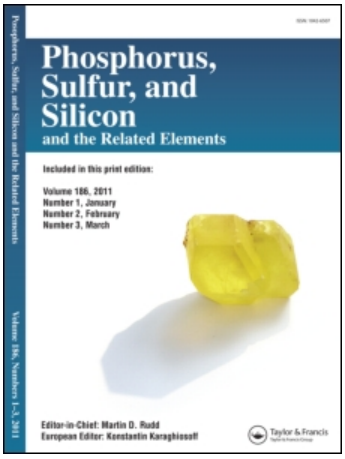

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IS SULFUR DICHLORIDE UNSTABLE? A Direct Experimental Answer

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IS SULFUR DICHLORIDE UNSTABLE?

A Direct Experimental Answer

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The nature of instability of sulfur dichloride was examined in the gas phase. Purification of this compound was performed by trap-to-trap condensation in the absence of light. In this condition, sulfur dichloride was quite stable for several days at room temperature and even up to 80°C in gas phase. The UV-Vis and IR spectra of the compound were reinvestigated. New data on the electronic absorption spectra of pure sulfur dichloride were obtained. Our observations reveal that the instability of sulfur dichloride is due to its photochemical decomposition until establishment of the equilibrium:

$$2SCl_2 \rightleftharpoons S_2Cl_2 + Cl_2.$$

Keywords: Sulfur dichloride; purification; thermal stability; absorption spectra; photochemical properties

INTRODUCTION

Products of direct chlorination of sulfur have attracted much attention after first investigation by Scheele at 1774. Although the existence of disulfur dichloride, that gives a golden yellow color, as the first product of this reaction, was generally accepted since the pioneering works by Aten[1] and also Ruff and Fischer,[2] the identity of the final product (a red species) of the reaction in excess chlorine was questioned for several years, due to variable properties of the compound. Following the extensive work by Lowery, Jessop and their co-workers on the

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absorption spectra,[3] dielectric constants[4] and some other properties of sulfur chlorides, it was found that the reddish compound is SCl_2. The authors attributed a complex behavior to the sulfur chlorides-chlorine system, because of the spontaneous decomposition of SCl_2 to S_2Cl_2 and Cl_2 until reaching equilibrium at about room temperature. A significant result on purification of SCl_2 was achieved by Rosser and Whitt, who found SCl_2 can be stabilized by addition of as little as 0.01% or greater PCl_5 or PCl_3 to a freshly distilled sample.[5]

Up to now, properties of SCl_2 have been studied extensively, including microwave spectra[6,7] IR[8–11] and Raman[9,12,13] spectra, UV-vis spectra,[14,15] photoelectron spectra,[14–16] mass spectra[17–19] electron diffraction[20–22] and its photolysis[23–25] and microwave discharge[26] products. For further information, cf. ref. 27.

As mentioned in all the reports, however, it seems that complete purification and spectral characterization of SCl_2 were hindered by the establishment of the equilibrium:

$$2SCl_2 \rightleftharpoons S_2 + Cl_2 \qquad (1)$$

In view of this long study period, it may be surprising that the nature of the chemical instability of SCl_2 is still uncertain. Our interest was roused by the fact that S_2Cl_2 is known to be more stable than SCl_2. Barton and Yost already investigated the dissociation of S_2Cl_2 vapor and found that no appreciable decomposition of S_2Cl_2 takes place at temperatures below 300°C.[28] As shown in Tables I and II, comparison of S-Cl bond dissociation energy and thermodynamic constants, reveals that SCl_2 may have similar stability with S_2Cl_2 or even be more stable. Thus we decided to investigate the origin of the chemical instability of SCl_2. Some new results on chemical stability and photochemistry of the molecule, obtained in the course of the study, are also included in this work.

Experimental Section

SCl_2 and S_2Cl_2 were prepared according to literature methods.[33] Purification of SCl_2 was achieved by trap-to-trap condensation under dynamic vacuum. Three

TABLE I Some thermodynamic data of SCl_2 and S_2Cl_2*

	T(°C)	*SCl_2*	*S_2Cl_2*
$\Delta H^\circ_{f\,(kJ/mol)}$	273.15	−22.4	−17.0
	298.15	−22.6	−17.2
$\Delta G^\circ_{f\,(kJ/mol)}$	273.15	−29.8	−28.1
	298.15	−30.5	−29.2

*The data are taken from ref. 12.

