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Elementary Reactions of the SCl Radical

Part 1.—Rate Constants and Mechanisms of the Reactions $Cl+C_2H_4S \rightarrow SCl+C_2H_4$, $SCl+SCl \rightarrow$ products and $SCl+Cl_2 \rightarrow SCl_2+Cl$

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The reaction of Cl atoms with ethylene sulphide, C_2H_4S, has been used as a source of SCl radicals in a discharge-flow system with detection of free-radical and molecular species by molecular-beam-sampling mass spectrometry. The rate constant for the overall reaction of Cl with C_2H_4S

$$Cl+C_2H_4S \rightarrow \text{products} \tag{1}$$

was found to be $k_1=(6.6\pm0.9)\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (1σ) at 292 K from the decay of C_2H_4S in an excess of Cl. By measuring the absolute yield of C_2H_4 from this reaction the branching ratio for the formation of SCl and C_2H_4 by the direct sulphur abstraction channel (1*a*) was found to be 0.70 ± 0.08 (1σ):

$$Cl+C_2H_4S \rightarrow SCl+C_2H_4. \tag{1a}$$

A minor hydrogen abstraction channel could be identified. The rate constant and branching ratio for the bimolecular self-reaction

$$SCl+SCl \rightarrow \text{products} \tag{2}$$

was also determined. This reaction proceeds mainly by disproportionation to S_2Cl+Cl (2*a*) with $\leqslant 11\pm4\%$ forming the disproportionation products SCl_2+S (2*b*). The four-centre reaction (2*c*) forming S_2+Cl_2 may also occur to some extent. A rate constant $(k_{2a}+k_{2c})=(6.0\pm2.4)\times10^{-11}$ cm^3 molecule^{-1} s^{-1} (1σ) was measured at 295 K, where k is defined by $-d[SCl]/dt=2k[SCl]^2$. The results are compared with the analogous reactions of the SF, SH and oxyhalide XO radicals (X = F, Cl, Br). In addition, the rate constant was estimated for the reaction

$$SCl+Cl_2 \rightarrow SCl_2+Cl; \quad k_3^{295}\approx 7\times10^{-14}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}. \tag{3}$$

This value of k_3 was used, together with available thermochemical data, to calculate an upper limit for the rate constant for the reverse reaction

$$SCl_2+Cl \rightarrow SCl+Cl_2 \tag{3'}$$

of 1×10^{-18} cm^3 molecule^{-1} s^{-1} at 295 K.

While a considerable amount of kinetic data exists for the reactions of the oxyhalide radicals, XO (where X = F, Cl, Br, I) owing to their importance in the atmosphere, relatively little is known about the reactivity of the isoelectronic sulphur halide radicals. Only recently has there been a study of the reactions of the SF radical,[1,2] whereas no information on the reactivity of the SCl radical currently exists. Spectroscopic data on the SCl radical is also sparse, and only recently was the radical first identified. In two early investigations, certain ultraviolet absorption bands which were observed following the photolysis of S_2Cl_2 in a hydrocarbon matrix[3] and in the gas phase[4] were tentatively attributed to SCl, but these assignments remain unconfirmed. More recently, Feuerhahn

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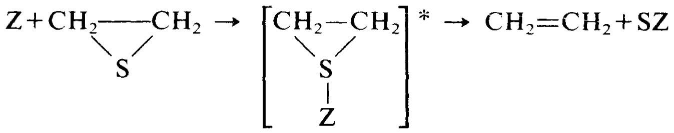
et al.[5] detected SCl radicals trapped in an argon matrix at 9 K by infrared absorption following the photolysis of either S_2Cl_2 or SCl_2. Their assignment was confirmed by Willner[6], who photolysed three different isotopically enriched SCl_2 samples in a neon matrix. Precise measurements of the molecular constants of the SCl radical in its $X\ ^2\Pi_{3/2}$ ground state were made by Yamada *et al.*,[7] who observed the fundamental absorption band of SCl in the gas phase at high resolution by infrared diode laser spectroscopy. In that study, SCl radicals were produced in the absorption cell by a d.c. discharge in a mixture of S_2Cl_2 or SCl_2, H_2 and He.

An earlier publication from this laboratory[8] reported the detection of SCl radicals by mass spectrometry as a product of the $Cl + H_2S$ reaction in a discharge-flow system. However, although the initial reaction was found to be rapid, the relatively slow rise of the SCl^+ ion signal indicated that SCl radicals were formed by secondary reactions involving other highly active species such as HS and S. This prompted a search for another rapid, but more direct source of SCl for kinetic studies in a flow system. The present work was initiated to assess the potential of the reaction between atomic chlorine and ethylene sulphide, C_2H_4S, as a possible source of SCl since ethylene sulphide is known to undergo a number of rapid desulphurisation reaction with various atomic species such as H, O and S.[9-11] Studies of these reactions have shown that the sulphur abstraction channels forming ethylene and SZ radicals (Z = H, O or S)



are overwhelmingly favoured and that they proceed with low or essentially zero activation energies. At the time the present work was initiated, the reaction of C_2H_4S with Cl atoms had not previously been investigated. Recently, however, Nava *et al.*[12] used the flash-photolysis-resonance-fluorescence technique to obtain a temperature-independent rate constant of $(1.02 \pm 0.10) \times 10^{-10}\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$ for this reaction, but obtained no information about reaction products. Although the $Cl + C_2H_4S$ reaction might be expected to proceed by sulphur abstraction to form $SCl + C_2H_4$, H-atom abstraction from C_2H_4S may also be an important pathway for this reaction since Cl is known to be efficient at abstracting H atoms from hydrocarbons such as C_2H_6 and C_3H_8.[13]

In the present work the rate constant for reaction (1)

$$Cl + C_2H_4S \rightarrow \text{products} \tag{1}$$

and the branching ratio for the sulphur abstraction channel producing SCl and C_2H_4 have been determined at room temperature in a discharge-flow system with detection of both free radical and molecular species by molecular-beam-sampling mass spectrometry. The rate constant and branching ratio of the SCl self-reaction (2) were also determined

$$SCl + SCl \rightarrow \text{products} \tag{2}$$

and the forward and reverse components of reaction (3) examined:

$$SCl + Cl_2 \rightleftharpoons SCl_2 + Cl. \tag{3}$$

Reaction (2) was earlier postulated as being responsible for formation of S_2 and S_2Cl in the $Cl + H_2S$ reaction.[8] The elementary reactions of SCl with a number of added reagents including NO_2, NO, O_2, $O(^3P)$ and $N(^4S)$ have also been investigated, and the results are presented in Part 2.[14]

Experimental

Methods

The experimental apparatus, including the sampling system and mass spectrometer, has been discussed elsewhere.[8] Briefly, it consists of a 2.6 cm internal diameter Pyrex discharge-flow system linked *via* a two-stage molecular-beam-sampling system to a quadrupole mass spectrometer. Typical flow conditions were 250-500 μmol s^{-1} of helium carrier gas near 1 Torr (133.3 Pa) total pressure at a flow velocity $\leq$2200 cm s^{-1}. The flow-tube pressure was measured at both ends by a capacitance manometer (M.K.S. Baratron, model 222) and the mean of the two readings taken. Reagent flowrates (C_2H_4S, ClNO, C_2H_4 and SCl_2, each diluted in He) were measured by a transducer-type mass flowmeter (Hastings, model H5-M) or by measuring the pressure drop across a narrow capillary. The latter type was used for C_2H_4S and ClNO after these reagents were found to contaminate severely the transducer-type flowmeter.

