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Energetic and Structural Aspects of the Solvation of Anions in Liquid SO_2

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Abstract: The solvation of halogen ions (F^-, Cl^-) in liquid SO_2 was investigated by means of ab initio calculations. Discrete complexes of one to four SO_2 ligands with a halide ion were optimized at various levels of theory. In the cases of the SO_2 molecule and the primarily formed halosulfite ions, the influence of the level of electron correlation and different basis sets on the structures and energies was studied by calculations at various levels of theory up to QCISD(T). The stabilities of the halosulfite ions were found to be −46.9 kcal/mol for the fluorosulfite ion (**1**) and −19.8 kcal/mol for the chlorosulfite ion (**2**). Higher complexes were optimized at the HF/6-31+G* and MP2/6-31+G* levels, and two different complexation patterns were obtained: complexation at the halogen or at an oxygen of the halosulfite ion. Almost independently of the type of complexation, each SO_2 ligand afforded a stabilization energy of 10−18 kcal/mol, thus proving that the high solvation energy is responsible for the ionogenic character of this solvent. The bonding situation in the complexes was studied by NBO analyses, and it was found that the stabilization is mainly due to electrostatic interactions, while charge transfer, covalent bonding, and orbital interactions make only minor contributions.

Introduction

Why is liquid SO_2 a highly suitable solvent for the support of heterolysis reactions? This is a basic question in many aspects of the chemistry of carbenium and phosphenium ions. Liquid SO_2 has been established as one of the most important aprotic, nonaqueous, and polar solvents since the first investigations on carbonium ions in this medium by Walden[1] and Gomberg.[2] The first studies on the dissociation and ionization processes in liquid SO_2 were published by Ziegler[3] and subsequently by Lichtin[4] who also measured the stability of carbonium ions in this solvent[5] and published an extensive review on the chemistry and the solvent properties of SO_2.[6] Further reviews on the properties of SO_2 have been published by Waddington,[7] Burow,[8] and Zingaro,[9] while a review by Tokura[10] summarizes organic synthesis in this solvent. The unique value of SO_2 as a solvent is due to its high solution power for both organic and inorganic solvates, its ionogenic character, low nucleophilicity, and pronounced tendency to form complexes of charge-transfer type.

In 1955, Seel et al.[11,12] first reported the formation of the fluorosulfites by dissolving metal fluorides in liquid SO_2, and these findings initiated intense research on the nature of halosulfite adducts (Scheme 1). While the compounds with Cl^-, Br^-, and I^- have been considered as complexes,[13] FSO_2^- was suggested to be a molecule ion of C_s structure on the basis of the infrared spectrum of isolated $KFSO_2$.[14] The high stability of the potassium salt supports this assumption, and the thermal dissociation enthalpy of 18.3 kcal/mol, as determined by Seel and Gölitz,[15] is of a comparable magnitude to those of some carbonates. Finally, investigations of the electronic and vibrational spectra of halosulfite solutions by Burow[16] provided some evidence that all halogen ions form molecule ions with SO_2 which may be further complexed by SO_2 molecules. On the other hand, measurements of the stabilities of the halosulfites of chlorine, bromine, and iodine in acetonitrile and DMSO suggested that these ions are only weakly complexed in these solvents.[17,18]

Scheme 1

$$F^- + SO_2 \rightleftharpoons \underset{\mathbf{1}}{FSO_2^-}$$

$$Cl^- + SO_2 \rightleftharpoons \underset{\mathbf{2}}{ClSO_2^-}$$

$$X^- + nSO_2 \rightleftharpoons X(SO_2)_n^-$$

Our investigations in phosphirenylium ion chemistry,[19] which took advantage of the strongly ionogenic properties of SO_2 as a solvent, prompted us to study the influence of solvation by means of ab initio theory, because calculations showed that the resulting Lewis acid-supported heterolysis reactions would be

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extremely endothermic without the inclusion of solvent effects. Because the preparatively used trifluoromethanesulfonate ions are far too large to be calculated as solutes at a high level of theory, we chose fluoride and chloride anions as models for our studies. Surprisingly little computational work has been done in the field of SO_2 complexes, although Schaefer III had calculated the H_3N-SO_2 complex as early as 1976.[20] No reports on calculations of the fluorosulfite ion were found whereas the chlorosulfite ion had been studied at a high level of theory.[21] An earlier investigation[22] of the latter anion is of little significance because the authors restricted the structure to C_{2v} symmetry while the C_s structure of this ion is well established from spectroscopic data.[16] Calculations of higher complexes of ions and SO_2 to simulate the effect of solvent molecules were not known previously and are published here for the first time.

Computational Methods

The solvation of F^- and Cl^- in liquid SO_2 was simulated by calculating the structures and energies of discrete complexes of solvate and solvent. Continuum models like that of Onsager[23] seemed to be insufficient for our purposes because they do not take into account the specific chemical interactions between solvate and solvent molecules like those investigated in the present study. Hence, we studied the influence of solvation of the ions in SO_2 by means of ab initio calculations of discrete complexes. Some of the complexes are rather large, and therefore, the level of theory employed must be a careful compromise between the quality and reliability of results and the expense of the calculations. To describe anions properly, it is necessary to use basis sets with diffuse functions to account for the more diffuse electron distribution.[24] Diffuse functions also improve the description of weak complexes. We chose the 6-31+G* basis set[25] that contains one set of diffuse p-orbitals and one set of d-orbitals as polarization functions at each heavy atom. In the case of SO_2 we tested the 6-311+G(2df) and Dunnings correlation consistent aug-cc-pVTZ[26] basis sets too. All structures were fully optimized at the RHF/6-31+G* level of theory and were verified to be real minima or transition states by subsequent frequency calculations.[27] Zero-point energies were scaled by the factor 0.89 and added to all relative energies to correct for the zero-point vibration.[28] Electron correlation must be assumed to be considerable because some fluoro compounds like FNO and FOOF show extremely strong correlation effects and are considered among the most challenging molecules for ab initio theory.[29] SO_2 and the fluoro- and chlorosulfite ions were optimized at various correlated levels using different basis sets to investigate the effects of electron correlation on the structures and energies. Unfortunately the sizes of the larger structures made it impossible to optimize them at a highly correlated level. For the larger (3:1) complexes, only single-point calculations at the MP2 level on the basis of the HF structures were performed to improve the quality of the energies. NBO analyses were performed to obtain a deeper insight into the electronic structures at the obtained geometries.[30] From the work of Weinhold et al.[31] it is known that this method gives an appropriate description of weak van der Waals complexes. We then used the natural charges[32] and the Wiberg bond indices[33] based on the NAO Fock matrix to investigate the nature of the binding in the treated structures.

