

Crossed beam reaction of atomic carbon $C(^3P_j)$ with hydrogen sulfide, $H_2S(X^1A_1)$: Observation of the thioformyl radical, $HCS(X^2A')$

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(Received 4 December 1996; accepted 16 January 1997)

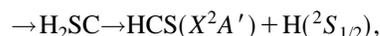
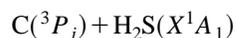
One of the simplest organosulfur reactions, that between ground state carbon atoms, $C(^3P_j)$, and hydrogen sulfide, $H_2S(X^1A_1)$, was studied at an average collision energy of 21.0 kJ mol^{-1} using the crossed molecular beams technique. The product angular distribution and time-of-flight spectra of $m/e=45$ ($HC^{32}S$) 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 kJ mol^{-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 X^2A' 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 nonequilibrium sulfur chemistry in the Jovian atmosphere, as well as combustion of sulfur containing coal. © 1997 American Institute of Physics. [S0021-9606(97)03412-0]

I. INTRODUCTION

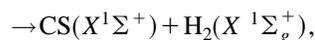
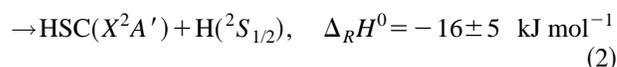
The sulfur chemistry in extraterrestrial environments is still an undiscovered country. Although 13 neutral sulfur containing species H_2S , CS, OCS, C_nS ($n=2, 3, 5$), SiS, NS, SO, SO_2 , CH_3SH , H_2CS , and HNCS, as well as the ions CS^+ and HCS^+ have been detected in the interstellar medium (ISM), 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 H_3S^+ , HCS^+ , H_3CS^+ , and SO^+ in comet P/Halley^{7,8} is well explained by cometary ion-molecule reactions and photochemistry, the formation mechanisms of the H_2S , CS, and H_2CS parent molecules have escaped a definite conclusion yet. Based on detailed maps of S_2 , CS, and H_2S outflows in comets Austin and Levy, Crosvisier and co-workers demonstrated that CS originates in a short-lived parent radical,⁹ but its solid assignment is still missing. Likewise, the source of sulfur compounds CS, CS_2 , COS, and S_2 detected in the upper Jovian atmosphere immediately after the impact of comet fragments of Shoemaker-Levy 9 (SL-9) into Jupiter¹⁰ is unknown. Here, detailed shock-wave chemistry models require in the Jovian atmosphere unobserved superfluous sulfur containing molecules such as thioformaldehyde H_2CS and the thioformyl radical 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

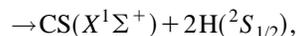
to ion-molecule reactions to form sulfur containing molecules in the ISM as well as in our solar system and explore the fundamental reaction dynamics underlying organosulfur chemistry. Here, we elucidate the chemical dynamics and reaction products of one of the simplest organosulfur reaction: the reaction of ground state atomic carbon $C(^3P_j)$ with hydrogen sulfide, $H_2S(X^1A_1)$, via H_2SC 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_2SC potential energy surfaces (PES) and thermochemistry:



$$\Delta_R H^0 = -181 \pm 10 \text{ kJ mol}^{-1} \quad (1)$$



$$\Delta_R H^0 = -462 \pm 2 \text{ kJ mol}^{-1} \quad (3)$$



$$\Delta_R H^0 = -26 \pm 2 \text{ kJ mol}^{-1}. \quad (4)$$

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_2S , 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 carbon star IRC+10216.^{16,17} Further, atomic carbon is ex-

