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Negative Ion–Molecule Reactions in Sulfuryl Halides

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Abstract: The negative ion–molecule reactions in sulfuryl chloride, sulfuryl fluoride, and sulfuryl chloride fluoride are described. Their mass spectra have been determined as a function of pressure and time at different ionization energies. In SO_2Cl_2 the most abundant primary ion is Cl^-. It reacts with SO_2Cl_2 forming the secondary ions Cl_3^- and SO_2Cl^-. SO_2Cl^- reacts with the neutral leading to the formation of Cl_3^-. Other secondary ions are formed in relatively small amounts. Equilibrium studies made it possible to estimate the heat of formation of Cl_3^- as -71.8 kcal/mol^{-1}. In sulfuryl fluoride $SO_2F_3^-$ is formed by two different processes: a three-body attachment reaction of F^- with SO_2F_2 and the reaction of F_2^- with SO_2F_2 leading to $SO_2F_3^-$ and F. In sulfuryl chloride fluoride the primary ions F^- and Cl^- react with SO_2ClF leading to the formation of SO_2F^-. Rate studies were made by varying both pressure and time, and rate constants were obtained for most of the principal reactions.

Introduction

Ion–molecule reactions of negative ions with neutrals have been proved to be of considerable value for the elucidation of thermochemical values, in particular heats of formation, electron affinities, and ion chemistry in the absence of solvent influences. In a preliminary communication[1] we described the ion–molecule reactions in sulfuryl chloride and the formation of the negative trihalide ion, Cl_3^-. The existence of some negative trihalide ions in the gas phase has been mentioned previously, but no thermochemical values have been reported: in 1928, Hogness and Harkness[2] reported the ion–molecule reactions in iodine and the formation of I_3^-. Melton and coworkers[3] observed the negative trichloride ion in pure chlorine. Since Eyring and Rollefson[4] have predicted the stability of the neutral Cl_3 and since this molecule has also been suggested as the active intermediate in a number of photochemical reactions of chlorine, Melton and co-workers[3] were not able to decide whether the Cl_3^- ion observed was the product of an ion–molecule reaction or resulted from direct electron attachment of Cl_3. Stockdale, Compton, and Reinhardt[5] described the reaction of SF_6^- with hydrochloric acid leading to the formation of F_2Cl^- and the existence of the Br_3^- ion was established by the three body attachment reaction of Br^- with bromine.[6] Tiernan and co-workers[7] observed the formation of several heteronuclear trihalide ions and concluded, from isotope distribution measurements in Cl_2^-, that the intermediate of the endoergic charge transfer reaction

$$Cl^- + Cl_2 \rightarrow Cl_2^- + Cl \qquad (1)$$

at low translational energies is Cl_3^-. Their data suggest that the Cl_3^- intermediate is linear in accordance with earlier theoretical calculations[8] and with IR and Raman studies[9,10] carried out with various salts of IX_2^- (X = Cl, Br) which indicated a linear structure of the negative trihalide ions. The formation of Cl_3^- in sulfuryl chloride has been mentioned by Beauchamp but no further details have been given.[11] Recently Sullivan and Beauchamp[12] reported studies of negative ion reactions in SO_2Cl_2, SO_2F_2, and SO_2FCl with results that are quite different from ours. Those results will be discussed subsequently and an attempt made to rationalize the differences.

This paper presents a comprehensive study of the ion–molecule reactions in sulfuryl halides. The measurement of the equilibrium constant of the main reaction in sulfuryl chloride made it possible to deduce the thermochemical properties of Cl_3^-.

Experimental Section

A 12-in. 60° sector field magnetic mass spectrometer, previously described,[13] was utilized for this study. Modification of the ion source made it possible to study ion–molecule reactions up to a source pressure of 100 mTorr. A pulsing device enabled us to change the reaction time at constant pressure. Pressures in the ionization region were measured by a MKS Type 77 Baratron pressure meter connected directly to the ion chamber through a 0.25-in. i.d. opening in the flange upon which the ion source was mounted. The ionization region was separated from this opening only by a backing electrode (repeller) made of highly porous mesh fine wire. Temperature measurements were carried out with a copper–constantan thermocouple attached directly to the source.

Variation of the residence time of the ion in the chamber was accomplished by delaying an ion draw-out pulse over a continuously variable range of 0 to several microseconds after shutting off the electron grid pulse. A modified Bendix TOF pulsing circuit delivered the necessary pulses: a narrow (0.3-μs fwhm) electron grid pulse, which enabled the electrons to enter the ionization region, and a broader (3-μs fwhm) source endplate pulse, to draw out the ions. The repetition rate was 10 kHz.

Reaction rates were determined by two methods: (1) varying the ion source pressure and (2) varying the reaction time. In the pressure studies, the reaction time was calculated as the free fall time of the reactant ion under the influence of an electric field (normally with field strengths of about 3–12 V cm^{-1}) which was symmetric with respect to the electron beam and so to the ion formation axis. In the pulsed operation of the ion source (time studies) reaction time was the sum of delay time and the free fall time of the particular ion in the draw-out field.

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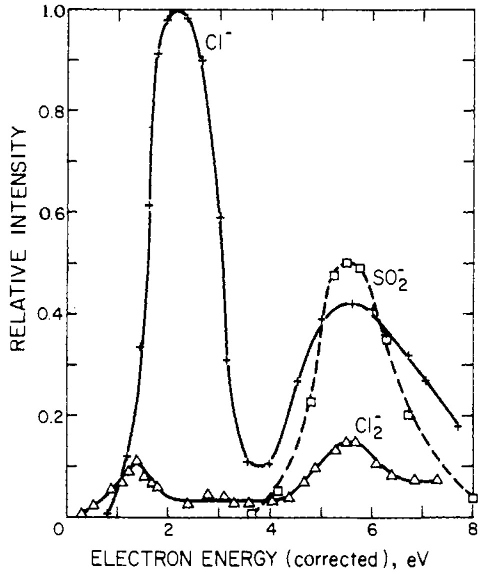

Figure 1. Ionization efficiency curves for negative primary ions in sulfuryl chloride.