Results and Discussion

Structures of SO_2 and Halosulfite Ions. Geometry optimizations of FSO_2^- (**1**) and $ClSO_2^-$ (**2**) result in the expected structures with C_s symmetry. The fluorosulfite ion shows an S−F bond length between 1.664 and 1.884 Å which indicates a single bond in accord with reported data (Table 1).[34] Compared to the free SO_2 molecule, the S−O bond of **1** is stretched and the O−S−O angle is slightly reduced at all levels of theory. In contrast, the molecule ion **2** shows a rather long S−Cl distance between 2.753 and 2.485 Å which is beyond the range of covalent single bonds. This is accompanied by slightly shorter S−O bond lengths and a wider O−S−O angle; these values are much closer to those of the free SO_2 than the parameters of **1**. It would appear that these bond lengths and angles give information about the nature of the bond formed between the halogen ion and the SO_2 molecule and indicate a shift of hybridization at the sulfur atom from sp^2 type to sp^3 character in the halosulfite ions.

From the work of Miaskiewicz and Steudel[21] it is known that the calculated structural parameters of **2** are sensitive to the choice of the basis set. To evaluate the influence and reliability of the computational method, we first optimized SO_2 at various levels of theory for which the structure and the dipole moment are well known from experimental data. Compared to the experimental S−O distance of 1.434 Å,[35] the HF method underestimates this bond length significantly and the measured dipole moment of 1.633 D[36] is overestimated. In contrast the MP2 approximation affords too long distances, and larger basis sets can compensate this error only in part. Nevertheless, the dipole moment is represented quite well by the MP2 method with larger basis sets. Pretty good structures are obtained by the CISD calculation with the 6-31+G* basis set, but enlargement of the basis set affords worse results. The CCD values show similar tendencies, but the bond length is found slightly longer than with CISD. Finally the QCISD method gives moderate results with the smaller basis set, but matches the experimental result almost exactly when the 6-311+G(2df) basis

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Table 1. Structural Parameters and Dipole Moments of SO_2 and Halosulfite Ions **1** and **2** from ab Initio Calculations at Various Levels of Theory

	SO_2[d]			**1**[e]				**2**			
	S−O (Å)	O−S−O (deg)	μ (D)	S−F (Å)	S−O (Å)	F−S−O (deg)	O−S−O (deg)	S−Cl (Å)	S−O (Å)	Cl−S−O (deg)	O−S−O (deg)
HF[a]	1.415	118.6	2.29	1.698	1.458	100.6	113.2	2.753	1.429	102.8	115.1
Hf[b]	1.398	118.7	1.98	1.664	1.440	100.5	113.0	2.603	1.415	101.9	114.8
MP2-FC[a]	1.482	119.3	1.88	1.844	1.498	100.6	113.9	2.667	1.493	102.8	115.1
MP2-FU[a]	1.481	119.3	1.89								
MP2-FC[b]	1.452	119.4	1.65	1.784	1.474	100.4	113.6	2.485	1.468	101.9	114.7
MP2-FU[b]	1.451	119.4	1.65								
MP2-FC[c]	1.464	118.8	1.65								
MP2-FU[c]	1.459	118.8	1.66								
CISD-FC[a]	1.444	118.7	2.17	1.747	1.476	100.3	113.4	2.651	1.457	102.5	114.8
CISD-FU[a]	1.443	118.7	2.17								
CISD-FC[b]	1.418	118.9	1.86								
CISD-FU[b]	1.414	118.9	1.87								
CCD-FC[a]	1.454	118.8	2.15	1.777	1.487	100.5	113.5	2.648	1.470	102.7	114.8
CCD-FU[a]	1.453	118.8	2.15								
CCD-FC[b]	1.428	119.0	1.83								
CCD-FU[b]	1.426	119.1	1.83								
QCISD-FC[a]	1.464	118.7	2.11	1.790	1.496	100.5	113.4	2.643	1.480	102.7	114.5
QCISD-FU[a]	1.462	118.7	2.11								
QCISD-FC[b]	1.436	118.9	1.80								
QCISD-FU[b]	1.434	118.9	1.80								
exptl	1.434	119.5	1.63	1.52	1.44 1.41	110.5					

[a] 6-31+G*. [b] 6-311+G(2df). [c] aug-cc-pVTZ. [d] Experimental data of SO_2 in the gas phase from electron diffraction (ref 35). [e] Experimental data of **1** from an X-ray structure of $Ph_3PCHF_2^+FSO_2^-$ (ref 38).

set is used. Nevertheless, the dipole moment is not well represented by the tested methods except MP2. Studies of other groups showed that for the accurate calculation of this electronic property of SO_2 very large or specially designed basis sets in combination with highly correlated methods like CCSD(T) or MRSD-CI are necessary.[37] The inclusion of core electrons in the correlation treatment seems to have only a minor influence on the structures and hence is neglected in all further calculations.

In the case of the fluorosulfite ion trends similar to SO_2 are found. The HF method affords the shortest S−F and S−O distances which must be expected to be too short. Although it must be mentioned that the only available X-ray structure of an FSO_2^- ion shows an even shorter bond length, this structure may be somewhat uncertain because of a disorder of the oxygen atoms.[38] With the MP2 approximation, much longer distances are obtained and at least the values of the MP2/6-31+G* calculation must be expected to be far too long. Calculations by Frenking et al.[39] revealed the same effect as we have found, namely, that, in the case of SO_2 and its complexes, the MP2 method overestimates the bond lengths, giving rise to S−O distances of 1.473 Å in SO_2 and 1.480 Å in the $Me_3N{-}SO_2$ complex while the experimental values are 1.434 Å[35] and 1.444 Å.[40] This indicates that a higher level of correlation must be employed to obtain a better accuracy of the structural data. The coupled cluster calculations, which are supposed to be superior to the MP2 method in the case of strong correlation effects,[41,42] result in significantly shorter bond distances, at least if compared to the MP2/6-31+G* results. The differences from the MP2/6-311+G(2df) values are less pronounced. The QCISD method affords distances which are slightly longer again and which even excede the values obtained from the MP2/6-311+G(2df) calculations. This is in perfect agreement with the results for SO_2, and hence we must expect that the correct bond lengths must be somewhat shorter. This assumption is confirmed by the CISD results which afford the best structures for SO_2 with the smaller basis set.

