

CROSSED-BEAM CHEMILUMINESCENCE: THE ALKALINE EARTH REARRANGEMENT REACTION $M + S_2Cl_2 \rightarrow S_2^* + MCl_2$

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The reaction of the heavier Group IIA metal atoms Ba, Sr, and Ca with S_2Cl_2 under crossed-beam conditions produces a chemiluminescent spectrum in which the $S_2 B^3\Sigma_u^- - X^3\Sigma_g^-$ emission bands are the most prominent feature. In addition, chemiluminescence is also observed from excited states of the alkaline earth monochlorides and from a "pseudo-continuum" which is believed to originate from an excited polyatomic metal halide, probably the alkaline earth dichloride. More than 100 bands are assigned to the $S_2 B-X$ band system; the vibrational levels of the $S_2 B$ state are found to be populated by the reaction in a non-thermal manner. The reaction forming S_2^* is determined to be first order with respect to both the ground state metal atom and the disulfur dichloride molecule. Phenomenological cross sections for removal of metal atoms from the metal beam by S_2Cl_2 are $162 \pm 20 \text{ \AA}^2$ for Ba, $105 \pm 20 \text{ \AA}^2$ for Sr, and $92 \pm 20 \text{ \AA}^2$ for Ca, which is consistent with an electron jump model if the vertical electron affinity of S_2Cl_2 is 3.25 eV. Absolute photon yield measurements indicate that less than 1% of the reaction products are S_2^* molecules that emit in the 2800–6000 Å region. From the single-collision chemiluminescence spectra the following dissociation energies are estimated: $D_0^0(Cl-S_2Cl) = 44.2 \pm 5 \text{ kcal/mole}$ and $D_0^0(S_2-Cl) = 54 \pm 5 \text{ kcal/mole}$. A speculation is offered that most of the reaction exoergicity appears in the S_2^* product when the S_2Cl_2M collision complex passes through a nearly-planar, five-member ring structure in separating to form products.

1. Introduction

In many elementary gas-phase atom-transfer reactions,



the newly-formed AB product is produced in an electronically excited state AB^* [1]. A spectroscopic analysis of the subsequent AB^* chemiluminescence provides direct information on the reaction dynamics provided collisions do not intervene between the time of AB^* formation and AB^* emission. Thus the rotational and vibrational internal state distributions of AB^* are most accurately studied in crossed-beam chemiluminescence experiments [2–12]. We report here the observation of $S_2 B^3\Sigma_u^- - X^3\Sigma_g^-$ chemiluminescence produced in a crossed-beam experiment utilizing the reactions of ground-state alkaline earth

atoms ($M = Ba, Sr, Ca$) with S_2Cl_2 under single-collision conditions. We conclude that among possible elementary reaction steps the following rather surprising rearrangement occurs



whereby most of the reaction exoergicity appears in the old S–S bond.

The $S_2 B-X$ band system, analogous to the Schumann–Runge system of O_2 [13], is well known [14–16]. The band system is readily observed in high-pressure flames containing sulfur vapor [14,17,18], and in shock-tube studies of sulfur compounds, SF_6 [19] and H_2S [20]. In these experiments the $S_2 B$ state is populated by the mechanism of inverse predissociation in which two sulfur atoms in their 3P ground states combine along a potential energy surface that makes a radiationless transition to the $S_2 B$ state. The only example for which it appears that the $S_2 B$ state might be populated directly in an elementary reaction step is the unpublished study by Setser [21] of the action of

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argon metastables on S_2Cl_2 vapor at a total pressure in the torr region. Unfortunately, insufficient information is available to permit a definitive conclusion whether or not S_2^* is formed in one collision. The present work indicates that the disulfur dichloride molecule, S_2Cl_2 , (commonly given the misnomer sulfur monochloride) may have special structural features which promote S_2 formation. The equilibrium geometry of S_2Cl_2 is like that of H_2O_2 or F_2O_2 , namely, a skew, chain structure [22] in which the two S-S-Cl planes are nearly perpendicular (see fig. 1). We will present some simple molecular orbital arguments to explain how the reaction exoergicity appears in the central S-S bond when the terminal Cl atoms are removed.

2. Experimental

2.1. Chemiluminescence spectra

The experimental setup, called LABSTAR, has been described previously [12]. A vertical metal beam is generated in a resistance-heated, disposable, stainless steel oven. The materials are purchased from Fisher and used without further purification. The temperature is chosen to give about 0.1–0.3 torr pressure of metal vapor, which escapes through a 6 mm long, 0.4 mm wide rectangular slit. An effusive beam of metal atoms enters the reaction chamber through a heated $1 \times 10 \text{ mm}^2$ slit and crosses a poorly collimated horizontal gas beam, produced in a multichannel, stainless-steel, capillary array. The reaction chamber is separately pumped by both a 6" diffusion pump and a large liquid-nitrogen-

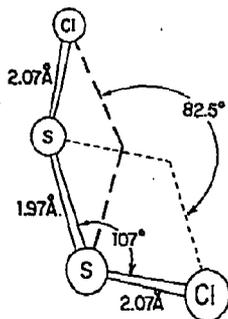


Fig. 1. Structure of disulfur dichloride. S_2Cl_2 has a skew, chain structure (C_2 symmetry) with a barrier to internal rotation about the S-S bond. The data are from Hirota [22].

cooled trap. The background pressure in the main chamber is in the 10^{-6} torr region with the beams on. The chemiluminescence is observed at right angles to both beams through a quartz window and collected by a 3.6 cm dia quartz lens of 24 cm focal length, which focuses light from the reaction zone onto the entrance slit of a spectrometer. This 1 m Interactive Technology Czerny-Turner spectrometer is operated in first order with a Bausch and Lomb 1200 groove/mm grating blazed at 5000 Å. The resolution of this instrument under our experimental conditions (1 mm slits) is 10 Å. For more accurate measurements of bandhead positions and for higher resolution studies of individual bands, spectra are taken with 100 μm slits corresponding to a resolution of 1 Å. In all cases the same cooled Centronic S20Q photomultiplier was used. The photomultiplier signal serves as the input to a fast picoammeter (Keithley Model 417) whose output drives a stripchart recorder.

The combined response of the spectrometer and photomultiplier was calibrated using a standard lamp. For this purpose we measured the intensity of a 200 W tungsten-iodine lamp (General Electric Model 6.6A/T4Q/1C1-200W) operated at a current of 6.5 A. The relative intensity of this lamp as a function of wavelength is taken from the work of Stair [23].

A calibrated cutoff filter was used to avoid contributions from the second order of the grating. Throughout the intensity measurements as a function of wavelength, the strength of the total chemiluminescence was continuously monitored in preliminary experiments to allow us to correct for any drifts caused by change in the S_2Cl_2 pressure or the metal beam flux. A correction by an amount of nearly $\pm 10\%$ was necessary for long-term drifts in beam intensities (we did not correct for variations in the detection efficiency), although typical drifts in the recording of a single spectrum (30 min or less) was closer to $\pm 3\%$.