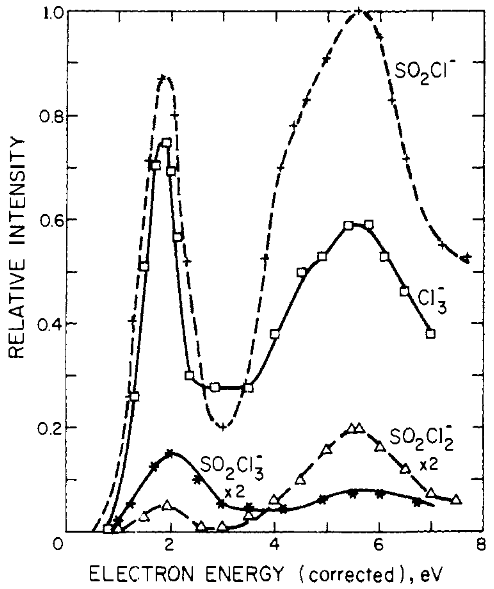

Figure 2. Ionization efficiency curves for negative secondary ions in sulfuryl chloride.

The sulfuryl chloride and sulfuryl chloride fluoride were obtained from the Aldrich Chemical Co., Inc. Sulfuryl chloride was purified by distillation and degassed on a vacuum line by several freeze-pump-thaw cycles. The positive mass spectrum showed only very little impurities (<0.5%) of hydrochloric acid and $SOCl_2$ (which probably gave SO^-, detected in low concentrations in some spectra at higher ionization energies). Sulfur dioxide and sulfuryl fluoride were obtained from the Matheson Co., Inc., and were used without purification.

As a check upon the reliability of our measurements, the rate of the reaction

$$S^- + COS \rightarrow S_2^- + CO \quad (2)$$

was determined by measuring the depletion of S^- and the formation of S_2^- as a function of time at constant ion source pressure and as a function of pressure at constant reaction time. Several measurements led to a value of k_2 of 4.1×10^{-10} cm^3 mol^{-1} s^{-1} in the pulsed source mode and of 4.3×10^{-10} cm^3 mol^{-1} s^{-1} with the ion source operated in the continuous mode. These values are in good agreement with the one of 3×10^{-10} cm^3 mol^{-1} s^{-1} reported earlier.[14]

Resonance capture potentials were determined at a source pressure of 1 mTorr for primary ions and of 17 mTorr for secondary ions. The electron energy scale was calibrated using the resonance maxima of S^- from COS at 2.2 eV[14] and of O^- from SO_2 at 5.0 and 7.4 eV.[15]

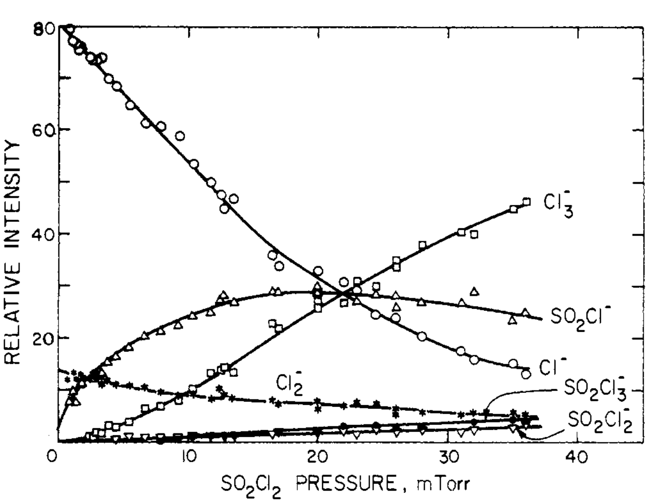

Figure 3. Fractional abundance of negative ions vs. SO_2Cl_2 pressure, with continuous source operation. Electron energy 1.6 eV; field strength 12 V cm^{-1}.

Table I. Heats of Formation Employed in This Study

M	ΔH_f(M), kcal mol^{-1}	ref
SO_2Cl_2	−84.8	16
SO_2	−70.9	16
Cl^-	−58.8	17
Cl_2^-	−56.7	18
Cl_3	25.7	19
SO_2F_2	−205	20
F	18.9	17
F^-	−62.2	21
F_2^-	−67.8	22
SO_2ClF	−133	16
ClF	−12.1	23

In the appraisal of various reactions thermochemical properties of various ions and molecules were needed. The values listed in Table I were employed for this purpose.

Results

A. Sulfuryl Chloride. Reactions. The dissociative resonance capture curves for the principal primary ions from SO_2Cl_2 are given in Figure 1. Minor amounts of SO_2Cl^- may also be formed as primary ions but at intensities too small to show here. It will be noted that Cl^- and Cl_2^- in the ratio of about 10:1 are the only primary ions of importance at the lower energy resonance; at the higher energy resonance these and SO_2^- are the important primary ions.

Figure 2 shows the ionization efficiency curves for the secondary negative ions formed in SO_2Cl_2 at a source pressure of 17 mTorr. The reactions leading to the formation of these ions will be discussed below.

Figures 3 and 4 show the variation of the intensities of the various ions with pressure and with retention time at the lower energy resonance. Both curves show that Cl^- is the direct precursor of both Cl_3^- and SO_2Cl^- and, further, that SO_2Cl^- also forms Cl_3^-. Thus

$$Cl^- + SO_2Cl_2 \rightleftarrows Cl_3^- + SO_2 \quad (3)$$

$$Cl^- + SO_2Cl_2 \rightarrow SO_2Cl^- + Cl_2 \quad (4)$$

$$SO_2Cl^- + SO_2Cl_2 \rightleftarrows Cl_3^- + 2SO_2 \quad (5)$$

Reactions 3 and 5 are shown as reversible which they appear to be when SO_2 is added.