A completely different behavior is obtained for the chlorosulfite ion. Here the longest S−Cl bond is found by the HF/6-31+G* calculation, and improvement of the method used leads to a shortening of this distance. This is valid as well for the enlargement of the basis set as for the treatment of electron correlation. The MP2 values of the S−Cl bond are remarkably smaller than the HF results while the S−O bonds are longer. The structures obtained from CCD and QCISD optimization are very similar and lie closer to the MP2/6-31+G* than to the MP2/6-311+G(2df) results. The CISD values, which we suppose to be quite accurate, are again close to the CCD and QCISD findings and show a slightly longer S−Cl bond and shorter S−O distances. Finally it is worth noting that only the bond distances show significant changes when optimized with different methods and basis sets while the bond angles are hardly affected by the level of theory.

Energies of Halosulfite Ions. It is obvious that larger complexes cannot be optimized at such highly correlated levels like QCISD, but it is important to know about the reliability of the energy values. Hence, we compare the relative energies of **1** and **2** at various levels of theory (Table 2).

At the HF level a surprisingly low energy of −54.4 kcal/mol is found for **1**, indicating that the fluorosulfite ion should be remarkably stable. At the MP2 level, **1** becomes less stable by about 10 kcal/mol, and the comparison of the energies obtained by MP2 single-point calculation, based on the HF structure, and those from MP2 optimization, respectively, shows that both MP2 values afford only a small difference. The relative energy of

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Table 2. Relative Energies (kcal/mol) of Halosulfite Ions Obtained from ab Initio Calculations at Various Levels of Theory

structure	ZPE[a]	HF/6-31+G*	MP2//HF[b]	MP2//MP2[b]	CCD//CCD[b]	QCISD//QCISD[b]	QCISD(T)//QCISD[b]
SO_2	4.44						
1	5.88	−54.37	−44.88	−43.54	−48.15	−47.38	−46.88
2	4.52	−16.28	−19.96	−19.02	−19.46	−19.45	−19.77

[a] Zero-point energies (kcal/mol) scaled by a factor of 0.89. [b] Basis set 6-31+G* is used. Relative energies with correction for zero-point vibration using the scaled zero-point energies from HF/6-31+G* calculations.

the optimized MP2 geometry is only 1.3 kcal/mol lower than that of the HF structure. Similar to the case of the bond lengths, the CCD energies lie between the HF and the MP2 approximations, giving a value of −48.1 kcal/mol. While the MP2 method underestimates the stability of **1**, according to the QCISD and QCISD(T) results, the CCD calculation finds a slightly too low energy. Nevertheless, the deviations between coupled cluster and quadratic CI are only small; thus, the results should be reliable. In **2** the differences between the various levels are much smaller, and in contrast to **1**, the HF method affords the highest energy of −16.3 kcal/mol. Both MP2 results show values of −19 to −20 kcal/mol, which are in excellent agreement with the experimental data reported by Fehsenfeld and Furguson[43] who measured a dissociation energy of 19.1 kcal/mol for **2**. The CCD value of −19.5 kcal/mol matches almost exactly the QCISD results, but inclusion of perturbative triples in the QCISD(T) calculation gives a further slight stabilization of **2**. It appears that the MP2 approximation is sufficient to describe **2** with the required accuracy, while with **1** it still gives some problems. Obviously the strong correlation effects operative in **1** make it necessary to use highly correlated methods such as CCD or QCISD in order to obtain accurate energy data. In the cases of the larger structures investigated here, it presently is impossible to perform calculations at such expensive levels of theory, and we decided that the MP2 energies would be sufficient for our purposes, but to calculate QCISD(T) energies where possible.

The high stability of **1** at all levels of theory seems to be somewhat surprising at first glance. But comparison between **1** and **2** on the one hand and SF_2 and SCl_2 on the other hand shows that this stability is reasonable. For both sulfur dihalides experimental heats of formation were measured which are −5.4 ± 0.5 kcal/mol for SCl_2[44] and −71.4 ± 2.5 kcal/mol for SF_2,[45] both at $T = 298.15$ K. This indicates that the S−F bond is much stronger than the S−Cl bond, leading to the conclusion that FSO_2^- must be much more stable than $ClSO_2^-$. Additionally Irikura calculated the heat of formation of SF_2 by use of G2(MP2) theory at $T = 0$ K and obtained an energy of −69.0 ± 1.5 kcal/mol[46] which compares very well with the measurements of Herron who obtained $\Delta H_f = -70.3 \pm 4.0$ kcal/mol (0 K).[47] This should be a confirmation that high-level ab initio calculations can provide quite accurate energies for systems like those investigated here.

Now the question arises as to what happens to a fluoride ion in SO_2 solution. Can a solvated F^- ion exist in this solvent, or will it react to form the fluorosulfite ion **1**? For this reason we tried to optimize the transition state for the cleavage of the S−F bond of **1**, but all attempts to locate a stationary point failed. Thus, we calculated a reaction coordinate at the HF/6-31+G* level by stretching the S−F bond in steps of 0.04 Å from a distance of 1.72 Å to a distance of 4.00 Å and further up to 6.00 Å in steps of 0.08 Å while optimizing the geometry at each point in C_s symmetry. This resulted in the energy curve depicted in Figure 1.

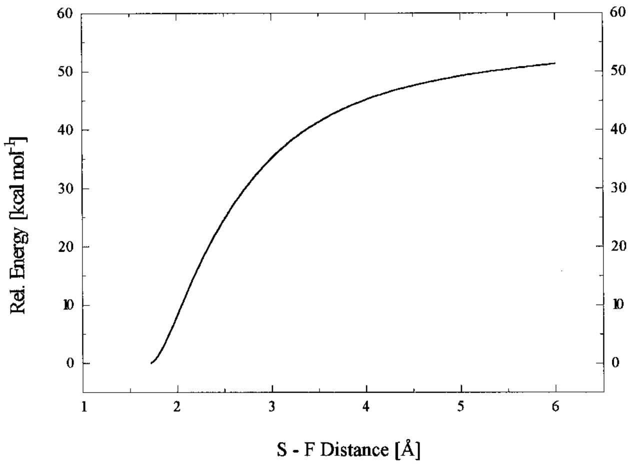

Figure 1. Energy profile of **1** dependent on the S−F bond distance at the HF/6-31+G* level of theory.

It can be seen that the slope of the curve increases up to a distance of about 2 Å and then continuously decreases until the final point at 6.00 Å. Instead of a saddle point, the energy curve shows asymptotic behavior, which confirms the assumption that no transition state exists. This leads to the conclusion that the formation of **1** from F^- and SO_2 is a reaction without a barrier.

Finally, we turned our attention to the bonding situation in the halosulfite ions and performed NBO analyses. For comparison, we first examined the free SO_2 molecule. As expected, the structure is strongly polarized with a positive sulfur atom (1.87) while the two oxygen atoms bear a negative charge of −0.93 each. The Wiberg bond indices show values of 1.456 for the S−O bonds and a bonding interaction of 0.222 between the two oxygen atoms.

