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Published in:
Astrophysical Journal

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DISSOCIATIVE RECOMBINATION OF THE THIOFORMYL (HCS\(^+\)) AND CARBONYL SULFIDE (OCS\(^+\)) CATIONS

H. Montaigne,\(^1,2\) W. D. Geppert,\(^1,3\) J. Semaniak,\(^4\) F. Österdahl,\(^5\) F. Hellberg,\(^1\) R. D. Thomas,\(^1\) M. af Ugglas,\(^1\) H. Roberts,\(^6\) T. J. Millar,\(^6\) V. Zhaunerchyk,\(^1\) M. Kamińska,\(^4\) A. Al-Khalili,\(^1\) A. Källberg,\(^7\) and M. Larsson\(^1\)

Received 2005 April 6; accepted 2005 May 18

ABSTRACT

Branching ratios and absolute cross sections have been measured for the dissociative recombination of HCS\(^+\) and OCS\(^+\) at the CRYRING ion storage ring. In the case of OCS\(^+\), the channel leading to CO + S (83\%) dominates, whereas the other exoergic pathways leading to CS + O (14\%) and C + SO (3\%) are of lesser importance. In the case of HCS\(^+\), fracture of the C−S bond is predominant (81\%), with the production of H + CS accounting for the remainder (19\%). The cross section of the reaction could be fitted by the expressions \( \sigma = 1.41 \times 10^{-15} E(eV)^{-1.11} \) and \( 4.47 \times 10^{-16} E(eV)^{-1.14} \text{ cm}^2 \) for HCS\(^+\) and OCS\(^+\), respectively. The derived energy dependences of the thermal reaction rate coefficients can be fitted by \( k(T) = 9.7 \times 10^{-7} (T/300)^{-0.57} \) and \( 3.5 \times 10^{-7} (T/300)^{-0.62} \text{ cm}^3 \text{ s}^{-1} \) for HCS\(^+\) and OCS\(^+\), respectively. We use these data to perform model calculations on the HCS\(^+\)/CS abundance ratio in dark clouds and find that the models using the UMIST and Ohio State University databases have even more difficulty in accounting for the large observed ratio.

Subject headings: astrochemistry — ISM: clouds — ISM: molecules

1. INTRODUCTION

Dissociative recombination (DR) is an important recombination process in a multitude of man-made and natural plasmas and is of special importance in planetary ionospheres and interstellar clouds. Since the process is very effective at low temperatures it can, in particular, have substantial effect on the abundances of molecules and ions in the low-temperature environment of interstellar clouds. Furthermore, DR is regarded as the primary mechanism for electron loss in the ionospheres of Mars and Venus (Cosby et al. 2001).

In DR reactions of polyatomic molecules, it is usual that several barrierless and exoergic fragmentation pathways of the intermediate neutral molecule exist, and these can lead to very different products. A detailed knowledge of probabilities with which all these pathways occur (i.e., branching ratios), as well as of the overall rate of the specific DR reaction, is therefore crucial for the accurate modeling of large interstellar reaction networks that incorporate these reactions (Millar et al. 1988). According to Bates (1986), the dissociative channels with the least rearrangement of valence bonds should be favored. This assumption has been now challenged by a multitude of measurements on branching ratios of DR reactions that do not fulfill these predictions, and processes regarded as improbable by Bates are, in fact, not uncommon (see, e.g., Larsson & Thomas 2001; Geppert et al. 2004b).

The DR of sulphur-containing interstellar ions deserves special interest. Models of gas-phase sulphur chemistry in translucent, dark, and dense clouds have, in many cases, failed to predict the observed abundances without resorting to substantial depletion of elemental sulphur. The degree of sulphur depletion is important for observational studies of star formation (Ruffle et al. 1999). It has been argued that sulphur-containing molecules can be used as tracers of early stellar evolution; e.g., in models of “hot cores” the abundances of sulphur-bearing molecules vary in time in a characteristic way (van der Tak et al. 2003). The chemistry of sulphur-containing compounds can also be used as a clock to understand the history of cold molecular clouds (Millar & Herbst 1990).

