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Organo-sulfur chemistry in dense interstellar clouds via S^+-hydrocarbon reactions

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Summary. Because S^+ is predicted via current model calculations to be an abundant ion in dense interstellar clouds, it might be expected to play a role in the synthesis of organo-sulfur compounds via ion-molecule reactions. In particular, the newly observed interstellar molecule CCS is probably formed via a reaction sequence initiated by the reaction between S^+ and acetylene (C_2H_2) to produce the organo-sulfur ion HC_2S^+ and H. The organo-sulfur ion can then undergo dissociative recombination with electrons to form CCS and H. Calculations based on models of dense interstellar clouds show that the abundance of CCS achieved via this synthesis may be only a factor of 6–7 below observation in TMC-1. An interesting and unexplored problem is whether reactions analogous to that between S^+ and C_2H_2 can initiate the production of other organo-sulfur compounds such as the newly observed CCCS. In order to assess the importance of S^+-hydrocarbon reactions in the chemistry of dense interstellar clouds, we have measured a variety of these reactions. In general, our results show that S^+-hydrocarbon reactions sometimes exhibit a sulfur-insertion channel leading to organo-sulfur ionic species but that other channels, especially charge exchange, tend to dominate for the larger and more saturated hydrocarbons studied.

Key words: atomic and molecular processes – chemical reactions – interstellar medium: molecules

1. Introduction

The recent laboratory and interstellar detection of the radicals CCS and CCCS (Saito et al., 1987; Yamamoto et al., 1987) are of significant importance to interstellar chemistry. In TMC-1, the fractional abundances of CCS and CCCS (assuming the column density of H_2 to be $\approx 1(22)\,cm^{-2}$) are $8(-9)$ and $2.5(-9)$ respectively. These values are far larger than the fractional abundances of CCO and CCCO in the same source, despite the greater elemental abundance of oxygen as compared with sulfur. Indeed, the radical CCO has not even been detected in the interstellar medium; the upper limit to its fractional abundance in TMC-1 is reported to be $1(-10)$ (Saito et al., 1987) whereas the observed value for CCCO in TMC-1 is also of this magnitude (Matthews et al., 1984). The CCCO fractional abundance has been calculated via ion-molecule schemes based on radiative association reactions involving hydrocarbon ions and CO (Herbst et. al., 1984). It is clear that analogous reactions involving the much less abundant CS cannot explain the greater abundances of CCS and CCCS. A more likely possibility is reactions involving the sulfur ion S^+. Unlike O^+, which reacts rapidly with molecular hydrogen, S^+ is calculated by dense cloud models (e.g. Herbst and Leung, 1986a,b) to have a moderately large fractional abundance in the range $4(-11)$–$2.5(-9)$ depending upon such variables as the age, temperature, visual extinction, and gas phase elemental depletion of the cloud. In addition, the reaction

$$S^+ + C_2H_2 \longrightarrow HC_2S^+ + H \qquad (1)$$

has been studied in the laboratory (Anicich and Huntress, 1986) and probably leads to CCS via the reaction

$$HC_2S^+ + e \longrightarrow CCS + H\,. \qquad (2)$$

One can easily estimate the fractional abundance of CCS produced via this mechanism using predicted abundances for S^+ and C_2H_2 from models, assuming that the dissociative recombination branching ratio to produce CCS + H is 0.5, and assuming that CCS is depleted via reactions with protonated ions and not by neutrals:

$$CCS + IH^+ \longrightarrow HC_2S^+ + I \qquad (3)$$

where $IH^+ = H_3^+$, HCO^+, etc. and only 50% of the HC_2S^+ ions produced in (3) do not cycle back to CCS. The fractional abundance of CCS with respect to H_2, designated f(CCS), is then given by the simple equation

$$f(CCS) = \{k_1 f(S^+) f(C_2H_2)\}/\{k_3 f(IH^+)\} \qquad (4)$$

where k_i is the rate coefficient for reaction (i) and $f(j)$ represents the fractional abundance with respect to H_2 of species j. The value of k_1 has been previously determined to be $9.8(-10)\,cm^3\,s^{-1}$ (Anicich and Huntress, 1986).

