

Potential Energy Surface of SOCl_3^- Steven M. Bachrach,^{*,†} Joseph M. Hayes,[†] Catherine E. Check,[‡] and Lee S. Sunderlin^{*,‡}*Department of Chemistry, Trinity University, 715 Stadium Drive, San Antonio, Texas 78212, and Department of Chemistry and Biochemistry, Northern Illinois University, DeKalb, Illinois 60115**Received: June 25, 2001*

Sulfur trichloride monoxide anion (SOCl_3^-) is stable in the gas phase. The G2 estimate of the energy for its dissociation to thionyl chloride and chloride anion is $102.8 \text{ kJ mol}^{-1}$. The potential energy surface for the reaction $\text{SOCl}_2 + \text{Cl}^- \rightarrow \text{SOCl}_3^-$ has just a single well corresponding to the product. Collision-induced dissociation observed using a flowing afterglow-tandem mass spectrometer indicates a $D_0(\text{SOCl}_2\text{--Cl}^-)$ bond energy of $85.4 \pm 7.6 \text{ kJ mol}^{-1}$, which is very similar to the previously determined bond energy $D_0(\text{SCL}_2\text{--Cl}^-) = 85 \text{ kJ mol}^{-1}$.

Introduction

Recent high-level calculations of nucleophilic substitution reactions at sulfur have indicated an addition–elimination reaction,^{1–4} characterized by a stable intermediate, which is formally a hypervalent⁵ species. Anticipating that electron withdrawing groups may stabilize such an intermediate, we reported a computational and experimental study of the reaction of SCL_2 with chloride.⁶ The potential energy surface for this reaction has a single well and the global minimum is SCL_3^- .

Nucleophilic substitution at sulfinyl centers has been exploited in the synthesis of chiral species including amino acids.⁷ This substitution proceeds with stereoinversion, usually associated with an $\text{S}_{\text{N}}2$ reaction.⁸ Miklojczyk has suggested that the mechanism involves a sulfurane that can pseudorotate before expelling the leaving group.⁹ Extrapolating from our previous work,⁶ we suspected that electron withdrawing groups might lead to an extremely stable sulfurane. Salama and co-workers have observed a weak complex of chloride with thionyl chloride in acetonitrile.¹⁰ We report here on the gas-phase reaction of thionyl chloride (SOCl_2) with chloride. The computed potential energy surface for this reaction has a single well, indicating that SOCl_3^- is a stable species. Mass spectral analysis confirms this: the bond dissociation energy for loss of chloride is 85.4 kJ mol^{-1} .

Computational Methods

We have examined a variety of nucleophilic substitution reactions with many computational methods and have found that all methods that include some electron correlation (MP2, CCD, B3LYP, B3PW91) consistently characterize the potential energy surface. Initial characterization of the potential energy surface for the reaction of SOCl_2 with Cl^- was carried out by optimizing the system with fixed distances between sulfur and the incoming chloride. This scan, performed at B3LYP/6-31+G*,¹¹ shows a single well, indicating a barrierless reaction to form SOCl_3^- . The local minimum energy structures of SOCl_2 and SOCl_3^- have C_s symmetry. The SOCl_3^- configuration having C_{3v} symmetry has two imaginary frequencies and is therefore a hilltop. These three critical points were reoptimized

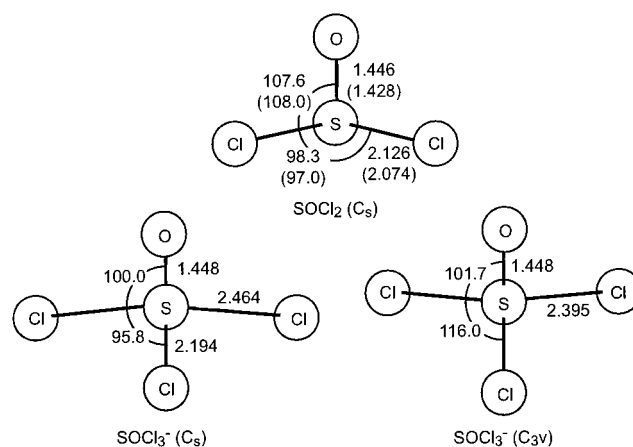


Figure 1. B3LYP/aug-cc-pVTZ optimized geometries of SOCl_2 and SOCl_3^- (C_s , left; C_{3v} , right). The experimental structure¹³ of SOCl_2 is given in parentheses. All distances are in Å and all angles are in degrees.