The OCS molecule has been detected in dense clouds (Palumbo et al. 1997), massive young stars and comets (Bockelée-Morvan et al. 2000), and hot molecular cores (Gibb et al. 2000). OCS can also be found in the terrestrial atmosphere, where it has a lifetime of approximately 2–3 yr (Griffith et al. 1998). OCS is oxidized in the stratosphere to form sulphate particles that may influence the radiation budget at the Earth’s surface as well as the stratospheric ozone cycle. It has also been found in soils, plants, oceans, volcanoes (Cadle 1980), and marshes (Steudler & Peterson 1985). In addition, it has been shown that the marine environment is the most important global source of atmospheric OCS (Kettle et al. 2002). Especially high concentrations of OCS in the atmosphere occur, e.g., in China, because of the extensive use of brown coal in heating processes. In particular, during the winter season domestic stoves and central heaters are important sources of OCS (Mu et al. 2004). The cycle of OCS through the atmosphere, oceans, and biosphere shows similarities with that of CO\(_2\). Further insights into the atmospheric cycle of both of these molecules will lead to further understanding of other long-lived compounds (Kettle et al. 2002). Therefore it is also interesting to compare DR branching ratios and reaction rates of OCS\(^+\) with those of CO\(_2\)\(^+\).
In the DR of OCS\(^+\), three exoergic channels exist at low relative translational energies:

\[
\text{OCS}^+ + e^- \rightarrow \text{CO} + \text{S}, \quad \Delta_h = -8.04 \text{ eV}, \quad (1a) \\
\rightarrow \text{CS} + \text{O}, \quad \Delta_h = -4.28 \text{ eV}, \quad (1b) \\
\rightarrow \text{SO} + \text{C}, \quad \Delta_h = -2.29 \text{ eV}. \quad (1c)
\]

The HCS\(^+\) ion has been observed in different interstellar environments and is one of the most important sulphur-containing ions there. It was first detected in 1981 in the Orion Nebula (Thaddeus et al. 1981) and subsequently in dark clouds (Irvine et al. 1983), diffuse clouds (Lucas & Liszt 2002), star-forming regions (Houde et al. 2000), and young stars (Nomura & Millar 2004), and the ionsphere of comet Halley (Marconi et al. 1991). According to McAllister (1978), the most important reactions forming HCS\(^+\) are the following:

\[
\text{CS}^+ + \text{H}_2 \rightarrow \text{HCS}^+ + \text{H}, \quad (2) \\
\text{C}^+ + \text{H}_2\text{S} \rightarrow \text{HCS}^+ + \text{H}, \quad (3)
\]

although proton transfer reactions such as

\[
\text{H}_3^+ + \text{CS} \rightarrow \text{HCS}^+ + \text{H}_2 \quad (4)
\]

and

\[
\text{HCO}^+ + \text{CS} \rightarrow \text{HCS}^+ + \text{CO} \quad (5)
\]

may dominate in dense molecular clouds (Millar et al. 1985). Furthermore, the DR of HCS\(^+\) is thought to account for the formation of the observed CS in diffuse clouds (Lucas & Liszt 2002). Since the abundance of HCS\(^+\) relative to CS in dark clouds has been found to be very high, \(\sim 0.1\) (Irvine et al. 1983), it was suggested that the DR of HCS\(^+\) must be very slow to account for this enhanced abundance (Millar 1983; Millar et al. 1985; Rowe et al. 1993). Theoretical calculations and an experimental estimation of \(5 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}\) at 300 K supported this theory (Millar et al. 1985). HCS\(^+\) is a relatively unreactive ion with most common interstellar molecules (Smith & Adams 1985), which is also consistent with its large abundances in molecular clouds. Three exoergic reaction channels exist in the DR of HCS\(^+\) at low relative kinetic energies:

\[
\text{HCS}^+ + e^- \rightarrow \text{CS} + \text{H}^+, \quad \Delta_H = -5.08 \text{ eV}, \quad (6a) \\
\rightarrow \text{HS} + \text{C}, \quad \Delta_H = -1.65 \text{ eV}, \quad (6b) \\
\rightarrow \text{CH} + \text{S}, \quad \Delta_H = -1.49 \text{ eV}. \quad (6c)
\]