Chlorine atoms were produced by passing Cl_2 diluted in the carrier gas through a microwave discharge (2.45 GHz, 50 W). The walls of the discharge tube were treated with H_3PO_4 to minimise atom recombination. The walls of the flow-tube were left untreated, but were conditioned by exposure to Cl atoms for up to 1 h before kinetic runs were performed each day. The chlorine atom concentration was measured using the rapid titration reaction, $Cl + ClNO \rightarrow Cl_2 + NO$. The decrease in the NCl^+ fragment ion (m/e 49) of ClNO, monitored using an electron energy of 30 eV, was measured when Cl atoms were added to an excess of ClNO.

Reagents

Helium (B.O.C. grade A, 99.995%) was passed through a molecular sieve at 77 K. Chlorine was maintained in a reservoir at 196 K which provided a constant vapour pressure of 52 Torr. Nitrosyl chloride was prepared by adding chlorine to an excess of nitric oxide. The residual NO was pumped from the ClNO which was condensed at 196 K. Ethylene sulphide (Aldrich, b.p. 55 °C) was degassed at 196 K and the vapour distilled by warming to 298 K, collecting only the middle fraction. Small amounts of polymer were present in the stored liquid, evident by a slight cloudiness. However, mass-spectrometric analysis revealed that only the monomer, C_2H_4S, was present in the vapour. Commercial sulphur dichloride (Aldrich, b.p. 59 °C) was degassed at 77 K and purified by several trap-to-trap distillations at 298 K. Some solid PCl_5 was added to the distillation and receiving vessels in order to remove impurities which catalyse the attainment of the equilibrium, $2SCl_2 \rightleftharpoons S_2Cl_2 + Cl_2$.[15] The vapour pressure of SCl_2 at 293 K is 180 Torr compared to 10.7 Torr for S_2Cl_2. Although this procedure does not remove all the S_2Cl_2 component of the sample, mass-spectrometric analysis revealed that the amount of S_2Cl_2 present in the vapour was small compared to SCl_2 and did not cause any complications in the calibration experiments which employed SCl_2.

Results

Rate Constants for the $Cl + C_2H_4S$ Reaction

The rate constant for reaction (1) was determined by adding C_2H_4S through a movable injector to an excess of Cl atoms and monitoring the disappearance of the $C_2H_4S^+$ ion peak at m/e 60 as the injector was moved away from the sampling pinhole. The range of injector-to-pinhole distances corresponded to reaction times of 1.5-14 ms. By using $[Cl]_0 > [C_2H_4S]_0$, the disappearance of C_2H_4S followed pseudo-first-order kinetics according to the expression

$$\ln([C_2H_4S]_0/[C_2H_4S]_t) = k_1' t$$

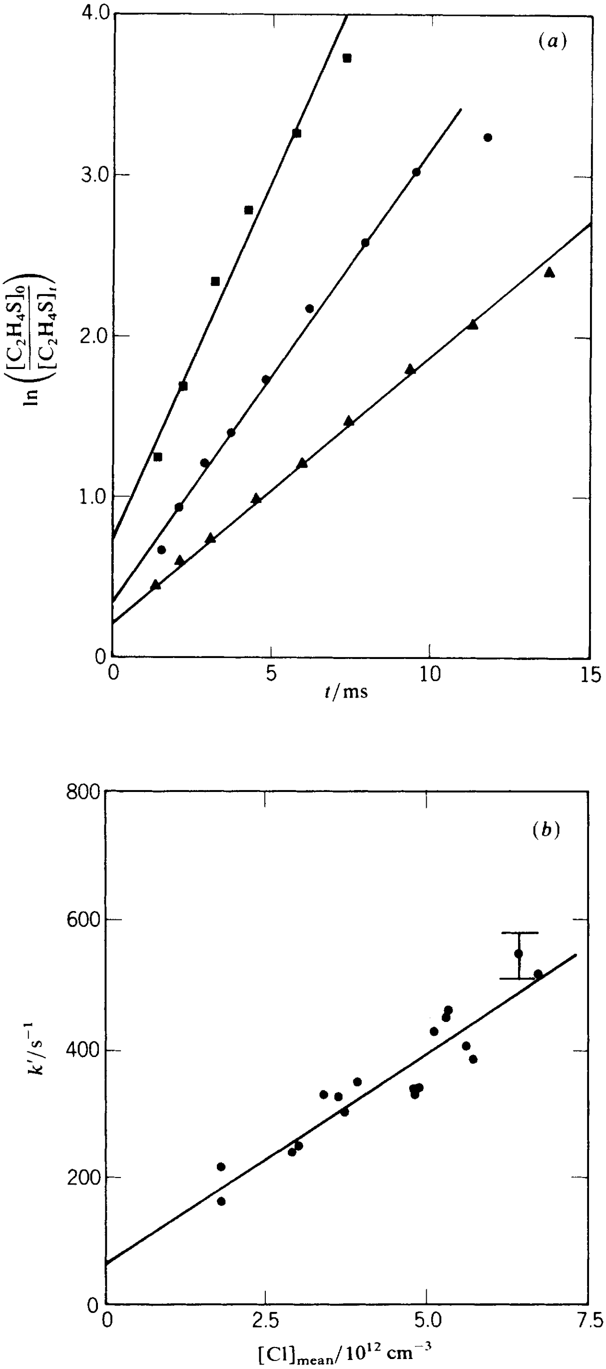


Fig. 1. Kinetics of reaction (1) at 292 K. (*a*) Typical first-order logarithmic decay plots of C_2H_4S in various excess concentrations of Cl atoms (10^{12} cm^{-3}) as follows: ▲, 1.8; ●, 3.7; ■, 6.7. (*b*) Summary plot for the variation of the pseudo-first-order rate constant k'_1 with $[Cl]_{mean}$.