Disulfur dichloride (S_2Cl_2) supplied by Fisher, with a purity higher than 99.5%, is used after distillation under vacuum. This is necessary in order to avoid chemiluminescence from possible impurities, especially Cl_2 and SCl_2 . The relatively low vapor pressure of S_2Cl_2 at room temperature (≈ 10 torr) and its extremely corrosive nature require special handling. The corrosion is minimized by using Kel-F grease and constructing the gas inlet system from only Teflon and stainless steel valves and fittings. The S_2Cl_2 is taken from a glass con-

tainer immersed in a temperature bath (20°C); the flow rate is controlled by a needle valve. This method maintains a uniform flow of reagent, as shown by the constant intensity of the chemiluminescence emission. The vapor pressure of S_2Cl_2 as a function of temperature is known [24]; to measure the dependence of the chemiluminescence intensity on S_2Cl_2 flux, the pressure inside the gas inlet system is varied by changing the temperature of the bath.

2.2. Cross section measurements

The phenomenological total cross section for removal of the atoms from the metal beam has been determined previously by measuring the change in the chemiluminescent intensity as a function of increasing gas pressure in a beam-gas arrangement [2,3,10]. A superior method is to direct the atomic beam into a long glass tube filled at a fixed (low) pressure of gas, and to record the chemiluminescent intensity as a function of distance along the tube (see fig. 2). This technique was used previously in the studies of alkaline earth reactions with chlorine dioxide [12]. The tube is 500 mm long and the atomic beam enters through a 2 mm hole, which collimates the metal beam so that it passes through the entire tube, and defines the length reference point ($x = 0$).

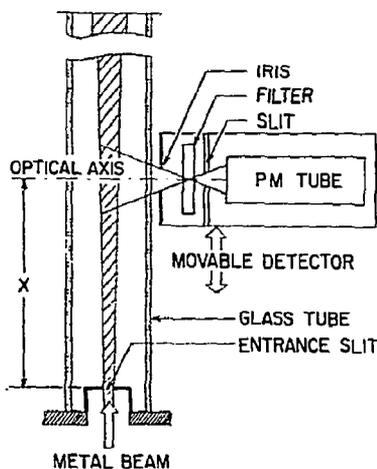


Fig. 2. Experimental arrangement for total cross section measurements. Different Corning filters are placed in front of the photomultiplier to isolate the wavelength region of interest. The distance x is measured from the collimating slit to the zone viewed by the photomultiplier.

In order to ensure that the movement of the optical detection system did not alter the detector sensitivity, the following test was made. The glass tube was filled with I_2 vapor to a pressure of $\approx 10^{-4}$ torr. The output of an argon ion laser at 5145 Å, expanded in diameter to match approximately the diameter of the metal beam, was directed through the center of the glass tube. The intensity of the well-known I_2 fluorescence series was then measured as a function of photomultiplier position. Only in the neighborhood of the entrance aperture ($x \leq 10$ mm) was it found that the fluorescent intensity was not constant, probably because of limited field of view.

The residual pressure in the glass tube was $\leq 2 \times 10^{-6}$ torr. The S_2Cl_2 is introduced directly from a trap containing liquid S_2Cl_2 at a temperature of 195–225 K, corresponding to a pressure of 5×10^{-6} to 2×10^{-4} torr. At low pressures, almost all metal atoms make at most one collision with an S_2Cl_2 molecule. We observe that the visible chemiluminescence is sharply confined to the volume intersected by the metal beam. This indicates that the major chemiluminescent species has a short radiative lifetime less than 10^{-5} s and that the contribution to the chemiluminescence from either secondary collisions or wall reactions is negligible under these conditions.

3. Results

3.1. Appearance of the chemiluminescent spectra

Fig. 3 presents a typical chemiluminescent spectrum obtained from the crossed-beam reaction $Ba + S_2Cl_2$. A broad feature beginning near 2800 Å, peaking around 4200 Å, and extending through the visible is seen to dominate the emission. On closer examination, this feature is observed to have many closely-spaced maxima and minima. Almost all the small peaks are found to correspond with the bandhead positions assigned by Kopp, Lindgren, and Rydh [25] to the $S_2 B^3\Sigma_u^- - X^3\Sigma_g^-$ system. In addition, the $BaCl A, B,$ and C states are identified from their characteristic transitions to the ground state. As will be discussed later, a pseudo-continuum originating from a polyatomic emitter appears to underlie the $S_2 B-X$ band system. Unfortunately, the contribution from this structureless continuum to the chemiluminescent spectrum seems to be comparable,

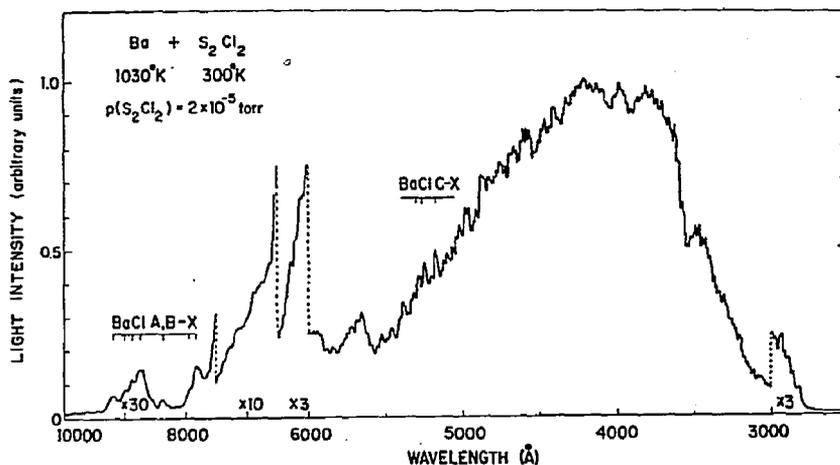


Fig. 3. The $\text{Ba} + \text{S}_2\text{Cl}_2$ chemiluminescence spectrum. Emission from the S_2 B state is seen from 2800–7000 Å; in addition, emission from the BaCl A, B, and C states is identified. The wavelength scale is compressed for the region 6000 Å–10 000 Å and the intensity scale is expanded as marked. The spectrum is taken with 10 Å resolution.

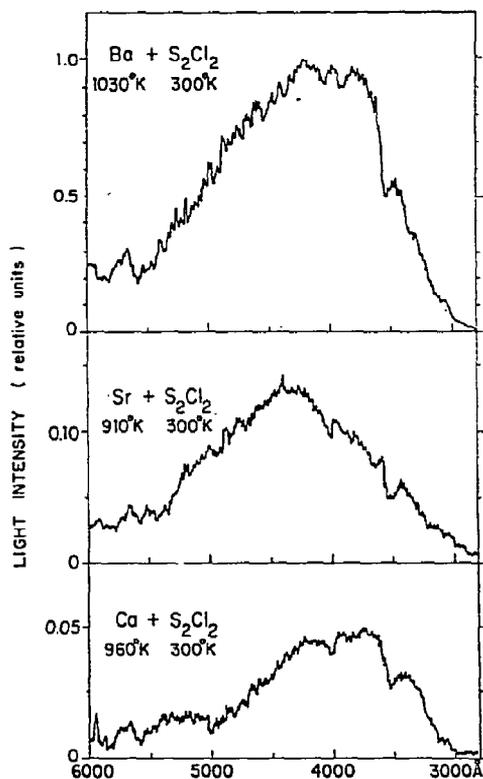


Fig. 4. Comparison of the chemiluminescent spectra for the three reactions studied. The relative intensities for the three reactions are marked. All spectra are normalized to the intensity maximum of the $\text{Ba} + \text{S}_2\text{Cl}_2$ emission. They are taken with 10 Å resolution and with a fixed S_2Cl_2 density of 2×10^{-5} torr.

thus complicating the analysis of relative band intensities in $\text{Ba} + \text{S}_2\text{Cl}_2$.