This paper presents an experimental determination of branching ratios, cross sections, and thermal reaction rate coefficients of the DR of OCS\(^+\) and HCS\(^+\).
The fragment energy spectrum of the DR reaction with the grid in front of the detector of OCS+ is shown in Figure 1. Apart from the peaks emerging from the CO and S, the different signals are reasonably resolved. Since the CO and S signals are emerging from the same reaction (1a) with the same intensity \( \frac{N_a}{C_0} = 0\), they were therefore treated as one feature with a relative intensity of 2. The grid in front of the detector of OCS+ is shown in Figure 1. Apart from the peaks emerging from the CO and S, the different signals had then to be treated as one feature and they are well separated from one another, their areas were determined by integration. From the overlapping of peaks separated by \( m/z = 1 \) it also follows that it is impossible to separate the reaction channels (6b) and (6c); only the sum of those pathways, from which an indication of the likelihood of rupture of the C–S bond is obtained, can be determined. The resulting evaluation matrix is as follows:

\[
\begin{bmatrix}
N(C + O + S) \\
N(C + O) + N(S) \\
N(C + S) \\
N(O + S) \\
N(O) \\
N(C)
\end{bmatrix}
= \begin{bmatrix}
T^2 & 0 & 0 \\
0 & T(1 - T) & 0 \\
0 & 0 & T(1 - T) \\
2T(1 - T) & 0 & 0 \\
0 & T(1 - T) & 0 \\
0 & 0 & T(1 - T)
\end{bmatrix}
\times \begin{bmatrix}
N_a \\
N_b \\
N_c
\end{bmatrix},
\tag{7}
\]

where \( N_a, N_b, \) and \( N_c \) are the branching ratios of reaction channels (1a), (1b), and (1c), respectively. There are more equations than variables in this matrix, but it contains two pairs of identical rows (third-fifth and fourth-sixth). A least-squares fit was employed to solve this matrix, which yields the branching ratios listed in Table 1.

A similar procedure was used to determine the branching ratios of HCS+. The fragment energy spectrum with the grid in place is shown in Figure 2. Unfortunately, the resolution of the detector is insufficient to distinguish between the signals arising from \( H + C + S \) (mass = 45) and \( C + S \) (mass = 44). The same thing applies for the peak pairs S (mass = 32) and S + H (mass = 33) and C (mass = 12) and C + H (mass = 13). Since the mentioned pairs of signals had then to be treated as one feature and they are well separated from one another, their areas were determined by integration.

### Table 1

<table>
<thead>
<tr>
<th>Reaction Channel</th>
<th>Branching Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCS+</td>
<td>0.83 ± 0.04</td>
</tr>
<tr>
<td>CS + O</td>
<td>0.14 ± 0.03</td>
</tr>
<tr>
<td>C + SO</td>
<td>0.03 ± 0.03</td>
</tr>
<tr>
<td>HCS+</td>
<td>0.19 ± 0.03</td>
</tr>
<tr>
<td>HC + S (HS + C)</td>
<td>0.81 ± 0.03</td>
</tr>
</tbody>
</table>

Using a least-squares fit as before, the branching ratios listed in Table 1 were obtained.

