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Experimental values of rate constants and ion product distributions for reactions of a series of ions with CS_2

Christopher D. Molek, Jason L. McLain, Nigel G. Adams*,
Lucia M. Babcock, Laura L. Gibbs

Department of Chemistry, University of Georgia, Athens, GA 30602, USA

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Abstract

Rate constants and product ion distributions have been determined in a Selected Ion Flow Tube (SIFT) for the reactions of He^+, $He_2{}^+$, Ar^+, $N_2{}^+$, N^+, CO^+, $CO_2{}^+$, O^+, D^+, CS^+, C^+, S^+, $CS_2{}^+$, $S_2{}^+$ and $D_3{}^+$ with CS_2 at 297 K. These ions have recombination energies varying from 2372 kJ/mol (24.58 eV) for He^+ to 903 kJ/mol (9.36 eV) for $S_2{}^+$. The reactions, except for the Ar^+, $S_2{}^+$ and $CS_2{}^+$ reactions proceed at, or close to, the collisional rate with charge transfer (both dissociative and non-dissociative) being an important mechanism. S^+ is a common product and, in the case of $D_3{}^+$, exothermic proton transfer is rapid. For the slower reaction of $CS_2{}^+$, ternary association occurs. The reactions are discussed relative to the reactivity of these ions with the analogues, OCS and CO_2.

Keywords: Ion-molecule reaction; Rate constant; Product distribution; Non-dissociative charge transfer; Dissociative charge transfer

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1. Introduction

Part of the rationale for this study was the significance of sulfur containing compounds in interstellar clouds (isc) [1,2] and comets [3]. To date, in the isc, 14 sulfur containing species have been detected (SO, NS, CS, H_2S, SO_2, OCS, C_2S, H_2CS, SiS, HNCS, C_3S, CH_3SH, SO^+, and HCS^+). However, this poses a problem since these only comprise <4% of the cosmic abundance [1,2,4] and therefore a considerable abundance of other sulfur containing species must be present. In a search for a solution to this problem, the reactions of S^+ [5], $S_2{}^+$ [6,7], SO^+ [8] and CS^+ [9] have previously been studied with a series of observed and likely interstellar molecules. These studies provided an insight into the problem suggesting that HS_2 and the protonated ion HS_2H^+, may be significant repositories of sulfur [10]. Not included in these studies were reactions with CS_2. CS_2 has not been detected in isc because its symmetry renders it unobservable in the infrared and the microwave, but the analogue, OCS has been detected. CO_2 is similarly undetected, although its protonated form $HCO_2{}^+$ has been seen [1,2,4]; thus, CS_2 is undoubtedly present. In order to provide a more complete database of reactions of sulfur containing species, we have studied the reactions of CS_2 with a series of fifteen ions (He^+, $He_2{}^+$, Ar^+, $N_2{}^+$, N^+, CO^+, $CO_2{}^+$, O^+, D^+, CS^+, C^+, S^+, $CS_2{}^+$, $S_2{}^+$, and $D_3{}^+$) and have determined the rate constants and percentage ion product distributions.

2. Experimental

These studies were conducted using a Selected Ion Flow Tube (SIFT) apparatus, which has been described previously [11] and this detailed discussion will not be repeated here. Fourteen of the fifteen ions ($He_2{}^+$ was generated by three body association of injected He^+) were generated by dissociative and non-dissociative ionization in an electron impact ion source, variously containing He (He^+, $He_2{}^+$), Ar (Ar^+), D_2 (D^+, $D_3{}^+$ by reaction $D_2{}^+ + D_2$), N_2 ($N_2{}^+$, N^+), CS_2 ($CS_2{}^+$, CS^+, C^+, S^+, $S_2{}^+$ by reaction $S^+ + CS_2$) and CO_2

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* Corresponding author. Tel.: +1 706 542 3722; fax: +1 706 542 9454.
E-mail address: adams@chem.uga.edu (N.G. Adams).