The chemiluminescent spectra from the reactions of Sr and Ca with S_2Cl_2 have the same gross appearance. Fig. 4 presents a comparison of the different alkaline earth metals in the spectral region 2800–6000 Å. Once again sharp peaks can be identified as arising from the S_2^* emitter (see table 1). However, the contributions from the pseudo-continua for Sr and Ca with S_2Cl_2 appear to be comparable and in any case are much less than that for Ba with S_2Cl_2 .

Emission from the A and B states of SrCl and CaCl are also seen. Higher resolution scans of the three alkaline earth monochloride spectra are presented in figs. 5–7 for selected bands. In each case the $\Delta v = 0$ sequence is shown since it is most prominent. The highest v' level observed is marked in each figure. This information will be used in section 3.3 to place lower bounds on the $\text{Cl}-\text{S}_2\text{Cl}$ bond energy.

We have attempted to compare in fig. 4 the relative intensities of the chemiluminescent features for the three alkaline earth metals. However, there are several complicating factors. First of all, the vapor pressure data for S_2Cl_2 given by Harvey et al. [24] may be uncertain. We have taken the special precaution of redistilling the S_2Cl_2 sample before usage to remove impurities. Since the source temperature was the same for the three different reactions, we believe that variations in S_2Cl_2

Table 1
Relative emission rates $n(v', v'')$ of the S_2 B-X (v', v'') bands observed in the reactions $M + S_2Cl_2$, $M = Ba, Sr, Ca$

v', v''	λ_{obs}	$q(v', v'')$	$n(v', v'')$		
			Ba	Sr	Ca
10,0	2786	0.049	0.16	0.08	<0.02
9,0	2830	0.040	0.26	0.28	<0.02
10,1	2860	0.057	0.19	0.13	<0.02
8,0	2886	0.030	0.44	0.51	0.07
7,0	2894	0.021	0.68	0.33	0.22
8,1	2918	0.069	0.47	0.42	0.09
6,0	2925	0.013	0.92	0.38	0.65
7,1	2952	0.064	0.65	0.39	0.17
5,0	—	0.007	—	—	—
6,1	2983	0.053	0.90	0.43	0.53
4,0	—	0.003	—	—	—
7,2	3015	0.057	0.60	0.45	0.19
5,1	3020	0.037	0.89	0.85	0.40
3,0	—	0.001	—	—	—
6,2	3056	0.071	0.82	0.40	0.55
4,1	3065	0.023	1.00	0.80	0.66
5,2	3089	0.073	0.83	0.79	0.45
3,1	3104	0.011	0.96	0.96	0.80
4,2	3130	0.060	0.99	0.69	0.66
2,1	—	0.004	—	—	—
5,3	3157	0.059	0.92	0.83	0.41
3,2	3173	0.039	0.84	0.93	0.94
4,3	3200	0.078	0.96	0.71	0.69
2,2	3219	0.019	0.96	0.97	1.00
3,3	3243	0.074	0.86	1.00	0.91
1,2	—	0.006	—	—	—
1,3	3335	0.026	0.48	1.00	1.00
2,4	3365	0.037	0.83	0.86	0.94
0,3	3386	0.011	0.27	0.80	0.92
1,4	3415	0.057	0.57	0.89	0.91
2,5	3450	0.034	0.98	0.82	0.83
0,4	3468	0.023	0.14	0.71	0.85
0,5	3555	0.009	0.11	0.64	0.79
0,11	4159	0.067	0.81	0.93	0.76
0,14	4437	0.073	0.73	0.87	0.67
2,17	4745	0.057	0.80	0.73	1.00
3,19	4938	0.069	1.00	0.94	0.69
4,21	5145	0.060	0.74	0.79	0.81
5,23	5358	0.054	0.91	0.63	0.38
6,24	5420	0.040	0.79	0.48	0.57
7,27	5840	0.051	0.42	0.17	0.24
8,29	6100	0.037	0.15	0.48	0.08
9,31	6383	0.029	0.43	0.34	<0.02
10,33	—	0.017	—	—	—

density cause little uncertainty in the measurement of the relative intensities, although the uncertainty in the vapor pressure does affect cross section and photon

yield measurements. Second, measurement of the relative metal beam fluxes requires extensive calibration. Although the temperature of the oven could be determined to a relative accuracy of $\pm 1\%$ from pyrometer and thermocouple readings, and the metal beam fluxes measured to a relative accuracy of $\pm 10\%$ using a film thickness monitor, other errors entering into the comparison of intensities may be more important. The metal fluxes in these experiments range from 2×10^{14} to 1×10^{16} atoms $cm^{-2} s^{-1}$ in the reaction zone, corresponding to densities between 5×10^{10} and 2×10^{12} atoms cm^{-3} . Possible changes in the metal beam profile with source pressure may alter the reaction zone viewed by the detection system. Finally, the difficulty of aligning the scattering chamber with respect to the oven chamber and the entire beam apparatus with respect to the spectrometer in a reproducible manner from run to run may also contribute to the uncertainty in the relative intensity measurements.

Despite the above problems and limitations, we can make the following statements about the relative chemiluminescent intensities: (a) The most intense emission observed in these studies is that from the S_2^* emitter for the reaction $Ba + S_2Cl_2$. Excluding the contribution from the underlying continuum, this emission is approximately one order of magnitude stronger than the S_2^* emission from the reaction $Sr + S_2Cl_2$ and almost two orders of magnitude stronger than the S_2^* emission from the reaction $Ca + S_2Cl_2$. (b) The inten-

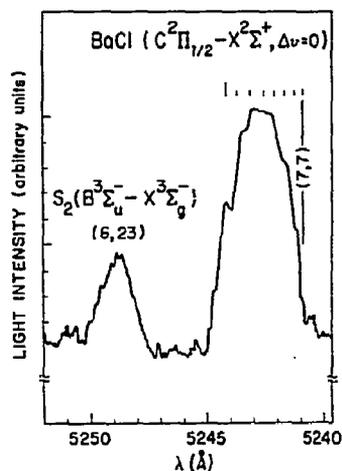


Fig. 5. High-resolution spectrum (2 Å) from $Ba + S_2Cl_2$, showing emission from the $\Delta v = 0$ sequence of the $BaCl C^2\Pi_{1/2} - X^2\Sigma^+$ band system.