Figures 5 and 6 show the effect of pressure and of time at the higher energy resonance. It will again be evident that re-

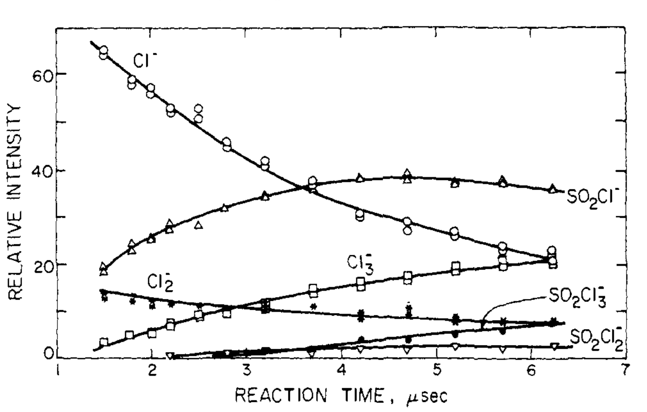

Figure 4. Fractional abundance of negative ions from SO_2Cl_2 vs. time. Electron energy 1.6 eV; source pressure 5.1 mTorr.

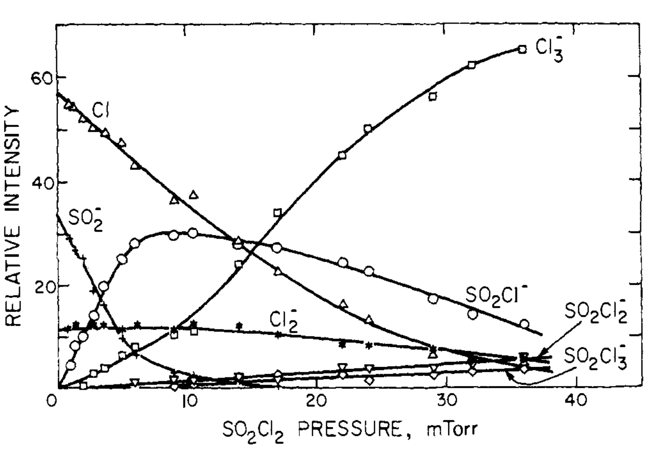

Figure 5. Fractional abundance of negative ions vs. SO_2Cl_2 pressure with continuous source operation. Electron energy 6.0 eV; field strength 8 V cm^{-1}.

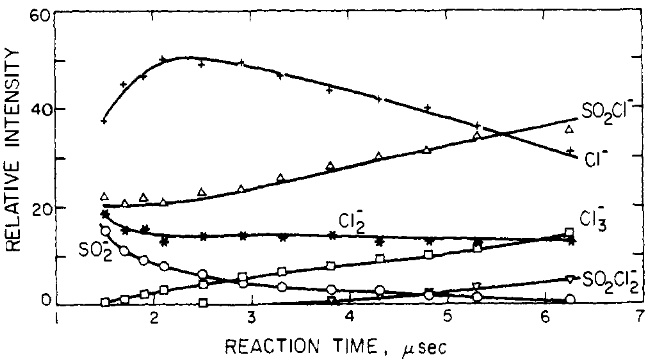

Figure 6. Fractional abundance of negative ions from SO_2Cl_2 vs. time. Electron energy 6 eV; source pressure 3 mTorr.

actions 3-5 occur. In addition Figure 6 shows that SO_2^- reacts primarily to form Cl^- by the reaction

$$SO_2^- + SO_2Cl_2 \rightarrow Cl^- + SO_2Cl + SO_2 \quad (6)$$

Figure 5 shows an extremely rapid decay of SO_2^- with a rate constant of 5×10^{-9} $cm^3/molecule{\cdot}s$. This is the largest second-order rate constant that we found with this system. This is reflected in the somewhat slower decay of Cl^- and the more rapid formation of SO_2Cl^- in this resonance as would be expected from the above mechanism. It is not clear from the data whether some SO_2Cl^- may be formed by reaction of SO_2^- with SO_2Cl_2.

The ions $SO_2Cl_2^-$, $SO_2Cl_3^-$, and $(SO_2)_2Cl^-$ were formed in small intensities as pressure or retention time was increased. The intensities in all instances were too small to permit a definite determination of the reaction(s) by which they were formed. However, reasonable deductions as to their precursors are possible.

It seems probable that $SO_2Cl_2^-$ is formed by charge exchange. The electron affinities of Cl^- and Cl_3^- (see below) are quite large (≥3.8 eV); if either of these ions transferred an electron to SO_2Cl_2, it would be necessary that $EA(SO_2Cl_2)$ be at least that great. If this were the case, other ions of lesser electron affinity (Cl_2^-, SO_2Cl^-, and SO_2^-) would also be expected to react rapidly to form $SO_2Cl_2^-$. This is not observed, so Cl^- and Cl_3^- are not the precursors of $SO_2Cl_2^-$.

The electron affinities of Cl_2 and SO_2Cl are in the neighborhood of 2.4-2.7 eV and seem more likely precursors of $SO_2Cl_2^-$ than Cl^- or Cl_3^-. Since Cl_2^- occurs as a primary ion and decreases in intensity very slowly with increasing pressure and time to about the extent at which $SO_2Cl_2^-$ is formed, it seems probable that $SO_2Cl_2^-$ is formed from it. However, SO_2Cl^- cannot be ruled out as a precursor of $SO_2Cl_2^-$.

Since $SO_2Cl_2^-$ is formed in the lower energy resonance, SO_2^- is not responsible for its formation in that energy range. At the higher energy resonance SO_2^- appears to transfer an electron to SO_2Cl_2 but with sufficient excess energy to cause $SO_2Cl_2^-$ to dissociate to Cl^- and SO_2Cl. Thus $SO_2Cl_2^-$ is probably formed by charge transfer from either Cl_2^- or SO_2Cl^-.