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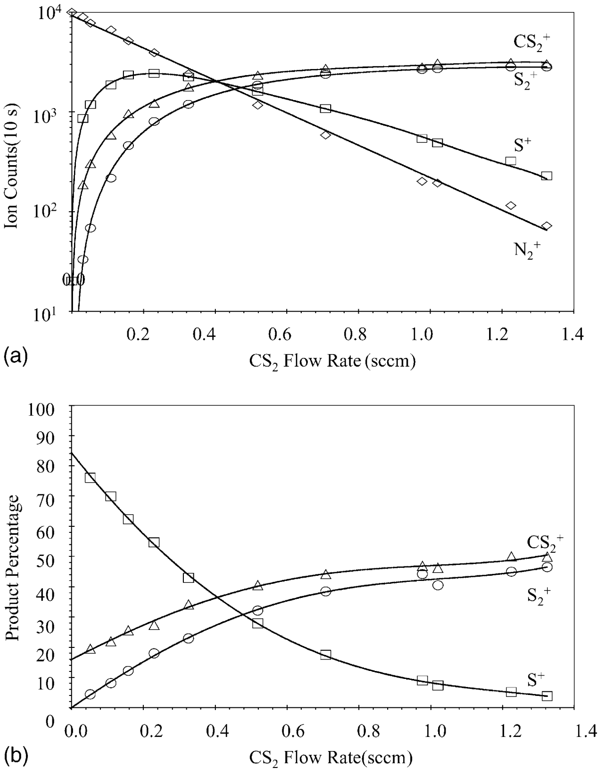

Fig. 1. (a) Variations of N_2^+ counts and product ion counts, and (b) percentage of the ion products, with CS_2 flow. In (a) the decay of N_2^+ show excellent linearity over two orders of magnitude decrease in counts. In (b) extrapolation to zero flow, using polynomial fits, gives the percent product ion distribution (shown in Table 1, together with those for the other CS_2 reactions). S^+ and CS_2^+ are primary products with the S^+ reacting further to give additional CS_2^+ and the secondary product S_2^+.

(CO_2^+, CO^+, C^+, O^+) and injected into the flow tube after mass selection in a quadrupole mass filter. Thence the ions were carried along the flow tube to a downstream mass spectrometer/ion counting detection system by a He carrier gas (at a throughput of 16 slm and a He pressure of 0.5 Torr). To study the reactions, controlled and accurately measured flows of CS_2 were added to the He carrier with reaction distances of 29.8, 59.6, and 83.6 cm depending on the rate of the reaction. The rate constants and percentage product ion distributions were determined in the usual way [12,13]. The rate constants are accurate to ±20% and the percentage product ion distributions to ±5 in the quoted percentage. The CS_2 had a purity of 99.9% and was further purified by freeze-pump-thaw cycles. Source gases were used without further purification. All measurements were made at room temperature (297 K).

3. Results

Rate constants were determined from semi-logarithmic ion count decays versus CS_2 flow that were linear from more than one order of magnitude up to three orders of magnitude. No evidence was seen for internal excitation in the reactant ions in terms of non-linearity of the semi-logarithmic plots or the detection of endothermic channels. An example for the reaction of N_2^+ with CS_2 is given in Fig. 1. Data for determining product distributions were taken using small flows of CS_2 so that they could be accurately determined. Kinetic information obtained in this study is given in Table 1.

Of these data obtained, only five (Ar^+, N_2^+, CO_2^+, CS_2^+, and D_3^+) of the fifteen reactions with CS_2 have been studied previously and these earlier data are also included in the table (note literature data for CS^+ is for an excited ion reaction with CS_2 [21] and therefore was not included in the table). For Ar^+, both the rate constants and product distributions are in agreement to within error with the previous study [22], but this study also indicates a slightly higher percentage of CS_2^+. For N_2^+, the rate constant is in agreement with that previously obtained in the same study as the Ar^+ measurement. However, although the same product ions are detected and with the same ion being dominant, the difference between the product percentages is outside the limits of experimental error. There is presently no explanation for this difference; it could, however, be due to differing corrections for mass discrimination. For the CO_2^+ and D_3^+ reactions, the same single charge transfer (c.t.) and proton transfer (p.t.) products, respectively, were detected and with the same rate constants as in previous studies [23,24]. For the CS_2^+ reaction, the literature values of 1.8 and 5.8 (−27) cm⁶/s, with O_2 and CO_2 third bodies, respectively, are consistent with the current value of 2.4(−27) cm⁶/s with He as third body [14–16]. The overall evidence indicates that the present measuring techniques are well calibrated.