The linear CCS radical has a dipole moment of 2.9 D (Murakami, 1987) and is expected to react rapidly with ions at low temperature if it is thermalized before reaction (Adams et al., 1985). We therefore assign a value for k_3 of $3(-8)\,cm^3\,s^{-1}$ at interstellar cloud temperatures. Herbst and Leung (1986b) have published a model for TMC-1 using rapid rates for reactions between ions and polar neutrals. For their "standard" early-time, low-metallic-abundance model, $f(S^+)$ is calculated to be $7.7(-11)$, $f(C_2H_2)$ to be $9.5(-7)$, and $f(IH^+)$ to be $6.0(-9)$. With these values, Eq. (4) leads to the prediction that f(CCS) =

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4(−10), which is a factor of 20 less than the observed value. Other models lead to similar CCS abundances. If the reactions between CCS and protonated ions occur at lower rates or if unmeasured reactions involving S^+ and other hydrocarbons which lead to CCS production are considered, one can obtain better agreement. A more realistic possibility is that dissociative recombination of HC_2S^+ leads only to CCS and H so that depletion of CCS *cannot* occur via its reactions with protonated ions such as H_3^+ and HCO^+ but only via reactions with ions of lesser abundances such as C^+, H^+, and He^+. In this instance, Eq. (4) with $f(IH^+)$ replaced by the sum of the fractional abundances of these latter ions leads to a prediction for f(CCS) of 1.2(−9), still somewhat below the observed value in TMC-1, but in reasonable agreement with it.

The production of CCS via S^+, while not leading to exact agreement with observation, appears to be faster than other ion-molecule formation schemes based on S, CS etc. The reason that S^+-based synthesis of CCS is more rapid than S-based synthesis is that the calculated S^+/S abundance ratio in interstellar cloud models normally exceeds the hydrocarbon ion/hydrocarbon neutral abundance ratio by a considerable factor. Thus, the $S^+ + C_2H_2$ reaction is likely to be more important than the (unmeasured) $S + C_2H_2^+$ reaction. However, the reverse may be true in circumstellar sources such as IRC + 10216 (Millar, private communication) where CCS and CCCS have also been observed (Cernicharo et al., 1987).

It is of interest to explore in the laboratory the ion-molecule chemistry between S^+ and neutral hydrocarbons to determine whether these reactions can lead to a rich organo-sulfur chemistry in dense interstellar clouds. In addition to the reaction between S^+ and C_2H_2, the only previously studied reaction of this class is $S^+ + CH_4$, which leads mainly to H_3CS^+ (Smith et al., 1981; Anicich and Huntress, 1986), a precursor of H_2CS. In this paper, we report experimental results on a number of reactions between S^+ and an assortment of hydrocarbons. In future work, we hope to be able to study reactions involving neutral sulfur and hydrocarbon ions.

2. Experiments

Measurements of the rate coefficients and ion product distributions for the reactions of S^+ in its ground electronic state with an assortment of hydrocarbon molecules (Table 1) were carried out at 300 K using our selected ion flow tube (SIFT) apparatus which has been described in detail elsewhere (Smith and Adams, 1979). The S^+ ions were derived from an electron impact ion source containing OCS and (after mass filtering) were injected into a helium carrier gas. A fraction of the injected S^+ ions ($\approx$20%) were in metastable electronic states (^2D, ^2P) as shown by their rapid reaction with H_2, which is unreactive with ground state S^+. To remove metastable S^+ ions, sufficient N_2 was added to the ion swarm upstream of the port via which the reactant hydrocarbon gases were introduced. The N_2 technique effectively relaxed the metastable ions into their ground state without introducing any chemical reactions since no exothermic channels for the reaction between S^+ and N_2 are available.

The method currently adopted to determine the flow rates of the hydrocarbon vapors requires values for the viscosities of these vapors. These values were not available for the larger hydrocarbon species and thus viscosity values equal to 0.5 of that of helium (a value typical of hydrocarbons) were adopted. This approximation is not likely to lead to large errors in the derived rate coefficients. Specifically, we estimate a maximum error of ±50% in the rate coefficients for the reactions of the

