convex, straight) can be separately described. The analytical expressions reveal the dependencies between both the nucleation and growth rates, and the structural parameters. They can provide information about possible changes caused by a change of physical conditions.

The only limitation to application of the above procedure occurs in the case of the simultaneous growth of several polymorphic forms with different growth rates. However, this class of processes can be described by introducing some modifications; e.g., for each value of the growth rate a separate conical zone should be constructed, and the fraction of the faster growing sites, nucleated in the space occupied by slower growing type, must be neglected. The reason for this is that these faster waves will overtake the slower waves, and be the first to arrive at other points of the sample.

In the case of anisotropic growth sites oriented randomly, another effect must be taken into account because some of the growth sites, although unable to reach the arbitrarily chosen point first, constitute a spatial obstacle for others, propagating toward that point more rapidly.

While the above considerations concern samples of infinite size (or samples llarge compared to the mean size of domains), they are also correct if only one dimension of the sample is infinite (or large). Setting the nucleation rate to zero outside the sample and integrating within the limits of the sample (see eq 2a), one can describe the nucleation and growth processes in plates, strips, etc. Although in this paper we refer mainly to the formation of radially growing structures, the mathematical approach and its modifications can be useful in the description of all phenomena involving nucleation and propagation.

Temperature Study of the Rates of the Reactions of Atomic Chlorine with H_2S and C_2H_4S

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Absolute rate constants for the reaction of atomic chlorine with hydrogen sulfide, $Cl + H_2S \rightarrow HCl + HS$ (1) over the temperature range 211 to 353 K, and with episulfide, $Cl + C_2H_4S \rightarrow C_2H_4 + SCl$ (3) over the temperature range 211 to 298 K, have been measured by the flash photolysis–resonance fluorescence technique. In both systems, the results were independent of substantial variation in reactant concentration, total pressure (Ar), and flash intensity (i.e., initial [Cl]). The rate constants were also shown to be invariant with temperature. The best representation of the reaction rate constant for the respective temperature range studied was found to be $k_1 = (6.29 \pm 0.46) \times 10^{-11}$ cm^3 molecule^{-1} s^{-1} and $k_3 = (1.02 \pm 0.10) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, respectively, where the errors are one standard deviation. An upper limit for the rate constant for the reaction $Cl + OCS \rightarrow SCl + CO$ (2) was also obtained at 298 K. The results for reactions 1 and 2 are compared to previous studies and the potential importance of the rate constants for these reactions in the atmospheric chemistry of Earth and Venus is considered.

Introduction

The prominence of both chlorine chemistry and sulfur chemistry in the atmosphere of Venus and in the atmosphere of Earth has recently generated interest in studying planetary atmospheric coupling between chlorine and sulfur chemistries. Chemical models of the atmosphere of Venus, such as earlier models by Prinn[1] and models recently refined by Prinn,[2] by Winick and Stewart,[3] and by Yung and DeMore[4] have suggested coupling of chlorine and sulfur chemistries in the Venus atmosphere. Species suggested for such interaction include molecules, atoms, and radicals such as HCl, Cl, ClO, S, SH, SO, and SO_2. Reactions of Cl, ClO, or OClO with sulfur species such as SO, SO_2, or OCS have already been suggested as links for chlorine and sulfur interaction in the ambient terrestrial stratosphere.[5,6]

Hydrogen sulfide (H_2S) is an additional sulfur molecule of interest for the atmospheres of Venus and Earth. Lewis[7] predicted the presence of H_2S (as well as of OCS), and Hoffman et al.[8] reported observational evidence of the presence of H_2S in the lower atmosphere of Venus. Yung and DeMore[4] have discussed the possibility of the generation of H_2S in the liquid phase by the exchange reaction $H_2S_2O_3 + H_2O \rightarrow H_2SO_4 + H_2S$. H_2S is a known constituent of the troposphere of Earth but rapid removal by reaction with the hydroxyl radical[9,10] prevents it from reaching the stratosphere. However, volcanic eruptions can inject large amounts of sulfur compounds into the stratosphere and the resulting SO_2 has been monitored in real time by using the total ozone mapping spectrometer (TOMS) on the Nimbus 7 satellite.[11] In the case of the El Chichon eruption the total SO_2 measured by the TOMS instrument was insufficient to account for the total sulfur estimated to be ejected from the volcano based on aerosol measurements. If only part of the missing sulfur was present as H_2S, there would be large, temporary injections of H_2S directly into the stratosphere. Recent in-situ measurements of plume constituents and atmospheric distribution from eruptions of the Augustine (Alaska), the Mount St. Helens (Washington), and the El Chichon (Mexico) volcanoes have shown that these volcanoes emitted not only SO_2, OCS, CS_2, and/or HCl gases which may locally enter the stratosphere[12–19] but that, under geochem-