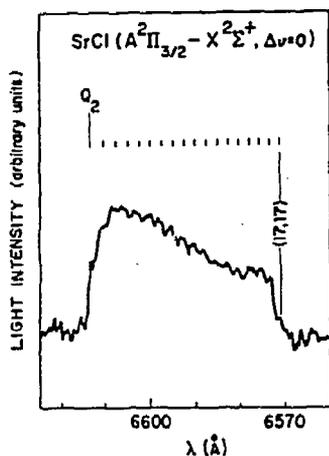


Fig. 6. High-resolution spectrum (1 Å) from Sr + S₂Cl₂, showing emission from the Δ*v* = 0 sequence of the SrCl A ²Π_{3/2} - X ²Σ⁺ band system.

sity of the polyatomic emitter tentatively identified as MCl₂^{*} from the similarity with the continuum emission seen for M + Cl₂ [25], is stronger for Ba + S₂Cl₂ than for either Sr or Ca with S₂Cl₂. (c) The emission from the BaCl C ²Π state is one order of magnitude less intense than the emission from the A ²Π and B ²Σ⁺ states of SrCl or CaCl. (d) The emission from the BaCl A ²Π and B ²Σ⁺ states also is greater than that from the BaCl C ²Π states when corrections are made for the rapid falloff in detector response above 9000 Å.

3.2. Reaction kinetics

3.2.1. Reaction order

It is important to demonstrate that the spectra shown in figs. 3–7 arise from single scattering events. Accordingly, a study is made of the chemiluminescent intensity at different wavelengths as a function of metal beam flux and S₂Cl₂ density. We examine the S₂^{*} feature at 3250 Å corresponding to the (3,3) and (4,3) B–X bands, and at 4300 Å, close to the maximum of the MCl₂^{*} chemiluminescence. We also examine the MCl^{*} feature at different wavelengths. The results are presented in figs. 8 and 9. All reactions show a linear rise in both gas pressure and metal beam flux, indicating the following bimolecular reaction mechanisms:

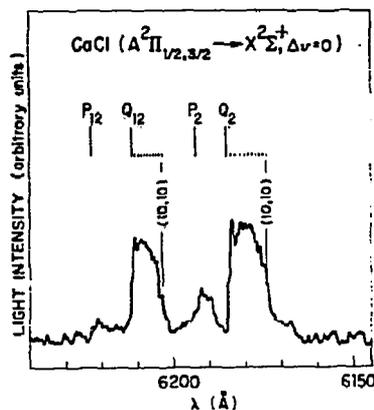
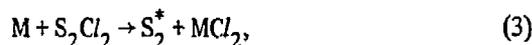


Fig. 7. High-resolution spectrum (1 Å) from Ca + S₂Cl₂, showing emission from the Δ*v* = 0 sequences of the CaCl A ²Π_{1/2,3/2} - X ²Σ⁺ band systems.

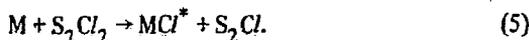


Fig. 8 shows a plot of the logarithm of the light intensity versus the reciprocal temperature of the metal oven. The data points at different wavelengths fit straight lines. The slopes represent the sum of the heat of vaporization of the metallic species and the activation energy of the reaction [6,10]. The values we obtain 44.5 ± 0.5 kcal/mole, 40.5 ± 0.5 kcal/mole, and 41.0 ± 0.5 kcal/mole for barium, strontium, and calcium, respectively, are in reasonable agreement with the literature values for the heats of vaporization [26]. We show in fig. 8 the dependence for MCl^{*} and S₂^{*} at 3250 Å. Similar results are obtained at 4300 Å and in other regions of the spectra. We conclude that the chemiluminescence is first order in the ground state alkaline earth atoms with no dependence on other (possible) beam components, such as M₂. In addition, the activation energies of the reactions shown in eqs. (3)–(5) are small.

Fig. 9 presents the corresponding study of the S₂Cl₂ concentration dependence. Once again the data points fit straight lines indicating that the reactions are first order in S₂Cl₂. Hence we conclude in particular that the S₂ B state is populated by a single collision between M and S₂Cl₂. We wish to stress that the S₂^{*} does not result from the recombination of two S atoms. Although the reaction exoergicities are sufficiently large to produce ground state S atoms by the reaction

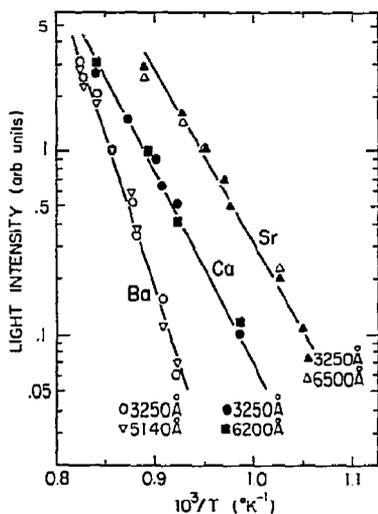
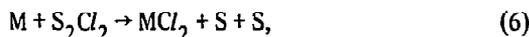


Fig. 8. Dependence of the logarithm of the chemiluminescence intensity at different wavelengths on reciprocal metal oven temperature. The S_2Cl_2 pressure is fixed at 2×10^{-5} torr. Straight lines indicate the linearity of the data points. Their slopes agree with literature values [39] for the heat of vaporization of barium and for the heat of sublimation of strontium and calcium, indicating that the reaction rates do not change with temperature in these regions.



the S_2 recombination is normally a three-body process. Hence the dependence of the S_2^* emission on M or S_2Cl_2 would not be expected to be linear. It might be argued that the S_2^* we observe results from two-body radiative association. This process does have a linear dependence on M and on S_2Cl_2 , but seems to be ruled out by the small probability of one S atom finding another in a secondary collision at these low rates of product formation. Assuming a gas kinetic cross section for reaction (6), the density of S atoms is only 10^{-11} torr in the reaction zone.

It is interesting to note how the chemiluminescent spectra changes for pressures of S_2Cl_2 greater than 10^{-4} torr. The S_2^* feature begins to level off at higher pressures but then increases in intensity once more. We speculate that we might be observing, in part, the onset of S atom recombination in this pressure regime. There are also many possibilities for energy transfer, such as emission from SCl^* or S_2Cl^* [27]. In addition, higher states of the MCl product appear in emission around 4000 Å, such as the $BaCl$ D-X system and the

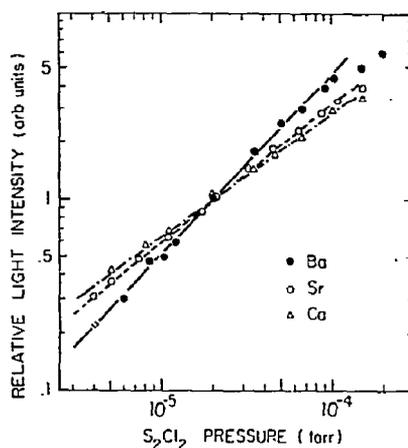


Fig. 9. Dependence of chemiluminescent intensity at 3250 Å on S_2Cl_2 pressure (log-log plot). The intensities for different metals are normalized to 1 at $p(S_2Cl_2) = 2 \times 10^{-5}$ torr. All curves are calculated from eq. (7) using the cross sections given in table 2 with the condition that the curves pass through the normalization point. The linearity of the data points demonstrates that these reactions are first order in S_2Cl_2 for a factor of twenty increase in the pressure.