at MP2/6-31+G* and B3LYP/aug-cc-pVTZ.¹² The geometries calculated at the three different levels are quite similar: bond distances differ by less than 0.02 Å and bond angles differ by less than 2° . The B3LYP/aug-cc-pVTZ geometry of thionyl chloride is in close agreement with the structure determined via microwave spectroscopy,¹³ confirming a previous study that DFT methods are quite appropriate for treatment of these types of compounds.¹⁴ The B3LYP/aug-cc-pVTZ geometries are shown in Figure 1. Analytical frequencies were calculated at all three levels to obtain zero-point vibrational energy (ZPE). The B3LYP/6-31+G* ZPEs were scaled by 0.96;¹⁵ all others were used without scaling. B3LYP/aug-cc-pVTZ frequencies and rotational constants were used in the experimental analysis described below.

Our previous study of SCL_3^- indicated that the bond dissociation energy calculated at B3LYP/aug-cc-pVTZ is overestimated by about 30 kJ mol^{-1} , but very close agreement with experiment is found at the G2 level.⁶ Therefore, we obtained optimized geometries and energies at G2 as well. The computed dissociation energies (including ZPE) are listed for the various methods in Table 1. The G2 energy includes all corrections for energetic determination at 298 K. All computations were performed using GAUSSIAN-98.¹⁶

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TABLE 1: Dissociation Energies^a (kJ mol⁻¹) SOCl₃⁻ → SOCl₂ + Cl⁻

| method | ΔE |
|-------------------|------------|
| MP2/6-31+G* | 123.1 |
| B3LYP/6-31+G* | 130.7 |
| B3LYP/aug-cc-pVTZ | 121.3 |
| G2 | 102.8 |
| expt | 85.4 ± 7.6 |

^a The MP2 and B3LYP computational energies include zero-point vibrational energies (scaled by 0.96 for B3LYP/6-31+G*). The G2 energy is evaluated at 298 K.

Experimental Methods

The flowing afterglow-tandem mass spectrometer used in these experiments consists of an ion source, a flow reactor, and a tandem mass spectrometer comprising a quadrupole mass filter, an octopole ion guide,¹⁷ a second quadrupole mass filter, and a detector. This instrument has been described in detail previously;¹⁸ a brief description follows.

The ion source used in these experiments is a direct current (dc) discharge that typically operates at 1500 V with 2 mA of emission current. The ions for these experiments were produced by adding SOCl₂ (Alfa, 97%, used as received) at the plasma source. Dissociative electron attachment to SOCl₂ gives Cl⁻, and attachment of the Cl⁻ to another molecule of SOCl₂ gives SOCl₃⁻. Approximately 10⁵ collisions with the buffer gas thermalize the ions. The buffer gas is typically 95% helium and 5% argon. Ions are sampled from the flow tube into the main chamber, which contains the tandem mass spectrometer. This chamber is differentially pumped to pressures sufficiently low that further collisions of the ions with the buffer gas are unlikely. The octopole passes through a gas cell that is filled with argon for collision-induced dissociation (CID) experiments.

Threshold Analysis. The threshold energy for a reaction is determined by modeling the intensity of product ions as a function of the reactant ion kinetic energy in the center-of-mass (CM) frame, E_{CM} . The laboratory energy E_{lab} is given by the octopole rod offset voltage measured with respect to the center of the Gaussian fit. Conversion to the CM frame is accomplished by use of $E_{CM} = E_{lab}m/(m + M)$, where m and M are the masses of the neutral and ionic reactants, respectively. This energy is corrected at low offset energies to account for truncation of the ion beam.¹⁹ Total cross sections for reaction, σ_{total} , are calculated as discussed previously.^{18,19}