Table 1. Results of S^+-hydrocarbon reactions

Hydrocarbon	Ionization Potential (eV)[a]	Products	Product Distribution	Rate Coefficient $cm^3\ s^{-1}$	Collisional Rate Coefficient $cm^3\ s^{-1}$
CH_4	12.6	**$H_3CS^+ + H$**	0.95	4.0(-10)[b]	1.2(-9)
		$HCS^+ + H_2 + H$	0.05		
C_2H_2	11.4	**$HC_2S^+ + H$**	1.0	9.8(-10)[c]; 9.5(-10)	1.1(-9)
C_2H_4	10.5	$HCS^+ + CH_3$	0.7	9.8(-10)	1.3(-9)
		$H_3C_2S^+ + H$	0.3		
C_2H_6	11.5	$C_2H_5^+ + SH$	0.7	9.9(-10)	1.3(-9)
		$H_3CS^+ + CH_3$	0.25		
		$H_5C_2S^+ + H$	0.05		
CH_3CCH	10.4	**$H_3C_3S^+ + H$**	0.6	1.7(-9)	1.6(-9)
		$C_3H_3^+ + SH$	0.2		
		$HCS^+ + C_2H_3$	0.15		
		$C_3H_4^+ + S$	0.05		
C_3H_6	9.7	$C_3H_5^+ + SH$	0.4	1.2(-9)	1.4(-9)
		$C_3H_6^+ + S$	0.3		
		$HCS^+ + C_2H_5$	0.1		
		$H_2CS^+ + C_2H_4$	0.1		
		$H_3C_2S^+ + CH_3$	0.05		
		$H_5C_3S^+ + H$	0.05		
C_3H_8	11.1	$C_3H_7^+ + SH$	0.9	1.1(-9)	1.4(-9)
		$H_3CS^+ + C_2H_5$	0.1		
C_4H_6	9.1	$C_4H_6^+ + S$	0.85	1.3(-9)[d]	1.5(-9)
		$C_3H_3^+ +$ neutrals	0.05		
		$HCS^+ + C_3H_5$	0.05		
		$H_5C_4S^+ + H$	0.05		
C_4H_8	9.6	$C_4H_8^+ + S$	0.35	9.7(-10)[d]	1.5(-9)
		$C_4H_7^+ + SH$	0.25		
		$H_2CS^+ + C_3H_6$	0.20		
		$H_3C_2S^+ + C_2H_5$	0.10		
		$H_5C_3S^+ + CH_3$	0.10		
C_4H_{10}	10.6	$C_4H_9^+ + SH$	0.65	1.6(-9)	1.5(-9)
		$C_3H_5^+ +$ neutrals	0.25		
		$C_3H_7^+ +$ neutrals	0.10		
c - C_5H_8	9.0	$C_5H_8^+ + S$	0.8	1.7(-9)[d]	--------
		$C_5H_7^+ + SH$	0.2		
cis - C_5H_8	8.6	$C_5H_8^+ + S$	1.0	1.9(-9)[d]	--------
c - C_6H_{10}	8.9	$C_6H_{10}^+ + S$	0.65	1.8(-9)[d]	1.6(-9)
		$C_6H_9^+ + SH$	0.20		
		$C_5H_8^+ + H_2CS$	0.10		
		$C_5H_7^+ +$ neutrals	0.05		
C_6H_6	9.2	$C_6H_6^+ + S$	0.70	1.6(-9)[d]	1.6(-9)
		$C_5H_6^+ + CS$	0.20		
		$C_6H_6S^+$	0.05		
		$H_4C_4S^+ + C_2H_2$	0.05		

[a] Ionization potential of atomic sulfur is 10.36 eV (See Rosenstock *et al.* 1977 for a useful compendium of atomic and molecular ionization potentials).

[b] Smith, Adams, and Lindinger (1981)

[c] previous ICR value by Anicich and Huntress (1986).

[d] calculated assuming a viscosity of 0.5 relative to helium.

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Table 2. Molecular polarizabilities and dipole moments

Hydrocarbon	Polarizability (Å^3) [a]	Dipole Moment (D) [b]
CH_4	2.59	0.0
C_2H_2	3.33	0.0
C_2H_4	4.26	0.0
C_2H_6	4.45	0.0
CH_3CCH	6.18	0.781
C_3H_6	6.26	0.366
C_3H_8	6.29	0.084
C_4H_6	8.64	0.0
C_4H_8	8.52	0.33
C_4H_{10}	8.20	0.05
c - C_6H_{10}	10.7	0.55
C_6H_6	10.53	0.0

[a] Miller (1986)
[b] Nelson, Lide, and Maryott (1967)

larger hydrocarbon species and $\pm 25\%$ for those reactions for which hydrocarbon viscosities were available. Note that in Table 1, in which our results are tabulated, the collisional rate coefficients k_c are also included except for two reactions for which the required molecular parameters for determination of k_c (Table 2) were also unavailable. For a few of the reactions in Table 1 the measured rate coefficient exceeds the collisional value by an amount smaller than our estimated error.