4. Discussion

As can be seen from Table 1, within these data there is a general trend of c.t. and dissociative c.t. products. Note that long-range c.t. is not an option in all cases since as the recombination energy of the reactant ion decreases, the long-range dissociation mechanism without complex formation becomes endothermic. The D_3^+ and CS_2^+ reactions are exceptions to this trend, with proton transfer and association being the only channels, respectively. The D_3^+ reaction proceeds at the collisional rate as is common for this mechanism [25], with the CS_2^+ association being relatively slow. CS_2^+ is a common c.t. product, although it is not observed for the highest recombination energy species (He^+ and He_2^+), where dissociative c.t. channels are exothermic. Note that the products could not be identified in the slow reaction of S_2^+ (no direct c.t. processes are energetically possible in this case), which proceeds at about 1% of the collisional rate. All other reactions proceed at, or close to, the collisional rate. Also, there is no consistent trend of increasing CS_2^+ product percentage with decreasing recombination

Table 1
Rate constants and percentage product ion distributions for the reactions of CS_2 with the ions indicated

Reactant ion	Product	Percentage		CS_2			OCS^b			CO_2^b		
		Present	Literature	k_{Expt} (cm^3/s)		$k_{Theor}{}^c$ (cm^3/s)	Product	Percentage	k_{Expt} (cm^3/s)	Product	Percentage	k_{Expt} (cm^3/s)
				Present	Literature							
He^+ (24.587)	S^+	58	–	2.07 (−9)		3.56 (−9)				C^+	2	1.0 (−9)
	CS^+	31	–							O^+	14	
	C^+	11								CO^+	78	
										$CO_2{}^+$	5	
$He_2{}^+$ (22.223)	S^+	$\sim$75				2.58 (−9)		–	–		–	–
	C^+	$\sim$25										
	CS^+	Small										
Ar^+ (15.759)	S^+	$\geq$93	88	3.70 (−10)	3.5 (−10)	1.36 (−9)	S^+		1.3 (−9)		–	4.8 (−10)
	$CS_2{}^+$	$\leq$7	12		2.6 (−10)		OCS^+			$CO_2{}^+$	100	
$N_2{}^+$ (15.581)	S^+	84	60	1.42 (−9)	1.2 (−9)	1.54 (−9)	S^+	80	1.36 (−9)		–	8.0 (−10)
	$CS_2{}^+$	16	40				OCS^+	20		$CO_2{}^+$	100	
N^+ (14.534)	S^+	12	–	1.55 (−9)	–	2.02 (−9)	S^+	22	1.4 (−9)		–	1.12 (−9)
	CS^+	8	–				CS^+	5		CO^+	18	
	$CS_2{}^+$	80	–				OCS^+	73		$CO_2{}^+$	82	
CO^+ (14.014)	S^+	71	–	1.56 (−9)	–	1.54 (−9)	S^+	10	1.41 (−9)	$CO_2{}^+$	100	1.10 (−9)
	$CS_2{}^+$	29	–				OCS^+	90				
$CO_2{}^+$ (13.777)	$CS_2{}^+$	100	100	1.39 (−9)	9.9 (−10) 1.3 (−9)	1.32 (−9)	OCS^+	100	9.60 (−10)		–	–
O^+ (13.618)	CS^+	40	–	1.56 (−9)	–	1.91 (−9)	S^+	3	6.70 (−10)	$O_2{}^+$	100	1.10 (−9)
	$CS_2{}^+$	60	–				OCS^+	97				
D^+ (13.603)	S^+	65	–	3.44 (−9)	–	4.98 (−9)		–	–	$CO_2{}^+$	100	3.5 (−9)
	DS^+	24	–									
	CS^+	11	–									
CS^+ (11.33)	$CS_2{}^+$	100	–	1.30 (−9)	–	1.32 (−9)	$CS_2{}^+$	100[d]	7.7 (−10)		–	–
C^+ (11.26)	CS^+	91	–	1.81 (−9)	–	2.16 (−9)	CS^+	80	2.0 (−9)	CO^+	90	1.1 (−9)
	$CS_2{}^+$	9	–				OCS^+	20		$CO_2{}^+$	10	
S^+ (10.36)	$S_2{}^+$	52	–	1.39 (−9)	–	1.46 (−9)	$S_2{}^+$	100	9.1 (−10)			<5 (−13)
	$CS_2{}^+$	48	–									
$CS_2{}^+$ (10.073)	$CS_2{}^+\cdot CS_2$	100	–	3.33 (−11)[a]	–	1.13 (−9)		–	–		–	–
$S_2{}^+$ (9.356)	N/A[e]		–	1.0 (−11)	–	1.18 (−9)		–	–		–	–
$D_3{}^+$	$DCS_2{}^+$	100	100	3.07 (−9)	3.1 (−9)	2.95 (−9)	HCO^+	<10	1.9 (−9)	$DCO_2{}^+$	100	1.74 (−9)
							$HCOS^+$	>90				