Table 1. Rate constant for reaction (1) at 292 K

run	$[Cl]_{mean}/10^{12}$ cm^{-3}	$[C_2H_4S]_0/10^{11}$ cm^{-3}	k_1'/s^{-1}
1	6.7	5.8	515
2	4.8	10.8	330
3	3.9	6.6	350
4	3.6	9.8	328
5	5.6	4.8	404
6	1.8	4.8	162
7	4.9	9.8	343
8	5.3	12.4	449
9	2.9	10.2	239
10	5.7	11.0	385
11	4.8	6.9	341
12	5.1	8.7	428
13	1.8	7.6	217
14	6.4	15.3	545
15	3.7	5.4	303
16	3.0	6.5	250
17	5.3	12.2	459
18	3.4	8.0	331

where $k_1' = k_1[Cl]_{mean}$ and $[Cl]_{mean}$ is the mean concentration of Cl atoms in the experiments. Use of $[Cl]_{mean}$ in this expression allows for the small depletion of Cl atoms by C_2H_4S that occurs in the experiments. Fig. 1(*a*) shows some typical semilogarithmic decay plots of C_2H_4S. Eighteen such decays were performed over a range of initial concentrations, with $3.0 \leq [Cl]_0/[C_2H_4S]_0 \leq 12$ and $2.1 \leq [Cl]_0/10^{12}$ cm$^{-3} \leq 7.0$. All the plots were linear over three 1/e lifetimes, but showed an intercept on the logarithmic axis and converged to a common origin at −1 ms on the time axis. This effect was observed in previous work with this system[8] and was assigned to the 'dead time' of the sampling system. Values of k_1' were obtained as the gradients of these plots using a least-mean-squares analysis of the data and were corrected for axial diffusion of C_2H_4S in the carrier gas, which results in the true value of k_1' being underestimated by *ca.* 7%. The range of low $[Cl]_0/[C_2H_4S]_0$ ratios was not ideal for pseudo-first-order conditions, but was limited by the rapidity of the reaction and the detection limit for C_2H_4S. Consequently, the corrections made to $[Cl]_0$ to obtain $[Cl]_{mean}$ were relatively large, ranging from 4 to 17%, depending on the $[Cl]_0/[C_2H_4S]_0$ ratio.

The relevant experimental details, including the values of $[Cl]_{mean}$ and corrected values of k_1', are listed in table 1 and a plot of k_1' against $[Cl]_{mean}$ is shown in fig. 1(*b*). The data can be fitted to a straight line reasonably well, thus demonstrating overall second-order behaviour. However, individual data points are rather scattered around the line which shows a substantial intercept on the k_1' axis. Least-mean-squares analysis of the data yields a bimolecular rate constant, k_1, of $(6.6 \pm 0.6) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} and an intercept of 60 ± 30 s^{-1}; the error in k_1' is one standard deviation of the slope. The scatter of the data is believed to be due to uncertainty in the measured value of $[Cl]_0$ as a result of instability in the NCl^+ signal calibration for the ClNO used to titrate the Cl atoms. The estimated error in $[Cl]_{mean}$ is 10% which when combined with the statistical error in k_1 results in a more realistic value of k_1 of $(6.6 \pm 0.9) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} at 292 K. Systematic errors arising from flow and pressure measurements were estimated to amount to 10%.

The cause of the large intercept is uncertain; if real, such an intercept implies that C_2H_4S decays along the flow tube in the absence of Cl atoms due to, for example, loss on the walls of the flow tube or reaction with impurities formed in the discharge;

however, no such decay was observed. Two other phenomena would cause an apparent intercept without altering the slope and hence the value of k_1. One is a first-order decay process which removes C_2H_4S only when Cl atoms are present, but with a rate independent of $[Cl]_0$; the second is one which, for reasons that are not known, results in the titration procedure routinely underestimating $[Cl]_0$ by *ca.* 1×10^{12} cm^{-3}. Neither of these explanations seem convincing even though they cannot be ruled out. An apparent intercept would also result from fitting the data to a straight-line plot, which is in fact curved either at high or low [Cl] as a consequence of incorrect measurements of $[Cl]_0$ or complications to the kinetics which affect the decay of C_2H_4S. Impurities formed in the Cl_2–He discharge such as O and H atoms were found to be present at concentrations too low ($<10^{11}$ cm^{-3}) to affect significantly either the measurements of [Cl] in the titration or the decay rate of C_2H_4S. It is also unlikely that [Cl] was being underestimated at low [Cl] owing to incomplete reaction with ClNO because the concentration of ClNO was sufficiently high (*ca.* 1×10^{13} cm^{-3}) that more than 99% of the Cl atoms would have been converted in the 15 ms reaction time allowed. Partial regeneration of C_2H_4S by secondary chemistry during kinetic runs might have caused k_1' to have been underestimated at high [Cl]. However, such an effect would also probably manifest itself as curvature in individual decay plots, and this was not observed. Furthermore, it is not possible to invoke a simple mechanism which could lead to regeneration of a stable species such as C_2H_4S. It is more conceivable that the plot is curved at low [Cl] because the values of k_1' for these runs were overestimated owing to removal of C_2H_4S by secondary reaction with a product of reaction (1). Experiments performed in an excess of C_2H_4S and described later in this paper showed that C_2H_4S reacts with SCl radicals, a major product of reaction (1). However, no curvature in the individual decay plots was observed at low [Cl] to substantiate this.

No matter which, if any, of the factors considered above was responsible for the intercept, all would either have left the slope unaltered or have reduced it. Therefore, the value of k_1 determined here should best be considered a lower limit. It should also be pointed out that the measurements of low Cl atom concentrations were subject to relatively large errors owing to the low detection sensitivity for the NCl^+ ion. Therefore, these data points should be considered to be less reliable from this standpoint alone in addition to being subject to possible kinetic complications. Nevertheless, it is felt that there is no compelling reason to reject any of the data from the analysis of k_1 and it is interesting to note that even if the two data points below $[Cl]_{mean} = 2.5\times10^{12}$ cm^{-3} are rejected for the reasons discussed above, the intercept and slope are virtually unaltered.

Product Analysis of the Cl + C_2H_4S Reaction

The products of reaction (1) were examined as a function of time by injecting C_2H_4S at different distances from the sampling pinhole for different concentrations of Cl and C_2H_4S. Fig. 2 shows ion signal *vs.* time profiles observed in (*a*) an excess of Cl and (*b*) an excess of C_2H_4S. An optimum electron energy of 15 eV was used to minimise fragmentation of parent ions while maintaining adequate signal-to-noise ratios. Even at this energy, small fragment peaks at *m*/*e* 28 ($C_2H_4^+$) and 58 ($C_2H_2S^+$) persisted in the mass spectrum of C_2H_4S so the product ion signals that were detected at these *m*/*e* values have been corrected (*ca.* 4%) for this small contribution. Note that the relative concentrations of the product species cannot be inferred from the relative peak heights owing to different detection sensitivities, but the general trends are informative.

