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Theoretical Evidence for the Nucleophilic Addition of Sulfur Dioxide to 1,2-Bridged Chloronium and Bromonium Ions

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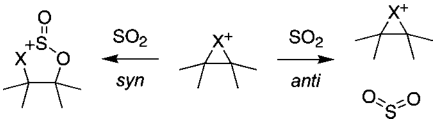
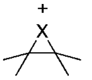
Received March 5, 2008



The nucleophilic addition of SO_2, SO_2ClF, and SO_2F_2 to carbenium ions and the nucleophilic addition of SO_2 to 1,2-bridged halonium ions are theoretically investigated by using B3LYP/6-311+G(d,p). On the basis of geometric changes in ion−solvent complexes compared to isolated molecules, the theoretical data for the addition of solvent to carbenium ions uniformly agree with experiments by Olah and Donovan. The relative reactivity of carbenium ions (methyl > ethyl > *iso*-propyl > *tert*-butyl) follows the familiar trend based on electron demand at the carbenium center. The theoretical data for the addition of SO_2 to 1,2-bridged halonium ions with use of similar methods indicate that this addition exhibits a reversed trend on the basis of the electron demand; SO_2 adds to 2,2-dimethylethylene chloronium and bromonium ions but does not add to the fluoronium analogue. Furthermore, the addition depends on the stereochemistry of the approaching SO_2. When SO_2approaches *syn* to the halogen atom on the halonium ion, addition is observed. When SO_2 is *anti*, addition is not observed. The reversed reactivity and stereochemistry of the addition of SO_2 to halonium ions can be explained by electron donation from the halogen atom to the sulfur atom of the approaching SO_2. This sulfur−halogen interaction activates the nucleophilicity of the approaching SO_2 and makes a normally unreactive tertiary carbenium carbon susceptible to addition. The theoretical evidence for covalently bound halonium ion−SO_2 complexes is discussed in the context of previously reported experimental evidence for the existence of equilibria involving β-halocarbenium ions.

Introduction

A fundamental question regarding the structure of 1,2-bridged halonium ions is whether they exist as a single symmetric structure with equal C−X bond orders (**a**) or as an equilibrium of asymmetric isomers with unequal bond orders (**b**).[1]



a

b

Since its initial proposal over 70 years ago,[2] the symmetric halonium ion has become an iconic example of how the structure of an intermediate can be used to explain stereospecific reactions. Though the symmetric halonium ion explains the stereospecificity of dihalogen addition to olefins, generalization of the mechanism based on a single intermediate is difficult because the reaction is sensitive to substituent effects, geometric constraints, and environmental influences.[3] To account for the mechanistic subtleties, several researches have proposed the existence of asymmetric structures, particularly β-halocarbenium ions.[4]

The direct observations in condensed phases have produced ambiguous data regarding the symmetry of halonium ions. In a landmark report, Olah and Bollinger were able to obtain NMR spectra of chloronium, bromonium, and iodonium ions under

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(1) (a) Olah, G. A. *Halonium Ions*; Wiley Interscience: New York, 1975; Chapter 7. (b) Olah, G. A.; Laali, K. K.; Wang, Q.; Prakash, G. K. S. *Onium Ions*; Wiley Interscience: New York, 1998; Chapter 6.

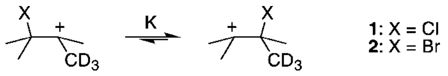
(2) Roberts, I.; Kimball, G. E. *J. Am. Chem. Soc.* **1937**, *59*, 947–948.

(3) (a) Ruasse, M. F. *Adv. Phys. Org. Chem.* **1993**, *28*, 207–291. (b) Brown, R. S. *Acc. Chem. Res.* **1997**, *30*, 131–137. (c) Chiappe, C.; Rebertis, A. D.; Jaber, A.; Lenoir, D.; Wattenbach, C.; Pomelli, C. S. *J. Org. Chem.* **2002**, *67*, 7066–7074.

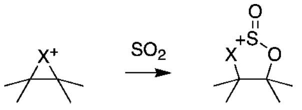
(4) (a) Bellucci, G.; Chiappe, C.; Lo Moro, G. *J. Org. Chem.* **1997**, *62*, 3176–3182. (b) Bellucci, G.; Bianchini, R.; Chiappe, C.; Brown, R. S.; Slebocka-Tilk, H. *J. Am. Chem. Soc.* **1991**, *113*, 8012–8016. (c) Ruasse, M. F. *Acc. Chem. Res.* **1990**, *23*, 87–93.

10.1021/jo800517b CCC: $40.75

SCHEME 1. Isotopic Perturbation of the Interconversion of *β*-Halocarbenium Ions



SCHEME 2. Sulfur Dioxide Addition to Halonium Ions



superacidic conditions.[5] However, the reported time-averaged NMR signals do not discriminate between a single structure and a rapid equilibrium of multiple structures. In a subsequent report, Olah et al. proposed an equilibrium involving the 2,2-dimethylethylene bromonium ion and its corresponding *β*-halocarbenium ions on the basis of temperature-dependent ^{13}C NMR shifts.[6] Petersen et al. proposed an analogous equilibrium involving 1,4-bridged halonium ions and their *δ*-halocarbenium ions on the basis of similar temperature-dependent shifts.[7] Brown et al. have reported X-ray crystallographic structures of adamantylideneadamantane bromonium and iodonium ions that appear to be sensitive to the position and nature of the counterion in the unit cell.[8] The bromonium ion complexed with tribromide is slightly asymmetric. By contrast, the ion complexed with triflate is essentially symmetric.

In a recent report, one of the authors investigated the structures of tetramethylethylene chloronium (**1**) and bromonium (**2**) ions by isotopic perturbation of equilibrium.[9] The NMR spectra of asymmetrically labeled ions exhibited ^{13}C NMR shifts that are consistent with a perturbation of a rapid equilibrium. These shifts were attributed to an equilibrium isotope effect on the interconversion of *β*-halocarbenium ions (Scheme 1). Attempts to theoretically determine the equilibrium isotope effect (K) produced the data presented herein and compel us to modify our initial interpretation of the equilibrium isotope effects.

In previous theoretical investigations, the coordinates for *β*-halocarbenium ions are conspicuously absent.[10] These ions are treated as nonstationary transitional structures that occur as halonium ions undergo 1,2-methyl shifts to form α-halocarbenium ions. The *β*-bromoethyl and *β*-chloroethyl carbenium ions were estimated to be about 15 kcal/mol less stable than the corresponding halonium ions.[11] Indeed, our initial attempts to calculate the equilibrium isotope effect (K) for **1** and **2** were unsuccessful because optimizations of asymmetric structures yielded halonium or α-halocarbenium ions rather than the desired *β*-halocarbenium ions.