C-X systems of $SrCl$ and $CaCl$. These weak diatomic band systems show a nonlinear dependence on M and/or S_2Cl_2 , consistent with an energy transfer mechanism.

3.2.2. Total cross sections

For a first-order chemiluminescent reaction in crossed beams, the rate of emission $dn_{v'}(\lambda)/d\lambda$ is proportional to the product of the differential cross section $d\sigma_{v'}(\lambda)/d\lambda$ for production of the excited state emitter at wavelength λ with the two beam densities, i.e.,

$$dn_{v'}(\lambda) = c d\sigma_{v'}(\lambda) n(M) n(S_2Cl_2). \quad (7)$$

In eq. (7) c is a constant factor provided the cross section is independent of velocity. The total cross section for production of excited states,

$$\sigma_{ex} = \int_{v'} d\sigma_{v'}(\lambda) d\lambda, \quad (8)$$

may be obtained by computing the total chemiluminescence

$$I/D = \int_{v'} dn_{v'}(\lambda) d\lambda, \quad (9)$$

where D is the detector response, found by using a

Table 2
Cross sections, branching ratios, and photon yields

Reaction	I/D ^{a)}		σ (10^{-16} cm ²)	I/D ^{a)}	
	Total S_2^*			Total S_2^*	
Ba + S_2Cl_2	1.00	1.00	162 ± 20	1.00	1.00
Sr + S_2Cl_2	0.08	0.12	105 ± 20	0.12	0.18
Ca + S_2Cl_2	0.03	0.02	92 ± 20	0.05	0.03

a) The relative excited state production rate, I/D and the branching rate, $I/(D\sigma)$, are for emission measured between 2800–7000 Å. To obtain absolute photon yields, i.e., the ratio of electronically excited products per reaction product, column 4 should be multiplied by 0.02 ± 0.01 .

standard lamp for calibration. Eq. (9) assumes that the lifetime of the emitter is sufficiently short so that all chemiluminescence occurs in the field of view seen by the detector system. The excited states of the alkaline earth monochlorides have lifetimes between 20 to 40 ns [28]; the lifetime of the S_2 B state is about 16 ns [29]. Thus this condition is met. The wavelength integration shown in eq. (9) was performed from 2800 to 7000 Å. Columns 1 and 2 of table 2 gives the relative values of I/D for the three reactions, i.e., the relative rate of total light emission and of S_2^* emission at constant metal beam flux and S_2Cl_2 density.

The total reaction cross section can be estimated from the attenuation of the chemiluminescent intensity as a function of path length when the metal beam traverses the long glass tube filled with S_2Cl_2 vapor (see fig. 2). If the metal atom M during its passage from the entrance slit to the observation region a distance x suffers at most only one collision, then the change of chemiluminescence with length is analogous to Beer's law for light absorption:

$$dI(x)/dx = k n_{ex} / dx = kI(0) \{1 - \exp [x\sigma n(S_2Cl_2)]\}, \quad (10)$$

where n_{ex} is the number density of excited products, σ is the total cross section for the removal of metal atoms from the beam and $n(S_2Cl_2)$ is the number density of target gas molecules. Fig. 10 shows a plot of $\ln [I(x) - I(0)]$ versus the length x for the three reactions at 3250 Å (the S_2^* B–X bands). In addition, the intensity variation of the BaCl C–X emission is also

given. The data show the linear dependence on length expected from eq. (10). The slopes yield the total cross sections given in column 3 of table 2. The error estimates are based on the uncertainties in the S_2Cl_2 vapor pressure. Because these cross sections are larger than gas kinetic, we equate these cross sections for metal beam removal to the total cross sections for reaction.

By dividing columns 1 and 2 of table 2 by the total reactive cross sections in column 3 we obtain the relative branching ratios for excited state production and for S_2^* production, shown in columns 4 and 5.

The $M + S_2Cl_2$ reaction system is seen to be characterized by large cross sections but the yield of excited reaction products is on the order of only 1%. It is well-known that the crossed-beam chemiluminescence technique detects only those collisions leading to electronically excited products. However, the sensitivity of this method is such that we easily see a single vibrational band produced with a cross section less than 10^{-19} cm². Although we observe directly only those (rare) collision processes producing emission, we nevertheless obtain information on the total cross section from the variation of the chemiluminescent intensity with beam path length.

The magnitudes of the total cross sections for all reactions are reminiscent of the alkali-atom-halogen-molecule reactions, suggesting that here, too, an electron jump mechanism is operative. According to this model, the total cross section σ (cm²) is related to the

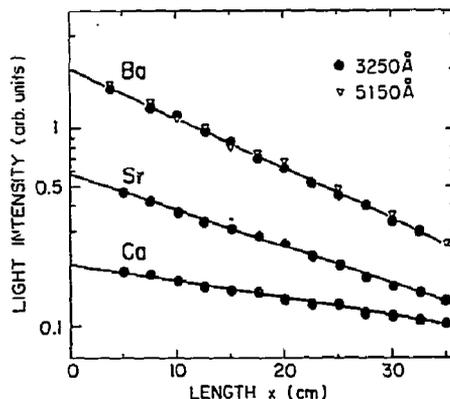


Fig. 10. Dependence of the logarithm of the chemiluminescent intensity at 3250 Å (S_2 B–X) and about 5150 Å (BaCl C–X) as a function of the path length x of the metal beam. The S_2Cl_2 pressure is fixed at 2×10^{-5} torr. Each solid line shows the best least-squares fit, yielding the cross section for the removal of different metal atoms (see table 2).

ionization potential IP (eV) of the metal atom and the vertical electron affinity EA (eV) of the S_2Cl_2 molecule by

$$\sigma = 6.50 \times 10^{-14} / (IP - EA)^2. \quad (11)$$

The ionization potentials of the alkaline earth atoms are well known but the vertical electron affinity of S_2Cl_2 appears not to have been measured. We note that the cross sections presented in table 2 are consistent with eq. (11) in that they decrease with increasing IP in the manner expected. Indeed, eq. (11) predicts the absolute cross sections to within 10% if we take the vertical electron affinity of S_2Cl_2 as 3.25 eV. Moreover, this assumption is very reasonable since the electron affinity of S_2Cl_2 might be expected to lie between the electron affinity of S (2.1 eV) and of Cl (3.6 eV).

3.3. Reaction energetics

3.3.1. S_2^* internal state distribution

It is possible to relate the intensity of a chemiluminescent feature to the concentration of emitters responsible for this feature provided the transition probability (Einstein A coefficient) is known. In the case of molecular emission the population of the v' level, denoted by $f(v')$ is related to the rate of emission $n(v', v'')$ of the (v', v'') band at the frequency $\nu(v', v'')$, by

$$n(v', v'') = C(\nu) f(v') R_e^2 q(v', v'') \nu^3(v', v''), \quad (12)$$

where R_e^2 is the square of the electronic transition moment, $q(v', v'')$ is the Franck-Condon factor of the band, and $C(\nu)$ is a proportionality constant including the variation of detector response with frequency. We have used eq. (12) to derive relative vibrational populations of the S_2 B state for the three different reactions from the measured $n(v', v'')$ values given in table 1. Here we assume that the radiation rates are given simply by the height of the peaks measured from the baseline.