TABLE II S-Cl bond dissociation energy (kJ/mol) of SCl_2 and S_2Cl_2

SCl_2	*Ref.*	S_2Cl_2	*Ref.*
242.7	29	249.8	30
		255.2	31
269.9	18	272.0	32

traps used, were cooled to −63.5, −95.0 and −196°C, respectively. Middle fraction (at −95.0°C) was pure SCl_2 without any impurities, such as S_2Cl_2, HCl, Cl_2 and so on. S_2Cl_2 purification was undertaken by a similar method, but the traps were chilled to −22, −63.5 and −196°C, respectively. The fraction at −63.5°C was pure S_2Cl_2. Vacuum apparatus equipped with Pirani gauge head (PRH10, Edwards), connected to a controller (Pirani-Penning 1005, Edwards), and valves with Teflon pistons. The above purifications were examined by direct sampling to an evacuated IR gas cell. All of the glass vacuum line and connections were protected from sunlight and any other light sources by proper covers.

A device described previously was used for vapor pressure measurement of SCl_2 at various temperatures.[34] IR spectra (gas phase) were recorded on a IFS-88 FT-IR spectrometer (Bruker) with gas cells of 50 or 100 mm path length equipped with KBr windows. Various spectral resolutions (4 to 1 cm^{-1}) were selected at 400–4000 cm^{-1} region. UV-Vis spectra were obtained at gas phase (Quartz gas cell, l = 50 mm) and recorded on a Lambda 9 UV-Vis-NIR spectrometer (Perkin-Elmer). The concentrations of SCl_2 and S_2Cl_2 within the IR and UV gas cells were calculated, assuming ideal gas behavior. For the study of thermal stability of SCl_2, the gaseous samples in IR or UV glass cells have been maintained on a temperature controllable medium (a thermostat oven).

Irradiations were carried out with a Black-Ray B-100A long wavelength UV lamp to the gaseous samples in IR glass (Duran) cell with KBr windows. No filters or lenses have been used. Photochemical changes were studied by synchronized irradiation and programmed FT-IR scanning. The incident beam from the UV lamp was perpendicular to the spectrometer beam.

RESULTS AND DISCUSSION

a) Purification

Although in our preliminary efforts on the purification of SCl_2, the trap for condensation of S_2Cl_2 was cooled (−63.5°C) enough for complete trapping of S_2Cl_2,[35] involved in crude SCl_2, but the IR spectrum of the purified SCl_2 shows

the presence of a little S_2Cl_2 impurity. Therefore, it was concluded that the S_2Cl_2 impurity arises from SCl_2 decomposition, even at low temperatures. The conversion of SCl_2 to S_2Cl_2 and Cl_2 studied at room temperature for a long time period (ca. a few days). In the time period, this reaction has not followed a systematic or ordered kinetic trend, so the rate of disappearance of SCl_2 or appearance of S_2Cl_2 IR absorption bands were faster in day with respect to night.

In this view, we concluded that SCl_2 decomposition may arise from the light sensitivity of the molecule. In this regard, purification of SCl_2 took place in absence of light. It is noteworthy that, in this condition, IR spectrum of purified SCl_2 (fraction of $-95°C$), shows any impurity of S_2Cl_2. According to these observations, now, crude sulfur dichloride can be purified reasonably without the addition of any stabilizers, such as PCl_3. This unique result led us to investigate the stability of SCl_2 by itself, and reinvestigate some properties of this commercially important chemical. Vapor pressures of purified SCl_2 have been measured at the -78.1 to $26.1°C$ temperature range. The data were fitted by the least-square method to the following equation with a correlation coefficient of 0.999:

$$\ln P\,(\text{mbar}) = -(3.658 \times 10^3)/T(K) + 17.885$$

The extrapolated boiling point is $60.5 \pm 0.5°C$.

b) Investigation of Thermal Stability

Rosser and Whitt reported that sulfur dichloride dissociates slightly at room temperature and extensively at boiling point, even in the presence of PCl_3 as stabilizer.[5] To our knowledge, apart from this observation, no studies on the stability of the sulfur dichloride have been reported. In order to determine the nature and extent of the dissociation as a function of temperature, a thorough investigation of the sulfur dichloride vapor under equilibrium conditions was conducted. These conditions are summarized in Table III.