The natural charge of the fluorine atom of **1** is only −0.67, and some negative charge is obviously transferred to the oxygens, which show enhanced negative charges of −1.13 each, while the sulfur is slightly more positive (1.94) than in free SO_2. The newly formed S−F bond shows a bond index of only 0.481, and the indices for the S−O bonds (1.208) and the O−O interaction (0.107) are distinctly reduced. Between the fluorine and the oxygens a very small overlap is noticed, as revealed by bond indices of 0.055. It seems that the bonding situation of the fluorine atom is a combination of weak covalent bonding, charge transfer complex, and electrostatic interaction. The situation in **2** is somewhat different, because here the chlorine is much more negative, showing a natural charge of −0.86, while the charge at sulfur (1.89) is hardly changed compared to that of free SO_2. The oxygen atoms (−1.02) carry a bit more negative charge than in SO_2 but still less than in **1**, indicating a much smaller amount of charge transfer. On the other hand the bond index of the S−Cl interaction (0.184) is of a magnitude comparable to that of the O−O interaction (0.176), which indicates only a small amount of covalent bonding, while the S−O bonds (1.357) stay noticeably stronger than in **1**. It seems

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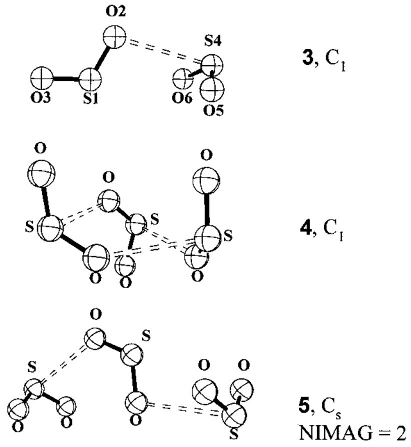

Figure 2. Structures of the SO_2 dimer and trimers optimized at the MP2/6-31+G* level of theory.

that in **2** the electrostatic interaction plays a larger role than in **1** while the importance of charge transfer and covalent bonding is reduced.

Interactions in the Pure Solvent (SO_2 Dimer and Trimer). Before the interactions between ions and solvent are investigated, the situation of complexation within the pure solvent needs to be studied, which was done just recently by investigating the SO_2 dimer and trimer. Nevertheless, two of the dimer studies may be of limited significance because the geometry of the dimer was restricted in symmetry although imaginary frequencies were obtained.[48] From experimental data the structure was suggested to contain two different SO_2 units and a plane of symmetry.[49] The calculations of Plummer[50] demonstrated that the suggested structure is nearly correct, but the two obtained minima on the potential energy surface are both of C_1 symmetry, thus differing slightly from the measured C_s symmetry which has been confirmed by our investigations (Figure 2).

The SO_2 dimer is a weak complex, stabilized by only 3.3 kcal/mol, which is "bonded" by one shorter and two longer S−O contacts (O2−S4 = 3.221 Å; S1−O5 = 3.651 Å; S1−O6 = 3.469 Å). The NBO analysis reveals that both SO_2 units are slightly more polarized than the free SO_2 molecule. Both sulfur atoms show natural charges of 1.89 which is only 0.02 more than in SO_2. In the first unit, the negative charge at O2 is enhanced (−0.97) while O3 shows a smaller value of −0.92. In the second unit, O5 shows the same charge as in SO_2 (−0.93), but O6 is more negative (−0.96). While the charge distribution within the two units is slightly changed upon dimerization, no intermolecular charge transfer is found. The calculated bond indices confirm that almost no covalent bonding is present between the units in dimer **3**. The index of the O2−S4 contact is only 0.005, and the other S−O contacts are 0.001 and smaller. In the covalent S−O bonds the effect of polarization becomes noticeable too. In the first unit the S1−O2 bond is slightly weakened (1.421) while the S1−O3 bond (1.473) is stronger than in the monomer (1.456). The same effect is found in the second unit with values of 1.430 (S4−O6) and 1.461 (S4−O5). The interaction of the two oxygens is reduced in both units as indicated by values of 0.215 (O2−O3) and 0.214 (O5−O6). From these findings it could be supposed that the dipole−dipole interaction plays an important role in the stabilization of the dimer. However, a closer look at the symmetry of the structure proves that an additional effect must be present. A pure dipole−dipole interaction should lead to a perfect colinear or antiparallel arrangement of the dipole moments, but this is obviously not the case in **3**. Indeed, several interactions of bonding orbitals and lone pairs between the two units are found. Obviously these orbital interactions determine the structure of **3**. Furthermore, if only electrostatic forces would be active, the energy of the complex could be calculated by the very simple expression

$$E(r) = \frac{1}{4\pi\epsilon\epsilon_0}\frac{\vec{\mu}_a\vec{\mu}_b}{{r_{ab}}^3}$$

With the experimentally determined dipole moment of 1.633 D and the calculated structural parameters of the dimer, this energy would be about 0.35 kcal/mol which is almost 10 times smaller than the energy calculated at the MP2/6-31+G* level of theory.

We expanded our investigations on the trimer to obtain additional information. According to Bone et al.[41a] the only obtained minimum without negative eigenvalues of the Hessian is a cyclic, C_1 symmetric structure, but the authors suggest the possibility of another acyclic minimum too. In fact we succeeded to optimize the cyclic structure **4** at HF and MP2 levels of theory and proved it to be a minimum. The linear arrangement of the trimer **5** was optimized in C_s symmetry but affords a Hessian index of 2. When the symmetry restriction was lifted, the calculation led to the cyclic trimer **4**. The structure of **4** affords a six-membered ring with alternating S−O distances of 1.48 and 2.93 Å. Two of the exocyclic oxygens are placed on one side of the ring while the third one is located on the opposite ring side (Figure 2). The O−S−O angles of the SO_2 units vary between 118.2° and 118.5° which is slightly reduced compared to the free SO_2 molecule. The natural atomic charges show that no charge transfer occurs between the SO_2 units and that the charge distribution within the SO_2 molecules is changed upon trimerization. While the sulfur charge of 1.85 is almost the same as in the monomer, the complexing oxygens afford a slightly enhanced charge of −0.96 which is compensated by a reduced charge of the noncomplexing oxygens (−0.89). The Wiberg bond indices are quite similar to that of the dimer. The complexing S−O bond of each unit is weakened (1.392−1.400) while the free S−O bond of the trimer (1.476−1.487) is stronger than in the free monomer. The O−O interaction of 0.218 is only slightly smaller than in the SO_2 molecule. Finally the analysis of the bond orbital interactions indicates that numerous interactions are found but all are of very small magnitude. Nevertheless, the calculated relative energy of **4** is −9.88 kcal/mol at the MP2/6-31+G* level of theory which indicates that electrostatic forces can be only a minor contribution to the binding energy like in the case of the dimer. It turns out that the relative energy of **4** is almost exactly 3 times the relative energy of **3**. This coincides with the fact that the trimer containes three interactions of the type found in the dimer. Obviously each of these interactions affords an energy gain of about 3.3 kcal/mol, and if the liquid SO_2 is ordered in such a way that every molecule interacts with two others, then each molecule should be stabilized by 3.3 kcal/mol. Of course the molecular dynamics will disturb this order and the stabilization will be less. But for our purposes we can use this value as an upper border.