To obtain *β*-halocarbenium ions as stationary points on the potential energy surface, a single molecule of the experimental solvent (SO_2) was added to differentially stabilize positive charge and break the symmetry. This approach has been recently applied to the norbornyl cation.[12] Instead of producing the desired *β*-halocarbenium ion, geometry optimization produced a structure in which the SO_2 added to the ion and formed a covalently bound complex (Scheme 2). In this ion−SO_2 complex, the formal charge resides on the sulfur atom and thus can no longer be described as either a halonium or a halocarbenium ion. The unexpected reactivity of SO_2 to halonium ions is remarkable considering the number of widely cited reports describing the NMR characterizations of 1,2-bridged halonium ions in SO_2.[1,5,6]

Although there are no reports of nucleophilic addition of SO_2 to halonium ions, addition of SO_2 to carbenium ions is well-known. The addition was initially identified in methyl fluoride−superacid mixtures in SO_2.[13] Subsequently, Olah and Donovan used ^{13}C NMR chemical shifts and carbon−fluorine coupling constants to systematically investigate the addition of common superacidic solvents (SO_2, SO_2ClF, and SO_2F_2) toward methyl, primary, secondary, and tertiary carbenium ions.[14] They determined that SO_2 added to more electron-deficient methyl and primary carbenium ions but did not add to tertiary carbenium ions. The other solvents (SO_2ClF, and SO_2F_2) were less nucleophilic but exhibited a similar reactivity trend that depended on the electron demand of the carbenium ion. A crystal structure of $CH_3OSO^+Sb_2F_{11}^-$ has been published and the bond distances and angles are consistent with the formation of a covalent oxygen−carbon bond.[15]

There are no reported theoretical investigations that directly address the nucleophilicity of superacidic solvents toward carbenium ions. However, Schleyer et al. investigated *O*-alkylated sulfur dioxide ($ROSO^+$) as a possible intermediate in the S_Ni reactions of alkyl chlorosulfite (ROSOCl).[16] They reported the dissociation of ROSOCl to form chloride and $ROSO^+$. Further dissociation of $ROSO^+$ to form SO_2 and R^+ was not investigated. The dissociation of CH_3OSO^+ to CH_3^+ and SO_2 (56 kcal/mol) has been reported, but no other alkylated SO_2 cations were investigated.[17]

Considering the general importance of carbenium and 1,2-bridged halonium ions, the demonstrated nucleophilic character of solvents used under superacidic conditions, and our recent evidence indicating that some halonium ions exist as equilibria, we now report theoretical evidence for the existence of covalently bound halonium ion−SO_2 complexes. This report presents the following: (1) a feasibility study of our computational methods by modeling experimental nucleophilic addition of SO_2, SO_2ClF, and SO_2F_2 to carbenium ions, (2) structural and energetic evidence for the addition of SO_2 to tetramethylethylene and 2,2-dimethylethylene halonium ions, and (3)

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(5) Olah, G. A.; Bollinger, J. M. *J. Am. Chem. Soc.* **1967**, *89*, 4474–4752.

(6) Olah, G. A.; Westerman, P. W.; Melby, E. G.; Mo, Y. K. *J. Am. Chem. Soc.* **1974**, *96*, 3565–3573.

(7) (a) Henrichs, P. M.; Peterson, P. E. *J. Am. Chem. Soc.* **1973**, *95*, 7449–7457. (b) McManus, S. P.; Peterson, P. E. *Tetrahedron Lett.* **1975**, *23*, 2753–2756. (c) Henrichs, P. M.; Peterson, P. E. *J. Org. Chem.* **1976**, *41*, 362–367.

(8) (a) Slebocka-Tilk, H.; Ball, R. G.; Brown, R. S. *J. Am. Chem. Soc.* **1985**, *107*, 4504–4508. (b) Brown, R. S.; Nagorski, R. W.; Bennet, A. J.; McClung, R. E. D.; Aarts, G. H. M.; Klobukowski, M.; McDonald, R.; Santarsiero, B. D. *J. Am. Chem. Soc.* **1994**, *116*, 2448–2456.

(9) Ohta, B. K.; Hough, R. E.; Schubert, J. W. *Org. Lett.* **2007**, *9*, 2317–2320.

(10) (a) Reynolds, C. H. *J. Am. Chem. Soc.* **1992**, *114*, 8676–8682. (b) Damrauer, R.; Leavell, M. D.; Hadad, C. M. *J. Org. Chem.* **1998**, *63*, 9476–9485. (c) Teberekidis, V. I.; Sigalas, M. P. *Tetrahedron* **2005**, *61*, 3967–3976.

(11) (a) Hehre, W. J.; Hiberty, P. C. *J. Am. Chem. Soc.* **1974**, *96*, 2665–2677. (b) Berman, D. W.; Anicich, V.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 1239–1248. (c) Hamilton, T. P.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1990**, *112*, 8260–8265.

(12) Hong, Y. J.; Tantillo, D. J. *J. Org. Chem.* **2007**, *72*, 8877–8881.

(13) (a) Peterson, P. E.; Brockington, R.; Vidrine, D. W. *J. Am. Chem. Soc.* **1976**, *98*, 2660–2661. (b) Olah, G. A.; Donovan, D. J.; Lin, H. C. *J. Am. Chem. Soc.* **1976**, *98*, 2661–2663. (c) Calves, J-Y.; Gillespie, R. J. *J. Am. Chem. Soc.* **1977**, *99*, 1788–1792.

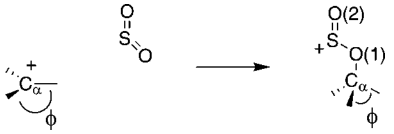
(14) Olah, G. A.; Donovan, D. J. *J. Am. Chem. Soc.* **1977**, *100*, 5163–5169.

(15) Gillespie, R. J.; Riddell, F. G.; Slim, D. R. *J. Am. Chem. Soc.* **1976**, *98*, 8069–9072.

(16) (a) Schreiner, P. R.; Schleyer, P. v. R.; Hill, R. K. *J. Org. Chem.* **1993**, *58*, 2822–2829. (b) Schreiner, P. R.; Schleyer, P. v. R.; Hill, R. K. *J. Org. Chem.* **1994**, *58*, 1849–1854.