TABLE III Experimental conditions for the study of thermal stability of SCl_2

No.	*P (mbar)*	*T(°C)*	*Time(h)*
1	20	50	48
2	20	60	48
3	25	70	72
4	25	80	72

It was found that in the absence of light, sulfur dichloride is stable at room temperature and even above this to its boiling point (Table III). This result is consistent with the close similarity between the thermodynamic parameters and S-Cl bond dissociation energy of SCl_2 and S_2Cl_2 (Tables I and II) and thermal stability of disulfur dichloride up to 300°C.[28] Therefore, it is obvious that decomposition of SCl_2 at least to 80°C is not due to thermal instability.

c) Infrared Spectrum

In several attempts[8–13] to obtain the vibration spectroscopy of SCl_2 it has not been possible to present the spectrum of the pure sample. However, there is no serious problem in interpretation of an impure sample spectrum, since the main impurity of SCl_2, i.e. S_2Cl_2, has no interfering bands in the region of fundamentals of SCl_2 at greater than 400 cm^{-1}. Figure 1 shows the IR spectrum of SCl_2 in gas phase at 400–1500 cm^{-1}. Out of three fundamentals, two stretching vibration bands of SCl_2 appear at wavenumbers greater than 400 cm^{-1}. Although, absorption bands of stretching modes are not resolved in the gas phase, but corresponding overtone bands appear at appreciable distances from each

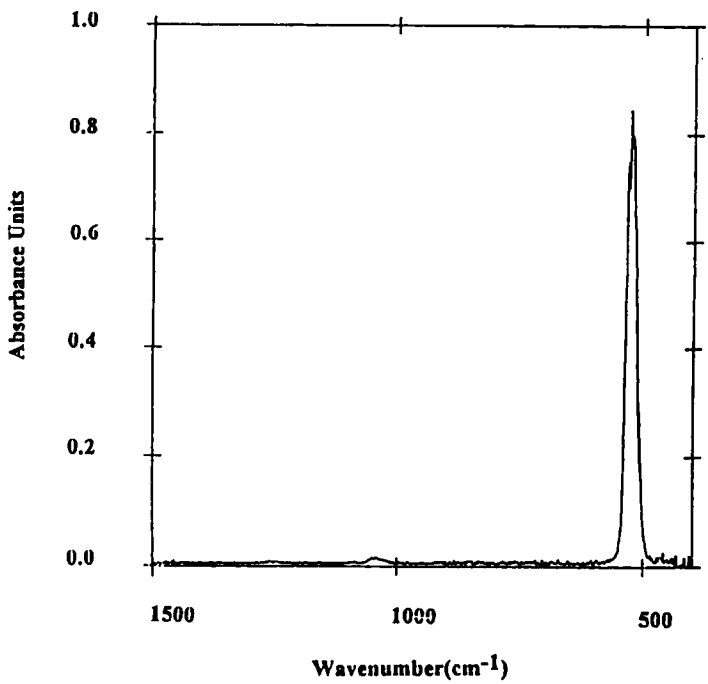

FIGURE 1 Gas phase IR absorption spectrum of SCl_2 at 27 °C (P = 20 mbar, l = 100 mm).

other, so it is possible to measure them precisely. Wavenumber of the overtone bands are 1039 and 1051 cm^{-1}, respectively related to symmetric and antisymmetric stretching vibrations.

The infrared spectrum in υ_1–υ_3 region of gaseous SCl_2, at 1 cm^{-1} resolution is reproduced in Figure 2. The three observed features arise from both υ_1 and υ_3 that are overlapped strongly. The fact was also reported by Savoie and Tremblay,[9] who carried out a full investigation on the IR and Raman spectra of four isotopic species of SCl_2. Intensity of absorption band of SCl_2 at center of the peak is a good criterion for concentration measurement of SCl_2 in gas phase. Therefore, we calculated the molar absorptivity of the middle branch at 525.5 cm^{-1}, that is:

$$\varepsilon_{max}\,(\upsilon = 525.5 \pm 0.1\ cm^{-1}) = 111.423 \pm 0.112\ (1/mol\ cm)$$

In order to obtain corresponding data of S_2Cl_2 for further experiments, we measured the molar absorptivity of S-Cl symmetric stretching vibration band at 461.1 cm^{-1}, that is:

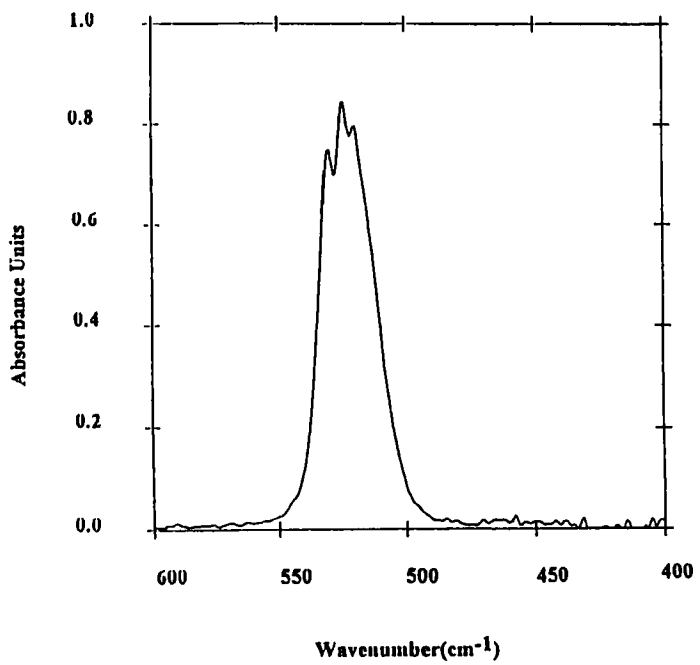

FIGURE 2 Gas phase IR absorption spectrum of SCl_2 in ν_1–ν_3 region at 27 °C (P = 20 mbar, l = 100 mm).

$$\varepsilon_{max}\ (\upsilon = 461.1 \pm 0.1\ cm^{-1}) = 206.88 \pm 0.11\ (1/mol\ cm)$$

d) UV Spectrum

In an earlier study, Koch reported same UV spectra for sulfur dichloride and disulfur dichloride in n-Hexane.[35] However, later report by Feher[15] was not consistent with that of Koch. Feher reported that the absorption spectrum of SCl_2 consists of three maxima at 200, 357 and 395 nm, in which the band at 395 nm has higher intensity than the 357 nm band. In an effort to interpret the electronic absorption spectra of sulfur halides, Colton and Rabalais have observed the 198, 335 and 388 nm bands for SCl_2, in which the band at 388 nm has lower intensity than the 335 nm band.[14] By considering an MO diagram, it was supposed that only two electronic transitions are possible in the long wavelengths UV region, $^1A_2 \leftarrow {}^1A_1$ (λ_{max} = 388 nm) and $^1B_1 \leftarrow {}^1A_1$ (λ_{max} = 335 nm). Therefore the low intensity of the 388 nm band was attributed to the symmetry forbidden transition of $^1A_2 \leftarrow {}^1A_1$. Also, the very intense band at 198 nm was assigned to symmetry allowed Rydberg electronic transition from $3b_1$ MO to a Rydberg series composed 3d, 4s or 4p orbitals or combinations of these. UV spectrum of SCl_2 is shown in Fig. 3.

Our examinations show all of the band intensities are not consistent with those reported by Colton and Rabalais (Table IV). These obvious differences, may arise from the fact that the SCl_2 sample used by Colton and Rabalais, contained considerable amount of S_2Cl_2 impurity. Indeed, existence of S_2Cl_2 in the SCl_2 sample, not only produced an undesirable band at 257 nm, but also its intense bands at 211 and 299 nm, increased the intensities of the 198 and 335 nm bands of SCl_2, respectively. In the other hand, the 3s orbital of sulfur is not incorporated in higher MOs by Colton and Rabalais. Following the work by Bock and coworkers on the photoelectron spectrum of SCl_2, another MO diagram was suggested based on Walsh molecular orbital predictions.[16,37] In view of this, we assigned two low intensity bands of SCl_2 at 347.4 and 388.4 nm to (..., $4b_1$, $9b_2$) $^1A_2 \leftarrow {}^1A_1$ and (..., $4b_1$, $12a_1$) $^1B_1 \leftarrow {}^1A_1$ transitions, respectively. The former is symmetry forbidden and the latter is a partially symmetry allowed transition. Hence, it is reasonable that the intensity of the band at 388.4 nm be relatively higher than the band at 347.4 nm.