The most intense product peaks were those at *m*/*e* 28, identified as belonging to C_2H_4 by its fragmentation pattern, and a pair at *m*/*e* 67 and 69 in the ratio 3 : 1, which corresponds to the isotopic peaks of SCl. The rapid rise of these peaks indicate that these species are formed as initial products of the reaction. The rapid decay of the SCl^+ signal and the relatively slow production of peaks at *m*/*e* 64, 99 and 102, corresponding

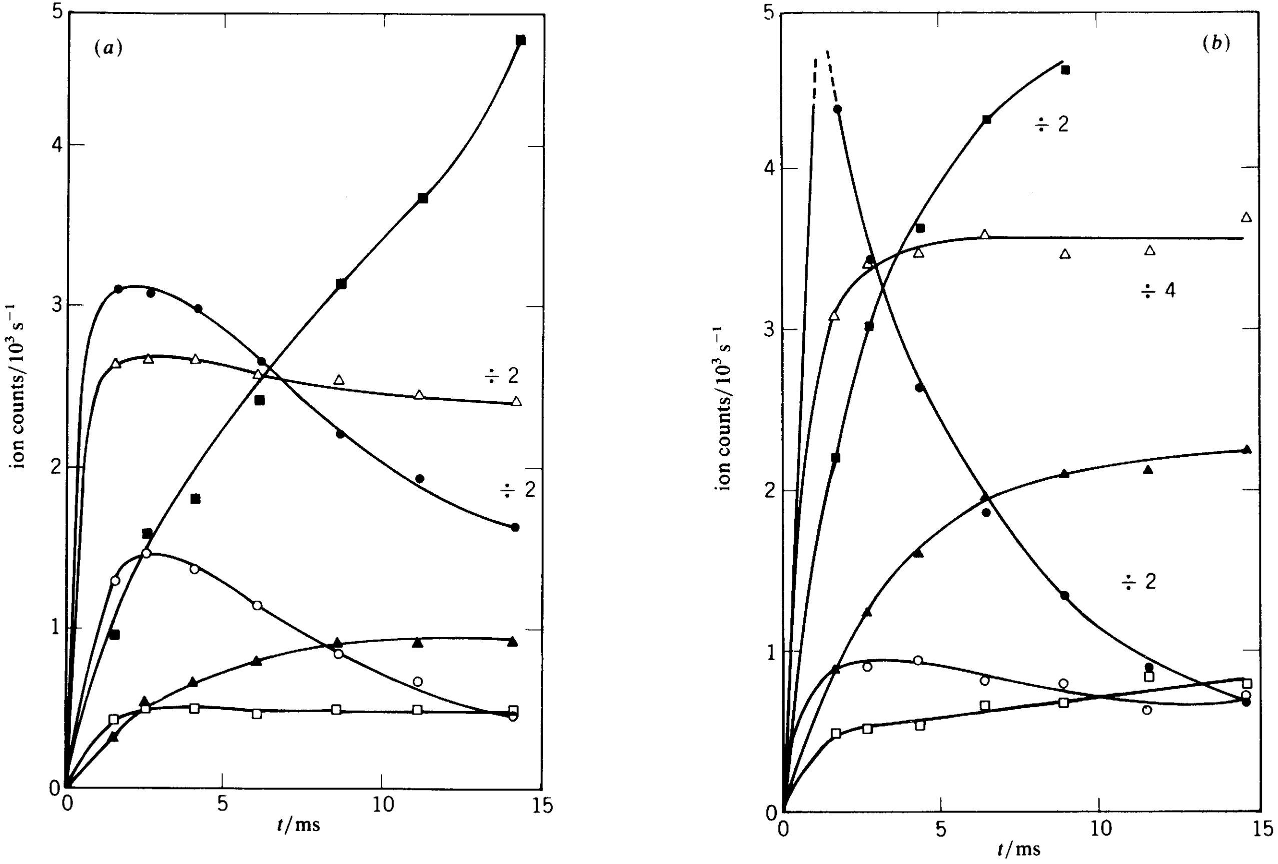


Fig. 2. Time dependence of radical species formed in the Cl + C_2H_4S reaction under conditions of: (*a*) an excess of Cl with $[C_2H_4S]_0 = 7.4 \times 10^{11}$ cm^{-3} and (*b*) an excess of C_2H_4S with $[Cl]_0 = 1.9 \times 10^{12}$ cm^{-3}. ■, S_2^+; △, $C_2H_4^+$; ●, SCl^+; ▲, S_2Cl^+; □, SCl_2^+; ○, $C_2H_2S^+$.

to S_2^+, S_2Cl^+ and SCl_2^+, respectively, suggest that these species are produced by secondary reactions involving SCl and will be discussed later in this paper.

While the above observations suggest that sulphur abstraction (1*a*) is certainly a dominant channel for reaction (1)

$$Cl + C_2H_4S \rightarrow SCl + C_2H_4 \qquad (1a)$$

the presence of a small, but significant peak at *m/e* 58, which corresponds to the species $C_2H_2S^+$, at short reaction times suggests that a hydrogen-abstraction channel must also occur to some extent. However, no peak was observed at *m/e* 59 corresponding to the C_2H_3S radical, the expected product of a simple elementary hydrogen-abstraction reaction by Cl from C_2H_4S. Two observations suggested that this was neither because C_2H_3S undergoes a rapid secondary hydrogen abstraction to form C_2H_2S, nor because C_2H_3S undergoes unimolecular decomposition to C_2H_2S. First, the $C_2H_2S^+$ signal was observed when $[C_2H_4S]_0 \gg [Cl]_0$, conditions which would preclude secondary H-atom abstraction by Cl. Secondly, no products were observed under any set of conditions from any reasonable reaction that could be proposed to explain the decay of the $C_2H_2S^+$ signal observed in an excess of Cl [fig. 2(*a*)]. A possible explanation for these observations is that C_2H_3S formed in the flow tube is dissociatively ionised to $C_2H_2S^+ + H$ in the ion source. Then the *m/e* 58 signal would be proportional to $[C_2H_3S]$ in the flow tube. The decay of the $C_2H_2S^+$ peak could be explained by the reaction of C_2H_3S with Cl_2 also present in the system, $C_2H_3S + Cl_2 \rightarrow C_2H_3ClS + Cl$, since this would also account for the small peak at *m/e* 94 corresponding to $C_2H_3ClS^+$ that was observed in this system and for the further decrease in the $C_2H_2S^+$ signal observed when additional amounts of Cl_2 was added downstream of the Cl_2-He discharge.

Branching Ratio for Reaction (1)

The branching ratio for the $Cl + C_2H_4S$ reaction was determined by measuring the yield of C_2H_4 produced by reaction (1). This was achieved by calibrating the $C_2H_4^+$ signal with known flows of C_2H_4 and then measuring the $C_2H_4^+$ signal on complete removal of known concentrations of C_2H_4S by an excess of Cl. The results are presented graphically in fig. 3. The yield of C_2H_4 varied in direct proportion to $[C_2H_4S]$ and there appeared to be no systematic dependence on $[Cl]_0$. The mean value of individual measurements of the ratio $[C_2H_4]_{\text{formed}}/[C_2H_4S]_0$ is 0.70 ± 0.08 where the error is one standard deviation of the mean. Several experiments were performed in an excess of C_2H_4S and the value of $[C_2H_4]_{\text{formed}}/\Delta[C_2H_4S]$, where $\Delta[C_2H_4S]$ is the decrease in $[C_2H_4S]$ when Cl atoms were added, was found to be larger than 0.70. This discrepancy is discussed later, but is believed to be due to increased formation of C_2H_4 by reaction of C_2H_4S with SCl radicals.