Higher Complexes. From aqueous solutions of salts, it is well known that the ions are separated from each other and

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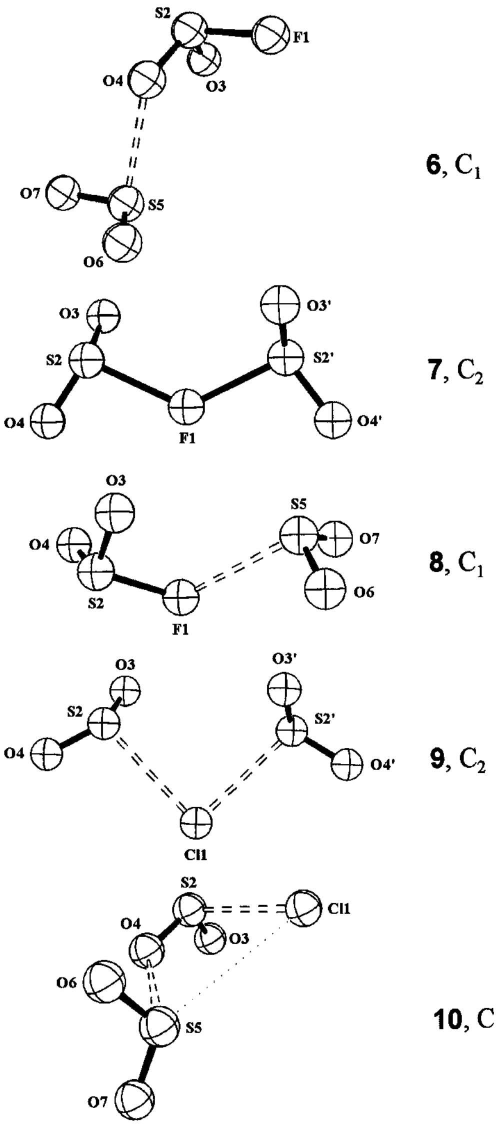

Figure 3. Structures of 2:1 complexes of SO$_2$ with fluoride and chloride anions from ab initio calculations. The geometries of **6**, **7**, **9**, and **10** were obtained from MP2/6-31+G* calculations; **8** was optimized at the HF/6-31+G* level of theory.

enclosed in a solvation shell.[51] The high complexation power of SO$_2$ can be expected to provide large energy gains when a solvation shell is formed, which should be the reason for the ionogenic character of this solvent. Thus, we investigated higher complexes of halide ions with SO$_2$ molecules to simulate the assumed effect of solvation and to obtain an estimation of the solvation energy. The first attempts to optimize a 2:1 complex of the fluoride ion in C_1 symmetry at the Hartree−Fock level unexpectedly resulted in structure **6** (Figure 3) which is obviously an SO$_2$ complex of the fluorosulfite ion **1**.

In this structure the S5 atom of the second SO$_2$ molecule complexes one oxygen (O4) of the fluorosulfite unit, resulting in an S5−O4 distance of 1.671 Å (Table 3). Compared to **1**, the S2−O4 bond is stretched to 1.475 Å while the second S−O bond (S2−O3) is slightly shortened to 1.454 Å and the O3−S2−O4 angle is reduced to 111.8°. In a second optimization attempt the two S−F bonds were restricted to have the same distance and the C_2 symmetric structure **7** was obtained at the HF level. The subsequent frequency calculation afforded one negative eigenvalue of the Hessian which proves **7** to be a transition state. Analysis of the vibrational mode corresponding to the imaginary frequency shows that this transition state belongs to the exchange of the fluoride ion between the two SO$_2$ units. The symmetry restriction was lifted and the geometry was reoptimized using analytical force constants, which finally resulted in the C_1 symmetric structure of **8**. In **8** the fluorine atom of a fluorosulfite ion is complexed by a second SO$_2$ molecule; this is expressed in an S5−F1 distance of 2.651 Å while the S2−F1 bond is weakened and has a length of 1.747 Å. In this case the O3−S2−O4 angle is hardly affected in comparison to **1**.

The relative energies corresponding to these three complexes show that complexation by the second SO$_2$ ligand effects a remarkable energy gain of approximately 11−15 kcal/mol at the Hartree−Fock level (Table 4). The barrier to the exchange process of the fluorine atom between the two SO$_2$ molecules is only 0.9 kcal/mol. Upon MP2 single-point calculations, a small but distinct difference of the energies is noticed. The total relative energy gain of complexation of the fluoride anion is reduced to values of about −60 to −63 kcal/mol, although the second SO$_2$ ligand gives a slightly larger energy gain of −15 to −18 kcal/mol at the MP2//HF level. More important is the fact that **7** is now lower in energy than **8** by 2.6 kcal/mol. Reoptimization of **7** at the MP2 level without any symmetry restrictions resulted in an equilibrium structure for **7** of approximately C_2 symmetry. The two slightly different S−F contacts show distances of about 2.14 Å which are beyond the range of covalent bonds. All S−O bonds are very similar to that of free SO$_2$ and have values of 1.488 Å. The geometry of **6** was also reoptimized at the MP2 level to facilitate a comparison of the structures. All bond lengths of the structure obtained are noticeably longer than the HF values, whereas the bond angles are hardly affected. The S−F distance (1.803 Å) within the fluorosulfite unit turns out to be noticeably longer than the sum of the covalent radii, and the second S−F interaction of 2.510 Å is far beyond the threshold for a usual single bond. A comparison with the structure of **7** reveals that the S−O bonds of the fluorosulfite unit of **6** are stretched more than in the complexing SO$_2$ ligands of **6** and **7**. Similar to the HF results, the S−O bond of the additional complexed oxygen (O4) has the longest distance found (1.513 Å). The shorter S−O distances of the SO$_2$ ligand in **6** compared to those of **7** indicate that this interaction is weaker than in **7**. This is in good agreement with the expectations, because the ligands in **7** stabilize the ion almost equally while the formation of the fluorosulfite unit in **6** must be expected to give a larger energy gain than a complexation by SO$_2$. Furthermore, it is found that the average of the sum of the two different S−F bond lengths in **6** comes close to the S−F distance in **7**. The MP2//MP2 relative energies of **6** and **7** are slightly higher than the MP2//HF values, but again **7** turns out to be the more stable structure by about 2.2 kcal/mol. QCISD(T) single-point calculations on the MP2 structures afforded slightly lower energies of the complexes and confirm that **7** is more stable than **6** by 1.7 kcal/mol.[52] This relatively small energy difference shows that both types of complexation give a comparable stabilization of the fluoride anion.

