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Crossed Beam Reaction of Atomic Carbon C(3Pj) with Hydrogen Sulfide, H₂S (X₁A₁): Observation of the Thioformyl Radical, HCS(X₂A')

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Crossed beam reaction of atomic carbon \( C(3P_j) \) with hydrogen sulfide, \( \text{H}_2\text{S} \) (\( \text{X}^1\text{A}_1 \)): observation of the thioformyl radical, \( \text{HCS}(\text{X}^2\text{A}') \)

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**ABSTRACT**

One of the simplest organosulfur reactions, that between ground state carbon atoms, \( C(3P_j) \), and hydrogen sulfide, \( \text{H}_2\text{S}(\text{X}^1\text{A}_1) \), was studied at an average collision energy of 21.0 kJmol\(^{-1}\) using the crossed molecular beams technique. The product angular distribution and time-of-flight spectra of m/e = 45 (\( \text{HC}^{32}\text{S} \)) were monitored. Forward-convolution fitting of our data yields an almost isotropic center-of-mass angular flux-distribution, whereas the center-of-mass translational energy flux distribution peaks at about 50 kJmol\(^{-1}\), indicating a tight exit transition state from the decomposing thiohydroxycarbene HCSH complex to the reaction products. The high energy cut-off of the translational energy flux distribution is consistent with the formation of the thioformyl radical HCS in its \( \text{X}^2\text{A}' \) electronic ground state. The first experimental verification of an existing thiohydroxycarbene intermediate and the rigorous assignment of the HCS radical product under single collision conditions explicitly suggest inclusion of the title reaction in chemical reaction networks of molecular clouds TMC-1 and OMC-1, the outflow of the carbon star IRC+10216, Shoemaker/Levy 9 impact-induced non-equilibrium sulfur chemistry in the Jovian atmosphere, as well as combustion of sulfur containing coal.
I. INTRODUCTION

The sulfur chemistry in extraterrestrial environments is still an undiscovered country. Although 13 neutral sulfur containing species $\text{H}_2\text{S}$, $\text{CS}$, OCS, $\text{C}_n\text{S}$ ($n = 2, 3, 5$), $\text{SiS}$, $\text{NS}$, $\text{SO}$, $\text{SO}_2$, $\text{CH}_3\text{SH}$, $\text{H}_2\text{CS}$, and $\text{HNCS}$, as well as the ions $\text{CS}^+$ and $\text{HCS}^+$ have been detected in the interstellar medium (ISM), the outcome of reaction models to reproduce observed abundances are unsatisfactory [1-6]. Most elementary processes of these ion-molecule-based networks are completely unstudied, and the large fraction of sulfur containing molecules supposed to be depleted on dust grains complicates this scenario [5]. Even in our solar system, the sulfur chemistry is far from being resolved. Although the production of $\text{H}_3\text{S}^+$, $\text{HCS}^+$, $\text{H}_2\text{CS}^+$, and $\text{SO}^+$ in comet P/Halley [7-8] is well explained by cometary ion-molecule reactions and photochemistry, the formation mechanisms of the $\text{H}_2\text{S}$, $\text{CS}$, and $\text{H}_2\text{CS}$ parent molecules have escaped a definite conclusion yet. Based on detailed maps of $\text{S}_2$, $\text{CS}$, and $\text{H}_2\text{S}$ outflows in comets Austin and Levy, Crosvisier and coworker demonstrated that CS originates in a short-lived parent radical [9], but its solid assignment is still missing. Likewise, the source of sulfur compounds $\text{CS}$, $\text{CS}_2$, COS, and $\text{S}_2$ detected in the upper Jovian immediately after the impact of comet fragments of Shoemaker-Levy 9 (SL-9) into Jupiter [10] is unknown. Here, detailed shock-wave chemistry models require in the Jovian atmosphere unobserved superfluous sulfur containing molecules such as thioformaldehyde $\text{H}_2\text{CS}$ and the thioformyl radical $\text{HCS}$, to reproduce at least observed CS production rates after the impact. But even their formation mechanism remains to be solved.