(17) Frank, A. J.; Turecek, F. *J. Phys. Chem. A* **1999**, *103*, 5348–5361.

SCHEME 3. Structural Parameters for Solvent Addition to Carbenium Ions



evidence that chlorine and bromine atoms activate the nucleophilicity of SO_2.

Computational Methods

All equilibrium structures were optimized at the B3LYP[18]/6-311+G(d,p)[19] level with default gradient tolerances. Frequency calculations were performed at all stationary points to confirm that the structures were potential energy minima and to obtain zero-point energy (ZPE) corrections. To get more accurate relative energy differences, MP2[20]/6-311+G(d,p) electronic energies were obtained for the B3LYP optimized geometries. Unless otherwise noted, all reported energies are ZPE corrected. NMR chemical shifts were calculated for B3LYP optimized geometries with use of the HF/6-31+G(d,p) level of theory. This method was chosen on the basis of previous analyses of the accuracy of various methods in predicting NMR shifts for electron-deficient carbon species.[21] All calculations were performed with Spartan04.[22]

Results

Carbenium Ions. Nucleophilic addition of solvent to carbenium ions (Scheme 3) was determined by the C_α−O(1) bond distance and geometric changes in the complex compared to the isolated solvent and carbenium ion. In the absence of addition, the C_α−O(1) bond distance was significantly greater than the sum of the covalent bonding radii and the geometry of the solvent−ion complex was comparable to the geometries of the solvent and ion in isolation. Additionally, the calculated chemical shift of C_α in the complex remained essentially unchanged compared to the calculated chemical shift of the isolated carbenium ion. In the presence of addition, the complex exhibited the following geometric characteristics: the C_α−O(1) bond distances were near the sum of the covalent bonding radii (1.50 Å),[23] the pyramidalization of C_α increased, and the S−O bond distances in the solvent became unequal. These geometric changes were accompanied by a decrease in chemical shift at C_α.

Table 1 lists the structural and spectroscopic data that were used to determine whether SO_2, SO_2ClF, or SO_2F_2 adds to methyl (**3**), ethyl (**4**), *iso*-propyl (**5**), and *tert*-butyl (**6**) carbenium ions. The geometries of the isolated carbenium ions are consistent with previously reported theoretical investigations including the structure of **4**, which forms a hydrogen-bridged cation.[24] The hybridization of the carbenium carbon, C_α, was monitored by $\sum\phi$, the sum of the bond angles involving C_α excluding the angles defined with C_α−O(1). For all isolated carbenium ions, the $\sum\phi$ values are 360°, the expected value for an sp^2 hybridized carbon. Increased pyramidalization of C_α causes $\sum\phi$ to be less than 360°; for an ideal sp^3 hybridized carbon, $\sum\phi$ is 328.5°.

TABLE 1. Structural and Spectroscopic Data for Carbenium Ions, Solvent Molecules, and the Ion−Solvent Complexes Optimized by Using B3LYP/6-311+G(d,p)[a]

compd	C_α−O(1)	S=O(2)	S−O(1)	$\sum\phi$	$\delta_{C\alpha\ calc}$	$\delta_{C\alpha\ exp}$
SO_2		1.458				
SO_2ClF		1.433				
SO_2F_2		1.426				
3				360.0	360.9	
3-SO_2	1.506	1.434	1.542	338.5	79.2	74.9
3-SO_2ClF	1.516	1.413	1.527	338.7	77.7	81.8
3-SO_2F_2	1.544	1.410	1.510	340.7	87.2	
4				360.0	143.9	
4-SO_2	1.563	1.431	1.540	341.1	102.3	94.8
4-SO_2ClF	1.607	1.421	1.517	343.5	113.4	
4-SO_2F_2	1.659	1.412	1.494	346.2	134.3	
5				360.0	336.9	
5-SO_2	1.745	1.441	1.510	348.3	177.8	125.2
5-SO_2ClF	2.324	1.430	1.458	358.7	301.0	320
5-SO_2F_2	2.728	1.420	1.442	360.0	318.3	321.5
6				360.0	339.4	
6-SO_2	3.777	1.463	1.463	359.9	350.2	334.6
6-SO_2ClF	2.8877	1.420	1.440	359.9	356.1	335.2
6-SO_2F_2	3.107	1.430	1.448	360.0	355.9	335.9

[a] Bond lengths are in Å, angles are in deg, and chemical shifts are in ppm.

For all ion−solvent complexes containing **3** or **4**, the geometric changes are consistent with solvent addition to the ion. In these complexes, the C_α−O(1) bond distances are between 1.66 and 1.51Å; the $\sum\phi$ values are between 339° and 346°; the S−O(1) bond length is greater than the S=O(2) by ≥0.08 Å. The calculated chemical shifts for C_α are between 77 and 135 ppm, significantly smaller than the calculated shifts for the isolated **3** and **4** (>300 ppm). The calculated chemical shifts for **3**-SO_2 and **4**-SO_2 are close to the experimental chemical shifts and the geometric parameters for **3**-SO_2 agree with the reported crystallographic data.[15]

For all ion−solvent complexes containing **6**, the geometric changes are consistent with the absence of solvent addition. In these complexes, the C_α−O(1) bond distances are >2.5 Å; the pyramidalization of C_α remains essentially trigonal planar, and the S−O bond distances are nearly equal and similar to the distances in the isolated solvents. The calculated chemical shifts are similar to the calculated chemical shift of the isolated ion and agree with the experimental chemical shifts.

For ion−solvent complexes containing **5**, the geometric changes are consistent with the absence of solvent addition with either SO_2ClF or SO_2F_2. The data for **5**-SO_2ClF and **5**-SO_2F_2 compare favorably to the data for isolated **5** and to that for unbound complexes containing **6**. The calculated chemical shifts in **5**-SO_2ClF and **5**-SO_2F_2 agree with the experimental values

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[18] (a) Becke, A. *J. Chem. Phys.* **1993**, *98*, 5648–5652. (b) Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B: Condens. Matter* **1988**, *37*, 785–789.

[19] Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650–654.