The analysis begins by examining the spectral region 2800–3500 Å where the contribution from the continuum emission can be most easily subtracted. Fig. 11 presents a trace of the chemiluminescent spectrum for Ba + S_2Cl_2 in this wavelength region at a resolution of 5 Å. The S_2 B–X band heads stand out and are readily

identified. The continuum contribution is indicated by the dashed curve in the figure. This curve has the same shape as for the Ba + Cl_2 continuum [25]. Different vibrational bands with the same v' value have different amounts of continuum. Thus the choice of the dashed curve in fig. 11 can be checked for consistency (see also table 1).

Unfortunately the S_2 B–X band system is heavily perturbed. Nevertheless, we assume that the transition moment does not vary with vibrational level in applying eq. (10). The S_2 B–X Franck-Condon factors, given in table 1, have been calculated using RKR potentials constructed from the molecular constants of Brabson and Volkmar [31]. The vertical bars in fig. 12 show the relative vibrational populations obtained for the three different reactions. These populations are based on peak height measurements. With the same Franck-Condon factors we have also derived the $f(v')$ distribution based on peak areas, measured as the area of a peak above the background envelope. The two procedures are in good agreement, but the second method shows more scatter.

For each reaction, the vibrational distribution is seen to peak at v' values greater than $v' = 0$. Hence, the internal state distribution cannot be described by a temperature. The question arises as to what extent the perturbations distort the relative vibrational distributions deduced. It is not a simple matter to answer this in detail. However, the S_2 B state becomes more

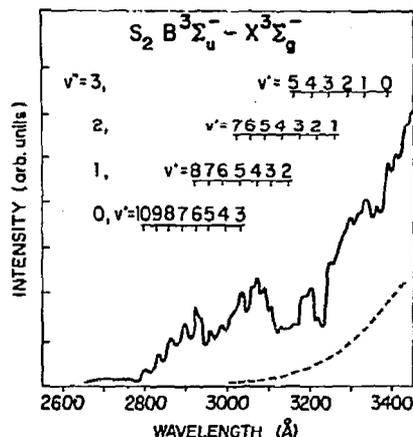


Fig. 11. High-resolution spectrum (5 Å) of the Ba + S_2Cl_2 chemiluminescence showing different v'' progressions of the S_2 B $^3\Sigma_u^- - X^3\Sigma_g^-$ system. The dashed line gives the underlying contribution from another emitter (see text).

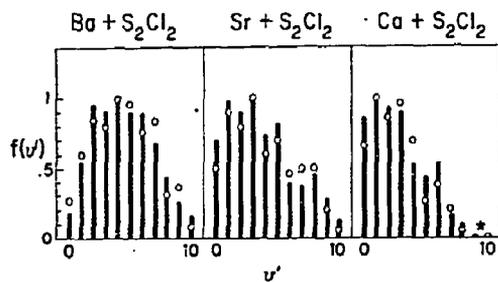


Fig. 12. Vibrational distribution $f(v')$ of the S_2 B state deduced from the chemiluminescent intensity for the three reactions studied. The vertical bars are found from peak heights; the open circles from peak areas. Each distribution is normalized to unity for the most populated v' level. The S_2 B-X system is not found in emission for $v' \geq 11$ because of extensive predissociation. Note that in the $Ca + S_2Cl_2$ reaction the $v' = 9$ and $v' = 10$ levels are not populated.

perturbed with increasing v' values. Thus, while the data in fig. 12 may not accurately represent the v' distribution of S_2^* produced in the chemical reaction, we believe we can conclude that $f(v')$ has approximately the form as shown. This distribution is not consistent with the equilibration of reaction exoergicity among the vibrational levels of a complex.

3.3.2. Dissociation energies

The chemiluminescent spectrum can be used to set lower bounds on the dissociation energies of the reactants or products provided single-collision events are studied and information is available about other bond energies [32]. In particular, for the reaction $M + S_2Cl_2 \rightarrow MCl^* + S_2Cl$, the $Cl-S_2Cl$ bond energy can be deduced from a knowledge of the MCl dissociation energy and the excitation energy required to populate the highest MCl^* v' level observed.

From conservation of energy arguments we write the inequality

$$D_0^0(Cl-S_2Cl) \geq D_0^0(MCl) - E_{int}^i(MCl) - E_{int}^i(S_2Cl_2) - E_{trans}^i \quad (13)$$

where E_{int} is the internal energy (electronic, vibrational, and/or rotational) of the species shown, and E_{trans}^i is the initial relative translational energy of the reactants. Eq. (13) would be an equality if we were able to include $E_{int}(S_2Cl)$ and E_{trans}^i .

The dissociation energies of MCl are taken to be $D_0^0(BaCl) = 110 \pm 3$ kcal/mole [33], $D_0^0(SrCl) = 105 \pm 3$ kcal/mole [34], and $D_0^0(CaCl) = 96 \pm 3$ kcal/mole [34]. The values of E_{int} are calculated from the highest vibrational level observed in the MCl chemiluminescent spectra shown in figs. 5–7, namely, $E_{int}(BaCl) = 61.1 \pm 1.5$ kcal/mole, $E_{int}(SrCl) = 58.3 \pm 1.0$ kcal/mole and $E_{int}(CaCl) = 56.8 \pm 0.5$ kcal/mole. The value of $E_{int}(S_2Cl_2)$ is calculated to be 1.5 kcal/mole at $T = 300$ K, where we take the average rotational energy as $\frac{3}{2}RT$ and we regard the vibrational energy as negligible except for the low-frequency (102 cm^{-1}) torsional mode [22] assumed to contribute RT to $E_{int}(S_2Cl_2)$. Finally, the initial relative translational energies are estimated [33] to be $E_{trans}^i = 1.6 \pm 0.8$ kcal/mole for $Ba + S_2Cl_2$, $E_{trans}^i = 1.8 \pm 0.9$ kcal/mole for $Sr + S_2Cl_2$, and $E_{trans}^i = 2.2 \pm 1$ kcal/mole for $Ca + S_2Cl_2$. With the above values, eq. (13) yields the following inequalities:

$$D_0^0(Cl-S_2Cl) \geq 44.8 \pm 5.5 \text{ kcal/mole}; \quad Ba + S_2Cl_2 \quad (14)$$

$$D_0^0(Cl-S_2Cl) \geq 43.4 \pm 4.9 \text{ kcal/mole}; \quad Sr + S_2Cl_2 \quad (15)$$

and

$$D_0^0(Cl-S_2Cl) \geq 35.5 \pm 4.5 \text{ kcal/mole}. \quad Ca + S_2Cl_2. \quad (16)$$

In eqs. (14)–(16) the error estimates include the uncertainty in the highest vibrational level observed in the different MCl^* spectra, the uncertainty in $D_0^0(MCl)$ and in E_{trans}^i .