In this communication, we begin to investigate the importance of neutral-neutral-reactions as an alternative route to ion-molecule reactions to form sulfur containing molecules in the ISM as well as in our solar system and explore the fundamental reaction dynamics underlying organosulfur chemistry. Here, we elucidate the chemical dynamics and reaction products of one of the simplest organosulfur reaction: the reaction of ground state atomic carbon $\text{C}(^{3}\text{P}_j)$ with hydrogen sulfide, $\text{H}_2\text{S}(X^{1}\text{A}_1)$, via $\text{H}_2\text{SC}$ isomers under
single collision conditions. These detailed insights in the reaction dynamics reveal possible reaction pathways to HSC/HCS-isomers as well as valuable information on the H$_2$SC potential energy surfaces (PES) and thermochemistry:

\[
\begin{align*}
C(^3P_j) + H_2S(X^1A_1) &\rightarrow H_2SC \rightarrow HCS(X^2A') + H(^2S_{1/2}) & \Delta_r H^0 = -181 \pm 10 \text{kJmol}^{-1} \quad (1) \\
\rightarrow HSC(X^2A') + H(^2S_{1/2}) & & \Delta_r H^0 = -16 \pm 5 \text{kJmol}^{-1} \quad (2) \\
\rightarrow CS(X^1\Sigma^+ ) + H_2(X^1\Sigma^+ ) & & \Delta_r H^0 = -462 \pm 2 \text{kJmol}^{-1} \quad (3) \\
\rightarrow CS(X^1\Sigma^+ ) + 2 H(^2S_{1/2}) & & \Delta_r H^0 = -26 \pm 2 \text{kJmol}^{-1} \quad (4)
\end{align*}
\]

This system represents the prototype reaction of ubiquitous interstellar carbon atoms with the simplest saturated sulfur molecule, hydrogen sulfide, to synthesize sulfur containing species via a single atom-neutral collision. H$_2$S, is ubiquitous in the ISM and has been observed, for example, in molecular clouds TMC-1 and OMC-1 [14-15], toward the star forming region SgrB2, and around the circumstellar envelope of the dying carbon star IRC +10216 [16-17]. Further, atomic carbon is expected to be formed in high quantities in SL-9 impact triggered shock waves with temperatures exceeding 5000 K [10]. Since H$_2$S is indigenous to Jupiter in form of stratospheric NH$_4$HS clouds thermolyzed to NH$_3$ and H$_2$S upon impact, the upwelling hydrogen sulfide is expected to react with atomic carbon.

Besides the extraterrestrial relevance, the title reaction holds strong ties to combustion processes with important consequences for tropospheric chemistry as well. Atomic carbon is formed via hydrogen abstraction of CH radicals by H atoms in combustion flames [11], and very likely reacts with sulfur containing molecules. Reaction with hydrogen sulfide in particular holds a room temperature rate constant of about $10^{10}$ cm$^3$s$^{-1}$ [12] and is expected to influence the combustion chemistry of sulfur containing coal chars profoundly. Although atomic and molecular oxygen are thought to dominate in chemical networks simulating flame chemistry [13], their rate constants range up to 3 orders of magnitude below those of carbon atoms with H$_2$S thus compensating the low concentration profile of C($^3P_j$).
II. EXPERIMENT AND DATA ACQUISITION