For comparison, equivalent data from the literature [14–16] are given for the analogous reactions of CO_2 and OCS with these ions. Also included are the theoretical rate constants determined using variational transition state theory [17] with polarizabilities and dipole moments taken from [18]. The number in parentheses beside each ion is the recombination energy in eV. The ionization energies for CS_2, OCS and CO_2 are 10.073, 11.18 and 13.777 eV, respectively [18].

[a] Effective binary k at $p_{He} = 0.493$ Torr and is equivalent to a ternary k of 2.4 (−27) cm^6/s with a He third body; literature values of 1.8 and 5.8 (−27) cm^3/s are available with O_2 and CO_2 third bodies [14].

[b] Experimental literature values [14–16].

[c] Theoretical capture value calculated using the model of Su and Chesnavich [17].

[d] Taken from Dzidic et al. [19] (note typographical error in the Anicich compilation [20]).

[e] Product distribution could not be determined for this slow reaction.

energy, and the other products indicate that the mechanism could be a mixture of direct/long range c.t. and complex formation.

4.1. He^+/He_2^+

He^+ and He_2^+ reactions proceed by exothermic dissociative c.t. giving the same product channels (S^+, C^+ and CS^+). The CS^+ product channel for the He_2^+ reaction is surprisingly much smaller than for the He^+ reaction, given the difference in recombination energy between the two reactants is only 228 kJ/mol (2.36 eV).

$$He^+ + CS_2 \rightarrow S^+ + CS + He + 932\,\text{kJ/mol} \quad 58\% \qquad (1a)$$

$$\rightarrow CS^+ + S + He + 839\,\text{kJ/mol} \quad 31\% \qquad (1b)$$

$$\rightarrow C^+ + 2S + He + 132\,\text{kJ/mol} \quad 11\% \qquad (1c)$$

$$\rightarrow C^+ + S_2 + He + 558\,\text{kJ/mol} \quad 11\% \qquad (1d)$$

$$He_2^+ + CS_2 \rightarrow S^+ + CS + 2He + 708\,\text{kJ/mol} \quad \sim 75\% \qquad (2a)$$

$$\rightarrow CS^+ + S + 2He + 614\,\text{kJ/mol} \quad < 1\% \qquad (2b)$$

$$\rightarrow C^+ + S_2 + 2He + 333\,\text{kJ/mol} \quad \sim 25\% \qquad (2c)$$

S_2^+ production, although exothermic in both cases, is not observed, probably because of the steric hindrance due to the two S atoms being at opposite ends of the reactant CS_2. Indeed, in the whole series of reactions, even where complex formation is required, S_2^+ is only observed as a product for the S^+ and CS^+ reactions where there is an additional source of S.

4.2. Ar^+/N_2^+

For Ar^+ and N_2^+, a comparison is interesting since the recombination energies are very similar (differing by only 17.4 kJ/mol (0.18 eV), with that of N_2^+ being the smaller). In these cases the product distributions are similar with S^+ being the dominant product and CS_2^+ production being small.