The formation of $SO_2Cl_3^-$ may occur by three-body addition of Cl^- to SO_2Cl_2 or by the transfer of Cl^- from SO_2Cl^- or Cl_3^- to SO_2Cl_2. We cannot be certain which of these reactions occurs. However, as will be seen subsequently, SO_2F_3 is formed both by addition of F^- in a three-body reaction and by transfer of F^- from F_2^-. It would not be surprising if $SO_2Cl_3^-$ were formed in a similar manner. However, as will be shown, $D(SO_2\text{-}Cl^-)$ and $D(Cl_2\text{-}Cl^-)$ are considerably less than $D(Cl\text{-}Cl^-)$, and so we expect that some of the $SO_2Cl_3^-$ is formed by the reactions

$$SO_2Cl^- + SO_2Cl_2 \rightarrow SO_2Cl_3^- + SO_2 \quad (7)$$

$$Cl_3^- + SO_2Cl_2 \rightarrow SO_2Cl_3^- + Cl_2 \quad (8)$$

The intensity of $S_2O_4Cl^-$ is too small to permit interpretation; however, it seems probable that this ion is formed by the reaction

$$SO_2Cl^- + SO_2Cl_2 \rightarrow S_2O_4Cl^- + Cl_2 \quad (9)$$

Reaction Rates. If SO_2 is added to the system, as we have done in several experiments, it is apparent that reactions 3, 5, 6, and 7 may be reversible. Of course, if Cl_2 is added, reactions 4 and 8 might also be reversible, but because of the corrosiveness of Cl_2 this was not attempted. The following equations can be written to express the rates of the most important processes:

$$d[Cl^-]/dt = -k_3[SO_2Cl_2][Cl^-] - k_4[SO_2Cl_2][Cl^-] + k_{-3}[SO_2][Cl_3^-] \quad (10)$$

$$d[Cl_3^-]/dt = k_3[SO_2Cl_2][Cl^-] - k_{-3}[SO_2][Cl_3^-] + k_5[SO_2Cl_2][SO_2Cl^-] - k_{-5}[SO_2]^2[Cl_3^-] \quad (11)$$

$$d[SO_2Cl^-]/dt = k_4[SO_2Cl_2][Cl^-] - k_5[SO_2Cl_2][SO_2Cl^-] + k_{-5}[SO_2]^2[Cl_3^-] \quad (12)$$

With the assumption that the reverse reaction rates are zero when no SO_2 is added, eq 10 leads directly to the sum of k_3 and k_4:

$$\ln \frac{[Cl^-]}{[Cl^-]_0} = (k_3 + k_4)[SO_2Cl_2]t \quad (13)$$

Replacing $[Cl^-]$ in eq 12, integrating and with the concen-

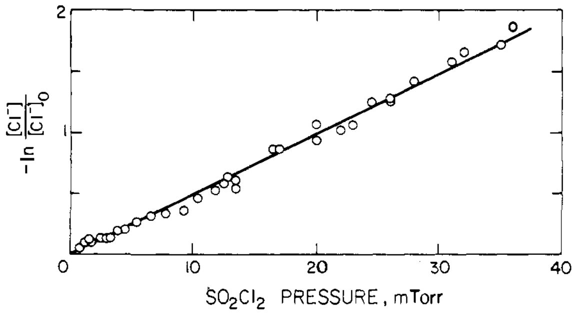

Figure 7. Typical plot for the determination of $k_3 + k_4$.

Table II. Values for k_3, k_4, and k_5 ($10^{10}\,k$, cm^3 mol^{-1} s^{-1}) Determined in This Study

electron energy, eV	$k_3 + k_4$	k_3	k_4	k_5
1.2	12	3	9	*a*
1.5	13	3	10	7
1.6	16	4	12	7
1.6	15	*b*	*b*	*b*
2.5	15	4	11	7
3.5	13	2	11	8
6.0	15	2	13	8

[a] Owing to small reaction time, the concentration of Cl$^-$ was too big to allow the calculation of k_5 (see text). [b] Pulsed source operation reaction time was not short enough to calculate k_4 and the concentration was too small to calculate k_5.

tration of SO_2Cl^- at time 0 equal to $[SO_2Cl^-]_0$, we get

$$\frac{[SO_2Cl^-]}{[Cl^-]_0} = \frac{k_4}{k_5 - k_3 - k_4}\{e^{-(k_3+k_4)[SO_2Cl_2]t} - e^{-k_5[SO_2Cl_2]t}\} + \frac{[SO_2Cl^-]_0}{[Cl^-]_0}e^{-k_5[SO_2Cl_2]t} \quad (14)$$

At low pressure or short reaction time, we can neglect reaction 5 and write

$$\frac{[SO_2Cl^-]}{[Cl^-]_0} = k_4[SO_2Cl_2]t + \frac{[SO_2Cl^-]_0}{[Cl^-]_0} \quad (15)$$

The ratio $[SO_2Cl^-]_0$:$[Cl^-]_0$ is constant and the slope of the ratio $[SO_2Cl^-]$:$[Cl^-]_0$ vs. pressure or time gives us k_4 and, since $k_3 + k_4$ is known, k_3.

On the other hand, at high pressure or long reaction time, the concentration of Cl$^-$ is small and we can neglect reactions 3 and 4. We then can write

$$\ln\frac{[SO_2Cl^-]}{[Cl^-]_0} = -k_5[SO_2Cl_2]t + \ln\left\{\frac{[SO_2Cl^-]_0}{[Cl^-]_0} - \frac{k_4}{k_5 - k_3 - k_4}\right\} \quad (16)$$

The semilogarithmic plot of $[SO_2Cl^-]$:$[Cl^-]_0$ vs. pressure or time gives us k_5.