The experiments were performed with a universal crossed molecular beam apparatus described in [18] in detail. Briefly, a pulsed supersonic carbon beam was generated via laser ablation of graphite [19]. The 266 nm output of a pulsed Nd-YAG laser (30 Hz) is focused onto a rotating graphite rod, and ablated carbon-atoms are subsequently seeded into neon gas released by a Proch-Trickl pulsed valve. The pulsed carbon beam with a velocity $v_0 = 2035 \pm 53$ ms$^{-1}$ and speed ratio $S = 4.0 \pm 0.1$ and continuous hydrogen sulfide beam ($v_0 = 738 \pm 5$ ms$^{-1}$, $S = 7.3 \pm 0.1$) at 263 ± 7 torr backing pressure pass through skimmers and cross at 90° in the interaction region. Reactively scattered species were monitored using a triply differentially pumped detector consisting of a Brink-type electron-impact-ionizer [20], quadrupole mass-filter, and a Daly ion detector [21] in 5.0° steps with respect to the carbon beam at m/e = 45 (HC$_{32}$S; hereafter: HCS) and m/e = 44 (C$_{32}$S; hereafter: CS). To gain information on the reaction dynamics, the time-of-flight (TOF) spectra and the laboratory angular distribution (LAB) were fit using a forward-convolution technique [22] yielding the translational energy flux distribution $P(E_T)$ and angular distribution $T(\theta)$ in the center-of-mass frame.

C. RESULTS

Reactive scattering signal was only observed at m/e = 45, i.e. HC$_{32}$S, c.f. Figs. 1-2. TOF spectra at m/e = 44 were monitored, but reveal identical patterns indicating that this signal originates in cracking of the parent in the ionizer, and that the thermodynamically accessible exit channels (3)-(5) are closed. The LAB distribution of the HCS product (Fig. 1) peaks at 47° near the center-of-mass angle of 45.8±1.0° and is very broad, extending at least 45° in the scattering plane. These findings imply a large energy release into translational degrees of freedom of the products as well as a $P(E_T)$ peaking away from zero. Comparison of the
scattering range with the limit circles of the HCS and HSC isomers strongly suggests formation of the HCS(\(X^2A'\)) radical.

This conclusion correlates with the center-of-mass translational energy distribution, Fig. 3. Best fits of our TOF spectra and LAB distributions were achieved with \(P(E_T)\)s extending to 220 - 320 kJmol\(^{-1}\), whereas the sum of the reaction exothermicity of reaction (1) and relative collision energy gives 210±30 kJmol\(^{-1}\) [23-25]. Even within the error limits, the 165±5 kJmol\(^{-1}\) less stable HSC(\(X^2A''\)) isomer can be ruled out. Further, the \(P(E_T)\) depicts a maximum at about 50 kJmol\(^{-1}\), clearly indicating a significant geometry as well as electron density change from the decomposing \(H_2SC\) complex to the products, resulting in a repulsive bond rupture from a tight transition state. In addition, this exit barrier is supported by the large fraction of energy released into translational motion of the reactants, here 38 ± 8 % (80±8 kJmol\(^{-1}\)).

The shape of the center-of-mass angular flux distribution \(T(\theta)\) can be utilized to gain further information on the chemical dynamics of the title reaction. Here, the \(T(\theta)\) is isotropic and symmetric around \(\pi/2\) implying an indirect reaction mechanism (complex formation). The decomposing \(H_2SC\) complex holds either a lifetime longer than its rotational period or the fragmenting intermediate rotates around a symmetry axis interconverting both H atoms. The weak \(T(\theta)\) polarization is the result of a poor coupling between the initial \(L\) and final orbital angular momentum \(L'\) indicating that most of the total angular momentum channels into rotational excitation of the HCS radical.

D. DISCUSSION

The schematic energy diagram in Fig. 4 shows two initial, prompt reaction pathways: addition of \(C(3P)\) to the non-bonding electrons forming triplet 1,1-dihydrothiocarbonyl \{1\} or insertion in the S-H-bond to triplet trans/cis thiohydroxycarbene \{2\} (\(C_1\) point group; \(^3A\) electronic state) or \{3\}. \{1\} can undergo
hydrogen migration to $\{2/3\}$, intersystem crossing (ISC) to singlet 1,1-dihydrothiocarbonyl $\{4\}$ followed by H-migration to singlet trans/cis thiohydroxycarbene $\{5\}$ ($C_s, \, ^1A'$) / $\{6\}$($C_s, \, ^1A'$), or decomposes to $\text{HSC}(X^2A') + \text{H}$. The final fate of both singlet and triplet trans/cis thiohydroxycarbenes results in C-H and/or S-H bond rupture to $\text{HSC}(X^2A')$ and/or $\text{HCS}(X^2A')$ and $\text{H}(^2S_{1/2})$ or a hydrogen migration to singlet/triplet thioformaldehyde $\{7\}$ ($C_{2v}, \, X^1A_1$) and $\{8\}$ ($C_s, \, ^3A'$). A final C-H-bond rupture in $\{7/8\}$ could yield $\text{HCS}(X^2A')$ and $\text{H}(^2S_{1/2})$ as well.