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ically suitable source conditions, some of their volcanic eruptions emitted H_2S as the dominant sulfur gas and may have directly injected H_2S into the Earth's stratosphere.[14b,19,20]

Interest in the potential coupling between chlorine and sulfur chemistries for the atmospheres of Venus and Earth led to a study of the kinetics of the reactions of atomic chlorine with H_2S, HS, and OCS in a discharge flow system.[21] Detection of free radical and molecular species was achieved via molecular beam sampling mass spectrometry. The rate of the reaction

$$Cl + H_2S \rightarrow HS + HCl \qquad (1)$$

was found to be very rapid at 296 K ($k_1 = 5.1 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}) while that for the corresponding reaction

$$Cl + OCS \rightarrow SCl + CO \qquad (2)$$

was immeasurably slow ($k_2 < 4 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}). These results confirmed previous room temperature studies of reaction 1 using laser photolysis–IR chemiluminescence[22] and discharge flow–resonance fluorescence.[23] The negative result for k_2 was also consistent with recent results of Eibling and Kaufman[6] based on a discharge flow–mass spectrometric study of the reaction.

In the present experiments, we report the first study of the temperature dependence of k_1. These results were obtained with the technique of flash photolysis–resonance fluorescence which has not previously been applied to this system. An upper limit for k_2 is obtained at 298 K. We also report measurement of the rate constant for the reaction

$$Cl + C_2H_4S \rightarrow SCl + C_2H_4 \qquad (3)$$

which has not been the subject of any previously reported study. This reaction is of interest as a direct route to production of the SCl radical, the sulfur analogue of ClO which plays a prominent role in atmospheric chemistry. The SCl radical was an expected product of reaction 2 and was also formed in the Cl/H_2S system[21] via reaction 1 followed by the sequence of rapid reactions $Cl + HS \rightarrow S + HCl$ and $S + Cl_2 \rightarrow SCl + Cl$.[24] Reaction 3 is expected to be rapid based on the results for the corresponding reactions of C_2H_4S with atomic oxygen[25] and with atomic hydrogen.[26]

Experimental Section

The method used in this kinetic study is flash photolysis coupled with time-resolved detection of atomic chlorine via resonance fluorescence (FP-RF). The apparatus has been described previously[27-29] and the application to the detection and monitoring of chlorine atoms has been discussed in detail.[30,31] Cl atoms were generated by flash photolysis of CCl_4. The photolysis wavelengths were determined by the absorption of CCl_4 above the wavelength cutoff of the MgF_2 window over the flashlamp ($\lambda \geq 115$ nm).

Chlorine atom resonance radiation was produced by a mixture of 0.1% Cl_2 in helium flowing through a microwave electrodeless discharge lamp at a pressure of 0.5 torr. The resonantly scattered fluorescent photons were detected at right angles to both the photolyzing and resonance light sources through a BaF_2 window ($\lambda \geq 135$ nm). Using multiple flashes, the signal from the photomultiplier was recorded by a multichannel analyzer operating in the multiscaling mode.

Preliminary experiments showed that the reactions of Cl atoms with both H_2S and C_2H_4S were fast ($k \sim 10^{-10}$ cm^3 molecule^{-1} s^{-1}) and thus small quantities of hydrogen sulfide and episulfide would have to be measured in order to prepare reaction mixtures. We therefore followed the same procedure developed in an earlier study of Cl atom reaction with H_2CO,[32] i.e., to prepare a fairly concentrated mixture of either H_2S or C_2H_4S in argon, and then subsequently prepare the reaction mixture, containing the necessary small amounts of the reactant, by further dilution techniques. Although this procedure increases slightly the systematic error, the total uncertainty in the concentration of H_2S or C_2H_4S is approximately ±3%. Reaction mixtures were flowed through the reaction cell at rates sufficient to replenish the mixtures every 1–2 flashes and hence to ensure against complications from accumulated photolysis products.