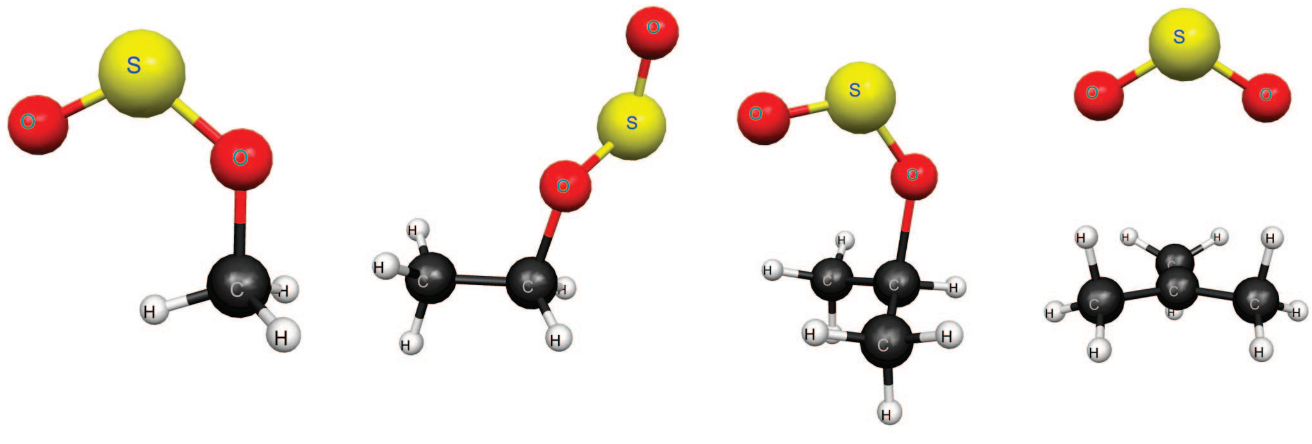
[20] Head-Gordon, M.; Pople, J. A.; Frisch, M. J. *Chem. Phys. Lett.* **1988**, *153*, 503–506.

[21] Gauze, G. F.; Pontes, R. M.; Basso, E. A. *THEOCHEM* **2004**, *712*, 91–100.

[22] *Spartan'04*; Wavefunction Inc.: Irvine, CA. Except for molecular mechanics and semiempirical models, the calculation methods used in Spartan'04 have been documented in: Kong, J.; White, C. A.; Krylov, A. I.; Sherrill, C. D.; Adamson, R. D.; Furlani, T. R.; Lee, M. S.; Lee, A. M.; Gwaltney, S. R.; Adams, T. R.; Ochsenfeld, C.; Gilbert, A. T. B.; Kedziora, G. S.; Rassolov, V. A.; Maurice, D. R.; Nair, N.; Shao, Y.; Beasley, N. A.; Maslen, P. E.; Dombroski, J. P.; Daschel, H.; Zhang, W.; Korambath, P. P.; Baker, J.; Byrd, E. F. C.; Van Voorhis, T.; Ouhi, M.; Hirata, S.; Hsu, C. P.; Ishikawa, N.; Florian, J.; Warshel, A.; Johnson, B. G.; Gill, P. M. W.; Head-Gordon, M.; Pople, J. A. *J. Comput. Chem.* **2000**, *21*, 1532–1548.

[23] Chang, R. *Chemistry*, 8th ed.; McGraw-Hill: New York, 2005; p 314.

[24] Schleyer, P. v. R., Maeker, C.; Buzek, P.; Sieber, S. In *Stable Carbocation Chemistry*; Prakash, G. K. S., Schleyer, P. v. R., Eds.; Wiley: New York, 1997; Chapter 2.



3-SO_2 **4**-SO_2 **5**-SO_2 **6**-SO_2

FIGURE 1. Structures of **3**-SO_2, **4**-SO_2, **5**-SO_2, and **6**-SO_2 optimized at the B3LYP/6-311+G(d,p) level.

TABLE 2. Binding Energies (in kcal/mol) of Carbenium Ion−Solvent Complexes[a]

cation	SO_2	SO_2ClF	SO_2F_2
CH_3^+	62.3	55.9	47.0
$CH_3CH_2^+$	26.6	25.2	16.2
$(CH_3)_2^+CH$	21.2	12.9	8.7
$(CH_3)_3C^+$	10.8	10.6	7.8

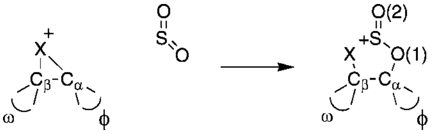
[a] Binding energies were evaluated at the MP2/6-311+G(d,p) level and are not ZPE corrected.

TABLE 3. Structural Data for Halonium Ions and Halonium Ion−SO_2 Complexes[a]

compd	C_α−O(1)	S=O(2)	S−O(1)	$\sum\phi$	$\sum\omega$	C_α−X	C_β−X	S−X
1				356.3	356.3	2.016	2.016	
syn-**1**-SO_2	1.557	1.442	1.561	340.7	338.8	2.776	1.904	2.656
anti-**1**-SO_2	3.567	1.462	1.463	356.7	356.3	2.031	2.016	6.267
2				356.0	356.0	2.181	2.181	
syn-**2**-SO_2	1.582	1.445	1.582	338.5	341.1	2.932	2.114	2.669
anti-**2**-SO_2	3.357	1.457	1.467	356.2	355.9	2.194	2.178	6.514
7				360.0	322.9	2.367	1.363	
7- SO_2	2.734	1.451	1.474	359.8	323.4	2.370	1.367	4.370
8				359.7	347.7	2.294	1.832	
syn-**8**-SO_2	1.596	1.437	1.551	341.5	330.5	2.790	1.814	2.885
anti-**8**-SO_2	2.902	1.452	1.474	359.9	345.9	2.348	1.832	6.085
9				359.3	349.6	2.387	1.994	
syn-**9**-SO_2	1.554	1.439	1.568	339.2	332.7	2.934	1.980	2.854
anti-**9**-SO_2	2.985	1.452	1.472	359.8	349.1	2.410	2.003	6.269

[a] Bond lengths are in Å and the sum of bond angles is in deg.

SCHEME 4. Structural Parameters for the Addition of SO_2 to Halonium Ions



and the calculated chemical shifts in **5**. Conversely, the geometric data for **5**-SO_2 suggest a weakly bound complex. The C_α−O(1) bond distance in **5**-SO_2 is longer than the distances in **3**-SO_2 and **4**-SO_2 but still near the covalent bonding limit. The other geometric and spectroscopic data are intermediate to the unbound and bound complexes described above. The optimized structures for **3**-SO_2, **4**-SO_2, **5**-SO_2, and **6**-SO_2 can be found in Figure 1.