It is assumed in this analysis that there are no other sources of C_2H_4 besides reaction (1) in this system, and also that C_2H_4 is not removed by Cl or Cl_2. The first assumption is reasonable when $[Cl]_0 \gg [C_2H_4S]_0$ while the absence of any dependence of the ratio on $[Cl]_0$ validates the second assumption. Further confirmation of the latter was also provided by the failure to observe any decrease in the $C_2H_4^+$ signal when an excess of Cl or Cl_2 was added to a known flow of C_2H_4. The $Cl + C_2H_4$ reaction proceeds entirely by addition to form an energy-rich C_2H_4Cl adduct which can be stabilised by collisions with the bath gas or decompose back to reactants. The rate constant for this reaction is *ca.* 1×10^{-10} cm^3 molecule^{-1} s^{-1} at atmospheric pressure,[16] increasing to 1.9×10^{-10} cm^3 molecule^{-1} s^{-1} at the high-pressure limit.[17] No measurements of the effective rate constant have been made at pressures close to 1 Torr, where the present observations were made, but under these conditions decomposition back to reactants is the dominant fate of the adduct, thus explaining why no loss of C_2H_4 was observed.

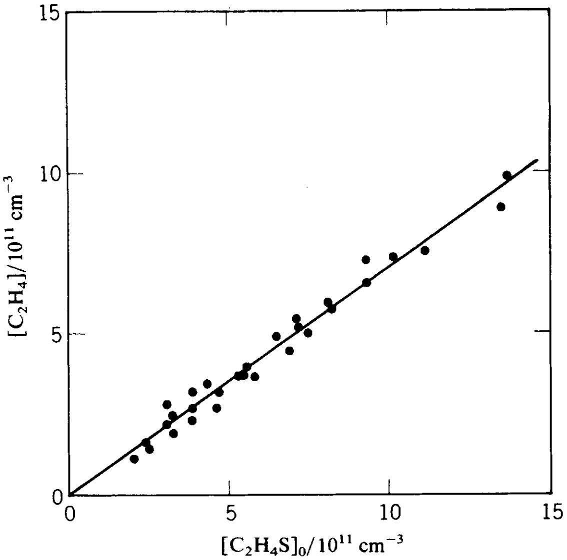


Fig. 3. Variation of $[C_2H_4]$ produced by reaction (1) with $[C_2H_4S]_0$ in an excess of Cl.

The SCl + SCl Reaction

The decay of SCl and the appearance of S_2Cl, SCl_2 and S_2 have been observed in the Cl + C_2H_4S reaction (1) and in a previous study of the Cl + H_2S reaction.[8] The kinetics of the decay of SCl were examined in both an excess of Cl and an excess of C_2H_4S by injecting C_2H_4S at different distances from the pinhole allowing at least 6 cm (*ca.* 3 ms) for reaction (1) to proceed to completion (>99%).

In an excess of Cl, plots of the reciprocal SCl^+ signal, monitored at m/e 67 using an electron energy of 15 eV, were found to be linear and parallel for different initial concentrations of C_2H_4S, indicating that the decay is second-order in [SCl]. The plots were unaffected by altering [Cl] or $[Cl_2]$, which suggests that reactions (3) and (4) are not major loss processes for SCl:

$$SCl + Cl_2 \rightarrow SCl_2 + Cl; \qquad \Delta H^{\ominus}_{298} = -52\ \text{kJ mol}^{-1} \tag{3}$$

$$SCl + Cl \rightarrow S + Cl_2; \qquad \Delta H^{\ominus}_{298} = 0\ \text{kJ mol}^{-1}. \tag{4}$$

The decay of SCl presumably occurs by the exothermic reactions:

$$SCl + SCl \rightarrow S_2Cl + Cl; \qquad \Delta H^{\ominus}_{298} = -112\ \text{kJ mol}^{-1} \tag{2a}$$

$$SCl + SCl \rightarrow SCl_2 + S; \qquad \Delta H^{\ominus}_{298} = -53\ \text{kJ mol}^{-1} \tag{2b}$$

$$SCl + SCl \rightarrow S_2 + Cl_2; \qquad \Delta H^{\ominus}_{298} = -184\ \text{kJ mol}^{-1}. \tag{2c}$$

The enthalpies of these reactions were calculated from data taken from the most recent JANAF Tables,[18] including an estimate of the heat of formation of SCl of 156 ± 17 kJ mol^{-1}. Reaction (2*c*) could account for all of the S_2 observed in this system, but similar four-centre reactions involving HS, SF and OH have been considered to be less probable than the disproportionation channels analogous to (2*a*) and (2*b*).[1,19] At long reaction times the S_2Cl^+ signal (m/e 99) decreased with increasing [Cl], with a concurrent increase in the S_2^+ signal (m/e 64), suggesting that the reaction

$$S_2Cl + Cl \rightarrow S_2 + Cl_2; \qquad \Delta H^\ominus_{298} = -71 \text{ kJ mol}^{-1} \tag{5}$$

contributes to the S_2 observed in this system in an excess of Cl. An additional contribution to the S_2^+ signal may be from fragmentation of S_2Cl in the ion source. This is expected to be significant even at 15 eV, since the appearance potential of S_2^+ from S_2Cl_2 is known to be only 9.2 eV.[20] A combination of these contributions probably explains the shape of the S_2^+ signal *vs.* time profile in an excess of Cl [fig. 2(*a*)]. An additional source of S_2 and SCl_2 could be the reaction $SCl + S_2Cl \rightarrow SCl_2 + S_2$ ($\Delta H^\ominus_{298} = -124$ kJ mol^{-1}).

In an excess of C_2H_4S the decay of SCl was generally more rapid, and the second-order plots showed significant curvature. Furthermore, the rate of decay was dependent on $[C_2H_4S]_0$, and higher S_2Cl^+ and S_2^+ signals were observed for initial SCl concentrations similar to those used in experiments where Cl atoms were in excess. These observations, and the higher fractional yield of C_2H_4 from C_2H_4S, suggest the occurrence of the reaction

$$SCl + C_2H_4S \rightarrow S_2Cl + C_2H_4. \tag{6}$$

Although the decay of SCl followed reasonable pseudo-first-order behaviour when C_2H_4S was present in a large excess, the first-order rate constants did not vary with $[C_2H_4S]_0$ in direct proportion, and were dependent on $[SCl]_0$. Thus the kinetics of the decay of SCl in an excess of C_2H_4S appear to be complex and probably involve reactions (2) and (6).