$$Ar^+ + CS_2 \rightarrow S^+ + Ar + CS + 80\,\text{kJ/mol} \quad \geq 93\% \qquad (3a)$$

$$\rightarrow CS_2^+ + Ar + 549\,\text{kJ/mol} \quad \leq 7\% \qquad (3b)$$

$$N_2^+ + CS_2 \rightarrow S^+ + N_2 + CS + 63\,\text{kJ/mol} \quad 84\% \qquad (4a)$$

$$\rightarrow CS_2^+ + N_2 + 531\,\text{kJ/mol} \quad 16\% \qquad (4b)$$

Bond formation in the product neutrals producing ArCS is not possible for Ar^+, but in the N_2^+ case this is a possibility yielding N_2CS. The major products in these distributions are associated with the less energetic pathway; the explanation can be found by looking at the potential energy surface for several electronic states of CS_2^+ [26]. In the non-dissociative c.t. pathway there is enough energy to excite CS_2^+ to the $B^2\Sigma_u^+$ electronic state, which intersects with the dissociative curve crossing yielding $S^+ + CS$.

4.3. D^+/O^+

D^+ and O^+ also have similar recombination energies, but in these cases, the products are very different with non-dissociative c.t. being dominant for the exothermic O^+ reaction and nonexistent for D^+even though it is similarly exothermic.

$$O^+ + CS_2 \rightarrow CS^+ + SO + 302\,\text{kJ/mol} \quad 40\% \qquad (5a)$$

$$\rightarrow CS_2^+ + O + 342\,\text{kJ/mol} \quad 60\% \qquad (5b)$$

and

$$D^+ + CS_2 \rightarrow S^+ + (DCS) + \text{N/A} \quad 65\% \qquad (6a)$$

$$\rightarrow DS^+ + CS + \text{N/A} \quad 24\% \qquad (6b)$$

$$\rightarrow CS^+ + DS + 139\,\text{kJ/mol} \quad 11\% \qquad (6c)$$

$$\rightarrow CS_2^+ + D + 341\,\text{kJ/mol} \quad 0\% \qquad (6d)$$

Note that in the D^+ reaction the DS^+ channel dominates over CS^+ as would be expected if multiple charge transfers occur as the products separate, since DS has a smaller ionization energy than CS by 87 kJ/mol (0.9 eV) and would be energetically favored (N/A indicates that insufficient literature data were available to calculate the reaction energetics). If this is so, it is surprising that SO^+ is not produced in the O^+ reaction since the ionization energy of SO is 100 kJ/mol (1.04 eV) less than that of CS. Even though no SO^+ is produced, the CS^+ + SO channel (5a) is of similar magnitude to the sum of channels (6b and c) consistent with a similar overall mechanism.

4.4. C^+/CS^+

C^+ and CS^+ also have similar recombination energies, however, here the reaction products appear very different, with CS_2^+ being small for the C^+ reaction and the only channel for the CS^+ reaction.

$$C^+ + CS_2 \rightarrow CS^+ + CS + 266\,\text{kJ/mol} \quad 91\% \qquad (7a)$$

$$\rightarrow CS_2^+ + C + 115\,\text{kJ/mol} \quad 9\% \qquad (7b)$$

$$CS^+ + CS_2 \rightarrow CS_2^+ + CS + 121\,\text{kJ/mol} \quad 100\% \qquad (8)$$

For the C^+ reaction, an S atom abstraction would yield the observed and dominant CS^+ product. However, the CS^+ reaction only proceeds by the non-dissociative c.t. channel. This channel has similar energy to the non-dissociative channel in the C^+ reaction, but the observed dominant

CS^+ product channel is energetically favored by 151 kJ/mol (1.57 eV).

4.5. N^+/CO^+

Although N^+ and CO^+ have relatively similar recombination energies (differing by only 50 kJ/mol (0.52 eV)), the product distributions for their CS_2 reactions are quite different.

$$N^+ + CS_2 \rightarrow S^+ + (NCS) + N/A \quad 12\% \tag{9a}$$

$$\rightarrow CS^+ + NS + 355\,kJ/mol \quad 8\% \tag{9b}$$

$$\rightarrow {CS_2}^+ + N + 430\,kJ/mol \quad 80\% \tag{9c}$$

$$CO^+ + CS_2 \rightarrow S^+ + (C_2OS) + N/A \quad 71\% \tag{10a}$$

$$\rightarrow {CS_2}^+ + CO + 380\,kJ/mol \quad 29\% \tag{10b}$$

In both cases S^+ and ${CS_2}^+$ are products, but the percentages are approximately reversed. The channel producing S^+ and N + CS is endothermic and thus the reaction requires complex formation with bonding in the neutral products, yielding NCS. In the reaction of N^+ with OCS, the analogous product channel S^+ + NCO was observed. Additionally, in the CO^+ reaction with CS_2, the channel producing S^+ and CO + CS is an endothermic process thus the reaction must yield C_2OS.