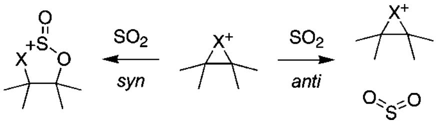
Table 2 lists the binding energies for carbenium ion−solvent complexes. For all complexes, the energy of the ion−solvent complex is lower than the energy of the isolated ion and solvent. On the basis of the geometric data, nucleophilic addition of the solvent to the carbenium ion occurs when the overall binding energy is greater than ~15 kcal/mol. The binding energies for complexes that exhibit nucleophilic addition are between 16 to 62 kcal/mol. Below 13 kcal/mol, the binding energy is due to purely electrostatic interactions between the solvent and carbenium ion, as opposed to chemical bonding.

Halonium Ions. Table 3 lists the relevant geometric parameters for tetramethylethylene chloronium (**1**) and bromonium (**2**) ions; 2,2-dimethylethylene fluoronium (**7**), chloronium (**8**), and bromonium (**9**) ions; and ion−SO_2 complexes. Due to the presence of the halogen, the table contains additional parameters associated with C_β, the carbon containing the shorter bond with the halogen atom (X). The sum of the bond angles about C_β is represented by $\sum\omega$. The computational methods used to obtain optimized halonium ion−SO_2 geometries are the same as the methods described for **3** thru **6**.

The structures of the isolated halonium ions in the gas phase are consistent with previously reported theoretical characterization (Scheme 4).[5] For **1** and **2**, the halogen atom symmetrically bridges the carbons of the ethylene fragment, C_α and C_β. For both ions, C_α and C_β are nearly trigonal planar: $\sum\phi$ and $\sum\omega$ are approximately 356°. For **8** and **9**, the halogen atom is asymmetrically bridged, the halogen bond to the more substituted carbon, C_α−X, is longer than the bond to the less substituted carbon, C_β−X. The hybridizations of C_α and C_β are consistent with the asymmetric bond lengths and indicate that C_α bears more positive charge than C_β. For **7**, the geometric data indicate that the fluorine does not bridge the carbons. In its lowest energy conformation, the C_β−F bond is orthogonal to the p orbital on C_α.

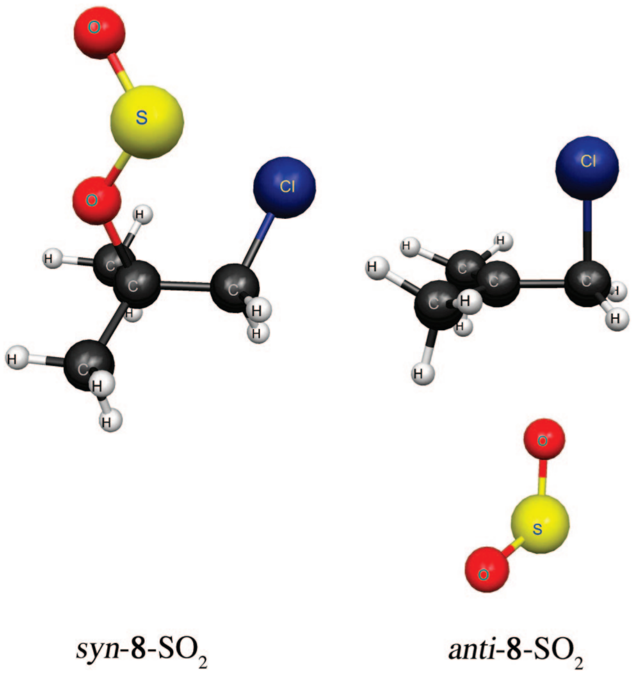
In the absence of addition, no significant geometric between the ion−solvent complex compared to the isolated ion and solvent were observed. In the presence of addition, the complexes exhibited similar geometric differences to the differences found for carbenium ion complexes: the C_α−O(1) bond distance approached the covalent bonding limit, the pyramidalization about C_α increased, and the S−O bond distances became unequal. Due to the presence of the halogen, the bound complexes exhibited the following additional geometric differences: the C_α−X bond distance increased, the C_β−X bond distance decreased, the pyramidalization of C_β increased, and the S−X bond distance decreased.

SCHEME 5. *Syn* and *Anti* Addition of Sulfur Dioxide to Tetramethylethylene Halonium Ions



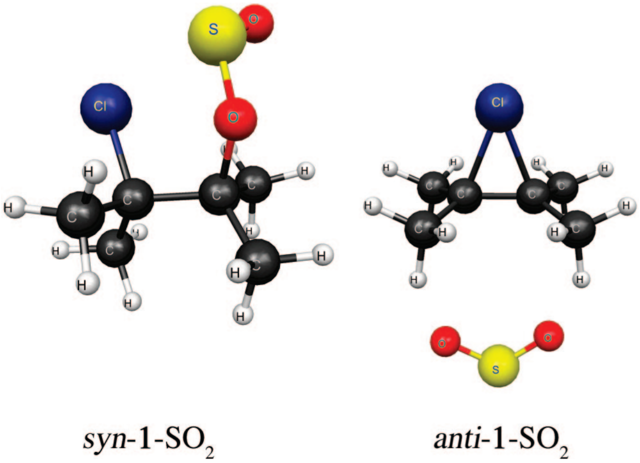
The data indicate that SO_2 adds to **8** and **9** but not to **7**. Furthermore, the addition depends on the orientation of the halogen atom relative to the approaching SO_2 (Scheme 5). When the SO_2 approaches from the same side of the halogen atom (*syn*-**8**-SO_2 and *syn*-**9**-SO_2), the geometric changes suggest that SO_2 adds to the halonium ions. The $C_\alpha-O(1)$ bonds are <1.6 Å, the S−O bond distances differ by >0.1 Å, and the pyramidalization about the C_α's increases ($\sum\phi$ values are approximately 340°). These values are comparable to those found in bound carbenium ion complexes. Additionally, the pyramidalization about the C_β's increases ($\sum\omega$ values are approximately 330°), the $C_\alpha-X$ bond distances increase by 0.5 Å, and the $C_\beta-X$ bond distance decreases by approximately 0.015 Å. The S−X bond distances are <2.9 Å and approach the sum of the covalent bonding radii (2.02 and 2.17 Å for S−Cl and S−Br, respectively).[23]