e) Observation of the Photochemical Decomposition

In this work the photochemical properties of SCl_2 were studied in order to investigate the origin of the instability of the molecule. Because of the room

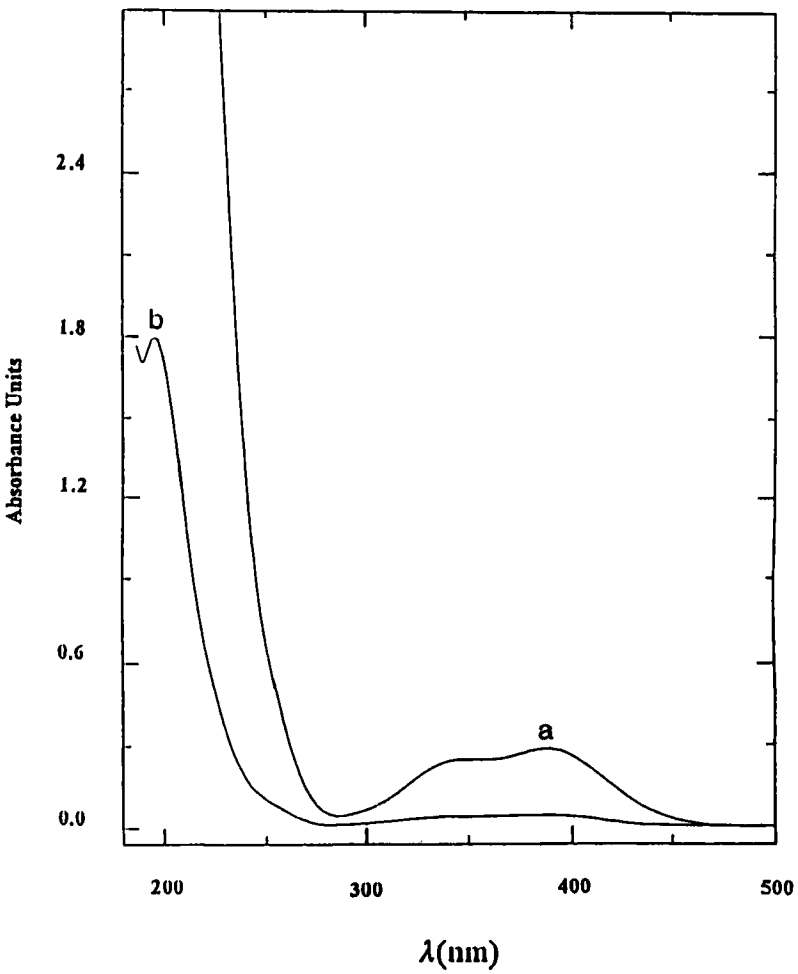

FIGURE 3 UV spectra of SCl_2 in gase phase (a) P = 70.2 mbar, (b) P = 10 mbar at room temperature (l = 50 mm).

TABLE IV UV absorption data for SCl_2

λ_{max}(nm)	ϵ(l/mol cm)	λ_{max}(nm)	ϵ(l/mol cm)	λ_{max}(nm)	ϵ(l/mol cm)	Ref.
200	3467	357	26	395	34	15[a]
198	2200	335	33	388	17	14[b]
195.5	900	347.4	18.5	388.4	21.3	This work[b]

a) Data obtained from spectrum in cyclohexane solution.
b) Data obtained from vapor spectrum.

light sensivity of SCl_2, it was concluded that the absorption bands which appear around 300 nm, can be responsible for the behavior. As already pointed out, these absorption bands were assigned to n (or π^*) $\rightarrow$ σ^* transitions. Followed by the transitions, the S-Cl bond will be weakened and photodissociated.

At daylight condition, photodecomposition of SCl_2 occurs in a few days, according to equilibrium (1). However, when an UV radiation source was employed, the equilibrium condition was achieved in a few minutes.

This phenomenon could be followed either by appearance of an intense band centered at 461.1 cm^{-1} (sym. stretching vibration of S-Cl) which is due to the formation of S_2Cl_2 or by decreasing the intensity of SCl_2 absorption band in the IR Spectrum (cf. Fig. 4).