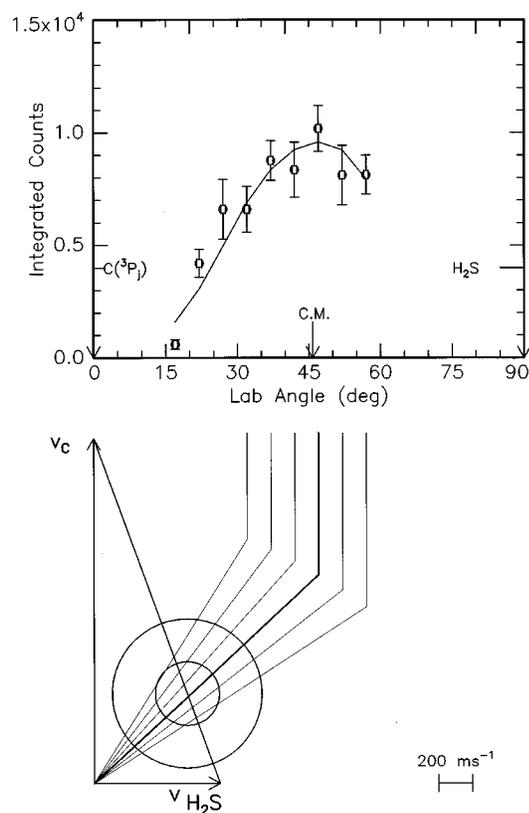


FIG. 1. Lower: Newton diagram for the reaction $C(^3P_j) + H_2S$ at a collision energy of 21.0 kJ mol^{-1} . The inner circle stands for the maximum center-of-mass recoil velocity of the HSC isomer, the outer circle for the thioformyl radical HCS in the CM reference frame. Upper: Laboratory angular distribution of $HC^{32}S$ at $m/e=45$. Circles and 1σ error bars indicate experimental data, the solid line the calculated distribution. C.M. designates the center-of-mass angle.

pected to be formed in high quantities in SL-9 impact triggered shock waves with temperatures exceeding 5000 K .¹⁰ Since H_2S is indigenous to Jupiter in form of stratospheric NH_4HS clouds thermolyzed to NH_3 and H_2S 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 present in combustion flames¹¹ very likely reacts with sulfur containing molecules. Reaction with hydrogen sulfide, in particular, holds a room temperature rate constant of about $10^{-10} \text{ cm}^3 \text{ s}^{-1}$ (Ref. 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_2S 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.¹⁸ Briefly, a pulsed super-

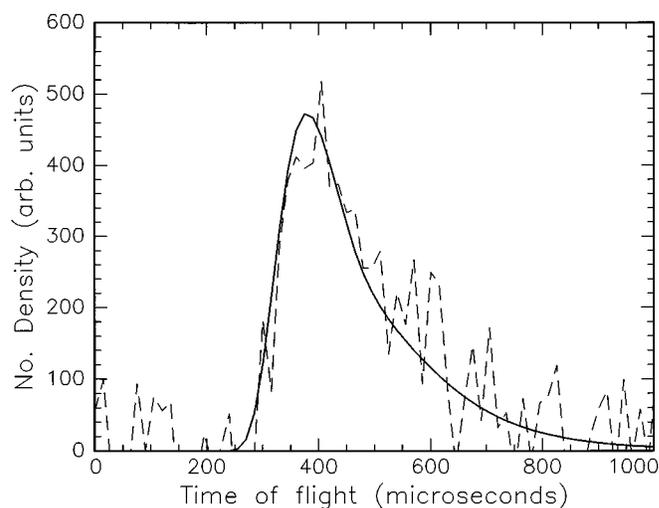


FIG. 2. Time-of-flight data at 47.0° . The dashed line indicates the experimental data, the solid line the fit.

sonic carbon beam was generated via laser ablation of graphite.¹⁹ The 266 nm output of a Nd-YAG laser is focused onto a rotating graphite rod, and ablated carbon-atoms are seeded into neon gas. The pulsed carbon beam with a velocity $v_0=2035 \pm 53 \text{ m s}^{-1}$ and speed ratio $S=4.0 \pm 0.1$ and continuous hydrogen sulfide beam ($v_0=738 \pm 5 \text{ m s}^{-1}$, $S=7.3 \pm 0.1$) 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 quadrupole mass spectrometer with an electron-impact ionizer^{20,21} 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 technique²² yielding the translational energy flux distribution $P(E_T)$ and angular flux distribution $T(\theta)$ in the center-of-mass frame.