When the SO_2 approaches from the opposite side of the halogen atom (*anti*-**8**-SO_2 and *anti*-**9**-SO_2), the complexes exhibit only slight geometric changes compared to the isolated ions suggesting that SO_2 does not add in this orientation. The $C_\alpha-O(1)$ bond distances are >2.5 Å, $\sum\phi$ and $\sum\omega$ differ by <3°, the S−O bond distances differ by <0.03 Å, and the $C_\alpha-X$ and $C_\beta-X$ bond distances differ by <0.05 Å. The structures of *syn*-**8**-SO_2 and *anti*-**8**-SO_2 are presented in Figure 2. Because the $C_\beta-F$ bond in **7** is orthogonal to the p orbital on the carbenium center, the *syn*/*anti* designation for the orientation of SO_2 is irrelevant. Analogous to *anti*-**8**-SO_2 and *anti*-**9**-SO_2, the geometry of **7**-SO_2 is comparable to **7** indicating the absence of addition.



syn-**8**-SO_2 *anti*-**8**-SO_2

FIGURE 2. Structures of *syn*-**8**-SO_2 and *anti*-**8**-SO_2 optimized at the B3LYP/6-311+G(d,p) level.



syn-**1**-SO_2 *anti*-**1**-SO_2

FIGURE 3. Structures of *syn*-**1**-SO_2 and *anti*-**1**-SO_2 optimized at the B3LYP/6-311+G(d,p) level.

TABLE 4. Binding Energies (in kcal/mol) of Halonium Ion−SO_2 Complexes[a]

	B3LYP	MP2
syn-**1**-SO_2	−2.8	4.3
syn-**2**-SO_2	−4.9	1.0
syn-**8**-SO_2	0.9	8.5
syn-**9**-SO_2	1.1	4.8
anti-**1**-SO_2	6.5	9.5
anti-**2**-SO_2	6.4	9.6
7-SO_2	9.5	13.0
anti-**8**-SO_2	8.2	10.7
anti-**9**-SO_2	7.9	10.5

[a] B3LYP/6-311+G(d,p) and MP2/6-311+G(d,p) binding energies were evaluated at the B3LYP/6-311+G(d,p) optimized geometries.

A similar dependence on the orientation of the approaching SO_2 is observed for the addition of SO_2 to **1** and **2**. The geometries of *syn*-**1**-SO_2 and *syn*-**2**-SO_2 are quantitatively similar to the geometries of *syn*-**8**-SO_2 and *syn*-**9**-SO_2, indicating the presence of addition. The $C_\alpha-O(1)$ bond distances are <1.6 Å, the $\sum\phi$ and $\sum\omega$ decrease to approximately 340°, the S−O bond distances differ by >0.1 Å, the $C_\alpha-X$ bond distances increase by >0.7 Å, and the S−X bond distances are <2.7 Å. Conversely, the absence of geometric changes in *anti*-**1**-SO_2 and *anti*-**2**-SO_2 compared to the isolated ions and SO_2 is analogous to the absence of changes for other *anti* complexes and **7**-SO_2. The $C_\alpha-O(1)$ bond distances (>3.5 Å) are longer than observed in the corresponding *syn* complexes, the $\sum\phi$ and $\sum\omega$ remain approximately 356°, the S−O bond distances are nearly equal, and the $C_\alpha-X$ bond distances remains unchanged. The structures of *syn*-**1**-SO_2 and *anti*-**1**-SO_2 are presented in Figure 3.

Table 4 lists the B3LYP and MP2 binding energies of halonium ion−SO_2 complexes. At the MP2 level of theory, the binding energies for the complexes are positive, indicating the complexes are more stable than the isolated solvent and ion. In the *anti* complexes, SO_2 stabilizes the halonium ion through electrostatic interactions. The binding energies associated with this interaction range from 9.5 to 13.0 kcal/mol. In the *syn* complexes, SO_2 adds to the halonium ions and the binding energies represent the change in enthalpy. The binding energies for *syn* complexes range from 1.0 to 8.5 kcal/mol.

Despite some fortuitous agreements, the calculated shifts for halonium ions and ion−solvent complexes were determined to be unreliable. Default GIAO calculations of some simple halogen-substituted alkanes and alkenes indicate that the calculation methods consistently overestimate carbon shifts compared to experiment (see the Supporting Information). In particular, the carbons that are directly bonded to the halogens are overestimated by as much as 15 ppm for chlorine and as much as 40 ppm for bromine. All other calculated carbon shifts for these halogenated species are underestimated compared to experiment, further suggesting that NMR calculations for such complex halogenated structures are not suitable for discriminating between halonium ions, halocarbenium ions, and ion−solvent complexes. A more thorough study of the factors that affect the accuracy of carbon NMR shifts for halogenated species is certainly needed.

Discussion

Method Evaluation. On the basis of geometric changes in the carbenium ion−solvent complexes, the theoretical determination of addition uniformly agrees with the experimental data from Olah and Donovan.[14] As further confirmation, the estimated chemical shifts for C_α also agree with the experimental shifts and suggest that our optimized structures are reasonably accurate. The only discrepancy was an overestimate of the chemical shift for C_α in **5**-SO_2. This result can be attributed to a comparatively longer C_α−O(1) bond length when optimized by using the B3LYP method. Optimization of **5**-SO_2 with MP2/6-311+G(d,p) produced a structure in which the C_α−O(1) bond distance is shorter (1.586 Å). With use of the MP2 optimized geometry, the calculated chemical shift (127.3 ppm) was found to be much closer to experiment. Despite this discrepancy between the MP2 and B3LYP methods for relatively weakly bound complexes, the B3LYP method accurately predicts the geometries of unbound and tightly bound carbenium ion complexes.

Gilbert and Carlier have independently cautioned that density functional methods underestimate bond distances for weak dative interactions.[25] Density functional optimization of halonium ion−SO_2 complexes produced structures with C_α−O bond distances similar to the distances found in tightly bound carbenium ion−solvent complexes and suggests that these complexes are tightly bound. However, both halonium ions and halonium ion−SO_2 complexes contain bonds that appear to have dative character: the C_α−X bonds in halonium ions and the S−X bonds in halonium ion−SO_2 complexes. Optimization of **1** and *syn*-**1**-SO_2 at the MP2/6-311+G(d,p) level produced structures that exhibited significant differences in the dative bonds compared to the B3LYP optimizations. The C−X bond in **1** decreased by 0.087 Å and the S−X bond in *syn*-**1**-SO_2 increased by 0.588 Å. Despite these geometric changes, the relative energies of the MP2 optimized structures differed by less than 0.2 kcal/mol compared to energies calculated at the MP2 level of theory at B3LYP geometries. Because the differences between MP2 and B3LYP optimized geometries produced only slight relative energy differences and did not materially affect the interpretation of the results, B3LYP optimizations with MP2 energy corrections were deemed to be adequate to model the addition of SO_2 to halonium ions.