### 3.2. Absolute Cross Section and Thermal Reaction Rate

During cross section measurements, the relative translational energy between the ions and the electrons was continuously varied between 1 and 0 eV. This was achieved by changing the cathode voltage linearly in the electron cooler over 1 s from a high value corresponding to a center-of-mass energy of 1 eV, the electrons being faster than the ions, down to a low value also corresponding to 1 eV but where the electrons were slower than...
the ions. Thus, a voltage corresponding to a center-of-mass energy of 0 eV is reached during the scan. Before the measurement was started, 3 s of cooling, with the electrons tuned to 0 eV collision energy, was carried out. The signal from the SBD was monitored by a single-channel analyzer. Its discrimination levels were adjusted to record only the pulses with a maximum height corresponding to the full kinetic energy of the ion beam, i.e., originating from DR reactions. The output signal was thereafter recorded by an MCS, yielding the number of counts versus the signals with the full kinetic energy, thus reducing the number of contributions of collisions with residual gas to the spectrum.

The experimental DR rate coefficient in the electron cooler is expressed by the formula (Neau 2002)

$$\langle v_{\text{cm}}\sigma \rangle = \frac{dN}{dt} \frac{v_e v_i e^2 r_e^2 \pi}{I_e I_i}$$

(9)

where $dN/dt$ is the number of counts per unit time, $v_i$ and $v_e$ are the electron and ion velocities, respectively, $r_e$ is the radius of the electron beam, $I$ is the length of the interaction region, and $I_e$ and $I_i$ are the electron and ion current, respectively. Continuous measurement of the count rate of neutral products originating from ion-residual gas collisions also allowed the decay of the ion beam to be monitored during each injection. From the resulting rate coefficients, the (comparatively) very small contribution to the data due to charge transfer processes had to be subtracted. Since the cross section of the DR is very low at a relative kinetic energy of 1 eV, all events registered at this energy were assumed to be due solely to charge transfer. Furthermore, the following corrections to the measured data had to be performed. (1) The voltage of the electron cooler cathode (and therefore $v_e$) had to be corrected for space charge effects. (2) The measured rate coefficient $\langle v_{\text{cm}}\sigma \rangle$ had to be adjusted because of the toroidal effect (Lampert et al. 1996). The toroidal effect stems from the zones at both ends of the interaction region where the electron beam is bent into or out of the ion beam. In these regions, the transversal electron velocity is higher than in the merged interaction region, leading to larger collision energies. (3) The electron beam has (in contrast to the ion beam) a nonnegligible energy spread, and the measured reaction rate coefficient $\langle v_{\text{cm}}\sigma \rangle$ has to be deconvoluted according to the formula

$$\langle v_{\text{cm}}\sigma \rangle = \int_{-\infty}^{\infty} v_e f(v_e) \sigma(v_e) d^3 v_e,$$

(10)

where $f(v_e)$ is the electron velocity distribution. (4) Drag force effects (Mowat 1988) were neglected due to the relatively large mass of the ions investigated. The obtained cross sections are presented in Figures 3 and 4 as a function of the relative kinetic energy. These data are best fitted by the expression $\sigma = (4.5 \pm 0.9) \times 10^{-16} E(\text{eV})^{-1.14}$ and $(1.4 \pm 0.3) \times 10^{-15} E(\text{eV})^{-1.11}$ cm$^2$ for OCS$^+$ and HCS$^+$, respectively. The thermal reaction rate coefficients can be deduced from the cross sections by applying the formula

$$k(T) = \frac{8\pi m_e}{(2\pi m_e k T)^{3/2}} \int_{0}^{\infty} E \sigma(E) e^{-E/kT} dE,$$

(11)

where $m_e$ is the mass of the electron. The absolute value and temperature dependence of the rate coefficients can then be fitted by the equations $k(T) = (3.5 \pm 0.7) \times 10^{-7} (T/300)^{-0.62}$ cm$^3$ s$^{-1}$ for OCS$^+$ and $k(T) = (9.7 \pm 2.9) \times 10^{-7} (T/300)^{-0.57}$ cm$^3$ s$^{-1}$ for HCS$^+$.