4.6. ${CO_2}^+/S^+$

The ${CO_2}^+$ reaction proceeds by the non-dissociative c.t. only. The S^+ reaction has a dissociative c.t. channel and a non-dissociative channel. The dissociative channel leads to ${S_2}^+$ production, which may be due to the S-atom abstraction.

$${CO_2}^+ + CS_2 \rightarrow {CS_2}^+ + CO_2 + 357\,kJ/mol \quad 100\% \tag{11}$$

$$S^+ + CS_2 \rightarrow {S_2}^+ + CS + 82\,kJ/mol \quad 52\% \tag{12a}$$

$$S^+ + CS_2 \rightarrow {CS_2}^+ + S + 28\,kJ/mol \quad 48\% \tag{12b}$$

This ${S_2}^+$ product is only observed in one other reaction in the series studied, that of CS^+, where the mechanism again does not require the formation of the ${S_2}^+$ from the two S atoms at opposite ends of the CS_2 molecule. That ${S_2}^+$ is not produced in any of the other reactions indicates that the coalescence of the two S atoms from CS_2 is sterically hindered and is not efficient. The S atoms in the ${S_2}^+$ product are then from both reactants indicating intermediate complex formation.

4.7. Comparison with literature data for the O containing analogs OCS and CO_2

In the Ar^+ reactions with CS_2 and OCS, S^+ and non-dissociative c.t. are both products, although the quantitative product distribution for OCS was not determined (see Table 1 for these and other literature data on the reactions with OCS and CO_2). ${CO_2}^+$ was the only product in the CO_2 reaction, since in this reaction, dissociation yielding O^+ is not energetically favorable. For ${N_2}^+$, the comparable channels with CS_2 and OCS have similar contribution to the product distribution, however ${CO_2}^+$ is the only product in the CO_2 reaction.

For the N^+ and CO^+ reactions, the rate constants are all close to collisional. For N^+, in all cases non-dissociative c.t. is dominant at ∼80%, the remaining channel in the CO_2 reaction being the strongly bonded CO^+. The analogous CS^+channel is observed in the CS_2 and OCS reactions. Additionally a S^+ channel is observed, which is possible in the OCS case by formation of NCO product neutral and therefore presumably possible with formation of NCS product neutral in the CS_2 reaction. Surprisingly the CO^+ channel is not seen in the OCS reaction. This may be partly due to sulfur having a lower ionization energy than CO. In comparison with N^+, in the CO^+ reaction with CS_2 there is a decrease in the non-dissociative c.t. as the recombination energy of the reactant ion decreases and with an increase in S^+ product channel. Comparing the $CO^+ + CS_2$ reaction to the analogous CO^+ reactions with OCS and CO_2, it is noticed that the OCS and CO_2 reactions have the non-dissociative c.t. channel as the dominant channel. The reason why this channel is not the dominant channel in the CO^+ reaction with CS_2 could not be explained and needs to be further investigated.

For the O^+, ${CO_2}^+$ and D^+ reactant ions, all the reactions are rapid (but with the OCS reaction being somewhat slower) except in the ${CO_2}^+$ reaction with CO_2 where only the undetectable resonant c.t. is possible. The D^+ reaction with OCS has not been studied. In the other ${CO_2}^+$ reactions, non-dissociative c.t. is the only product. For the O^+reactions with CS_2 and OCS non-dissociative c.t. is observed along with dissociative channels. Additionally, only the dissociative channel is observed in the O^+ reaction with CO_2. Note that CO^+ is not a product, which may be due to O_2 having a lower ionization energy. The combination of a small difference in recombination energy between ${CO_2}^+$ and O^+ and dissociative product channels only existing in the O^+ reactions may imply that formation of an intermediate complex occurs in the O^+ case.