The decay constants obtained from the Cl atom decay plots produced in both the H_2S and C_2H_4S kinetic studies are composite. In addition to reaction with H_2S or C_2H_4S, the Cl atoms were also lost by diffusion out of the reaction zone viewed by the photomultiplier. Independent determination for the diffusional correction k_d was made for each set of experiments by flash photolyzing mixtures of CCl_4 and argon, in the absence of reactant, at the respective temperature and pressures used to obtain the reaction data.

Preliminary experiments at temperatures above room temperature exhibited two problems which initially prevented quantitative measurements. First, there was a rapid deterioration of signal with time which was traced to the formation of deposits on the cell windows. A second and more serious problem was the consumption of atomic chlorine on a time scale too rapid to be attributable to the added reactant H_2S or C_2H_4S. This rapid loss at high temperatures was also observed in the absence of reactant, i.e., for mixtures of CCl_4 and argon used to measure the diffusional correction k_d. Both effects most likely had a common origin—the evolution of reactive material from the hot walls of the reaction cell which consumed Cl and formed deposits on the somewhat cooler cell windows. These effects were alleviated but not completely eliminated by the following procedures: pumping the cell and flowing argon through the cell while heating; replacing the old black teflon coating of the reaction cell with a fresh coating; cleaning or replacing the lines leading to and from the reaction cell. In addition, effects of varying the flow rate were assessed over nearly an order of magnitude both for diffusion and for reaction experiments. Resultant values of k_{obsd} for both the diffusion mixtures and the reaction mixtures, respectively, were invariant (to within one standard deviation) over the range of flow rates employed. The net result of incorporating the above procedures was a significant improvement in the signal problem which enabled us to make measurements over a still somewhat limited temperature range. This limitation was not serious, however, since neither $Cl + H_2S$ nor $Cl + C_2H_4S$ exhibited a measurable temperature dependence.

Argon (Cryogenic Rare Gas Labs, Inc., 99.9995%) and helium (Ideal Gas Products, 99.9999%) were used without further purification. Chlorine (Matheson, High Purity >99.5%) was further purified by bulb-to-bulb distillation at 195 K with a middle fraction being retained for use in preparing resonance lamp mixtures. The following reagents were also purified by bulb-to-bulb distillation at the respective temperatures listed with the middle fraction being collected and retained: CCl_4 (Fisher, 99 mol %) at 233 K; H_2S

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TABLE I: Rate Data for the Flash Photolysis-Resonance Fluorescence Study of the Reaction Cl + H_2S

T/K	$[H_2S]$/ mtorr	$[CCl_4]$/ mtorr	[Ar]/ torr	flash energy/ J	no. of experiments	k_{bi}[a]/ 10^{-11} cm^3 molecule^{-1} s^{-1}
211	0.079	17.7	25	36–144	3	6.90 ± 0.47
	0.157	17.7	25	20–144	5	6.72 ± 0.51
	0.159	35.3	50	36–144	4	6.21 ± 0.31
	0.315	35.3	50	20–144	5	5.98 ± 0.60
	0.238	53.0	75	36–144	4	6.55 ± 0.46
	0.472	53.0	75	36–144	4	6.35 ± 0.52
					25	6.43 ± 0.54[b]
298	0.079	12.5	25	7–29	4	6.18 ± 0.16
	0.082	12.5	25	7–29	11	6.51 ± 0.43
	0.105	37.5	25	36–144	6	6.32 ± 0.24
	0.101	22.5	30	36–144	9	6.20 ± 0.28
	0.201	33.8	30	36–144	6	6.16 ± 0.34
	0.260	33.8	30	56–144	7	6.06 ± 0.21
	0.198	35.0	40	81–144	3	6.59 ± 0.13
	0.235	40.0	50	56–127	3	6.06 ± 0.24
	0.200	45.0	60	81–144	4	6.13 ± 0.31
	0.403	67.5	60	56–144	4	6.41 ± 0.16
	0.520	67.5	60	81–144	5	6.54 ± 0.37
	0.357	60.0	75	56–144	2	6.59 ± 0.28
	0.395	70.0	80	81–144	4	6.41 ± 0.07
	0.470	80.0	100	95–127	3	6.32 ± 0.68
					71	6.31 ± 0.34[b]
353	0.836	25.3	20	56–144	5	5.70 ± 0.32
	0.132	42.2	40	56–144	6	6.67 ± 0.76
	0.737	36.9	50	56–144	6	5.74 ± 0.29
	0.900	36.9	50	110–182	3	6.54 ± 0.38
	0.795	50.7	100	56–144	6	5.92 ± 0.22
					26	6.08 ± 0.59[b]

[a] Error limit is one standard deviation. [b] Mean value of reaction rate at that temperature.