3. Results and discussion

From Table 1, it can be seen that the overall rate coefficients for the reactions between S^+ and hydrocarbon molecules are normally near or at the collisional limiting value. This is itself an interesting phenomenon because one might expect the high spin multiplicity (quartet) of ground state S^+ to lead to difficulties in correlation with ground or low-lying product electronic states. However, it would appear either that high-multiplicity, low-lying product excited states abound and/or that spin flipping is not an uncommon occurrence.

A second observation is that as the hydrocarbon reactants increase in size, the number of product channels can become quite large, with charge exchange playing a major if not an absolutely dominant role when it is exothermic. From the point of view of interstellar chemistry, the most important synthetic product channel is simple sulfur insertion into the hydrocarbon species with the attendant removal of atomic hydrogen. This channel, shown in boldface in Table 1, is quite significant for CH_4 and two unsaturated two-carbon hydrocarbons studied (C_2H_2, C_2H_4). It is not significant for the saturated hydrocarbons ($C_2H_6, C_3H_8, C_4H_{10}$). For the unsaturated three-carbon hydrocarbons, sulfur insertion occurs readily with C_3H_4 (methyl acetylene) but is only a minor channel for C_3H_6 (propene), where charge exchange and H^- transfer dominate, and is even less important for C_4H_6 (butadiene). Sulfur insertion is also minor to non-existent for the larger unsaturated hydrocarbons.

Both limited observation and gas phase theory show that dense interstellar cloud hydrocarbons are primarily exceedingly unsaturated and often radical in nature. These very unsaturated hydrocarbons are difficult to produce in the laboratory when more than a few carbon atoms are involved and we are unable to study their reactions with S^+. From our experimental results, which chiefly involve more saturated hydrocarbons, it is unclear whether or not the strongly unsaturated hydrocarbons will insert sulfur readily, as do the small unsaturated hydrocarbons C_2H_2 and C_3H_4, or whether they will undergo charge exchange and H^- transfer predominantly, as the larger and more saturated hydrocarbons do. Charge exchange is likely if the ionization potential of the hydrocarbon is less than that of sulfur, but ionization potentials for many of the strongly unsaturated hydrocarbons of interstellar interest are not known. From the known ionization potentials of the unsaturated acetylenic hydrocarbons C_4H_2 and C_6H_2 (Rosenstock et al., 1977), it would appear that charge exchange with S^+ is likely for hydrocarbons in this family. We are not aware, however, of studies of the ionization potentials of hydrocarbons of the type C_nH_2 where n is odd.

If the reaction between S^+ and the abundant interstellar species c-C_3H_2 (cyclopropenilydene) contains an important sulfur insertion channel which also leads to ring breakage:

$$S^+ + \text{c-}C_3H_2 \longrightarrow HC_3S^+ + H, \tag{5}$$

it can lead to the production of CCCS via a subsequent dissociative recombination reaction. Note that reaction (5) would also have to undergo a spin flip or produce HC_3S^+ in a triplet state. To estimate the abundance of CCCS produced, we can assume that it is depleted at the same rate as CCS. Then

$$f(\text{CCCS})/f(\text{CCS}) = k_5 f(\text{c-}C_3H_2)/\{k_1 f(C_2H_2)\}. \tag{6}$$