Rate Constant for Reaction (2)

In the light of the above observations the rate constant for the SCl + SCl reaction was determined in an excess of Cl. Under these conditions S atoms formed by reaction (2*b*) can regenerate SCl by reaction(7):

$$S + Cl_2 \rightarrow SCl + Cl \tag{7}$$

for which $k^{298} = 1.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}.[21] The reaction $S + SCl \rightarrow S_2 + Cl$ is probably rapid, but will not compete with reaction (7) for S atoms because the concentration of Cl_2 (*ca.* 10^{13} cm^{-3}) is two orders of magnitude higher than SCl. Reaction (3) and the reverse reaction

$$SCl_2 + Cl \rightarrow SCl + Cl_2 \tag{3'}$$

were found to be too slow, as shown later in this paper, to affect significantly the decay of SCl, and were neglected in the analysis.

Using reactions (2*a*)-(2*c*) and (7) and a steady-state approximation for [S], the decay of SCl can be described by the equation

$$-\frac{d}{dt}[SCl] = (2k_{2a} + 2k_{2c} + k_{2b})[SCl]^2$$

and

$$\frac{1}{[SCl]} = \frac{1}{[SCl]_0} + k_2 t$$

where $k_2 = (2k_{2a} + 2k_{2c} + k_{2b})$. To obtain the value of k_2 it was necessary to convert the SCl^+ signal into absolute concentrations. This was achieved by calibrating the signal, by completely converting known amounts of C_2H_4S to SCl with a large excess of Cl at short reaction times (*ca.* 2 ms) to minimise loss of SCl by reaction (2). The variation of the SCl^+ signal with $[C_2H_4S]_0$ was found to be linear up to $[C_2H_4S] = 1 \times 10^{12}$ cm^{-3}.

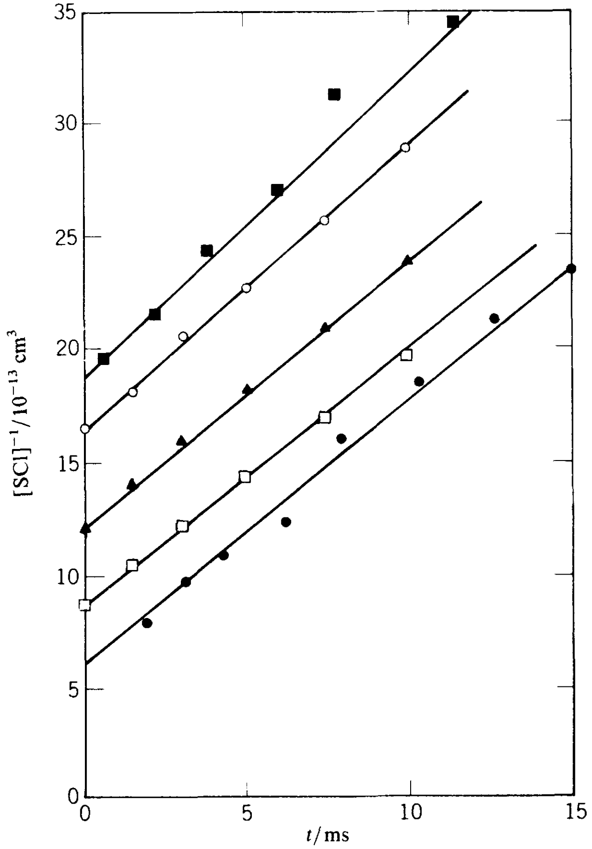


Fig. 4. Kinetics of the SCl + SCl reaction at 295 K under conditions of excess Cl. Typical plots of $[SCl]^{-1}$ against time. The different symbols refer to the runs numbered in table 2, as follows: ■, run 18; ○, run 19; ▲, run 9; □, run 16; ●, run 17.

To account for the 70% conversion efficiency for C_2H_4S into SCl, the SCl^+ signal was plotted against $[C_2H_4]_{formed}$. The detection limit for SCl using 14 eV† electrons was estimated to be 2×10^{10} cm^{-3} for a signal-to-noise ratio of one and a 10 s integration time. The sensitivity of the mass spectrometer was too low to permit electron energies below the appearance potential of 12.0 eV for SCl^+ from SCl_2 to be employed.[20] The SCl^+ signals were therefore corrected for the estimated contribution from fragmentation of SCl_2 formed in reaction (2*b*), by simultaneously measuring the SCl^+ and SCl_2^+ signals and using the ratio $(SCl^+)/(SCl_2^+)$ determined independently from a sample of SCl_2. The value of ths ratio was typically 0.3 using 14 eV electrons, which resulted in corrections of $\leqslant 7\%$.

Fig. 4 shows some plots of 1/[SCl] against time. The initial Cl atom concentration was $>2\times10^{13}$ cm^{-3}, so that >98% of the C_2H_4S reacted in a reaction time of 3 ms. The origin $t = 0$ corresponds to injection of C_2H_4S 10 cm from the pinhole, thus allowing 5 ms for the source reaction (1) to go to completion before measurements were made. The plots were linear over at least 15 ms and were parallel for a range of initial concentrations $5.5 \leqslant [SCl]_0/10^{11}$ cm$^{-3} \leqslant 22.1$. The value of k_2 was determined as the

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† 1 eV = 1.602 18 × 10^{-19} J.

Table 2. Rate data for the SCl+SCl reaction at 295 K

run	$[\mathrm{SCl}]_0/10^{11}\ \mathrm{cm}^{-3}$	$k_2/10^{-11}\ \mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1}$
1	5.5	16.4
2	7.7	13.7
3	9.2	14.6
4	5.6	16.0
5	11.9	10.9
6	12.6	12.4
7	8.9	13.0
8	9.0	13.3
9	8.2	13.0
10	12.3	12.1
11	6.7	14.9
12	22.1	12.0
13	9.8	15.1
14	13.0	12.6
15	12.7	12.4
16	11.7	13.6
17	13.9	13.6
18	5.2	13.3
19	5.9	13.6
20	10.5	10.8
21	16.5	9.5
22	8.1	10.3
23	12.0	10.9
24	19.4	10.6
25	9.1	11.9
26	10.0	11.7
27	15.3	11.4
28	6.7	12.7
29	6.2	13.9

mean value of $k_2 = (12.8 \pm 1.7) \times 10^{-11}\ \mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1} (1\sigma)$

gradient of these plots using a least-mean-squares analysis, and the results are listed in table 2 for 29 such runs. The mean value of individual measurements of k_2 at 295 K was $(12.8 \pm 2.4) \times 10^{-11}\ \mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1}$, where the error is composite of one standard deviation of the mean and estimated errors in the SCl calibration (11%).