A typical semilogarithmic plot of the ratio $[Cl^-]\cdot[Cl^-]_0$ vs. pressure is presented in Figure 7. The slope is $k_3 + k_4$. The values for the rate constants k_3, k_4, and k_5 are summarized in Table II for various electron energies.[26] The data indicate that the rate constants are independent of translational or excitational energy of the reacting ions. This is supported in part by the fact that, when an inert gas, argon, was added to a pressure of 80 μm, the extents of the various reactions were not affected. However, in this experiment the number of collisions of a moderately energetic Cl$^-$ ion with argon would be five or less depending upon the initial energy, and thus the kinetic energy of Cl$^-$ may not have been significantly reduced.

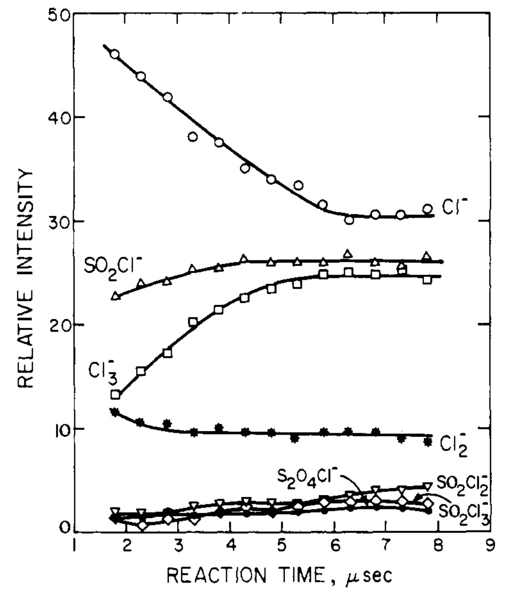

Figure 8. Typical plot of the fractional abundances of the negative ions vs. time from a mixture of SO_2Cl_2 and SO_2 ($[SO_2Cl_2]$:$[SO_2]$ = 1). Ion source pressure was 40 mTorr.

The value of the rate constant for reaction 6 was calculated from

$$[SO_2^-]/[SO_2^-]_0 = e^{-k_6[SO_2Cl_2]t} \quad (17)$$

k_6 measured to be 5×10^{-9} cm^3 mol^{-1} s^{-1}. It is the fastest reaction in this system.

Energetics. In an effort to ascertain whether reactions 3 and 5 were reversible and to try to approach equilibrium in these reactions, several experiments were performed employing mixtures of SO_2Cl_2 with SO_2 in various ratios. Results of a typical experiment are given in Figure 8, in which a 50:50 mixture of SO_2Cl_2 and SO_2 at a source pressure of 0.4 Torr was introduced into the source and various ion retention times employed. Obviously the intensities of Cl$^-$, SO_2Cl^-, and Cl_3^- attained steady-state intensities at retention times in the order of 5-7 μs.

At the steady state which Cl$^-$ appears to have reached at the higher energies, $d(Cl^-)/dt = 0$ and eq 10 becomes

$$k_{-3}(SO_2)(Cl_3^-) = (k_3 + k_4)(SO_2Cl_2)Cl^- \quad (18)$$

Rearranging,

$$\frac{(Cl_3^-)}{(Cl^-)} = \frac{(k_3 + k_4)(SO_2Cl_2)}{k_{-3}(SO_2)} \quad (19)$$

In the special case shown in Figure 8 $(SO_2) = (SO_2Cl_2)$ and at the steady state $(Cl_3^-)/(Cl^-) = 0.82$. Taking k_3 and k_4 as 0.4 and 1.6×10^{-9}, respectively, we obtain $k_{-3} = 1.96 \times 10^{-9}$.

$$K_{eq} = k_3/k_{-3} = 0.205 \text{ and } -\Delta G = -0.95 \text{ kcal/mol}$$

Since there is no change in the number of molecules in reaction 3, very little error will be introduced if it is assumed that $\Delta S = 0$ and hence that $\Delta H_r = 0.95$ kcal/mol, from which we compute $\Delta H_f(Cl_3^-)$ to be -71.7 kcal/mol. Employing the values given in Table III, we obtain the values of K_3 shown and from these an average value of ΔG of 0.86 kcal/mol and an average $\Delta H_f(Cl_3^-)$ of -71.8 kcal/mol.

Since SO_2Cl^- seems to disappear by some reactions other than reaction 5, eq 12 cannot be successfully treated by the method employed with eq 10. However, if reaction 5 were

Table III. Values for the Equilibrium Constant K_3 and the Free Energy Changes ΔG_3 Determined in This Study

(SO_2Cl_2), mTorr	(SO_2), mTorr	temp, K	I_{Cl^-}	$I_{SO_2Cl^-}$	$I_{Cl_3^-}$	K_3	ΔG_3, kcal mol^{-1}
25	24	363	0.23	0.28	0.30	0.31	0.71
25	26	353	0.26	0.27	0.25	0.25	0.73
20	20	350	0.30	0.27	0.24	0.20	0.97
20	30	353	0.33	0.28	0.21	0.24	0.86
20	30	360	0.35	0.31	0.21	0.25	0.82
20	21	358	0.31	0.30	0.24	0.20	0.96
						av	0.86

approaching equilibrium

$$k_5(SO_2Cl_2)(SO_2Cl^-) = k_{-5}(SO_2)^2(Cl_3^-) \quad (20)$$

which, when (SO_2Cl_2) = (SO_2), yields $k_5/k_{-5} = K_{eq}$ = (SO_2), which at 0.02 Torr is 2.6×10^{-5} atm and would result in ΔG = 6.3 kcal/mol. This is too large a value to permit reaction 5 to approach equilibrium at the conditions employed in these studies, so we are unable to obtain a reasonable value of k_{-5} or K_{5eq}. In spite of this it is possible to approach values for the heats of formation of some product ions.