(Matheson, 99.5%) at 150 K; C_2H_4S (Aldrich, 99%) at 298 K; and OCS (Matheson, 97.5%) at 150 K.

Results

All of the reported experiments of the reaction of atomic chlorine with, respectively, hydrogen sulfide and with episulfide were carried out under pseudo-first-order conditions with [reactant] >> [Cl]. Thus, the decay of Cl atoms is given by

$$\ln\,[\mathrm{Cl}] = -k_{\mathrm{obsd}}t + \ln\,[\mathrm{Cl}]_0 \qquad (4)$$

where [Cl] is proportional to fluorescent counts and values of k_{obsd} are obtained by using linear least-squares analysis of plots of the logarithm of accumulated fluorescent counts against time. The pseudo-first-order decay constant with hydrogen sulfide is represented by

$$k_{\mathrm{obsd}} = k_1[\mathrm{H_2S}] + k_{\mathrm{d}} \qquad (5)$$

while that for episulfide is

$$k_{\mathrm{obsd}} = k_3[\mathrm{C_2H_4S}] + k_{\mathrm{d}} \qquad (6)$$

where k_1 and k_3 are respectively bimolecular rate constants for reactions 1 and 3, and k_d is the first-order rate constant for Cl atom loss by processes other than reactions 1 and 3. As mentioned in the previous section, this includes not only the usual loss by Cl atom diffusion out of the viewing zone of the photomultiplier but also a small contribution from the reaction of Cl with impurities from the reaction cell walls. Values of k_d for reaction 1 were generally ≤5% of k_{obsd} for experiments at 211 and 353 K and ≤15% at 298 K, while k_d corrections for reaction 3 were typically ≤10% of the k_{obsd} values for all temperatures and pressures employed.

Typical results of first-order decay plots are illustrated in Figure 1 for chlorine atom diffusion and reaction with H_2S at 211 K. The linearity of these plots confirms the pseudo-first-order conditions. The values for k_1 and k_3 respectively are calculated from eq 5 and 6 by substituting the experimentally determined values of k_{obsd}, k_d, and the respective $[H_2S]$ or $[C_2H_4S]$.

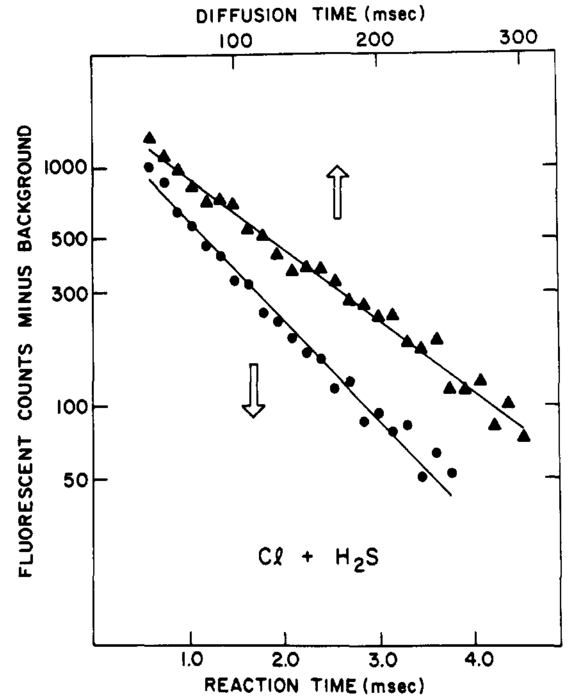

Figure 1. Examples of first-order decay plots for the reaction (●) of Cl + H_2S and for Cl atom diffusion (▲) at 211 K. The lines are determined from linear least-squares analysis of the data points; errors in the decay constants are one standard deviation. Both experiments were carried out at a total pressure of 75 torr, P_{CCl_4} = 53 mtorr, and a flash energy of 144 J. P_{H_2S} = 0.472 mtorr for the reaction experiment. k_{obsd} = 933 ± 19 s^{-1} and k_d = 10 ± 1 s^{-1}.