Branching Ratio of Reaction (2)

The branching ratio for reaction (2*b*) forming $\mathrm{SCl}_2 + \mathrm{S}$, $R = k_{2b}/(k_{2a} + k_{2b} + k_{2c})$, was determined by measuring the increase in the absolute concentration of SCl_2 as a fraction of the decrease in [SCl] measured over the same reaction time. Absolute SCl_2 concentrations were obtained by calibrating the SCl_2^+ signal against known flows of SCl_2. Table 3 lists the results obtained for 12 of the runs listed in table 2, where $\Delta[\mathrm{SCl}]$ and $\Delta[\mathrm{SCl}_2]$ refer to changes in concentrations of these species over typical reaction times of 15 ms. The branching ratio is given by $R = -2\Delta[\mathrm{SCl}_2]/\Delta[\mathrm{SCl}]$. The factor of two arises because two SCl radicals react to form one SCl_2. The mean value of R was 0.11 ± 0.04, where the error is one standard deviation of the mean. From this and the value of k_2 determined previously, a value of $k_{2b} = (7.4 \pm 3.0) \times 10^{-12}\ \mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1}$ (1σ) is obtained at 295 K. Similarly, a value of the sum of individual rate constants for the other channels, $(k_{2a} + k_{2c}) = (6.0 \pm 2.4) \times 10^{-11}\ \mathrm{cm}^3\ \mathrm{molecule}^{-1}\ \mathrm{s}^{-1}$ (1σ) can be derived.

The $SCl + Cl_2 \rightleftharpoons SCl_2 + Cl$ Reactions (3)

The analysis used above for determining the rate constant and branching ratios for reaction (2) assumes that there are no other reactions forming or removing SCl_2, such as reaction (3) and the reverse reaction (3′). These reactions were examined independently.

The Reaction $SCl + Cl_2 \rightarrow SCl_2 + Cl$

Although the second-order plots for SCl in an excess of Cl were not affected by increasing the flow of Cl_2 through the discharge, a small increase in the SCl_2^+ signal was observed when Cl_2 was added through a separate side-arm downstream of the Cl_2 discharge. When corrected for the contribution from fragmentation of SCl_2, a small decrease in the SCl^+ signal was observed on increasing the Cl_2 flow. The decrease was too small to allow a systematic kinetic study as a function of time, so the rate constant for reaction (3) was estimated by measuring the decrease in the corrected SCl^+ signal as a function of Cl_2 added at a constant reaction time. The largest decrease observed was 12% over a reaction time of 22 ms for $[Cl_2] = 8.4 \times 10^{13}$ cm^{-3}. This corresponds to a pseudo-first-order rate constant of 6 s^{-1} and hence a bimolecular rate constant $k_3 \approx 7 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1} at 295 K.

The Reaction $SCl_2 + Cl \rightleftharpoons SCl + Cl_2$

Monitoring the SCl_2^+ signal while varying the reaction time up to 17 ms did not reveal any consumption of SCl_2 when an excess of Cl up to 3×10^{13} cm^{-3} was added to a flow of SCl_2. At higher [Cl] the SCl_2^+ signal actually increased, suggesting that SCl_2 is formed by reaction of Cl with sulphur deposited on the walls of the flow tube or by a heterogeneous reaction in the sampling system. Because heterogeneous formation of SCl_2 could have obscured any decrease in SCl_2 due to reaction (3′), it was not possible to estimate even a meaningful upper limit for the rate constant of reaction (3′), $k_{3'}$. A value of $k_{3'}$ can be estimated from the equilibrium constant for the equilibrium $SCl + Cl_2 \rightleftharpoons SCl_2 + Cl$ and the rate constant for the forward reaction, k_3. Using thermochemical data from the most recent JANAF Tables,[18] an equilibrium constant $K_p = 2.7 \times 10^8$ is obtained, although because of the large uncertainty in the heat of formation of the SCl radical, K_p could be as low as 5.5×10^4. The lower limit for K_p can be combined with the value of k_3 of 7×10^{-14} cm^3 molecule^{-1} s^{-1} to give an upper limit for $k_{3'}$ of 1×10^{-18} cm^3 molecule^{-1} s^{-1} at 295 K.

Table 3 shows that although the increase in $[SCl_2]$ was small, typically 4×10^{10} cm^{-3} between 5 and 20 ms of the $Cl + C_2H_4S$ reaction time, corresponding to the 15 ms that the decay of SCl and formation of SCl_2 was observed, the amount of SCl_2 formed in the first 5 ms of the source reaction (1) was comparatively high. Typical values of $[SCl_2]_0$ were $>1 \times 10^{11}$ cm^{-3}. The values of k_3 and $k_{3'}$ indicate that neither the forward or reverse reaction (3) will contribute significantly to SCl_2 formation or removal. Other sources of SCl_2 such as $SCl + S_2Cl \rightarrow SCl_2 + S_2$ and the recombination reaction $SCl + Cl + M \rightarrow SCl_2 + M$ are unlikely to be significant sources at short reaction times over all the range of relative Cl and C_2H_4S concentrations that the SCl_2^+ was observed. One possible explanation is that SCl_2 is formed by heterogeneous reactions involving SCl and Cl in the flow tube or in the sampling system, particularly as this was observed in the $Cl + SCl_2$ reaction. Note that in a mass-spectrometric study of the $SO + OClO$ reaction using a similar sampling system, MacRobert[22] observed a spurious $SClO^+$ signal which was attributed to a heterogeneous reaction in the sampling system. The occurrence of such reactions in this system indicates that the branching ratio for reaction (2*b*) should best be considered as an upper limit.

Table 3. SCl_2 yields from reaction (2*b*)[a]

run	$[SCl]_0$	$[SCl_2]_0$	$-\Delta[SCl]$	$\Delta[SCl_2]$	*R*
18	5.2	0.65	2.1	0.15	0.14
19	5.9	1.8	3.0	0.1	0.07
20	10.5	2.9	6.3	0.3	0.10
21	16.5	5.6	10.6	0.5	0.09
22	8.1	1.9	4.3	0.2	0.09
23	12.0	3.9	7.6	0.4	0.11
24	19.4	8.5	14.3	0.4	0.06
25	9.1	2.0	5.3	0.4	0.15
26	10.0	1.3	5.7	0.3	0.11
27	15.3	1.9	10.1	0.5	0.10
28	6.7	0.9	3.2	0.1	0.06
29	6.2	0.9	3.0	0.3	0.20

mean value of $R = 0.11 \pm 0.04\ (1\sigma)$

[a] All concentrations are in units of 10^{11} cm^{-3}.

Discussion

The present work has shown that abstraction of sulphur from C_2H_4S by Cl is as fast or faster than that by other atomic species such as $H(^2S)$, $O(^3P)$ and $S(^3P)$ for which the rate constants (in units of cm^3 molecule^{-1} s^{-1}) are 1.17×10^{-12},[9] 1.2×10^{-11},[10] and 4.47×10^{-11},[11] respectively, at room temperature. The present result for k_1 of $(6.6\pm0.9)\times10^{-11}$ cm^3 molecule^{-1} s^{-1} at 292 K may be compared with a recent value obtained by Nava *et al.*[12] using the flash-photolysis-resonance-fluorescence technique. These authors obtained a value of $(1.02\pm0.10)\times10^{-10}$ cm^3 molecule^{-1} s^{-1} by monitoring the disappearance of Cl in an excess of C_2H_4S. The rate constant was found to be independent of temperature and pressure over the range 211-298 K and 20-60 Torr. These two independent results are not in substantial disagreement considering the rapidity of the reaction and relative conditions employed. Furthermore, several factors considered earlier could have resulted in k_1 being slightly underestimated in the present work, so that the agreement may be better than the two values indicate. The rate constant is surprisingly high in view of the fact that the reaction is almost thermoneutral ($\Delta H^{\ominus}_{298} = +4 \pm 17$ kJ mol^{-1}). As pointed out by Nava *et al.*,[12] the greater reactivity of Cl compared to $O(^3P)$, which also has essentially no activation energy, must be due entirely to the larger *A* factor for the Cl reaction.