Comparable calculations were performed for the 2:1 complexes of SO$_2$ with a chloride ion. In contrast to the fluorine case, the C_2 symmetric structure **9** was obtained as a real minimum of the Hartree−Fock potential energy surface, and

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(52) The size of the systems allowed only QCISD(T)/6-31G* single-point calculations to be performed. To improve the energies, we calculated the MP2-QCISD(T) difference of the total energy with the 6-31G* basis set and added this QCISD(T) increment to the MP2/6-31+G* energy.

Table 3. Selected Bond Lengths (Å) and Angles (deg) of 2:1 Complexes of SO_2 with Fluoride and Chloride Anions from ab Initio Calculations at the MP2/6-31+G* Level of Theory[a]

structure	X1−S2	S2−O3	S2−O4	S5−O6	S5−O7	S5−O4	S5−X1	O3−S2−O4	O6−S5−O7
6	1.803	1.493	1.513	1.487	1.487	2.510		112.9	116.2
	(1.671)	(1.454)	(1.475)	(1.426)	(1.425)	(2.461)		(111.8)	(115.5)
7	2.140	1.488	1.488					115.5	
	2.138								
8	(1.747)	(1.456)	(1.450)	(1.422)	(1.423)		(2.651)	(113.5)	(115.9)
9	2.847	1.489	1.488					116.0	
	(2.948)	(1.424)	(1.424)					(115.8)	
10	2.618	1.490	1.498	1.486	1.487	2.730	3.641	114.8	116.4
	(2.661)	(1.428)	(1.437)	(1.422)	(1.423)	(2.808)	(3.845)	(114.6)	(116.0)

[a] HF/6-31+G* values in parentheses.

Table 4. Relative Energies (kcal/mol) of Complexes of SO_2 with Fluoride and Chlorid Anions Obtained from Ab Initio Calculations at Various Levels of Theory

structure	ZPE[a]	HF/ 6-31+G* [b]	MP2// HF[c]	MP2// MP2[c]	QCISD(T)// MP2[c]
3	9.35	−2.73	−3.48	−3.28	
4	15.28	−7.85		−9.88	
5	14.07	−4.84			
6	11.15	−69.75	−60.42	−57.91	−61.66
7	9.42[d]	−65.68[d]	−63.07	−60.11	−63.39
8	10.81	−66.56	−59.54		
9	9.99	−27.98	−33.21	−32.47	−33.22
10	9.99	−26.94	−32.56	−30.88	−32.15
11	14.38	−81.99	−75.31		
12	15.41	−74.87	−75.51		
13	20.96	−91.87			

[a] Zero-point energies (kcal/mol) scaled by a factor of 0.89. [b] Relative energies (kcal/mol) with correction for zero-point vibration. [c] Basis set 6-31+G* is used. Relative energies (kcal/mol) with correction for zero-point vibration using the scaled zero-point energies from HF/6-31+G* calculations. [d] Transition state (NIMAG = 1).

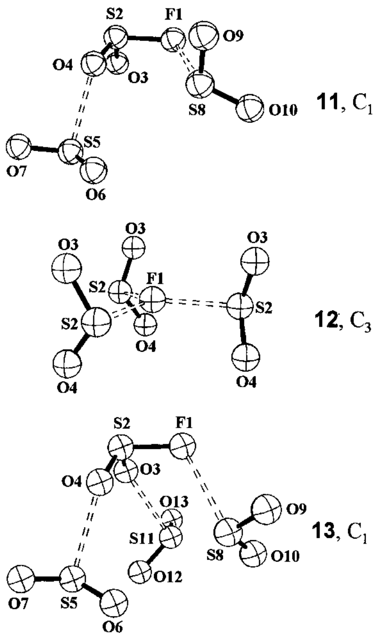

Figure 4. Structures of 3:1 and 4:1 complexes of SO_2 with fluoride from ab initio calculations. The geometries of **11**, **12**, and **13** were obtained from HF/6-31+G* calculations.

no structure analogous to **8** was found. The two S−Cl bonds show rather long distances of 2.948 Å which are shortened to 2.847 Å upon MP2 optimization, and the S−X−S angle of 80.1° in **9** is noticeably smaller as compared to 128.4° in **7**. On the other hand the S−O distances of 1.489 and 1.488 Å (MP2 values) in **9** are almost exactly the same as those in the fluoro compound. A second stationary point of C_1 symmetry is found which, at a first glance, seems to be the analogue of **6**. A closer look at the structure of **10** reveals some distinct differences from **6**. The S2−Cl1 distance of 2.661 Å is significantly longer than the sum of the covalent radii, and the S5−O4 bond length of 2.808 Å is noticeably stretched as compared to **6**. In contrast to the fluorine case, these distances are found to be shorter at the MP2 level—showing values of S2−Cl1 = 2.618 Å and S5−O4 = 2.730 Å. In **10** the second SO_2 ligand is tilted in such a way that an additional contact of 3.641 Å (MP2 value) between S5 and C11 is formed, thus indicating a weak complex contact. The two S−O bonds of the chlorosulfite unit of **10** are somewhat shorter than the comparable bonds in **6**, but the S−O distances in the second SO_2 ligand show almost exactly the same values in both complexes. The relative energies of **9** and **10** appear to be only of about half the magnitude of the fluoro structures and show values of −32 to −33 kcal/mol. Like in the fluoro case the QCISD(T) energies compare very well with the MP2//HF results, indicating the reliability of the latter values. Nevertheless, complexation with the second SO_2 molecule gives an energy gain of approximately −13.5 kcal/mol which is only 25% less than in the fluorine case.

We then expanded our investigations to 3:1 complexes but treated only the fluoride ion. We were not able to optimize the structures at the MP2 level due to the large size of 10 heavy atoms. The first attempt to optimize such a complex started from a trigonal pyramidal arrangement of three SO_2 units around a fluoride ion as shown in **12** but without any symmetry restrictions, and this resulted in the C_1 symmetric structure **11**. The depicted structure of **11** (Figure 4) clearly shows a fluorosulfite unit which is complexated by SO_2 ligands at the fluorine atom and at one oxygen atom.