It is particularly pleasing to us that the lower bounds to the $Cl-S_2Cl$ bond energy derived from two of the independent chemiluminescence studies are so close. We suggest that these lower bounds are good approximations to the true dissociation energy and adopt the value

$$D_0^0(Cl-S_2Cl) = 44.2 \pm 5 \text{ kcal/mole}. \quad (17)$$

Unfortunately, there appears to be no previous measurements of this bond energy. Donovan, Husain, and Jackson [27] estimate $S-Cl$ bond energies based on the Pauling additive mean rule [35] combined with the electronegativities of S and Cl, which are in good agreement with those based on the Mulliken scale [36]. They find for disulfur dichloride, $D_0^0(Cl-S_2Cl) = 48$ kcal/mole. On the other hand, Perona, Setser and

Johnson [37] place an upper bound of $D_0^0(\text{Cl}-\text{S}_2\text{Cl}) \leq 52$ kcal/mole from infrared chemiluminescence studies. Eq. (17) is consistent with both these estimates, giving us further confidence in our value for $D_0^0(\text{Cl}-\text{S}_2\text{Cl})$.

With a knowledge of this bond energy we are able to estimate $D_0^0(\text{S}_2-\text{Cl})$ from the thermochemical cycles shown in fig. 13. We calculate that the reaction $\text{S}_2\text{Cl}_2 \rightarrow \text{S}_2 + \text{Cl}_2$ is endothermic by 41 kcal/mole. This value is found using the bond energies of SCI [27], S_2 [38], Cl_2 [39], and $\text{ClS}-\text{SCI}$ [27], the last being based on the standard heat of formation $\Delta H_f^0(\text{S}_2\text{Cl}_2) = -13.9 \pm 0.5$ kcal/mole [40]. From the lower cycle we deduce

$$D_0^0(\text{S}_2-\text{Cl}) = 54 \pm 5 \text{ kcal/mole.} \quad (18)$$

Eq. (18) shows that the first $\text{S}-\text{Cl}$ bond in the formation of S_2Cl_2 is stronger than the second $\text{S}-\text{Cl}$ bond, as would be expected by analogy with F_2O_2 [39].

The observation that $v' = 8$ is the highest populated level of the S_2 B state in the reaction $\text{Ca} + \text{S}_2\text{Cl}_2$ permits us to calculate the internal energy remaining in the CaCl_2 product. From energy conservation we have

$$\begin{aligned} E_{\text{int}}(\text{CaCl}_2) &= D_0^0(\text{Cl}-\text{CaCl}) + D_0^0(\text{CaCl}) \\ &- D_0^0(\text{S}_2-\text{Cl}) - D_0^0(\text{Cl}-\text{S}_2\text{Cl}) - E_{\text{int}}(\text{S}_2) \\ &- E_{\text{int}}(\text{S}_2\text{Cl}_2) - E_{\text{trans}}^i + E_{\text{trans}}^f. \end{aligned} \quad (19)$$

Here $E_{\text{int}}(\text{S}_2) = 100.3$ kcal/mole and $D_0^0(\text{Cl}-\text{CaCl}) + D_0^0(\text{CaCl}) = 214.7 \pm 2$ kcal/mole [41,42]. Using the previous values for $E_{\text{int}}(\text{S}_2\text{Cl}_2)$, E_{trans}^i , $D_0^0(\text{S}_2-\text{Cl})$, and $D_0^0(\text{Cl}-\text{S}_2\text{Cl})$, we obtain

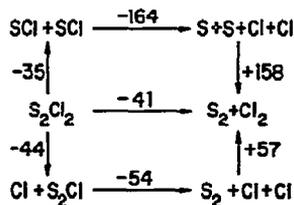
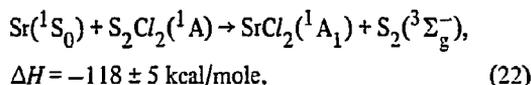
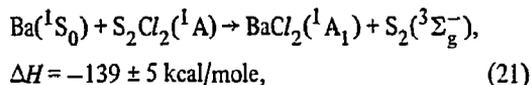


Fig. 13. Thermochemical cycles for the formation of S_2 and Cl_2 from S_2Cl_2 . All energies are in kcal/mole. The upper cycle is based on literature values (see text); the lower cycle is used to determine $D_0^0(\text{S}_2-\text{Cl})$ from our value of $D_0^0(\text{Cl}-\text{S}_2\text{Cl})$.

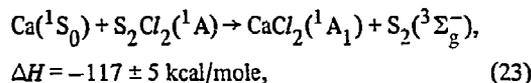
$$E_{\text{int}}(\text{CaCl}_2) = 12.7 \pm 7 \text{ kcal/mole,} \quad (20)$$

where we have neglected E_{trans}^f . This result indicates that the CaCl_2 product is internally excited to an appreciable extent even when the S_2^* product is produced in its highest vibrational level. Moreover, this suggests that the average internal energy of CaCl_2 is much higher.

The knowledge of the $\text{Cl}-\text{S}_2\text{Cl}$ and S_2-Cl bond energies also permit us to calculate the following reaction exoergies



and



where the bond energies of the alkaline earth dichlorides are based on vapor pressure data [39]. Eqs. (19)–(21) show that the formation of the metal dichloride provides sufficient energy to excite the S_2 molecule to the B state (91 kcal/mole) or even to dissociate the S_2 product (101.7 kcal/mole). It should be pointed out that the S_2 product may also be formed in a number of other electronic states, but the observed S_2 emission could only be attributed to the $\text{B}-\text{X}$ transition. On the other hand, the reaction $\text{M} + \text{S}_2\text{Cl}_2 \rightarrow \text{MCl} + \text{S}_2^* + \text{Cl}$ is so endothermic (≥ 76 kcal/mole) that it cannot be responsible for causing the S_2^* emission. We also conclude from the reaction energetics that the formation of MCl^* must be accompanied by the formation of S_2Cl .

4. Discussion

Gas-phase chemical reactions generally proceed by a sequence of elementary steps, each of which require the making and breaking of one chemical bond at a time. Consequently, much modern kinetics concentrates on the identification and detection of transient

Table 3
Some multi-center reactions of barium with polyhalide molecules
under single-collision conditions

Reaction system ^{a)}	Observed chemiluminescent product ^{b)}
Ba + (CdCl ₂)	BaCl ₂ [*] (m)
Ba + (CdBr ₂)	BaBr ₂ [*] (m)
Ba + (CdI ₂)	BaI ₂ [*] (s); CdI [*] (m)
Ba + (HgCl ₂)	BaCl ₂ [*] (m)
Ba + (HgBr ₂)	BaBr ₂ [*] (w)
Ba + (HgI ₂)	BaI ₂ [*] (m); HgI [*] (w)
Ba + SOCl ₂	BaCl ₂ [*] (m); BaCl [*] (s)
Ba + SCl ₂	BaCl ₂ [*] (s); BaCl [*] (s)
Ba + SO ₂ Cl ₂	BaCl ₂ [*] (m); BaCl [*] (m)
Ba + S ₂ Cl ₂	BaCl ₂ [*] (s); BaCl (m); S ₂ [*] (s)
Ba + S ₂ Br ₂	BaBr ₂ [*] (s); BaBr [*] (m); S ₂ [*] (w)

^{a)} The CdX₂ and HgX₂ may occur in part as dimers, i.e. $n = 1$ or 2.