Solvent Addition to Carbenium Ions. The carbenium ion results suggest that, for a given solvent molecule, electron demand of the carbenium carbon determines whether the solvent will add. All solvents add to electron deficient carbenium ions **3** and **4** whereas no solvent adds to the least electron deficient ion **6**. For complexes containing **5**, only **5**-SO_2 exhibits the geometric characteristics consistent with solvent addition suggesting that SO_2 is more nucleophilic than either SO_2ClF or SO_2F_2.

The calculated binding energies are consistent with the theoretical determination of addition. All complexes are more stable than the isolated molecules whether or not the solvent adds to the ion. In the absence of addition, the lowered energy results from electrostatic interactions. These interactions account for approximately 8−13 kcal/mol of stabilization, depending on the nature of the ion and solvent. In the presence of addition, the binding energy represents the enthalpy difference for the bonding changes that occur during addition: forming the C_α−O(1) σ bond, rehybridization of C_α, and breaking the S═O π bond. The binding energies range from 16.2 to 62.3 kcal/mol. Complexes containing **4** are exceptional due to the stabilization associated with the hydrogen bridge in the isolated ion. Consequently, the reported binding energies for **4** are underestimated compared to those of the ethyl carbenium ion.

Solvent Addition to Halonium Ions. Substitution of a hydrogen atom on **6** with a halogen atom provides a model compound that can test whether halogens can affect the reactivity of the carbenium center. A reasonable hypothesis is that a more electronegative halogen atom increases electron demand at the carbenium center and makes these ions susceptible to addition. Indeed, the geometric data indicate that SO_2 adds to **8** and **9**. However, the data also indicate that SO_2 does not add to **7** despite fluorine being more electronegative than either bromine or chlorine.

This reversed reactivity of these ions can be explained by a sulfur−halogen interaction that activates the nucleophilicity of the SO_2. In the bound complexes *syn*-**8**-SO_2 and *syn*-**9**-SO_2, the sulfur and halogen atoms are near the sum of the covalent bonding radii. This interaction can be disrupted if the halogen is oriented away from the SO_2 as demonstrated in *anti*-**8**-SO_2 and *anti*-**9**-SO_2. In these complexes, the SO_2 does not add and stabilizes the complex through electrostatic interactions only. In other words, SO_2 does not perform the typical backside addition to the halonium ion. Rather, SO_2 attacks from the same side as the halogen atom, analogous to S_Ni reactions.[16,26] The reversed reactivity of the halogen-substituted carbenium ions can be attributed to fluorine's inability to donate electron density to the sulfur atom and activate the approaching SO_2. The evidence for bound complexes *syn*-**8**-SO_2 and *syn*-**9**-SO_2 supports the possibility that the nucleophilic addition of SO_2 to 1,2-bridged chloronium and bromonium ions is a general phenomenon. Indeed, optimized geometries of *syn*-**1**-SO_2 and *syn*-**2**-SO_2 resemble *syn*-**8**-SO_2 and *syn*-**9**-SO_2 by exhibiting all the characteristics of bound ion−solvent complexes.

The binding energies of the halonium ion−SO_2 complexes can be understood in the framework of two different ion−SO_2 interactions. For *anti* complexes, the SO_2 molecule behaves like a solvent and adopts the most stable conformation of a single molecule in the primary solvent shell. The energies represent the electrostatic stabilization of the halonium ion with the dipole of the SO_2 and are comparable to the electrostatic stabilization observed in **6**-SO_2. By contrast, the energies for the *syn* complexes represent the enthalpy change that accompanies

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[25] (a) Gilbert, T. M. *J. Phys. Chem. A* **2004**, *108*, 2550–2554. (b) Carlier, P. R.; Deora, N.; Crawford, T. D. *J. Org. Chem.* **2006**, *71*, 1592–1597.

[26] Moss, R. A.; Fu, X.; Tian, J.; Sauers, R.; Wipf, P. *Org. Lett.* **2005**, *7*, 1371–1374.

nucleophilic addition of SO_2 to the halonium ion. These changes are considerably more complex than that for addition to carbenium ions. In addition to forming the $C_\alpha-O(1)$ bond and breaking the S=O π bond, changes to both carbon halogen bonds and the formation of a weak S−X bond also contribute to the enthalpy for forming the bound complex. Because the nature of the ion−SO_2 interaction is different, the binding energies of *syn* complexes cannot be directly compared to those of *anti* complexes. The bound *syn* complexes should be considered a unique chemical species that can be stabilized through ion−dipole interactions similar to the stabilization observed in the *anti* complexes. Our calculations include a single solvent molecule and cannot account for the full stabilization due to solvation each ionic species will experience from all the solvent molecules in the solvation shell.

Entropy Effects. The calculated binding energies in Table 4 do not account for the entropic contribution to the overall free energy of binding in the halonium ion−SO_2 complexes. A binding energy correction for entropy that accounts for the dissociation of *syn*-**1**-SO_2 to **1** and SO_2 at infinite distance was calculated to be −9.1 kcal/mol at 200 K (−9.5 kcal/mol for the dissociation of **2**). The entropy corrected binding energy for **1** is −4.8 kcal/mol under the experimental conditions (−8.5 kcal/mol for **2**), thus making dissociation favored. Because the calculation only accounts for a single molecule of SO_2, the foregoing correction for entropy represents a lower limit. The actual entropic contribution should be attenuated by the presence of several nearby molecules of SO_2 that can reinsert into the halonium ion. Additionally, the halonium ion−SO_2 complex would not dissociate to infinite distance but would return the dissociating molecule of SO_2 into the primary solvent shell. A more realistic estimate of the correction for entropy is achieved by comparing the *syn* and *anti* complexes, which represents the process of transferring bound SO_2 to the primary solvent shell. The binding energy corrections for this process were calculated to be −3.8 and −3.2 kcal/mol at 200 K for **1** and **2**, respectively; the entropy corrected binding energies are 0.5 and −2.2 kcal/mol.

Halonium Ion−SO_2 Complexes versus β-Halocarbenium Ions. The experimental data that suggest the presence of asymmetric halocarbenium ions present a serious challenge for gas phase calculations. The symmetric halonium ions are 15 kcal/mol more stable than the corresponding β-halocarbenium ions, effectively making the concentration of halocarbenium ions undetectable by NMR. Alternatively, the bound halonium ion−SO_2 complexes are comparable in energy to the halonium ion and, even with entropy correction, are more stable than β-halocarbenium ions.