To derive CID threshold energies, the threshold region of the data is fitted to the model function given in eq 1, where $\sigma(E)$ is the cross section for formation of the product ion at

$$\sigma(E) = \sigma_0 \sum_i [g_i P_D(E, E_i) (E + E_i - E_T)^n / E] \quad (1)$$

center-of-mass energy E , E_T is the desired threshold energy, σ_0 is a scaling factor, n is an adjustable parameter related to the shape of the cross section, P_D is the probability of an ion with a given amount of energy dissociating within the experimental window (ca. 30 μ s), and i denotes rovibrational states having energy E_i and population g_i ($\sum g_i = 1$). P_D is calculated using the RRKM formalism. The CRUNCH program is used in the threshold analysis described above.²⁰ The thermal motion of the collision gas and the kinetic energy distribution of the reactant ion are also included in the fitting procedure. The effect of secondary collisions is accounted for by linear extrapolation of data taken at several pressures to a zero pressure cross section.²¹ The calculated rotational constants and vibrational frequencies (Table 2) at the B3LYP/aug-cc-pVTZ level were used in this analysis.

TABLE 2: Vibrational Frequencies (cm⁻¹) of SOCl₂ and SOCl₃⁻ Calculated at B3LYP/Aug-cc-pVTZ

| SOCl ₂ | SOCl ₃ ⁻ |
|-------------------|--------------------------------|
| 174.44 | 69.89 |
| 269.19 | 120.79 |
| 327.07 | 128.89 |
| 432.67 | 199.40 |
| 476.13 | 208.41 |
| 1246.09 | 278.66 |
| | 376.57 |
| | 419.11 |
| | 1236.06 |

The uncertainty in the reaction thresholds due to the internal energy of the reactant ions is 1.35 kJ mol⁻¹, as estimated by determining the threshold with the calculated reactant frequencies multiplied by 0.8, 1.0, and 1.2. Also, the uncertainty in the energy scale is 14.5 kJ mol⁻¹ in the lab frame. The uncertainty associated with 20% changes in the dissociation transition state frequencies, as well as a factor of 3 change in the 30 μ s time window for dissociation, is negligible (<1 kJ mol⁻¹). These uncertainties are combined with the standard deviation of the thresholds derived from different data sets to give the overall uncertainty in reaction energetics.

Results

The potential energy surface for the reaction of thionyl chloride and chloride anion is very simple: reactants combine to form SOCl₃⁻ without any barriers or intermediates. The optimized structure of SOCl₂ has C_s symmetry and is drawn in Figure 1. The minimum energy structure of SOCl₃⁻ has C_s symmetry, as shown in Figure 1. This structure is of the “seesaw” type, consistent with VSEPR theory. Addition of chloride to thionyl chloride results in no change of the S–O distance and a slight lengthening of one of the S–Cl bonds. The other S–Cl bond lengthens by more than 0.3 Å.

The C_{3v} configuration of SOCl₃⁻ is a hilltop having two imaginary frequencies (see Figure 1). At B3LYP/aug-cc-pVTZ, it lies 7.4 kJ mol⁻¹ above the C_s configuration (15.7 kJ mol⁻¹ at G2). The imaginary frequencies correspond to motions that scramble the axial and equatorial chlorides in the C_s form.

CID Results. The data for collision-induced dissociation of SOCl₃⁻ as a function of translational energy are shown in Figure 2. The reactions observed are given in eqs 2–5,



where the neutral products are assumed on thermodynamic grounds. Reaction 2 is dominant over the entire energy range examined, while reaction 5 is observed in only trace amounts. The minor products have sufficiently small cross sections in the reaction threshold region such that they can be ignored in the threshold fitting procedure; analysis of these products to determine further thermochemistry is in progress.²² The optimized fitting parameters are $E_T = 85.4 \pm 6.8$ kJ mol⁻¹ and $n = 1.3 \pm 0.1$. The threshold energy corresponds to a bond energy (loss of Cl⁻) of 85.4 ± 7.6 kJ mol⁻¹ after other sources of error are included.