Both types of coordination are similar to that found for the 2:1 complexes, indicating that these patterns can be generalized for the interaction of a fluoride ion in liquid SO_2 as solvent. In the 3:1 complex **11** the S2−F1 distance of 1.695 Å (Table 5) and the two long contacts S5−O4 (2.502 Å) and F1−S8 (2.870 Å) are stretched compared to the 2:1 complexes, while the covalent S−O bonds are hardly affected. When the structure was restricted to C_3 symmetry, the geometry optimization afforded structure **12** and subsequent frequency calculation proved this stationary point to be a minimum. In **12** the central fluorine atom is slightly pyramidalized and the O−S−O planes stand almost perpendicularly to the S−F bonds. The S−F distances of 2.291 Å show approximately the average value of the two different S−F contacts in **11**. The S−O distances are only slightly longer than in the free SO_2 molecule, and the values are comparable to those of the weakly bound SO_2 units in **6** and **8**, while the S−O bonds in the fluorosulfite units are distinctly longer. According to the total relative energies, complex **11** is appreciably more stable than **12** at the Hartree−Fock level, but the MP2 energy is almost the same for both complexes. This behavior is similar to that of **6** and **7**, where the structure without covalent bonds to the fluorine atom

Table 5. Selected Structural Parameters of 3:1 and 4:1 Complexes of SO_2 with a Fluoride Anion Obtained from HF/6-31+G* Optimization

distance (Å) or angle (deg)	**11**	**12**	**13**
F1−S2	1.695	2.291	1.686
S2−O3	1.450	1.425	1.462
S2−O4	1.473	1.426	1.463
O4−S5	2.502		2.626
S5−O6	1.425		1.423
S5−O7	1.423		1.423
F1−S8	2.870		2.912
S8−O9	1.421		1.423
S8−O10	1.423		1.420
O3−S11			2.619
S11−O12			1.422
S11−O13			1.422
O3−S2−O4	112.0	115.5	111.8
O6−S5−O7	115.8		115.9
O9−S8−O10	116.0		116.2
O12−S11−O13			116.2

becomes more stable only at the electron correlated level. Obviously the HF approximation favors the fluorosulfite structure, and from the energetic data of fluorosulfite ion **1** it must be supposed that the HF method overestimates its stability. Again the complexation by one additional SO_2 ligand gives a considerable energy gain of −13 to −15 kcal/mol, and the total relative energy of −75 kcal/mol indicates a remarkable stabilization of the ion.

Finally, we were able to optimize one 4:1 complex of a fluoride anion at the HF/6-31+G* level of theory. Again the central unit is a fluorosulfite ion which is complexed by three different SO_2 ligands, one at fluorine and one at each oxygen atom. The obtained S−F bond length of 1.686 Å is shorter than that of the free fluorosulfite ion (**1**) and those of the F-complexed structures of **8** and **11**. The complex bond F1−S8 of 2.912 Å is rather long, as are the S−O complex contacts. While the S−O bonds within the fluorosulfite unit are slightly stretched as compared to **1**, all three SO_2 ligands show quite similar S−O distances between 1.420 and 1.423 Å which are comparable with the values of all previously discussed SO_2 ligands. Unfortunately this was the only structure of a 4:1 complex that could be obtained. We did not succeed in the optimization of a pseudotetrahedral arrangement of four SO_2 molecules around a fluorine. As already mentioned, the HF method seems to favor the formation of a fluorosulfite unit over a complex containing more or less equivalent ligands. Nevertheless, the energy of −91.3 kcal/mol found for **13** shows that this structure should be very stable. The complexation by the fourth SO_2 molecule affords an additional energy gain of approximately 10 kcal/mol. This value confirms the tendency of the energy to change dependent on the number of ligands as may be concluded from the data of the calculated complexes. The first coordination gives the largest energy gain, which in the case of fluorine is not a complexation but a formation of a single bond, resulting in an extreme stabilization. Every further ligand reduces the energy of the system by an amount of 75−85% of the preceding stabilization. Of course, this is only a model for the first-order solvation shell, and second-order effects will reduce the energy further. On the other hand the stabilization of the SO_2 molecules in the pure liquid must be taken into account. For every complexing contact of the ligand to the central ion, the stabilization energy must be reduced by about 1.6 kcal/mol according to our findings for the SO_2 dimer and trimer. Nevertheless, the large stabilization by the first-order shell shows that, in this case, mainly the distinct chemical and the physical properties of every solvent molecule in the solvation shell are responsible for the stabilization of the solvate.

Bonding Situation in the Complexes. As in the cases of the halosulfite ions, we also performed NBO analyses for the higher complexes to obtain an insight into the bonding situation of these structures. The natural charges (Table 6) give information about the charge transfer while the bond indices (Table 7) indicate the magnitude of covalent bonding. Complex **6** shows the typical structure increment of a fluorosulfite ion, as do **8**, **11**, and **13**. The charges at S2 show values between 1.95 and 2.00 and are slightly more positive than in **1**. The charges of fluorine and the oxygens O3 and O4 differ only slightly from the values of **1**, although a small enhancement of the negative charge of the complexed oxygens can be noticed. The same complexation at the oxygens seems to reduce the negative charge at F1, but a complexation at fluorine causes the opposite effect. While the changes within the fluorosulfite unit are only minor, the SO_2 ligands undergo larger deviations from the free SO_2 molecule. The charges of the sulfur atoms within the ligands vary between 1.93 and 1.95 which is distinctly more positive than in the SO_2 molecule (1.87). But this higher positive charge is compensated by the enhanced negative charge of the oxygens (−0.97 to −1.00). As a result, there is only a very small charge transfer from the fluorosulfite unit to the SO_2 ligands which lies between 0.00 and −0.01 for complexation at fluorine and between −0.03 and −0.06 for complexation at oxygen. Hence, the changes within the ligands are only due to a strong polarization.