4. DISCUSSION

According to Bates (1986) the dissociative channels involving the least rearrangement of valence bonds are the most favored. In the case of OCS$^+$ this prediction is fulfilled, since channel (1a) leading to CO + S dominates. Consequently, channel (1c), which involves the breakup of two double bonds and forming a new one, shows the smallest branching ratio. The DR of HCS$^+$, on the other hand, does not follow Bates's prediction. The branching ratio of channel (6a), leading to CS + H, which should be the most favored channel, is only 19%. Because of the impossibility of separating pathways (6b) and (6c) only the sum of their branching ratios could be determined (81%). However, since channel (6b) involves a considerable rearrangement of the intermediate molecule, it can be conjectured that the majority of this sum is made up by channel (6c).
It is interesting to compare the present findings with those obtained with other isovalent ions, which, for OCS\(^+\), include the CO\(_2\)\(^+\) ion. For CO\(_2\)\(^+\), both DR rates and branching behavior have recently been reported by Seiersen et al. (2003). In the DR of this ion, two pathways, one leading to CO + O, the other one yielding C + O\(_2\), exist, and also the presence of radiative recombination has been discussed by the authors. They report the former as the major pathway (branching ratio 87%). The contribution of the C + O\(_2\) channel, which correlates to the C + SO channel in OCS\(^+\), is also present to a smaller extent (9%). Seiersen et al. also reported a small contribution of radiative recombination leading to CO\(_2\) (3%). Such a process was not observed with OCS\(^+\) in our experiment. In a new study of the branching ratios of the DR of CO\(_2\)\(^+\), Viggiano et al. (2005) found the CO + O channel to account for 98% and no conclusive evidence for radiative recombination. These results can be compared with our findings for OCS\(^+\), where the sum of the analogous channels (channels [1a] and [1b]) amounts to 97%.

Furthermore, the obtained rate coefficients in the DR of OCS\(^+\) and CO\(_2\)\(^+\) can be compared. Apart from differences in branching ratios, isovalent ions can show unlike reaction rates. For example, the DR rates of HCO\(^+\) and N\(_2\)H\(^+\) differ by more than a factor of 2 (Geppert et al. 2004b; Mitchell 1990). Conversely, the rates of DOCO\(^+\) and N\(_2\)OD\(^+\) are fairly similar (Geppert et al. 2004a, 2004c). Such behaviors can serve as benchmarks for future theoretical investigations in the DR processes of such species. Our value of \(k(T) = 3.5 \times 10^{-7} \text{cm}^3 \text{s}^{-1}\) at 300 K is somewhat smaller than that obtained by Seiersen et al. (2003) for CO\(_2\)\(^+\) (6.5 \times 10^{-7} \text{cm}^3 \text{s}^{-1}), but is very similar to the values obtained in microwave and flowing afterglow measurements that lie between 3.1 and 4.0 \times 10^{-7} \text{cm}^3 \text{s}^{-1} (Weller & Biondi 1967; Gutchuck & Zipf 1973; Geoghegan et al. 1991; Gougousi et al. 1997). It also compares favorably with the value of 4.2 \times 10^{-7} \text{cm}^3 \text{s}^{-1} obtained by Viggiano et al. (2005).

In the case of HCS\(^+\) a comparison with the isoelectronic ions HCO\(^+\) and HN\(_2\)\(^+\) is rewarding. Consistent with the present findings, the breakup of the bond between the two heavy atoms is favored in the DR of HN\(_2\)\(^+\) (Geppert et al. 2004b). This is not the case for HCO\(^+\) and DCO\(^+\), where all available data point to an overwhelming dominance of the H(\(D\)) + CO channel (Adams et al. 1991; Geppert et al. 2004c). This preference of rupture is even more surprising since, according to Marquèlès (2003), HCS\(^+\) has probably the shortest (and therefore strongest) CS bond of any known molecule. Similarly, the CO bond length in HCO\(^+\) ranks among the shortest CO bonds. The lesser propensity of HCS\(^+\) to undergo dissociation of the H–C bond in the DR process might be due to the fact that the repulsive potential energy surface leading to H + CO crosses those of the HCO\(^+\) ion at a comparatively short H-C distance (Talbi et al. 1988). In HCS\(^+\) this crossing occurs at a longer H-C distance and should therefore be less favorable for channel (6a). The absence of the HC + O (DC + O) channel in the DR of HCO\(^+\) (DCO\(^+\)) is very probably due to the fact that this pathway is, unlike the analogous processes in HCS\(^+\) and HN\(_2\)\(^+\), endoergic. If one compares the thermal rate coefficients of the reactions, the DR of HCS\(^+\) is considerably faster than the DR of the other isoelectronic ions.