The existence of halonium ion−SO_2 complexes can be used to explain all previously reported experimental data that indicate the presence of an equilibrium involving β-halocarbenium ions in superacidic solutions. For example, Olah et al. observed the chemical shift for C_α in **9** increased 4.6 ppm as the temperature was raised from −80 to −40 °C.[6] They attributed this temperature dependence to an equilibrium between **9** and the corresponding open β-bromocarbenium ion. However, a rapid equilibrium of **9** and *syn*-**9**-SO_2 can also be used to explain the temperature-dependent shifts without involving the open β-bromocarbenium ion. On the basis of entropic considerations, an equilibrium of **9** and *syn*-**9**-SO_2 favors dissociated products at high temperatures. To explain the temperature-dependent NMR shifts, this argument requires that the chemical shift of C_α in **9** is larger than that in *syn*-**9**-SO_2, a reasonable assumption considering C_α in **9** is more sp^2-like compared to that of *syn*-**9**-SO_2.

Additionally, the results from an isotopic perturbation of equilibrium investigation of isotopically labeled **1** and **2** were initially attributed to equilibria of β-halocarbenium ions.[9] The geometry optimization and binding energies of *syn*-**1**-SO_2 and *syn*-**2**-SO_2 suggest that these results can also be reinterpreted as a rapid equilibrium involving interconverting ion−SO_2 complexes or a rapid equilibrium involving both halonium ions and ion−SO_2 complexes. Estimation of the relative stability of symmetric halonium ions to ion−SO_2 complexes on the basis of the isotope shifts is possible but requires knowledge of the ^{13}C chemical shifts in both the halonium ion and the ion−SO_2 complex. Calculated NMR chemical shifts using standard GIAO methods are too inaccurate for a meaningful estimation of the relative energy. Considering the theoretical evidence that β-halocarbenium ions are high-energy species on the potential energy surface, we believe the existence of ion−SO_2 complexes provides a preferred explanation for experimental evidence that indicate an equilibrium when SO_2 is present in the system.

Counterion Effects on Symmetry. Though counterion effects have thus far been omitted from the discussion, they may play a role in determining the symmetry of halonium ions. The crystal structures of adamantylideneadamantane halonium ions indicate that the symmetric displacement of the counterion within the unit cell can affect the symmetry of the halonium ions.[8] In the crystal structure of the bromonium ion containing tribromide as a counterion, the unit cell contains a single bromonium ion in which the C−Br distances differ by 0.08 Å. In this structure, the tribromide anion is asymmetrically displaced off the σ_v plane of the olefin and the carbon closer to the anion possesses the longer C−Br bond. In the crystal structures containing triflate as a counterion, the unit cell contains two bromonium ions, one hydronium ion, and three triflate anions. The C−Br bond lengths are within experimental error making each bromonium ion essentially symmetric. Notwithstanding, the counterion's effect on the symmetry appears to be minor despite relatively close packing of the counterion and the halonium ion. For comparison, nucleophilic addition of SO_2 to the halonium ion produces an asymmetric structure in which the differential C−Br bond distances are 10 times the differential bond distances found in the asymmetric crystal structure.

Conclusions

Theoretical determination of the nucleophilic addition of SO_2, SO_2ClF, and SO_2F_2 to carbenium ions can be feasibly modeled by using geometries optimized at the B3LYP level of theory and energy calculations at the MP2 level of theory. The determination of addition supports the notion that, for a given solvent, electron demand of the carbenium center determines whether the addition occurs. When applying the same theoretical

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(27) (a) Humbel, S.; Sieber, S.; Morokuma, K. *J. Chem. Phys.* **1996**, *105*, 1959–1967. (b) Svensson, M.; Humbel, S.; Froese, R. D. J.; Matsubara, T.; Sieber, S.; Morokuma, K. *J. Phys. Chem.* **1996**, *100*, 19357–19363. (c) Dapprich, S.; Komaromi, I.; Byun, K. S.; Morokuma, K.; Frisch, M. J. *THEOCHEM* **1999**, *462*, 1–21.

(28) (a) Day, P. N.; Jensen, J. H.; Gordon, M. S.; Webb, S. P.; Stevens, W. J.; Krauss, M.; Garmer, D.; Basch, H.; Cohen, D. *J. Chem. Phys.* **1996**, *105*, 1968–1986. (b) Gordon, M. S.; Freitag, M. A.; Bandyopadhyay, P.; Jensen, J. H.; Kairys, V.; Stevens, W. J. *J. Phys. Chem. A* **2001**, *105*, 293–307. (c) Gordon, M. S.; Slipchenko, L.; Li, H.; Jensen, J. H. *Annu. Rep. Comp. Chem.* **2007**, *3*, 177–193.

methods to halonium ions, the results indicate that the addition of SO_2 to halonium ions exhibits a reversed trend on the basis of the electron demand; fluorine-substituted carbenium ions do not react but chlorine and bromine compounds react. The reversed reactivity of halonium ions can be understood on the basis of a sulfur–halogen interaction that activates the nucleophilicity of the approaching sulfur dioxide. The formation of halonium ion–SO_2 complexes is consistent with previously reported data that indicate the existence of rapid equilibria involving β-halocarbenium ions in SO_2. On the basis of our evidence for solvent binding to halonium ions, we conclude that previously reported characterizations of 1,2-bridged halonium ions in SO_2 should be reinterpreted as a rapid equilibrium involving halonium ion–SO_2 complexes.

The theoretical evidence for nucleophilic addition of the solvent presents a challenge to future calculations that include multiple discrete solvent molecules in this system. Our results suggest that the calculations must allow at least one solvent molecule to react with the halonium ion. The results also suggest that simple solvation models (e.g., polarizable continuum model or PCM) are inappropriate for halonium ions due to the observed reactivity of these ions to relatively unreactive solvents. To get a more definitive picture of the role solvent plays in these systems, a more complex method involving conformational sampling (e.g., molecular dynamics or Monte Carlo) with a discrete solvation model such as ONIOM[27] or Effective Fragment Potentials (EFP)[28] is needed.

Acknowledgment. The authors thank the Department of Chemistry and the College of Liberal Arts and Sciences at Villanova University for financial support of this research.

Supporting Information Available: A table of calculated and experimental NMR chemical shifts for a few halogenated hydrocarbons, along with Cartesian coordinates of all structures reported in this work. This material is available free of charge via the Internet at http://pubs.acs.org.

JO800517B