The bond indices (Table 7) show larger differences upon complexation of the fluorosulfite ion. The S−F bond is obviously strengthened by ligands at the oxygens as in **3** and weakened by complexation at the fluorine atom (**8**). In **6**, **11**, and **13** the covalent S−O bond of the complexed oxygen is always weakened while the strength of the attached S−O bond of the fluorosulfite unit is enhanced. The bond index of the O3−O4 contact is reduced in all three cases. In contrast to these findings, in **8** both the covalent S−O bonds and the O3−O4 interaction are strengthened. This shows that the ligands disturb the covalent bonding of the fluorosulfite ion, and a comparison of the ligands with free SO_2 reveals that all its bonds

Table 6. Natural Charges of Complexes from Natural Population Analysis at the HF/6-31+G* Level of Theory

	natural atomic charge (au)												
structure	X1	S2	O3	O4	S5	O6	O7	S8	O9	O10	S11	O12	O13
6	−0.65	1.98	−1.12	−1.15	1.94	−1.00	−1.00						
7[a]	−0.76	1.91	−1.02	−1.01									
8	−0.69	1.95	−1.13	−1.11	1.95	−0.98	−0.98						
9	−0.86	1.91	−0.99	−0.99									
10	−0.82	1.89	−1.01	−1.06	1.94	−0.97	−0.97						
11	−0.66	1.98	−1.11	−1.16	1.94	−1.00	−0.99	1.94	−0.97	−0.97			
12	−0.82	1.95	−1.00	−1.00									
13	−0.66	2.00	−1.14	−1.15	1.95	−0.99	−0.98	1.93	−0.97	−0.97	1.94	−0.99	−0.98

[a] Structure optimized at the MP2/6-31+G* level of theory.

Table 7. Wiberg Bond Indices of Complexes from NBO Analysis at the HF/6-31+G* Level of Theory

bond	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
X1−S2	0.512	0.166	0.422	0.093	0.233	0.480	0.087	0.491
S2−O3	1.223	1.351	1.215	1.390	1.365	1.243	1.379	1.169
S2−O4	1.125	1.344	1.243	1.394	1.293	1.120	1.386	1.163
O3−O4	0.061	0.162	0.113	0.189	0.163	0.100	0.177	0.097
O4−S5	0.075				0.015	0.063		0.037
S5−O6	1.386		1.417		1.420	1.385		1.398
S5−O7	1.389		1.411		1.418	1.402		1.413
O6−O7	0.182		0.195		0.199	0.185		0.191
X1−S8 (S5)			0.022		0.002	0.009		0.008
S8−O9						1.420		1.421
S8−O10						1.424		1.429
O9−O10						0.200		0.201
O3−S11								0.038
S11−O12								1.406
S11−O13								1.412
O12−O13								0.192

are weakened too. Nevertheless, the small bond indices of 0.002−0.075 for the complex contacts indicate that there is only a very minor part of covalent interaction between the central ion and its ligands. The strong polarization of the ligands, the almost negligible charge transfer, and the very weak covalent bonding show that the stabilizing effect of the SO_2 ligands must be due to strong electrostatic interactions to a great extent.

In the structures **7** and **12**, where no fluorosulfite ion but a symmetrically complexed fluoride ion is present, the charge transfer from the fluorine to the ligands is smaller than in **1**, **6**, **8**, and **13** as indicated by the stronger negative charge at F1. The result of this is that the ligands bear only slightly more negative charge (−0.12 and −0.05, respectively) than in the previous cases. The bond indices for the S−F contacts are noticeably larger than the complexing ones of **8**, **11**, and **13**, but are still much smaller than the values of the F1−S2 bonds within the fluorosulfite units. Again the conclusion must be that mainly the electrostatic interactions are responsible for the remarkable stability of these structures.

The chlorine complexes **9** and **10** show even less charge transfer which is indicated by the high negative charge at chlorine. This is accompanied by a less polarized charge distribution within the chlorine bound SO_2 ligands. Only the ligand at O4 in structure **10** is as polarized as the comparable SO_2 units of the fluorine complexes. The S2−Cl1 bond index of **9** is very small, but in **10** this bond shows a larger covalent interaction than in the free chlorosulfite ion, in parallel to the findings for **6**. Again, all bond indices of the SO_2 units are smaller than in the free SO_2 molecule, but this loss of covalent bonding is larger than the effect of the new S−Cl bonds. As in the case of the fluorine complexes, it is found that the electrostatic interactions provide the major contributions to the stabilization of the structures while charge transfer and covalent bonding are only of minor importance. The smaller polarization compared to the fluorine case should result in smaller stabilization energies, and this is in very good agreement with the calculated energies presented here.

Conclusion

In this study we have attempted to obtain a closer insight into the solvation of halide anions in liquid SO_2 on a molecular scale and to find explanations for the solvent properties of liquid SO_2, especially for its high solvation power for anions and its ionogenic character. It is found that the formation of halosulfite ions is a favored process which gives, at least in the case of the fluoride ion, high energy gains and takes place without an activation barrier. The halogen ion or the halosulfite ion, respectively, interacts with further solvent molecules which can be investigated by calculation of discrete complexes of the ion and SO_2 ligands. It is found that complexation can take place either at the halogen or at an oxygen of the halosulfite ion. In both cases stabilization energies of comparable magnitude are obtained. While the fluorosulfite formation affords an energy gain of about 44 kcal/mol at the MP2 level (47 kcal/mol at the QCISD(T) level), the stabilization by each further SO_2 ligand is found to be 19.6, 12.4, and 9.9 kcal/mol (HF), respectively. For the largest calculated complex (**13**) a relative energy of −91.9 kcal/mol is obtained at the HF level of theory which, after consideration of the interactions in the pure solvent, leads to a total stabilization of 83.9 kcal/mol. It may be supposed that in the real solution this stabilization is even larger, because our model cannot give an approximation of the complete solvation shell. Nevertheless, our results show that the stabilizing effects are based mainly on electrostatic interactions of the ions and molecules, but a considerable assistence by charge transfer, covalent, and orbital interactions must be active too.

The calculated stabilization energies can be used to estimate reaction energies of heterolysis reactions in this solvent. Usually, such processes show highly endothermic energies in the gas phase and hence in ab initio calculations too. To estimate the energy of a real reaction in SO_2, the energy of the solvated ions must be used. In the case of a fluoride ion, a stabilization by solvation of about 85−90 kcal/mol can be considered. The chloride ion is obviously less stabilized by the solvent. The 2:1 complex gives an energy gain of 33 kcal/mol, and the value for a possible 4:1 complex is suggested to be about 55 kcal/mol if the trend of the stabilization by each further ligand is taken into account. Consideration of the interaction in the pure solvent reduces the stabilization to approximately 47 kcal/mol. If complexes of the counterions are calculated too, a crude estimation of the total reaction energy can be derived. Hence, the present investigation gives not only a better understanding of the solvent properties of SO_2, but also a practical tool to estimate heterolysis energies too.

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Supporting Information Available: Tables listing the total energies of SO_2, halide and halosulfite ions, and complexes of SO_2 with fluoride and chloride anions obtained at various levels of theory (2 pages). See any current masthead page for ordering and Internet access instructions.

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