Even at the lowest electron energies at which Cl^- is detected, excess energy has been introduced into the molecule. In a preliminary measurement in this laboratory Wang[24] has found that Cl^- is formed with approximately 10 kcal/mol of kinetic energy over the lower energy resonance. The center of mass collision energy of Cl^- with SO_2Cl_2 would then be 8 kcal/mol. Thus from reaction 4 we can now compute $\Delta H_f(SO_2Cl^-) \leqslant -136$ kcal/mol. On the other hand, from reaction 5, employing the heat of formation of Cl_3^- determined above, we calculate $\Delta H_f(SO_2Cl^-) \leqslant -129$ kcal/mol. Further, the fact that SO_2Cl^- appears to be stable at the conditions employed in these studies means that $\Delta H_f(SO_2Cl^-)$ must be less than -130 kcal/mol, or else it would dissociate to Cl^- and SO_2. Thus it seems reasonable that $\Delta H_f(SO_2Cl^-)$ must be near -135 kcal/mol.

As was discussed earlier, $SO_2Cl_3^-$ may be formed by one or more of the following reactions:

$$SO_2Cl^- + SO_2Cl_2 \rightarrow SO_2Cl_3^- + SO_2 \quad (7)$$

$$Cl_3^- + SO_2Cl_2 \rightarrow SO_2Cl_3^- + Cl_2 \quad (8)$$

$$Cl_2^- + SO_2Cl_2 \rightarrow SO_2Cl_3^- + Cl \quad (21)$$

$$Cl^- + SO_2Cl_2 \rightarrow SO_2Cl_3^- \quad (22)$$

Reactions 7 and 22 require $\Delta H_f(SO_2Cl_3^-)$ to be less than -149 kcal/mol, assuming $\Delta H_f(SO_2Cl^-)$ to be -135 kcal/mol. Reactions 8 and 21, which appear not to occur, set lower limits on $\Delta H_f(SO_2Cl_3^-)$ of -157 and -169 kcal/mol, respectively. Thus, we conclude that $\Delta H_f(SO_2Cl_3^-)$ lies between -149 and -157 kcal/mol.

If $S_2O_4Cl^-$ is formed by reaction 9, a postulate that is certainly not proved, we find that $\Delta H_f(S_2O_4Cl^-) \leqslant -220$ kcal/mol.

B. Sulfuryl Fluoride. Figure 9 shows the relative ion currents of the negative ions in sulfuryl fluoride as a function of source pressure. The dominant secondary ion in SO_2F_2 is $SO_2F_3^-$. It is formed by two different reactions:

$$F^- + SO_2F_2 \xrightarrow[k_{23}]{SO_2F_2} SO_2F_3^- \quad (23)$$

and

$$F_2^- + SO_2F_2 \xrightarrow{k_{22}} SO_2F_3^- + F \quad (24)$$

The third-order rate constant is calculated as 1.3×10^{-27} cm^6 mol^{-2} s^{-1} and k_{24} is 8.6×10^{-11} cm^3 mol^{-1} s^{-1}.

Again $SO_2F_2^-$ is formed via a charge-transfer process the nature of which is not known. It is likely that F_2^- is responsible for this charge exchange reaction. In that case, k_{24} represents the sum of the two rate constants. The concentration of SO_2F^- does not change with increasing pressure indicating that the reaction of SO_2F^- with SO_2F_2 forming $SO_2F_3^-$ is endothermic. Reaction 23 sets an upper limit of -292 kcal/mol for $\Delta H_f(SO_2F_3^-)$. Reaction 26 (see below) sets an upper limit of -192 kcal/mol for $\Delta H_f(SO_2F^-)$. Since SO_2F^- does not react to give $SO_2F_3^-$, the lower limit of $\Delta H_f(SO_2F_3^-)$ must be -326 kcal/mol.

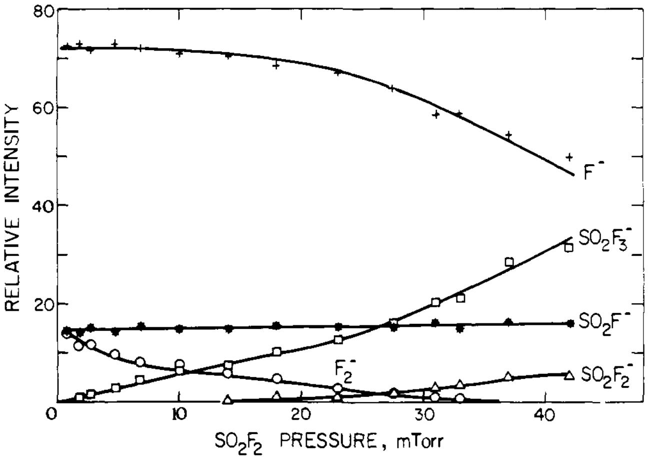

Figure 9. Relative intensities of the negative ions vs. pressure from sulfuryl fluoride. Continuous source operation with a field strength in the ionization chamber of 3.3 V cm^{-1}

C. Sulfuryl Chloride Fluoride. The primary ions in SO_2ClF formed by dissociative electron attachment processes at an electron energy of 3.2 eV are F^- and Cl^- with SO_2F^- and ClF^- formed in low abundances. With increasing pressure in the reaction chamber (Figure 10) SO_2F^- is formed by reactions of F^- (reaction 25) and Cl^- (reaction 26) with SO_2ClF.

$$F^- + SO_2ClF \rightarrow SO_2F^- + ClF \quad (25)$$

$$Cl^- + SO_2ClF \rightarrow SO_2F^- + Cl_2 \quad (26)$$

The data in Figure 10 indicate that the reaction of F^- with the neutral leads also to the formation of Cl^-

$$F^- + SO_2ClF \rightarrow Cl^- + SO_2F_2 \quad (27)$$

No other secondary ions were observed. Reaction 26 leads to a calculated upper limit of the heat of formation of SO_2F^- of -192 kcal mol^{-1}

The depletion of the F^- concentration as a function of ion source pressure allowed us to calculate the sum of the rate constants k_{25} and k_{27}. Again the slope of the semilogarithmic plot of $[F^-]/[F^-]_0$ vs. pressure or time gives us $k_{25} + k_{27}$, which we find to be 2.1×10^{-9} cm^3 molecule^{-1} s^{-1}.