The results at 211, 298, and 353 K for reaction 1 are presented in Table I and those at 211, 249, and 298 K for reaction 3 are presented in Table II. The internal consistency of the data over a moderate range of, respectively, H_2S and C_2H_4S reactant concentrations, as well as the general agreement with results of previously reported studies of k_1 (see Discussion) indicate that, for the temperature ranges reported in Tables I and II of the present study, there was no significant loss of reactant. For both reactions, the respective results show that k_{bi} is invariant with

TABLE II: Rate Data for the Flash Photolysis–Resonance Fluorescence Study of the Reaction Cl + C_2H_4S

T/K	[C_2H_4S]/ mtorr	[CCl_4]/ mtorr	[Ar]/ torr	flash energy/ J	no. of experiments	k_{bi}[a]/ 10^{-11} cm^3 molecule^{-1} s^{-1}
211	0.233	33.9	30	81–144	3	11.00 ± 1.43
	0.310	33.9	30	81–163	4	9.86 ± 0.73
	0.350	50.8	45	81–163	4	10.81 ± 0.89
	0.185	42.4	50	56–144	4	9.87 ± 0.08
	0.273	42.4	50	81–144	4	9.56 ± 0.34
					19	10.18 ± 0.89[b]
249	0.250	29.9	20	81–144	3	9.49 ± 0.37
	0.291	44.9	30	56–110	2	9.70 ± 0.24
	0.203	57.5	60	81–144	4	9.57 ± 0.91
	0.333	57.5	60	81–144	3	9.49 ± 0.08
					12	9.55 ± 0.51[b]
298	0.097	31.3	25	81–144	4	12.05 ± 0.44
	0.145	31.3	25	81–144	4	10.98 ± 0.43
	0.191	18.8	30	110–144	4	9.81 ± 0.57
	0.242	18.8	30	110–144	3	11.52 ± 0.56
	0.193	62.5	50	81–144	4	9.76 ± 0.61
	0.290	62.5	50	81–144	3	10.50 ± 0.65
	0.383	37.5	60	81–144	4	9.93 ± 0.51
	0.484	37.5	60	110–144	3	9.31 ± 1.08
					29	10.49 ± 1.05[b]

[a] Error limit is one standard deviation. [b] Mean value of reaction rate at that temperature.

TABLE III: Comparison of Rate Data for the Reaction Cl + $H_2S \rightarrow$ HS + HCl (1)

$10^{11}k_1$/ cm^3 molecule^{-1} s^{-1}	T/K	species monitored	method[a]	ref
7.3 ± 0.9	298	HCl	LP-CL	22b
4.00 ± 0.08	296	Cl	DF-RF	23
5.1 ± 0.7	296	H_2S	DF-MS	21
6.29 ± 0.46	211–353	Cl	FP-RF	this study

[a] LP, laser photolysis; CL, chemiluminescence; DF, discharge flow; RF, resonance fluorescence; MS, mass spectrometry; FP, flash photolysis.

temperature, gas composition, total pressure, and flash intensity (i.e., initial [Cl]) within one standard deviation. The value for k_1 over the temperature range studied is thus represented by (6.29 ± 0.46) × 10^{-11} cm^3 molecule^{-1} s^{-1} while that for k_3 is (1.02 ± 0.10) × 10^{-10} cm^3 molecule^{-1} s^{-1}, where in each case the error is the standard deviation of the mean.

Some effort was also given toward studying the rate of a third Cl atom reaction, namely,

$$\mathrm{Cl + OCS \rightarrow SCl + CO} \qquad (2)$$

Experiments were conducted at 298 K at pressures of OCS between 100 and 300 mtorr. We were not able to observe any net loss of Cl above that due to diffusion and results yielded a room temperature k_2 of $<1 \times 10^{-14}$ cm^3 molecule^{-1} s^{-1}. A more extensive study of this reaction was prohibited by the inability to adequately purify the OCS of small amounts of H_2S, an impurity which, as can be seen in Table I, undergoes very rapid reaction with atomic chlorine.