In TMC-1, c-C_3H_2 is measured to have a fractional abundance of $\approx 1.5(-8)$, in good agreement with theory at "early time" (Herbst and Leung, 1986a,b). Using the calculated value for $f(C_2H_2)$, we obtain that $f(\text{CCCS})/f(\text{CCS}) = 0.02\, k_5/k_1$. Since c-$C_3H_2$ is decidedly polar (dipole moment = 3.43 Debye; Kanata, Yamamoto, and Saito 1987), one might expect k_5 to exceed k_1 at low temperature. If one assumes k_5 to be $\approx 1(-8)\,\text{cm}^3\,\text{s}^{-1}$ (Herbst and Leung, 1986b) at the temperature of TMC-1, then $f(\text{CCCS})/f(\text{CCS}) \approx 0.2$, which is in good agreement with the observed abundance ratio of 2.5/8. Study of reaction (5) in the laboratory is, of course, urgently needed. If this reaction is slow, an alternate possibility is the reaction between S^+ and C_3H_4 which produces the ion $H_3C_3S^+$ with a branching ratio of 0.60 (Table 1). Methyl acetylene (C_3H_4) has an abundance approximately one-third that of cyclopropenilydene in TMC-1 (Irvine et al., 1987) although it is considerably less polar. In addition, the ion $H_3C_3S_3^+$ would have to dissociate considerably in a dissociative recombination reaction to produce CCCS. Although this mechanism cannot be ruled out, it does not appear rapid enough to explain the observed abundance ratio between CCCS and CCS. It would, however, be a likely synthetic pathway for species such as HCCCS and H_2CCCS if they are stable.

If reaction (5) is found to proceed at a large rate, then it might be profitable to study the reactions between S^+ and larger unsaturated hydrocarbons. For example, the reaction between S^+ and C_4H_2 might lead to C_4S via the pathway

$$S^+ + C_4H_2 \longrightarrow HC_4S^+ + H \tag{7}$$

$$HC_4S^+ + e \longrightarrow C_4S + H. \tag{8}$$

One possible problem with this synthesis is the fact that the ionization potential of C_4H_2 is slightly lower than that of S, so that charge transfer may dominate reaction (7). If charge transfer

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is found to be the dominant channel in reactions (5) and (7), then the alternative mechanism of reactions between S and hydrocarbon ions would have to be investigated for larger organosulfur compounds.

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References

Adams, N.G., Smith, D., Clary, D.C.: 1985, *Astrophys. J. Letters* **296**, L31

Anicich, V.G., Huntress, Jr., W.T: 1986, *Astrophys. J. Suppl.* **62**, 553

Cernicharo, J., Guélin, M., Hein, H., Kahane, C.: 1987, *Astron.* Astrophys. **181**, L9

Herbst, E., Leung, C.M.: 1986a, *Monthly Notices Roy. Astron. Soc.* **222**, 689

Herbst, E., Leung, C.M.: 1986b, *Astrophys. J.* **310**, 378

Herbst, E., Smith, D., Adams, N.G.: 1984, *Astron. Astrophys.* **138**, L13

Irvine, W., Goldsmith, P.F., Hjalmarson Å.: 1987, in *Interstellar Processes*, eds. D.J. Hollenbach, H.A. Thronson, Jr., Dordrecht, Reidel, p. 561

Kanata, H., Yamamoto, S., Saito, S.: 1987, *Chem. Phys. Letters* **140**, 221

Matthews, H.E., Irvine, W.M., Friberg, P., Brown, R.D., Godfrey, P.D: 1984, *Nature* **310**, 125

Miller, T.M.: 1986, in *CRC Handbook of Chemistry and Physics, 67th Ed.*, Chemical Rubber Publishing Co., p. E66

Murakami, A.: 1987, private communication to Saito et al. (1987)

Nelson, R.D., Jr., Lide, D.B., Jr., Maryott, A.A.: 1967, *Selected Values of Electric Dipole Moments for Molecules in the Gas Phase*, National Standard Reference Data Series-National Bureau of Standards (US)-10

Rosenstock, H.M., Draxl, K., Steiner, B.W., Herron, J.T.: 1977, *J. Phys. Chem. Ref. Data* **6**, Supplement No. 1

Saito, S., Kawaguchi, K., Yamamoto, S., Ohishi, M., Suzuki, H., Kaifu, N.: 1987, *Astrophys. J. Letters* **317**, L115

Smith, D., Adams, N.G.: 1979, in *Gas Phase Ion Chemistry*, ed. M.T. Bowers, New York: Academic Press, Vol. **1**, p. 1

Smith, D., Adams, N.G., Lindinger, W.: 1981, *J. Chem. Phys.* **75**, 3365

Yamamoto, S., Saito, S., Kawaguchi, K., Kaifu, N., Suzuki, H, Ohishi, M.: 1987, *Astrophys. J. Letters* **317**, L119

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