Discussion

We are concerned to find that our results differ considerably from those published by Beauchamp and his associates. In an

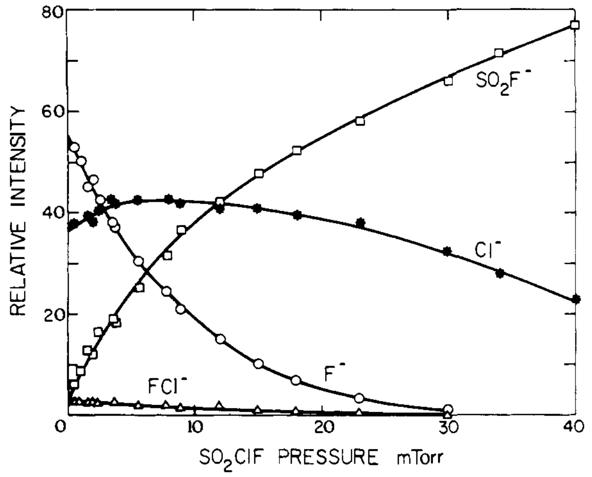

Figure 10. Relative abundances of the negative ions vs. pressure from SO_2ClF. Ionization energy was 3.2 eV and the field strength in the source was 4.7 V cm^{-1}

earlier paper[11] he reported without elaboration the observation of reaction 3. In a more recent paper Sullivan and Beauchamp[12] reported a more detailed study of negative ion reactions in SO_2F_2, SO_2Cl_2, and SO_2ClF. In their studies they employed an ICR spectrometer in which 70-eV electrons ionized the gas. The secondary electrons were thought to be thermalized by many collisions before undergoing dissociative attachment reactions with the gases under investigation.[25] In our study a conventional sector field mass spectrometer was employed at electron energies suitable to bring about dissociative resonance capture reactions. Although we attempted to study the formation and reactions of the various ions over the electron energy range of the resonances, we could not detect ions from any of the three molecules at electron energies as low as thermal, whereas Sullivan and Beauchamp were able to do so.

The primary ions reported by Sullivan and Beauchamp[12] and those found in this study differ considerably except in the case of SO_2F_2. With SO_2F_2 both groups found F^- SO_2F^-, and F_2^- in similar proportions and decreasing abundance in the order given. This is also the order of increasing endothermic heat of reaction. The fact that F_2^- is formed requires that the electron energy be $\geqslant 41$ kcal/mol (using $\Delta H_f(SO_2F_2) = -181$ kcal/mol as used by Sullivan and Beauchamp), or $\geqslant 65$ kcal/mol employing our value. This value, incidentally, is only slightly less than the electron energy that we employed.

With SO_2Cl_2 in the lower energy resonance we found only Cl^- and Cl_2^- ions in the ratio of about 9:1 Sullivan and Beauchamp[12] found Cl^-:SO_2Cl^-: Cl_2^- in the ratio 49:43:8. Since, even with thermal electrons, the formation of all of these ions is exothermic, it is not surprising that, at electron energies of 1.5–2 eV, the SO_2Cl^- would have sufficient internal energy to dissociate into $Cl^- + SO_2$ and thus account for our failure to detect SO_2Cl^- as a primary ion.

With SO_2ClF Sullivan and Beauchamp[12] reported only Cl^- and SO_2F^- in the ratio 16:84. In this study we find Cl^-:F^-: SO_2F^-· FCl^- = 36:55:4:4. If we assume that Cl^- and F^- are formed along with SO_2 and F or Cl, we find that these reactions are about equally endoergic. The formation of SO_2F^- is slightly exoergic and that of SO_2Cl^- is slightly endoergic. Thus with electrons of sufficiently low energy we would expect to find an abundance of SO_2F^- ions and perhaps some SO_2Cl^-. However, if there were a small amount of excess energy, SO_2Cl^- would dissociate into $Cl^- + SO_2$ whereas nearly 2 eV of internal energy is required if SO_2F^- is to be dissociated into F^- and SO_2. Thus with the lower electron energies employed by Sullivan and Beauchamp it is not surprising that they found principally SO_2F^- along with some Cl^- whereas with our higher energy electrons both SO_2Cl^- and SO_2F^- could be dissociated to give principally Cl^- and F^- ions.

In addition to differences in primary ions between our results and those of Sullivan and Beauchamp,[12] there are also differences in the ion-molecule reactions observed. Again, the greatest similarities occur with SO_2F_2 in which both groups observed the formation of SOF_3^- by reaction 24. In addition, we detected the attachment of F^- to SO_2F_2 by a third-order reaction. Sullivan and Beauchamp did not report this reaction, as would be expected since the time between collisions in ICR cells is usually so great that the excited attachment product dissociates before it can undergo a stabilizing collision.