Discussion

The present determination of k_1 may be compared with previous results obtained for the reaction Cl + $H_2S \rightarrow$ HS + HCl (1) at 298 K only. This comparison is given in Table III and shows that the temperature-independent result obtained here, k_1 = (6.29 ± 0.46) × 10^{-11} cm^3 molecule^{-1} s^{-1}, lies between the higher value reported by Nesbitt and Leone[22b] and the lower values of Clyne and Ono[23] and Clyne et al.[21] The results are only in moderate agreement; the range of values considerably exceeds the quoted uncertainty of the individual determinations. Considering the wide range of species monitored and techniques employed, this moderate agreement is probably acceptable and there is no compelling reason to reject any one of the four measurements. A simple average of the results shown in Table III yields k_1 = (5.7 ± 1.4) × 10^{-11} cm^3 molecule^{-1} s^{-1} which should be applicable over the temperature range 200 to 350 K. The results of Leone and co-workers[22] showed vibrational excitation predominantly in the newly formed HCl bond. In their view, Cl initially attacks the S atom but during the time scale of the collision one of the H atoms rotates around to react with Cl and departs with it along the exit channel. By analogy with other fast reactions, they expect the presence of an initially attractive energy surface and the absence of any significant activation barrier. The present study showing the rate constant to be independent of temperature confirms their expectation. The temperature independent value of k_1 = 6.3 × 10^{-11} cm^3 molecule^{-1} s^{-1} measured in this study may be compared with previous work from this laboratory on fast H atom abstraction reactions by Cl with molecules such as H_2CO,[32] CH_3OH,[31] CH_3OCH_3,[31] and CH_3OOCH_3.[33] All these molecules react with atomic chlorine with a temperature-independent rate constant which is within a factor of 2 of 1 × 10^{-10} cm^3 molecule^{-1} s^{-1}.

Our negative result for Cl + OCS $\rightarrow$ SCl + CO (2) is consistent with two previous estimates of the upper limit for k_2 at room temperature. A low value for k_2 is also consistent with the fact that reaction 2 is about 8 kcal/mol endothermic. Eibling and Kaufman[6] suggest $k_2 \leq 10^{-16}$ cm^3 molecule^{-1} s^{-1} based on monitoring Cl in a discharge flow–mass spectrometric (DF-MS) study with OCS in excess. Clyne et al.[21] also used the DF-MS technique but monitored OCS with Cl in excess and obtained the result $k_2 < 4 \times 10^{-15}$ cm^3 molecule^{-1} s^{-1}. The present study employed a different source for Cl (flash photolysis of CCl_4) and a different monitoring technique (resonance fluorescence). A larger upper limit of $k_2 < 10^{-14}$ cm^3 molecule^{-1} s^{-1} was observed due to the presence of a small residual impurity of H_2S in the purified reagent grade OCS.

There are no published results with which our determination of the rate constant for Cl + $C_2H_4S \rightarrow$ SCl + C_2H_4 (3) may be compared. Recent unpublished work by Murrells[34] employed this reaction to prepare the SCl free radical in a discharge flow–mass spectrometric study of the reactions of this radical. He measured k_3 by monitoring C_2H_4S under pseudo-first-order conditions with Cl > C_2H_4S and obtained the result k_3 = (6.6 ± 0.9) × 10^{-11} cm^3 molecule^{-1} s^{-1} at 298 K. This is in moderate agreement with the present temperature-independent result of k_3 = (1.02 ± 0.10) × 10^{-10} cm^3 molecule^{-1} s^{-1}. Our result for Cl + C_2H_4S may be compared with previous work from this laboratory on the rate of the reaction of O(^{3}P)[25] and H[26] with C_2H_4S. The comparison is summarized in Table IV. All are fast reactions with k(298 K) for O(^{3}P) being an order of magnitude faster than that for

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TABLE IV: Comparison of Rate Data for the Reaction of Atomic Species with C_2H_4S Obtained by the Flash Photolysis-Resonance Fluorescence Technique

atomic species	k(298 K)/ cm^3 molecule^{-1} s^{-1}	A/ cm^3 molecule^{-1} s^{-1}	E/ cal/mol	ref
H	1.17×10^{-12}	2.87×10^{-11}	1880	26
$O(^3P)$	1.26×10^{-11}	1.26×10^{-11}	0	25
Cl	1.02×10^{-10}	1.02×10^{-10}	0	this study