Since the separator magnet in the ion source cannot distinguish between ions with the same mass ratio, the question of isomerism arises; e.g., for HCO\(^+\) a stable isomer HOC\(^+\) exists. In the case of HCS\(^+\), the isomeric ion HSC\(^+\) is not stable and HSC\(^+\) can isomerize to HCS\(^+\) with an isomerization barrier of only 0.1 kcal mol\(^{-1}\) (Sumathi et al. 1999), which is easily surmounted at the temperature present in the ion source. On the other hand, a significant barrier between HSC\(^+\) and HCS\(^+\) exists in the triplet state. This state, however, is situated 83.7 kcal mol\(^{-1}\) above the ground state and therefore unlikely to be populated to a great extent under the present ion source conditions. Since OCS\(^+\) is produced directly, a contribution of an isomeric CSO\(^+\) ion (with a sulphur atom in the center) is unlikely but cannot be ruled out. The small presence of the C + SO channel might point in that direction, but can also be due to rearrangement of the intermediately produced OCS neutral molecule during the DR process.

5. IMPLICATIONS FOR INTERSTELLAR CHEMISTRY

The difference of the abundance ratios of HCO\(^+\)/CO and HCS\(^+\)/CS in interstellar clouds was commonly considered as a consequence of a difference in rate coefficients of proton transfer and DR reactions involving these ions (Millar 1983; Millar et al. 1985; Talbi et al. 1989). The proton transfer rate coefficients are enhanced at low temperatures if the neutral molecule, such as CS, possesses an appreciable permanent electric dipole moment. Furthermore, it has been shown that the large proton affinity of CS ensures that HCS\(^+\) does not undergo proton transfer with most of the common interstellar molecules, including H\(_2\), CO, and N\(_2\), but only with strong proton acceptors such as NH\(_3\) and CH\(_3\)OH (Smith & Adams 1985), a process that should also enhance the HCS\(^+\)/CS abundance ratio. Standard models for interstellar chemistry, e.g., in dark interstellar clouds, use a fairly low value of 5 \times 10^{-8} \text{cm}^3 \text{s}^{-1} (Herbst 2003; Markwick et al. 2000) for the rate coefficient for the DR of HCS\(^+\). The application of such a low rate is now challenged by the present data, and we explore here how this affects sulphur chemistry in dark clouds through calculating a pseudo–time-dependent chemical kinetic model using both the UMIST RATE99 (R99) and OSU New Standard Model (NSM) databases (Le Tuff et al. 2000; Herbst 2003). These two databases use identical DR rate coefficients for HCS\(^+\) and OCS\(^+\) ions but differ in that the NSM database adopts rate coefficients for ion-neutral reactions that are enhanced by “ion-dipole” effects, typically by a factor (T/300)^{-1/2}. Both databases also include the reaction

\[
\text{HCS}^+ + \text{O} \rightarrow \text{OCS}^+ + \text{H}.
\]

This process is assumed to be 100 times faster in NSM compared to R99 and therefore dominates DR as the loss for HCS\(^+\) in the NSM model; it also results in an abundance of OCS\(^+\) some 50 times larger in the NSM model than in R99. Although this reaction is thought to be exothermic, it has not been measured in the laboratory. At steady state, a consideration of the formation and destruction rates of HCS\(^+\) shows that the HCS\(^+\)/CS abundance ratio can be approximated by

\[
\frac{[\text{HCS}^+]}{[\text{CS}]} = \frac{k_{12}[\text{H}_3]}{k_5(e^-) + k_{11}[\text{O}]}.
\]
formation mechanism of CS at steady state in the NSM model, which assumes that 50% of recombination events produce CS. Since these calculated abundance ratios are much less than observed in dark clouds, we neglect reaction (12) in order to investigate the effect of our new measured rate coefficients on dark cloud chemistry.