III. RESULTS

Reactive scattering signal was only observed at $m/e=45$, i.e., $HC^{32}S$, cf. Figs. 1 and 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) and (4) are closed. The LAB distribution of the HCS product (Fig. 1) peaks at 47° near the center-of-mass angle of $45.8 \pm 1.0^\circ$ 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 $P(E_T)$ 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 as a major channel. 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 $220\text{--}320 \text{ kJ mol}^{-1}$, whereas the sum of

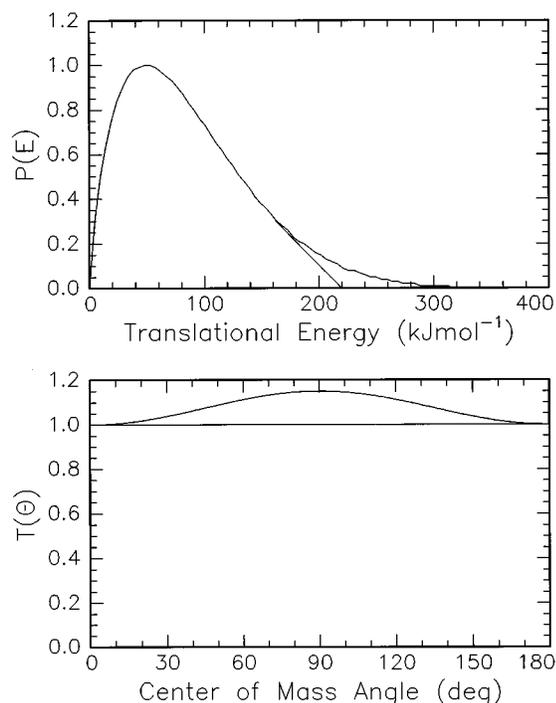


FIG. 3. Lower: Center-of-mass angular flux distribution for the reaction $C(^3P_j) + H_2S$. Upper: Center-of-mass translational energy flux distribution for the reaction $C(^3P_j) + H_2S$. Both solid lines limit the range of acceptable fits within 1σ error bars.

the reaction exothermicity of reaction (1) and relative collision energy gives $210 \pm 30 \text{ kJ mol}^{-1}$ (Refs. 23–25). Even within the error limits, the $165 \pm 5 \text{ kJ mol}^{-1}$ less stable $HSC(X^2A)$ isomer can be ruled out as a major contribution. Further, the $P(E_T)$ depicts a maximum at about 50 kJ mol^{-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 $38 \pm 8\%$ ($80 \pm 8 \text{ kJ mol}^{-1}$).

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 nearly 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.

IV. DISCUSSION

The schematic energy diagram in Fig. 4 shows two prompt reaction pathways: addition of $C(^3P_j)$ to the non-bonding electrons forming triplet 1,1-dihydrothiocarbonyl

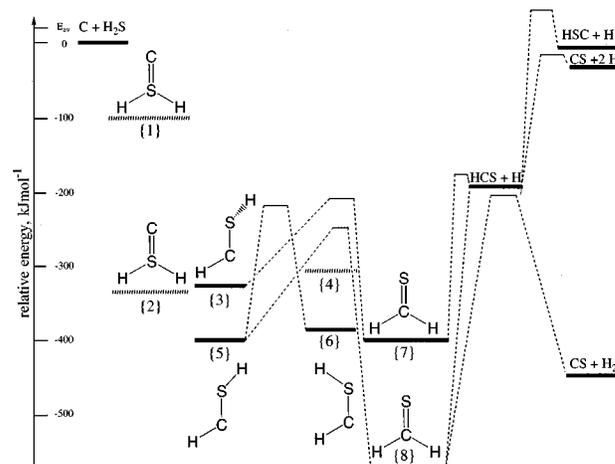


FIG. 4. Schematic energy level diagram for the reaction $C(^3P_j) + H_2S$. Enthalpies of formation are taken from Refs. 24–29. Solid dashed lines: no *ab initio* calculations have been performed on these structures. E_{av} indicates the total available energy.