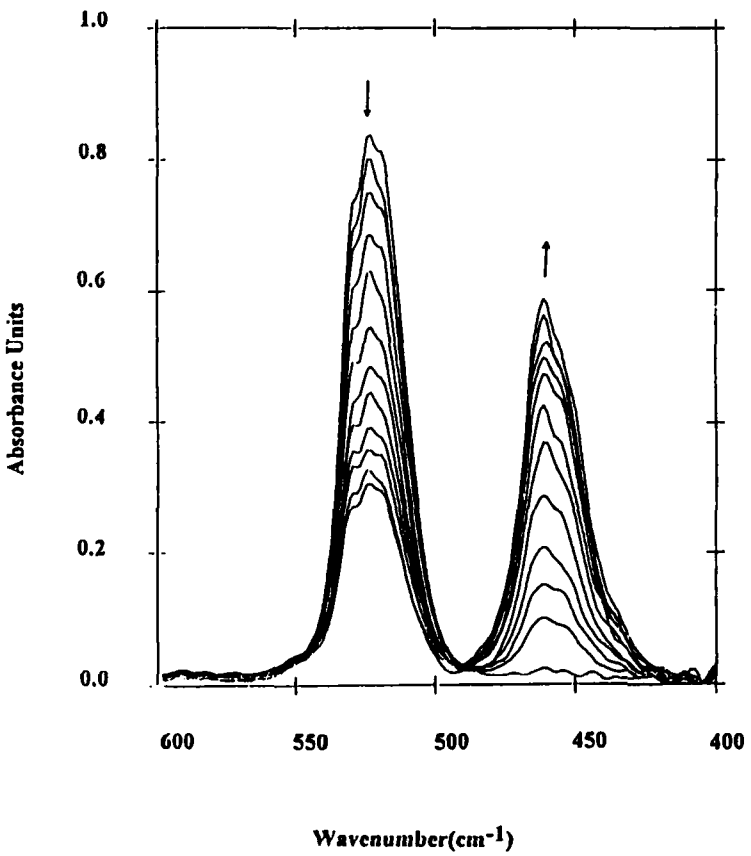

FIGURE 4 IR spectrum of a photolysed sample of SCl_2 as function of irradiation time. The curves (from top to bottom at 525.5 cm^{-1}) are for irradiation times: 0, 60, 120, 180, 300, 420, 540, 660, 780, 900, 1080 and 1560 (sec.) respectively. (P = 20 mbar, l = 100 mm, at 26.5 °C).

Returning to relative concentrations of SCl_2 and S_2Cl_2 during photolysis of SCl_2, it can be concluded that no other compound with a long life time has been formed (with the exception of Cl_2 which is undetectable by IR spectroscopy).

Although the photodecomposition products of SCl_2 (i.e. SCl and Cl) are energetic enough for fast elementary reactions in gas phase, but the overall rate of the processes is relatively low and depends on intensity of the radiation source. This mainly arises from the low intensity of SCl_2 absorption bands at 300–400 nm (cf. Fig. 1). Following the process:

$$SCl_2 \xleftarrow{h\nu} SCl + Cl \qquad (2)$$

several SCl self-reactions and reactions with other species can be thought in this system, including:

$$SCl + Cl \longleftarrow S + Cl_2 \qquad (3)$$

With the exception of SCl_2 and S_2Cl_2, other species in the above equations are

$$SCl + Cl_2 \longrightarrow SCl_2 + Cl \qquad (4)$$

$$SCl + SCl \longrightarrow \begin{cases} S_2Cl + Cl & (5a) \\ SCl_2 + S & (5b) \\ S_2 + Cl_2 & (5c) \end{cases}$$

$$SCl + SCl + M \longrightarrow S_2Cl_2 + M \qquad (6)$$

$$SCl + SCl_2 \longrightarrow \begin{cases} S_2Cl_2 + Cl & (7a) \\ S_2Cl + Cl_2 & (7b) \end{cases}$$

very reactive and have a short life time,[38] so detection of IR active species was impossible by the conventional FT-IR spectrometry in the gas phase.

Kinetics of some of the elementary reactions have been studied by Murrelles and coworkers, who used reactions of atomic chlorine with C_2H_4S [38] and H_2S [39] as sources of SCl radical in a discharge flow system with mass spectrometry detection. According to these reports, reactions of (5a,5b and especially 5c) have

been suggested as the major pathways for SCl loss in excess Cl or Cl_2 at short time scale (~10 μsec.). However, no further mechanistic details are provided until equilibrium condition.