Since the thioformyl isomer $\text{HCS}(X^2A')$ was identified unambiguously, H-loss of $\{1\}/\{4\}$ yielding the $\text{HSC}(X^2A')$ isomer and atomic hydrogen can be clearly dismissed. Further, high level electronic structure calculations [27-29] show that the C-H-bond rupture in thioformaldehyde proceeds without a barrier (singlet surface, $\{7\}$) or holds a barrier of about 12 kJmol$^{-1}$ (triplet surface, $\{8\}$). Since the P(E$_T$) indicates the barrier for the H-loss channel to $\text{HCS}(X^2A')$ is about 50 kJmol$^{-1}$, decomposing complexes $\{7\}$ and $\{8\}$ must be ruled out as well. Therefore, none of the four remaining $\text{H}_2\text{CS}$ isomers $\{2\}$, $\{3\}$, $\{5\}$, and $\{6\}$ has a rotation axis to interconvert both H-atoms, and the symmetric center-of-mass angular distribution, Fig. 3, is the result of a decomposing complex holding a lifetime longer than its rotational period. The preferential S-H-bond rupture in the fragmenting thiohydroxycarbene complex to $\text{HCS}(X^2A') + \text{H}$ instead of a C-H-cleavage forming $\text{HSC}(X^2A') + \text{H}$ is consistent with S-H-bonds, about 120 - 180 kJmol$^{-1}$ weaker than C-H bonds.

At the present stage, we cannot identify the reaction pathway to $\text{HCS}(X^2A')$ unambiguously, i.e. a) addition to $\{1\} \rightarrow \{2\}/\{3\}$, b) addition to $\{1\} \rightarrow \{4\} \rightarrow \{5\}/\{6\}$, c) insertion to $\{2\}/\{3\}$ or d) insertion to $\{2\}/\{3\} \rightarrow \{5\}/\{6\}$ followed by decomposition to $\text{HCS} + \text{H}$. Since the insertion process is symmetry forbidden and is expected to hold a significant entrance barrier, insertion of $C(^3P_J)$ into the S-H bond of hydrogen sulfide is very unlikely, but cannot be excluded definitely based on our present data. Future experiments will be performed at higher collision energies to probe the existence of an osculating complex and could reveal if more than one channel is involved in the chemical dynamics to HCS and/or if minor amounts of $\text{HSC}$ are formed. Likewise, the increased collision energy might induce decomposition of HCS.
radicals. Finally, high level electronic structure calculations on the singlet and triplet H₂SC surfaces will be used to quantify the entrance and exit barriers as well as the nature of the initially formed H₂SC collision complex. The frequencies of the exit transition state(s) will be employed to fit our data with RRKM and phase space theory to identify the fragmenting complex and hence the role of intersystem crossing.

Understanding the combustion of sulfur containing fuel will assume a critical importance in the coming century as sulfur-rich coals inevitably assume a larger role in energy production. The title reaction represents the first step to a detailed understanding of the chemistry of organosulfur combustion that leads ultimately to acid rain. The HCS radical identified here might represent the missing link between sulfur containing molecules in coal and sulfur-hetero polycyclic aromatic hydrocarbons formed in the combustion process. In this process H₂S, for example, is transformed into hitherto undetected and highly unstable thioformyl intermediates HCS, which can decompose to H atoms and extremely reactive CS. The latter was detected in hydrocarbon flames [37-38], but the source has not yet been resolved, and might react with four and five carbon atom containing hydrocarbon radicals to the very first thio-penta and/or hexacycle. In addition, the open shell species HCS is expected to react without entrance barrier with atomic oxygen with rate constants in the order of 10⁻¹⁰ cm³s⁻¹, possibly transforming HCS into in OCS detected in combustion processes [38]. Hence, the role of the reaction chain (5)-(6)

