.54
μ_{TS}	5.94	5.94	6.37	6.96

[a] Single point calculations on the 4-31G/S* structures; attempts to optimize the TS structures were unsuccessful due to persistent convergence problems with the PSSC routine. *E* is the molecular energy (hartrees); μ is the dipole moment (D); ε is the relative permittivity; ΔE_π is the difference in energy between the reactants and the respective π-complex and ΔE_{TS} is the difference in energy between the reactants and the respective transition state (both given in kcal mol^{-1}). MP2 and PSSC are defined in Methods of calculations.

C–S and C–O bond lengths here of 1.437, 2.087 and 2.376 Å respectively *versus* 1.543, 1.835 and 1.405 Å in the product of the reaction, tetrafluoroethane sultone **2f**, and 1.297 Å for the double bond found in tetrafluoroethene **1f**. The transition state here occurs later along the reaction coordinate and is more product-like as the C1–C2 bond length is closer to that found in the sultone **2f**.

However, because the energies of both transition states are considerably higher than expected for room temperature reactions, the energies were re-evaluated using single point calculations on the 4-31G/S* structures at the Moller–Plesset MP2 level.[13,16] This refinement resulted in a substantial lowering of the molecular energies of the reactants and the transition state structure, formed between ethene and sulfur trioxide, to give a new saddle point which is higher than the original value at 23.9 kcal mol^{-1} above the isolated reactants (Table 6). The corresponding saddle point for the reaction of tetrafluoroethene with sulfur trioxide at 30.4 kcal mol^{-1} shows the opposite trend and is lower than the original value (Table 6). This could be an indication that the RHF geometries are, in this case, quite different from the MP2 optimized geometries. The gas phase results clearly do not match the experimental data, particularly for the closely related reaction of octadec-1-ene with sulfur trioxide to form the corresponding octadecane sultone,[28] which has an experimentally determined activation energy of 6.22 kcal mol^{-1}.

A further series of calculations were carried out using the Tomasi method,[17] coded in the GAMESS program, to assess the effect of solvent on the activation energy, as both reactions commence in the presence of an excess of reactants, which have a relatively low relative permittivity, and end in the presence of an excess of products which have a relatively high relative permittivity (see Methods of calculation). In this solvation model,[17] the solute molecule is embedded in a cavity constructed from the intersecting van der Waals spheres of the component atoms surrounded by a dielectric continuum of permittivity ε. The surface between the continuum and the solute is then partitioned into a large number of segments and the interaction between the charge density at points on each segment polarizes the surrounding medium and produces a reaction field which in turn acts on the solute to modify the molecular energy.

The dipole moments of the molecular species involved in the alkene reactions increase from zero for each of the reactants to 7.79 and 5.95 D for the transition states derived from ethene and tetrafluoroethene respectively (Table 6), and then decrease to 6.59 D for ethyl sultone **2a** and 1.45 D for tetrafluoroethyl sultone **2f** (Table 4). It follows that the stability of the polar transition states would be expected to increase with increasing relative permittivity of the reaction medium, with that derived from ethene showing a greater effect than that derived from tetrafluoroethene. Initial calculations on the reactants and corresponding transition state from ethene using the relative permittivity of either ethene ($\varepsilon = 1.48$)[15] or sulfur trioxide ($\varepsilon = 3.11$)[15] confirm these predicted trends, with a lowering of the energy barrier from 17.03 kcal mol^{-1} in the absence of solvent to 11.28 and 3.33 kcal mol^{-1}, respectively, in their presence (Table 6). These results are now more consistent with the experimentally determined activation energy of 6.22 kcal mol^{-1} for the related reaction of octadec-1-ene with sulfur trioxide.[28] However, solvent appears to have a smaller effect on the energy of the corresponding transition state derived from the reaction of tetrafluoroethene with sulfur trioxide, as the transition state is only stabilized by 2.04 and 4.93 kcal mol^{-1} on moving from a relative permittivity of 1.48 to 3.11 (Table 6), possibly because the van der Waals radius of fluorine is larger than that of hydrogen (1.35 *versus* 1.20 Å),[14] resulting in a smaller stabilizing interaction energy at the surface.