The D^+ reaction with CO_2 is very different giving only non-dissociative c.t. Here for ${O_2}^+$ to be a product would require the more weakly bonded CD to be produced, and also the 2 O atoms to bond from opposite ends of the O=C=O. It was noted earlier that in reactions with CS_2, the ${S_2}^+$ product channel is only seen if the reactant ion contains a S atom, presumably for the same reason.

The C^+ and CS^+ reactions are all rapid (the reaction of CS^+ with CO_2 has not been studied). Although the recombination energies of the ions are getting smaller, non-dissociative c.t. is not becoming more prevalent except for the CS^+ reaction with CS_2, where it is the only channel. The same ${CS_2}^+$ product ion is similarly observed in the CS^+ reaction with OCS, indicating a S-atom abstraction reaction (note that the product ion was incorrectly reported in a recent compilation [20]). In the reaction of C^+ with CS_2 the dominant dissociative channel is energetically favored over the non-dissociative c.t. channel by 151 kJ/mol (1.57 eV). A dominant dissociative channel is similarly seen in the reactions of C^+ with OCS and CO_2. The C^+ reaction with OCS forms the CS^+ product ion and neutral CO, presumably because CS has a lower ionization energy than CO. Similarly the C^+ reaction with CO_2 produces CO^+ as the dominant product ion.

In the S^+ reactions, the ${S_2}^+$ product channel for CS_2 and OCS presumably take place by a S-atom abstraction. No equivalent O-atom abstraction occurs for the CO_2 reaction even though the strongly bonded CO would be produced. The S^+ reaction with OCS produces 100% ${S_2}^+$ in contrast to the S^+ reaction with CS_2 where the large channel is due to the non-dissociative charge transfer. The ${S_2}^+$ channel produced in the OCS reaction is exothermic by 217 kJ/mol (2.25 eV) and the analogous channel in the CS_2 reaction is exothermic by 82 kJ/mol (0.85 eV), which is only 55 kJ/mol (0.57 eV) larger than the competitive non-dissociative c.t. product channel. No literature data are available for the ${CS_2}^+$ reaction. Literature data are also not available for the ${S_2}^+$ reaction.

The ${D_3}^+$ reactions proceed almost exclusively by proton transfer as might be expected. Only in the case of the OCS reaction is there another channel with the likely neutral product being D_2S. This would imply that the proton attacks the electronegative O-atom and would then lead to the isomer COD^+ rather than DCO^+ and this needs to be investigated.

5. Conclusions

Of the fifteen reactions studied, a majority of the reactions proceed by a non-dissociative charge transfer. There was no clear trend by which this channel became more prevalent with a decreasing recombination potential of the reactant ion. However, there is an expected consistency between the product distribution abundances and the energetics. The comparison between the CS_2 reactions and previously studied OCS and CO_2 reactions is consistent with similar mechanisms taking place between the reactant ion and neutrals as dictated by the energetics.

In the CS_2 reactions, the major products, S^+, ${S_2}^+$, C^+, CS^+, and ${CS_2}^+$ are all significant in chemical models of the interstellar medium. S^+ and ${S_2}^+$ are involved in further ion-molecule reactions, which have been discussed by Decker et al. [5–7]. The reaction products C^+ and CS^+ react with H_2 to give CH^+ and HCS^+ [20], respectively, both of which have been detected in isc [1,2]. Also, ${CS_2}^+$ reacts with atomic H to produce HCS^+ and this reaction could play an important role in diffuse clouds where atomic H is prevalent. Additionally, photo-fragmentation of ${CS_2}^+$ could occur leading to smaller ion fragments, which could react with H_2 producing observed isc species such as CH^+ and HCS^+. In dense clouds, where atomic H is much less prevalent than H_2, ${CS_2}^+$ can be a long lived species allowing dissociative electron-ion recombination to occur, as has been studied recently (Plasil et al., 2004, in preparation). In addition, ${CS_2}^+$ could react with abundant CO, which has not been investigated in the laboratory. CS_2 reactions may play an important role in contributing to the observed sulfur containing molecules in the isc and therefore the unobservable CS_2 may partly contribute to the difference in the cosmic abundance of sulfur and the abundance of observed sulfur species in the isc.

Acknowledgements

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