\[
\begin{align*}
C( ^3P_\text{j}) + H_2S(X^1\text{A}_1) & \rightarrow H_2SC \rightarrow HCS(X^2\text{A}') + H(^2S_{1/2}) \\
HCS(X^2\text{A}') & \rightarrow CS(X^1\Sigma^+) + H(^2S_{1/2}) \\
HCS(X^2\text{A}') + O( ^3P_\text{j}) & \rightarrow OCS(X^1\Sigma^+) + H(^2S_{1/2})
\end{align*}
\]

must be included in future combustion flame modeling.

The formation of the HCS isomer under single collision conditions employing the crossed beams technique presents the first "clean" synthesis following previous in situ HCS production via successive H atom abstraction by F atoms from dimethylthioether (CH₃)₂S [30] and thiomethanol CH₃SH [31]. The HCS
radical is an excellent candidate for hitherto unassigned microwave transitions toward IRC +10216, unidentified lines in the extended ridge of OMC-1, and in the SL-9 impact into Jupiter as well as in comets Austin and Levy as a CS precursor. Terrestrial based microwave spectra of HCS radicals could be simply recorded during pulsed discharges of H₂S/He/CO-mixtures and should be compared with previous charted interstellar regions. Further, the title reaction represents a strong alternative to hitherto postulated, but never studied reactions to form interstellar HCS thru S + CH₂ → HCS + H [32-33] or C₂H₃ + S₂ → HCS + H₂CS in the gas phase or S⁺ + SH → HCS + H on interstellar grains [34]. In addition, at higher collision energies, HCS might decompose to CS + H, a pathway to form CS as observed in the shock wave chemistry in the Jovian atmosphere upon SL-9 impact. Finally, the reaction of C(^3P_J) with H₂S on interstellar grains might resolve the anticorrelation of H₂CS and H₂S in carbon rich dark clouds TMC-1. Since H₂S is very likely formed on interstellar grains [15, 35-36], implanted carbon atoms from the gas phase very likely react to a thiohydroxycarbene intermediate. Its lifetime is expected to be longer in a solid matrix as compared to our crossed beam experiments, and a second H-migration to thioformaldehyde might take place.

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Fig. 1. Lower: Newton diagram for the reaction \( \text{C}^3\text{P}_1 + \text{H}_2\text{S} \) at a collision energy of 21.0 kJmol\(^{-1}\). The inner circle stands for the maximum center-of-mass recoil velocity of the HSC isomer, the outer circle for the thioformyl radical HCS in the CM reference frame. Enthalpies of formation of the HCS/HSC radicals were taken from refs. [23-25]. Upper: Laboratory angular distribution of HC\(^{32}\text{S} \) at m/e = 45. Circles and 1\(\sigma\) error bars indicate experimental data, the solid line the calculated distribution. C.M. designates the center-of-mass angle. The solid lines originating in the Newton diagram point to distinct laboratory angles whose TOFs are recorded.

Fig. 2. Time-of-flight data at 47.0\(^\circ\). The dashed line indicates the experimental data, the solid line the fit.

Fig. 3. Lower: Center-of-mass angular flux distribution for the reaction \( \text{C}^3\text{P}_1 + \text{H}_2\text{S} \) at a collision energy of 21.0 kJmol\(^{-1}\). Upper: Center-of-mass translational energy flux distribution for the reaction \( \text{C}^3\text{P}_1 + \text{H}_2\text{S} \) at a collision energy of 21.0 kJmol\(^{-1}\). Both solid lines limit the range of acceptable fits within 1\(\sigma\) error bars.

Fig. 4. Schematic energy level diagram for the reaction \( \text{C}^3\text{P}_1 + \text{H}_2\text{S} \). Enthalpies of formation are taken from refs. [24-29]. Solid dashed lines: no ab-initio calculations have been performed on these structures.