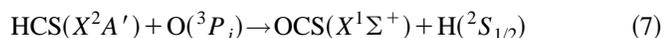
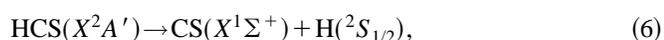
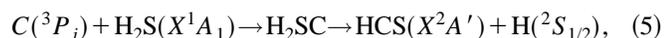
{1} or insertion in the S–H-bond to triplet *trans/cis* thiohydroxycarbene {3} (C_1 point group; 3A electronic state) or {4}. {1} can undergo hydrogen migration to {3/4}, intersystem crossing (ISC) to singlet 1,1-dihydrothiocarbonyl {2} followed by H-migration to singlet *trans/cis* thiohydroxycarbene {5} (C_s , $^1A'$)/{6} (C_s , $^1A'$), or decomposes to $HSC(X^2A') + H$. The final fate of the thiohydroxycarbene results in C–H and/or S–H bond rupture to $HSC(X^2A')$ and/or $HCS(X^2A')$ and $H(^2S_{1/2})$ or a hydrogen migration to singlet/triplet thioformaldehyde {8} (C_{2v} ; X^1A_1) and {7} (C_s ; $^3A'$). A final C–H-bond rupture in {7/8} could yield $HCS(X^2A')$ and $H(^2S_{1/2})$ as well.

Since the thioformyl isomer $HCS(X^2A')$ was identified, H-loss of {1}/{2} yielding $HSC(X^2A')$ and atomic hydrogen can be dismissed. Further, high level electronic structure calculations^{27–29} show that the C–H-bond rupture in thioformaldehyde proceeds without a barrier (singlet surface, {8}) or holds a barrier of about 12 kJ mol^{-1} (triplet surface, {7}). Since the $P(E_T)$ indicates the barrier for the H-loss channel to $HCS(X^2A')$ is about 50 kJ mol^{-1} , decomposing complexes {7} and {8} must be ruled out as well. Therefore, none of the four remaining H_2CS isomers {3–6} 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 $HCS(X^2A') + H$ instead of a C–H-cleavage forming $HSC(X^2A') + H$ is consistent with S–H-bonds, about 120 – 180 kJ mol^{-1} weaker than C–H bonds.

At the present stage, we cannot identify the reaction pathway to $HCS(X^2A')$ via an initial addition to the S-atom or insertion into the H–S-bond of hydrogen sulfide unambiguously. Since the insertion process is symmetry forbidden and is expected to hold a significant entrance barrier, this pathway is very unlikely. 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 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 H_2SC surfaces will be used to quantify the entrance and exit barriers as well as the nature of the initially formed H_2SC 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 H_2S , 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 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-heterocyclic compound. In addition, the open shell species HCS is expected to react without entrance barrier with atomic oxygen with rate constants in the order of $10^{-10} \text{ cm}^3 \text{ s}^{-1}$, possibly transforming HCS into in OCS detected in combustion processes. Hence, the role of the reaction chain (5)–(6)



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 from $(CH_3)_2S$ (Ref. 30) and CH_3SH (Ref. 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 $H_2S/He/CO$ - 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 $S + CH_2 \rightarrow HCS + H$ ^{32,33} or $C_2H_3 + S_2 \rightarrow HCS + H_2CS$ in the gas phase or $CH^+ + SH^- \rightarrow HCS + H$ 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 H_2S on interstellar grains might resolve the anticorrelation of H_2CS and H_2S in carbon rich dark clouds TMC-1. Since H_2S is 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.

ACKNOWLEDGMENT

This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

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