The only ion-molecule reactions in SO_2Cl_2 reported by Sullivan and Beauchamp[12] are reactions 4 and 7. We detected reaction 4 and also observed the formation of $SO_2Cl_3^-$ in small amounts, probably by reaction 7. We detected reaction 4 and also observed the formation of $SO_2Cl_3^-$ in small amounts, probably by reaction 7. However, we also observed the formation of Cl_3^- by both reactions 3 (also reported by Beauchamp[11]) and 5 as well as the formation of $SO_2Cl_2^-$ and $(SO_2)_2Cl^-$ by reactions that could not be definitely established. Since $SO_2Cl_3^-$ is obviously stable, it would not be surprising if it were formed as an intermediate in reactions 3, 4, and perhaps 5. With precursor ions having some kinetic energy such as occurred in our experiments, the excited $SO_2Cl_3^-$ might be expected to dissociate either to $Cl_3^- + SO_2$ or to $SO_2Cl^- +$ Cl_2. However, with the less energetic ions employed in the experiments of Sullivan and Beauchamp,[12] the $SO_2Cl_3^-$ might well be stable when formed by reaction 7 but not when formed by reactions 3 and 4, where the Cl^- precursor must have been formed with some kinetic energy, even under the conditions in the ICR instrument. If this interpretation is correct, it would appear that a small amount more of energy must be required to form Cl_3^- than SO_2Cl^- from $SO_2Cl_3^-$. This would be in keeping with the fact that in Beauchamp's instrument Cl_3^- was formed by reaction 3 in some experiments but not in others as would occur if small differences in energy occurred. It thus appears that the differences in behavior can be rationalized if, as appears probable, the primary (and to a lesser extent the secondary) ions in our instrument occurred with more energy than those in the ICR instrument.

The ion-molecule reactions observed in the two studies of SO_2ClF are quite different. This is due to the fact that, because of the difference in electron energies, the primary ions that are formed are different and probably contain quite different amounts of energy. Thus with the lower electron energy employed by Sullivan and Beauchamp[12] only Cl^- and SO_2F^- were formed as primary ions. The Cl^- ion formed reacted to produce SO_2F^- as was found in our study. We detected SO_2F^- in only very small initial intensity but found that it was formed rapidly by reaction of both F^- and Cl^- with the parent neutral. Presumably, at our conditions there was enough excess energy to cause any primary SO_2F^- to dissociate further to F^- and SO_2. We also found that some Cl^- is formed by reaction 27. Since at Sullivan and Beauchamp's conditions no F^- ion was formed, neither reaction 25 nor 27 could have been detected by them. On the other hand, they observed a very slow reaction of SO_2F^- with the parent molecule to produce SO_2Cl^- whereas we did not Possibly the SO_2F^- at our conditions had enough excess energy to dissociate any SO_2Cl^- that might have been formed, but this, of course, is no more than speculation.

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Gas Phase Nucleophilic Displacement Reactions of Negative Ions with Carbonyl Compounds

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Abstract: The rates of a number of nucleophilic displacement reactions $X^- + RCOY \rightarrow Y^- + RCOX$ have been studied with pulsed ion cyclotron resonance spectroscopy, where X = F, Cl, CH_3O, CN, SH; R = CH_3, C_2H_5, $(CH_3)_2CH$, $(CH_3)_3C$, C_6H_5, CF_3; Y = Cl, Br. The results suggest that the potential surfaces contain at least two minima separated by a barrier. The kinetic model is analyzed using RRKM theory, which provides an estimate of the barrier height. The estimated stability of the "tetrahedral intermediate" is examined critically in terms of ions of comparable structure.

Introduction

The carbonyl group plays a central role in chemistry because of its participation in a wide variety of reactions of chemical and biochemical importance.[1] Thus, over the years, there has been considerable activity in the mechanistic study of reactions of carbonyl groups. Of the many reactions usually undergone by carbonyl substrates, nucleophilic displacements have been among the most extensively investigated, especially because of their relevance to the enzymatic catalysis of reactions of carboxylic acid derivatives.[2]

Most of these studies have been in solution with the attendant complications of the solvent system and our work was motivated by the thought that a systematic study of these reactions under solvent-free conditions would improve our understanding of the intrinsic factors controlling the reactivity of carbonyl substrates. We have therefore undertaken a detailed study of gas phase ionic nucleophilic displacement reactions at carbonyl centers using ion cyclotron resonance (ICR) spectroscopy.

There have been studies by other workers on some aspects of the reactions of ionic nucleophiles with carbonyl substrates in the gas phase. For example, Bowie and co-workers have reported the formation of adducts of acetic and trifluoroacetic anhydrides which are suggested to be collisionally stabilized tetrahedral adducts.[3] Riveros and co-workers have investigated reactions of ionic nucleophiles with some carbonyl substrates and found that other pathways in addition to conventional nucleophilic displacement at the carbonyl center are important in many cases.[4] Comisarow has also shown[5] that nucleophilic attack of CD_3O^- on $CF_3CO_2CH_3$ and $C_6H_5CO_2CH_3$ in the gas phase leads to displacement of $CF_3CO_2^-$ and $C_6H_5CO_2^-$ rather than CH_3O^-.

In a previous paper on this subject, we focused our attention on the formation and detection of adducts of nucleophiles with acyl halides.[6] In that paper, we showed that at least in one case the addition complex has structurally equivalent halides, which suggests a tetrahedral structure. Thermochemical estimates which are reported in this paper show, however, that some acyl halide addition complexes must have structures other than tetrahedral—presumably loose association complexes. In this paper, we also report on our kinetic and mechanistic studies of reactions of ionic nucleophiles toward carbonyl substrates in the gas phase. Variations in the nucleophile (X^-), leaving group (Y^-), and alkyl substrate (R) are found to affect the rate constants in a manner which is not consistent with the single minimum surface postulated from solution and theoretical studies. The similarities and differences in gas-phase structure-reactivity behavior from solution behavior are discussed.

Experimental Section

Instrumentation. A Varian V-5900 drift mode ion cyclotron resonance spectrometer was used for the nonkinetic experiments reported in this work.[7] The auxiliary equipment has been described previously[8] and typical operating parameters are as described earlier.[6] For the nonkinetic and some of the kinetic experiments, the pulsed double resonance and ion ejection techniques[9] were used either to confirm a particular reaction or to eliminate one reaction while monitoring another.

The kinetic experiments were done using a pulsed ion cyclotron resonance spectrometer.[10] Marginal oscillator frequencies of 153.5

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