Ethylene and SCl radicals are the major products of the $Cl + C_2H_4S$ reaction, although hydrogen abstraction does also occur to some extent. The relatively inert nature of ethylene under the low-pressure conditions used in these experiments and the fact that SCl does not appear to react with Cl or Cl_2 at appreciable rates make reaction (1) a useful source of SCl radicals for kinetic and spectroscopic studies of this radical.

Note that the reaction

$$H + SCl_2 \rightarrow SCl + HCl; \qquad \Delta H^{\ominus}_{298} = -137\ \text{kJ mol}^{-1}$$

could in principle be used as a source of SCl. This reaction has been studied by Sung and Setser[23] who, by monitoring relative produce HCl chemiluminescence in a flowing afterglow system, obtained a rate constant of 1.5×10^{-11} cm^3 molecule^{-1} s^{-1}. However, the presence of SCl_2 cannot be tolerated in the present system owing to extensive fragmentation of SCl_2 to SCl^+ in the ion source at low ionising electron energies. For the same reason, a simple discharge in SCl_2 used by Hirota and coworkers[7] to generate SCl could not be used.

Table 4. Disproportionation of SCl and similar diatomic radicals

		$\Delta H^{\ominus}_{298}$/kJ mol^{-1}	k^a/cm^3 molecule^{-1} s^{-1}	ref.
SCl+SCl	$\rightarrow S_2Cl+Cl$	−112	6.0×10^{-11}	this work
	$\rightarrow S_2+Cl_2$	−184		
	$\rightarrow SCl_2+S$	−53	$\leqslant 7.5\times10^{-12}$	
SF+SF	$\rightarrow SF_2+S$	−45	2.52×10^{-11}	1
SH+SH	$\rightarrow H_2S+S$	−36	1.3×10^{-11}	19
ClO+ClO	→ ClOO+Cl	6	1.2×10^{-14}	24
BrO+BrO	→ BrOO+Br	−28	2.8×10^{-12}	25
FO+FO	→ FOO+F	−88	7.5×10^{-12}	25

[a] k is defined by the equation $-d[A]/dt=2k[A]^2$.

The results for the SCl self-reaction (2) may be compared to the analogous reactions of SF, SH, and the isoelectronic oxyhalide radicals ClO, BrO and FO. The results for these reactions are summarised in table 4 which shows the major disproportionation channels observed for each reaction. The much higher rate constant for the SCl+SCl reaction compared to the ClO+ClO reaction can be explained by the higher exothermicity of the channel (2*a*) forming S_2Cl+Cl than the ClO+ClO channel producing ClO_2+Cl. The reactivities of the SCl, SF and SH radicals are similar in magnitude, but increase in order of increasing exothermicity. A similar trend can be noted for the disproportionation reactions of the oxyhalide radicals. However, in contrast to the SF and SH radicals which disproportionate mainly by transfer of the F or H atoms, SCl preferentially disproportionates by transfer of the S atom. This channel is energetically favoured over the chlorine transfer channel (2*b*) by almost 60 kJ mol^{-1} and is analogous to the oxygen transfer mechanism by which the oxyhalide radicals disproportionate. However, whereas the S_2Cl radical is observed in the SCl system, the analogous XOO radical in the XO systems (X = Cl, Br, F) is unstable and is collisionally dissociated to $X+O_2$, so that the overall reactions becomes $XO+XO\rightarrow 2X+O_2$. The increased stability of S_2Cl compared to ClOO suggests that the reaction $SCl+SCl\rightarrow 2Cl+S_2$ is unlikely to be important in this system. In the presence of an excess of Cl, the ClOO radical may persist sufficiently long to react with Cl to form stable molecular products Cl_2+O_2, which is analogous to reaction (5) identified as a source of S_2 in the present system.

The extent to which S_2 is formed directly by the four-centre reaction (2*c*) is uncertain. Such reactions are considered minor for SF[1] and SH[19] compared with the disproportionation channels. However, it does appear that direct formation of the molecular products Cl_2+O_2 (for which $\Delta H^{\ominus}_{298}=-204$ kJ mol^{-1}) is a significant channel in the ClO+ClO reaction, although the relative importance of this and the radical disproportionation channel (ClOO+Cl) is not well established. Based on an estimate of the yield of atomic chlorine from this reaction in a low-pressure discharge-flow study, Clyne and coworkers[26] concluded that the radical disproportionation channel accounts for at least 50% of the total reaction pathway, and later suggested[27] that this channel is dominant at low and high pressures. Conversely, in a modulated photolysis study of the ClO+ClO reaction at atmospheric pressure, Cox and Derwent[28] found that the molecular channel accounts for 50% of the total reaction pathway. The BrO+BrO reaction is also known to proceed *via* both radical disproportionation and four-centre molecular product channels,[29,30] although the quantitative studies of Sander and Watson[29] show that only 16% of the reaction proceeds by the latter. Formation of the molecular products Br_2+O_2 by this channel is thought to occur *via* a cyclic BrOOBr transition state. The negative entropy of activation involved in forming such a complex is believed to be compensated for by the large exothermicity of this channel ($\Delta H^{\ominus}_{298} = -256$ kJ mol^{-1}). The rate constant of $(6.0 \pm 2.4) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} determined in the present work for the SCl+SCl reaction is the sum of the individual rate constants for the radical and molecular channels (2*a*) and (2*c*). It was not possible to determine the contribution made by each of these channels, but note that the molecular channel (2*c*) is not so energetically favoured over the radical channel (2*a*) as it is for the oxyhalide radicals and therefore may not make as large a contribution to the overall decay of SCl.

It is also worth noting that the ClO+ClO reaction is known to have a pressure dependence above 25 Torr which suggests that a termolecular channel forming a ClO dimer, Cl_2O_2, becomes competitive with the bimolecular channels at higher pressures.[31-33] The dimer, whose ultraviolet and infrared absorption spectra have recently been observed,[33-35] appears to possess moderate stability (*ca.* 1 s lifetime) at room temperature and atmospheric pressure and is analogous to sulphur monochloride, S_2Cl_2, which is the most stable form of the sulphur chlorides. No S_2Cl_2 product from the recombination of two SCl radicals was observed in the present work, which suggests that such a process is slow at low pressures (<2 Torr). This channel may become more important at higher pressures, but given the high rate constant for the bimolecular channels, it is unlikely to become the dominant process.

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