Figures 5 and 6 show the time-dependent evolution of the fractional abundances of several sulphur-bearing species for the RATE99 and NSM models for both the old and new rate coefficients. It can be seen that there are significant differences in the time-dependence of the abundances of several molecules when comparing R99 results to those using NSM, particularly in those of CS and SO. The reasons for these differences, which relate to the use of enhanced ion-dipole rate coefficients, have been discussed by Roberts et al. (2004) and serve to underline the uncertainties in sulphur chemistry in interstellar clouds. At steady state, use of the old rates and branching ratios leads to abundance ratios of ~0.01 (NSM) and ~0.001 (RATE99). The larger ratio in NSM, although still an order of magnitude less than that observed in TMC-1 (Irvine et al. 1983), is a direct result of the use of an enhanced rate coefficient for the proton transfer reaction, which forms HCS+. The adoption of the new branching ratio (0.2) for the production of CS from HCS+ might naively be expected to lead to a large reduction in the abundance ratio. However, the total DR rate coefficient is now, from our measurements, estimated to be about 10 times faster at 10 K than the old rate coefficient. Nevertheless, the reductions calculated, around 3–5, do exacerbate the discrepancy between observation and theory. The reduction in the HCS+ abundance does lead in the R99 model to the reaction between C and SO being the most important formation mechanism for CS at steady state.

Finally, we note that these results are only applicable if the reaction between HCS+ and O atoms is negligible. If this is not the case, then DR will not be the dominant loss for HCS+ except in regions of high depletion.

6. CONCLUSIONS

The DR of OCS+ in collisions with low-energy electrons leads mainly to CO + S (83%), whereas in the DR of HCS+ the rupture of the CS bond dominates. The reaction cross sections at low relative translational energies of the reactants follow the equations

\[ \sigma = 4.47 \times 10^{-16} (eV)^{1.14} \] and \[ 1.41 \times 10^{-15} (eV)^{1.11} \] cm² for OCS+ and HCS+, respectively. No perceptible resonances appear in the plots of the cross section versus the relative kinetic energy of the reactants. From these expressions thermal reaction rate coefficients of \( k(T) = 3.5 \times 10^{-7} (T/300)^{-0.62} \) and \( 9.7 \times 10^{-7} (T/300)^{-0.57} \) cm³ s⁻¹ are derived for OCS+ and HCS+, respectively. The rate coefficient for the DR of OCS+ was therefore found to be similar to that of CO₂, whereas the DR rate of HCS+ was substantially larger than those of other iso-electronic ions, such as HN₂⁺ and DCO⁺. Application of these new results to models of the chemical evolution of dark clouds shows that the discrepancy between theory and observation is worsened. Our understanding of sulphur chemistry in molecular clouds appears to be very incomplete.

The authors want to thank the Swedish Research Council and the Swedish Institute for funding. W. D. Geppert acknowledges the European Union (EU) for granting a “Marie Curie Individual Fellowship” under the EU program “Improving Human Potential,” contract number HMPF-CT-200201583. Support from the EU IHP Research Training Network program under contract HPRN-CT-2000-0142 is also gratefully acknowledged. J. Semaniak and M. Kaminska acknowledge partial support by the State Committee for Scientific Research, Poland. Molecular astrophysics at the University of Manchester is supported by a grant from PPARC. The authors also want to thank the staff at Maunie Siegbahn Laboratory for excellent technical assistance.

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Manne Siegbahn Laboratory for excellent technical assistance.