The process (1) gives SCl and Cl in equal quantity, which is a more probable condition for SCl self reactions than Murrelles' experiments. Accordingly, if reaction (5c) proceeded with significant efficiency, it was expected some S_2 would be converted to S_8 precipitation. But no observable deposited sulfur was obtained in our study.

Also, on the bases of Murrelles' results, the rate of reaction (3) and (4) are much smaller than SCl self reactions and possibility of termolecular pathway (6) was rejected.

Formation of S_2Cl_2 from reaction (7a) and Cl_2 from (7b) are other pathways which may contribute to equilibrium (1), especially at the beginning of photolysis of SCl_2. However, it seems that the mechanism of photochemical equilibriation of SCl_2, S_2Cl_2 and Cl_2 are more complicated than the elementary reactions of SCl in excess Cl or Cl_2.

Photolysis of S_2Cl_2 is another parameter which may affect the reversible reaction (1) under exposure of UV irradiation. In spite of extensive works on the photochemistry of S_2Cl_2, there are controversies about the photolysis mechanism and succesive reactions.

Some authors have suggested photolysis of S_2Cl_2 may involve S-S bond breaking [40–41] and other proposed cleavage of S-Cl.[42–44] In either case, vibrationaly excited state of S_2 was one of the most important products of the photolysis.

The UV spectrum of S_2Cl_2 contain three absorption bands with maxima located at 211, 269 and 299 nm. The latter band has lower intensity than the two former. Molar absorptivity of 299 nm band is drastically reduced at higher wavelength and reaches to less than 1 at 350 nm.

According to a very recent qualitative MO diagram of S_2Cl_2 the band at 299 nm can be assigned to a $n_{SCl} \rightarrow \sigma^*_{SCl}$ transition.[45]

Also, it was found recently that the photolysis of S_2Cl_2 with 514 nm laser at temperatures higher than 540 K is initiated by generation of S_2Cl.[46] Consequently, the probability of S-Cl bond breaking is higher than S-S under long wavelength UV radiation. IR spectrum of a photolysed sample of S_2Cl_2 is shown in Fig. 5. Photolysis was accompanied by the appearence of the SCl_2 absorption band and deposited sulfur on the gaseous cell wall. However, investigation of this process is beyond the scope of the present study, but it reveals that, conversion of S_2Cl_2 to SCl_2 and sulfur is continued until enough SCl_2 that is produced for establishment of equilibrium (1). After this point, no significant change was observed with repetition of irradiation.

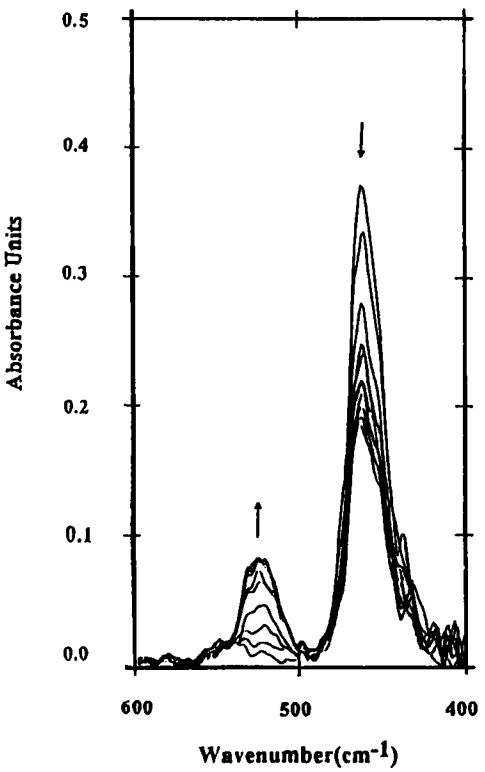

FIGURE 5 IR spectrum of a photolysed sample of S_2Cl_2 as function of Irradition time. The curves (form top to bottom around 460 cm^{-1}) are for irradiation times: 0, 47, 160, 358, 564, 771, 1063, 1558, 2157, 2818 and 3514(s) respectively (P = 10 mbar, l = 50 mm, at 27.5°C).

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