Bond Energy. The calculated energy for loss of Cl⁻ using the standard computational methods (MP2 and B3LYP) range from 121 to 130 kJ mol⁻¹ (Table 1). This value is much larger

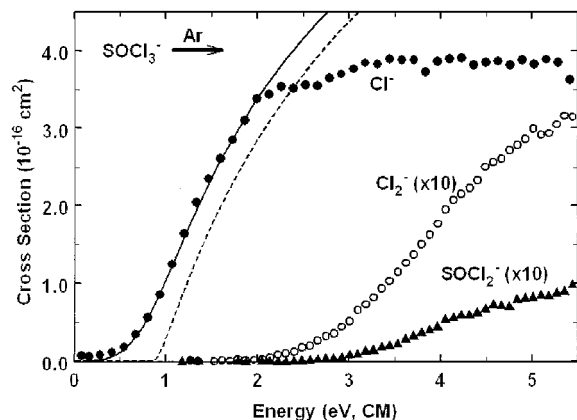


Figure 2. Appearance curves for collision-induced dissociation of SOCl_3^- as a function of kinetic energy in the center-of-mass frame. The solid line is the model appearance curve calculated using eq 1 and convoluted as discussed in the text. The dashed line is the unconvoluted fit. The fitting parameters for this data set are $n = 1.30$ and $E_T = 0.89$ eV.

TABLE 3: NPA Charges

| atom | SCl_2^a | $\text{SCl}_3^-^a$ | SOCl_2 | SOCl_3^- |
|------|------------------|--------------------|-----------------|-------------------|
| S | 0.25 | 0.22 | 1.26 | 1.32 |
| O | | | -0.82 | -0.85 |
| Cl | -0.13 | -0.20 | -0.22 | -0.31 |
| | | -0.51 (ax) | | -0.58 (ax) |

^a See ref 6.

than the experimental bond dissociation value of 85.4 kJ mol^{-1} . The overestimation also was found for the bond dissociation energy of SCl_3^- .⁶ In that case, we recalculated the energy at G2, which gave a value of 99.0 kJ mol^{-1} , within the combined error limits of the experimental value of 85 kJ mol^{-1} . The G2 estimate of the bond dissociation energy of SOCl_3^- is $102.8 \text{ kJ mol}^{-1}$. Again, the computational estimate is higher than the experimental value, but just within the sum of the uncertainties.

The bond dissociation energy of SCl_2 is 293 kJ mol^{-1} ,²³ about 3 times larger than the bond dissociation energy of SCl_3^- or SOCl_3^- . This is reflected in the S-Cl bond distances, which are much shorter in SCl_2 (2.072 \AA) than in the two hypervalent species. The two long S-Cl bonds in the ions are in the axial position and are consistent with 3-center, 4-electron bonding. These bonds are expected to be weaker than typical S-Cl bonds.

The bond dissociation energies of SCl_3^- and SOCl_3^- are essentially identical: 85 kJ mol^{-1} . This at first may seem surprising, since the latter ion is larger and should better accommodate the negative charge. The charge distribution, evaluated using natural population analysis (NPA),²⁴ is shown in Table 3. When the chloride adds to SCl_2 , the charge on S changes little, and the excess negative charge resides mostly on the two axial chlorines.⁶ Similar charge redistribution occurs when chloride adds to thionyl chloride. Sulfur becomes slightly more positive, but oxygen gains almost no negative charge. Rather, the excess negative charge is again borne by the axial chlorines. Oxygen does not assist in delocalizing the anionic charge, so SOCl_3^- is not stabilized relative to SCl_3^- . Thus, they have similar bond energies. The analogous molecules PCl_3 and POCl_3 also have similar chloride affinities.²⁵

Gas-phase nucleophilic substitution at sulfur in sulfides, disulfides, and trisulfides proceeds by an addition-elimination pathway, having a triple-well potential energy surface.¹⁻⁴ When many electron withdrawing groups are placed on the central sulfur atom, the surface can alter and, as found for the reaction of SCl_2 with chloride, become a single well. The reaction studied here, SOCl_2 with chloride, is consistent with the previous result.

Further studies are under way to examine the nature of the reaction when the substrate carries electroneutral substituents.

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