Conclusions

Calculations using the 4-31G/S* basis set appear to give a reasonable account of the structures, molecular energies and electronic properties of a series of substituted fluoroalkenes and the corresponding alkane sultones derived from the addition of sulfur trioxide to the double bond. Both the calculated charge distributions at carbon and the calculated enthalpies of the addition process show a good correlation with the observed selectivity of electrophilic attack by the sulfur atom of sulfur trioxide, especially for alkenes where there are two possible sites of addition. Mechanistically, the reactions of ethene and tetrafluoroethene with sulfur trioxide proceed *via* formation of stable π-complexes to give transition states with activation energies which are comparable to experimental data.

References

1 D. W. Roberts and D. L. Williams, *J. Chem. Soc.*, *Perkin Trans. 2*, 1985, **81**, 389.

2 I. L. Knunyants and G. A. Sokolski, *Angew. Chem., Int. Ed. Engl.*, 1972, **11**, 583.

3 D. C. England, M. A. Dietrich and R. V. Lindsey Jr., *J. Am. Chem. Soc.*, 1960, **82**, 6181.

4 D. W. Roberts and D. L. Williams, *Tetrahedron*, 1987, **43**, 1027.

5 E. E. Gilbert, *Chem Rev.*, 1966, **62**, 549.

6 M. A. Dmitriev, G. A. Sokolski and I. L. Knunyants, *Khim. Nauka Prom.*, 1958, **3**, 826; *Chem. Abstr.*, 1959, **53**, 11211.

7 M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899.

8 M. J. S. Dewar, E. G. Zoebisch, E. F. Healy and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902.

9 J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 209.

10 M. J. S. Dewar and Y.-C. Yuan, *Inorg. Chem.*, 1990, **29**, 3881.

11 (*a*) J. O. Morley and M. H. Charlton, *Int. J. Quantum Chem.*, 1995, **55**, 361; (*b*) J. O. Morley, *Int. J. Quantum Chem.*, 1998, **66**, 141.

12 *MOPAC 93*, J. J. P. Stewart, Fujitsu Limited, Tokyo, Japan, 1993, obtained from QCPE, Department of Chemistry, Indiana University, Bloomington, Indiana 47405, USA.

13 See for example: W. J. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople, *Ab Initio Molecular Orbital Theory*, John Wiley and Sons, New York, 1986.

14 M. F. Guest and P. Sherwood, *GAMESS*, an *ab initio* program, The Daresbury Laboratory, Warrington, UK.

15 See C. Wohlfarth, *CRC Handbook of Chemistry and Physics*, ed. D. R. Lide and H. P. R. Frederiske, CRC Press, Boca Raton, Florida, 1998, 78th edn., pp. 6–139.

16 (*a*) C. Moller and M. S. Plesset, *Phys. Rev.*, 1934, **46**, 618; (*b*) J. E. Rice, R. D. Amos, N. C. Handy, T. J. Lee and H. F. Schaefer, *J. Chem. Phys.*, 1986, **85**, 963; (*c*) J. D. Watts and M. Dupuis, *J. Comput. Chem.*, 1988, **9**, 158.

17 S. Miertus, E. Scrocca and J. Tomasi, *Chem. Phys.*, 1981, **55**, 117.

18 *SYBYL*, Ver. 6.2, Tripos Inc., 1699 S. Hanley Road, St. Louis, Missouri, 63144-2913, USA.

19 S. Nagase and K. Morokuma, *J. Am. Chem. Soc.*, 1978, **100**, 1666.

20 A. Bottoni, *J. Chem. Soc., Perkin Trans. 2*, 1996, 2041.

21 D. Suarez, J. A. Sordo and T. L. Sordo, *J. Phys. Chem.*, 1996, **100**, 13462.

22 J. O. Morley and D. W. Roberts, *J. Org. Chem.*, 1997, **62**, 7358.

23 *Cambridge Structural Database*, Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, UK CB2 2EW.

24 R. M. Schonk, B. H. Bakker and H. Cerfontain, *Recl. Trav. Chim. Pays-Bas*, 1992, **111**, 478.

25 K. A. Potekhin, Yu. T. Struchkov, A. S. Koz'min, V. V. Zhdankin, V. D. Sorokin and N. S. Zefirov, *Sulf. Lett.*, 1988, **8**, 55.

26 S. Fleck, R. Gockel and A. Weiss, *J. Mol. Struct.*, 1987, **161**, 139.

27 C. W. Bock, P. George, G. J. Mains and M. Trachtman, *J. Chem. Soc., Perkin Trans. 2*, 1979, 814.

28 T. Miyauchi, T. Kikuchi, T. Ogoshi, R. Susuki and H. Kataoka, *J. Chem. Eng. Jpn.*, 1971, **4**, 44.

Paper 9/02645B