H and k(298 K) for Cl an order of magnitude faster than that for $O(^3P)$. The enhanced reactivity of $O(^3P)$ compared to H is attributable to the absence of an energy barrier for the former reaction. However, the greater reactivity of Cl compared to $O(^3P)$ is due entirely to the much larger A factor for the Cl reaction since both reactions occur with essentially no activation energy. A comparably larger A factor is also observed for Cl + H_2S (6.3×10^{-11} cm^3 molecule^{-1} s^{-1} from the present study) compared to that for $O(^3P) + H_2S$ (1.0×10^{-11} cm^3 molecule^{-1} s^{-1} from Singleton et al.[35] and Whytock et al.[36]). Both the H + C_2H_4S reaction[26,37] and the $O(^3P) + C_2H_4S$ reaction[25] involve the abstraction of a sulfur atom. Thus by analogy we would expect a major channel for the Cl reaction to be the abstraction of S:

$$Cl + C_2H_4S \rightarrow SCl + C_2H_4 \qquad (3)$$

The present experiments provide no evidence for this but the mass spectrometric study of Murrells[34] provides direct confirmation of the formation of SCl. The present results and the study of Murrells demonstrate that reaction 3 is a convenient source of the SCl radical for kinetic or spectroscopic investigations.

The implications of these results for atmospheric science is that for any system containing appreciable levels of H_2S, whether constant in time or transitory in nature, there could be significant coupling between chlorine and sulfur chemistry via this reaction. Since the reaction $Cl + H_2S \rightarrow HS + HCl$ (1) is not only rapid but temperature independent, this statement applies equally to both high-temperature atmospheric systems such as Venus and low-temperature atmospheric systems such as Earth. Modeling considerations[38] suggest that the relative rates of reaction of H_2S with, respectively, Cl (Table I) and OH[10] may enable the Cl + H_2S reaction to be more important relative to that of the OH + H_2S reaction in the middle and upper stratosphere than in the lower stratosphere. Another specific example of Cl-S coupling would be the temporary injection of H_2S into the stratosphere of the Earth by volcanic eruption. After compositionally suitable volcanic eruptions, reaction 1 could become more important if OH is depleted in the stratosphere because of processes such as $OH + SO_2 + M \rightarrow HOSO_2 + M$ and $OH + HCl \rightarrow H_2O + Cl$ while Cl could likely be enhanced due to added HCl.[16] Within such a system, reaction 1 might be a significant complementary reaction to OH radical, O atom, or photolysis conversion processes for H_2S in attempting to better understand pathways and time values for volcanic sulfur gas conversion to stratospheric sulfate aerosols. Another aspect which may be of interest for atmospheric modeling is that of the effects which nonambient H_2S could have upon Cl chemistry, particularly as a potentially competitive loss process, along with methane, for Cl atoms and resultant implications concerning chlorine-catalyzed ozone perturbations. Volcanic-induced perturbations may, therefore, include effects upon tropospheric or stratospheric reaction chemistry of sulfur-, chlorine-, and oxygen-containing source species, the reaction couplings of which could be quite complex. The very slow reaction rate for Cl + OCS appears to preclude coupling of atmospheric chlorine and sulfur chemistries through this reaction.

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Registry No. H_2S, 7783-06-4; OCS, 463-58-1; C_2H_4S, 420-12-2; Cl, 22537-15-1; HCl, 7647-01-0; HS, 13940-21-1; C_2H_4, 74-85-1; CO, 630-08-0; SCl, 14989-32-3.

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Molecular Dynamics Simulation of Disorder Transitions in Lipid Monolayers

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A 78-ps molecular dynamics simulation of a model lipid monolayer using an umbrella sampling method has been performed in order to calculate the free energy, potential energy, and entropy profiles for kink transitions and other hydrocarbon chain rotational isomerizations. A novel feature of umbrella sampling employed here is the determination of a free energy surface as a function of two torsions which are coupled to form a kink disorder. This method allows the calculation of equilibrium populations of interior gauche and kink conformers of greater statistical significance than the usual unbiased molecular dynamics or Monte Carlo simulations. Isolated gauche conformations are found to be nearly as thermally accessible as kink disorders because they are accommodated by ubiquitous surrounding chain tilting. Such tilting may occur even in the absence of complete torsional isomerization within chains. Gauche conformations further serve as intermediates in the formation of kinks and account for the substantial positive entropy of activation of kink transitions. Chain-tilting disorders are thus coupled to and essentially modulate rotational isomerization in lipid aggregates and are yet another example of a gated reaction mechanism. The results are of particular significance with respect to the nucleation of disorder phase transitions in monolayers.

I. Introduction

It is well-known that lipid monolayers and bilayers exhibit a fairly pronounced phase transition from a highly ordered gel state, with hydrocarbon chains in all-trans conformation, to a more disordered liquid crystalline state, in which many chain bonds are rotated into gauche conformations.[1] The role of this transition in biological function is under widespread investigation. A complete understanding of both the structural and dynamical aspects

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