^{b)} Relative emission intensities are indicated by s = strong, m = medium, and w = weak.

intermediates. However, there is a special class of elementary reaction steps, called concerted reactions, in which two or more bonds are made and/or broken simultaneously. Concerted reactions are of much interest not only because of their seeming rarity but also because their occurrence appears often to be governed by simple symmetry considerations [43]. The $M + S_2Cl_2 \rightarrow MCl_2 + S_2^*$ rearrangement where M is an alkaline earth atom (Ca, Sr, or Ba) involves the rupture of two S–Cl bonds and the formation of two M–Cl bonds during the course of a single collisional encounter. Recently, it has become increasingly apparent that multi-center reactions are less rare than once believed [44,45]. Indeed, the divalency of the Group IIA atoms leads to a number of concerted reactions in the sense defined above. In table 3 we list some examples we have observed under single-collision conditions. However, the $M + S_2Cl_2$ rearrangement has the unique characteristic that the excess reaction energy appears in the *old* S–S bond of the original ClSSCl reactant, rather than in the *new* M–Cl bonds of the MCl₂ product. In what follows we offer a possible explanation for this unusual finding based on simple molecular orbital arguments and the conservation of orbital symmetry in concerted reactions.

The disulfur dichloride molecule may be regarded as

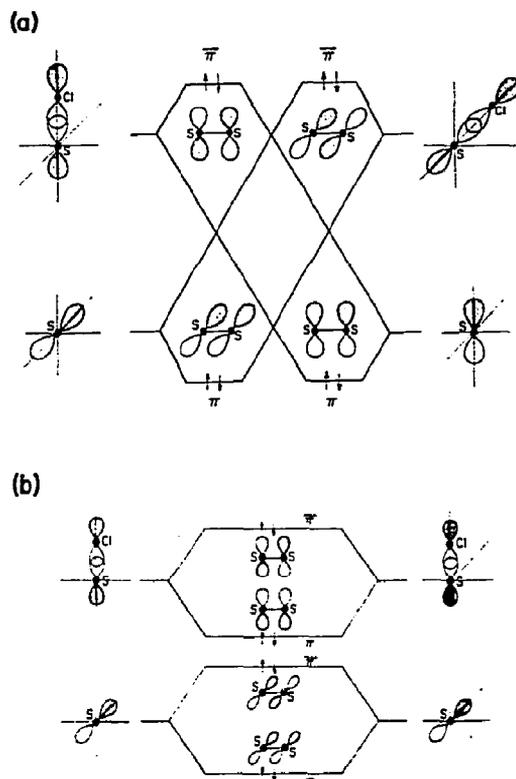
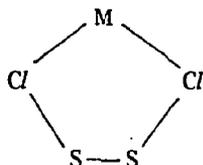


Fig. 14. The building up of molecular orbitals for ClSSCl from SCl subunits: (a) skew, C₂ structure; and (b) planar, C_{2v} structure. Only the π orbitals of the S–S backbone are shown.

formed from two sulfur monochloride subunits which are brought together in the orientation corresponding to the ground-state geometry of ClSSCl (fig. 1). We indicate in fig. 14a how the molecular orbitals of S₂Cl₂ are built up from those of SCl where we concentrate our attention only on the π orbitals of the S–S backbone. The ground state configuration of S₂Cl₂ is $\pi^4\bar{\pi}^4$. Here the departure of the Cl atoms requires one to remove one electron from each paired filled $\bar{\pi}$ orbital. This leaves the S–S linkage in the configuration $\pi^4\bar{\pi}^2$, which correlates with the X³ Σ_g^- ground state of S₂. The $\pi^4\bar{\pi}^2$ configuration also gives rise to the a¹ Δ_g and the b¹ Σ_g^+ states of S₂. In any case, a reaction of M with ClSSCl in which the Cl atoms are removed by the M atom in a concerted manner from the S₂Cl₂ molecule in its ground state geometry (C₂ symmetry) would not be expected to cause the S₂ product to be formed in the electronically excited B³ Σ_u^- state.

The disulfur dichloride molecule has a sizable barrier to internal rotation about the S—S backbone (≈ 17 kcal/mole [22]) presumably caused by the repulsive effect of the *Cl* nonbonding electrons. However, with the approach of the alkaline earth atom *M*, the transition state may deform toward a planar five-member ring structure



The corresponding molecular orbital diagram for this geometry of *ClSSCl* is shown in fig. 14b. It should be recalled that the localized S—*Cl* bond corresponds to forming a linear combination of π_u and $\bar{\pi}_g$, where the center of inversion refers only to the S—S bond. Thus, simultaneous removal of the two *Cl* atoms leaves the S—S linkage in the $\pi^3\bar{\pi}^3$ configuration, which correlates with the $B^3\Sigma_u^-$ excited state of S_2 . Hence, to the extent the transition state involves planar rather than skew *ClSSCl*, the formation of S_2 B state products is made more likely.

It is to be noted that the equilibrium geometry of the Group IIA dichlorides is linear for $CaCl_2$, but bent for $SrCl_2$ and $BaCl_2$ [46]. Thus, it is also reasonable to find that the $CaCl_2$ product retains some of the reaction exoergicity as internal (vibrational) energy. In agreement with the experimental results.

We also note that this model predicts that FSSF and BrSSBr behave similarly to *ClSSCl* in forming S_2^* products, but that the thionyl halides ($SOCl_2$ and $SOBr_2$) with their C_{2v} structures would not lead to SO^* products (see table 3). It would be interesting in future studies to explore the reaction system $M + FOOF$, as the above considerations suggest that the O_2 product would appear in the $B^3\Sigma_u^-$ excited state.

The $M + S_2Cl_2 \rightarrow MCl_2 + S_2^*$ reaction formally violates the spin conservation rules, since the reactants approach on a singlet surface and the products depart on a triplet surface. It appears that the cross section for the formation of S_2^* is much smaller than gas kinetic, in keeping with the spin-forbidden character of the reaction. Presently, we have no means of judging from our experimental data to what extent the $M + S_2Cl_2$ collision complex is long-lived. We cannot say

if the *M* atom first attacks one *Cl* atom and then the other by some snarled trajectory or if the attack is on both *Cl* atoms simultaneously. However, the energization of the S_2 product suggests an electronic rearrangement of the type that could be expected if the $M + S_2Cl_2$ collision complex approaches a planar five-member ring structure in separating to form reaction products. Although relatively common for organic reactions, the $M + S_2Cl_2 \rightarrow MCl_2 + S^*$ rearrangement presented here appears to be one of the few well-proven instances [47] of orbital symmetry control in inorganic reactions.

Acknowledgement

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