Crossed beam reaction of atomic carbon C(3Pj) with hydrogen sulfide, H2S(X1A1): Observation of the thioformyl radical, HCS(X2A′)

R. I. Kaiser, W. Sun, and A. G. Suits

Department of Chemistry, University of California, Berkeley, California 94720 and Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720

(Received 4 December 1996; accepted 16 January 1997)

One of the simplest organosulfur reactions, that between ground state carbon atoms, C(3Pj), and hydrogen sulfide, H2S(X1A1), 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 (HCl−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 X2A′ 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.

[Received 4 December 1996; accepted 16 January 1997]

I. INTRODUCTION

The sulfur chemistry in extraterrestrial environments is still an undiscovered country. Although 13 neutral sulfur containing species H2S, CS, OCS, C3S (n=2, 3, 5), SiS, NS, SO, SO2, CH3SH, H2CS, and HNCS, as well as the ions CS+, HCS+ and H2S+, 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.3 Even in our solar system, the sulfur chemistry is far from being resolved. Although the production of H2S+, HCS+, H2CS+, and SO+ in comet P/Halley7,8 is well explained by cometary ion-molecule reactions and photochemistry, the formation mechanisms of the H2S, CS, and H2CS parent molecules have escaped a definite conclusion yet. Based on detailed maps of S2, CS, and H2S outflows in comets Austin and Levy, Crosovies 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, CS2, COS, and S2 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 H2CS 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(3Pj) with hydrogen sulfide, H2S(X1A1), via H2SC 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 H2SC potential energy surfaces (PES) and thermochemistry:

C(3Pj) + H2S(X1A1) → H2SC−→ HCS(X2A′) + H(3S1/2),

ΔRHO = −181 ± 10 kJ mol−1 (1)

→ HSC(X2A′) + H(3S1/2), ΔRHO = −16 ± 5 kJ mol−1 (2)

→ CS(X1Σg+) + H2(X1Σg+), ΔRHO = −462 ± 2 kJ mol−1 (3)

→ CS(X1Σg+) + 2H(3S1/2), ΔRHO = −26 ± 2 kJ mol−1. (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. H2S, 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-
expected to be formed in high quantities in SL-9 impact triggered shock waves with temperatures exceeding 5000 K. 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 present in combustion flames 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$^{-1}$ (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, 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($^3P_f$).

II. EXPERIMENT AND DATA ACQUISITION

The experiments were performed with a universal crossed molecular beam apparatus. Briefly, a pulsed super-sonic carbon beam was generated via laser ablation of graphite. 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 $v_0=2035\pm53$ m s$^{-1}$ and speed ratio $S=4.0\pm0.1$ and continuous hydrogen sulfide beam ($v_0=738\pm5$ m s$^{-1}$, $S=7.3\pm0.1$) 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 in 5.0° steps with respect to the carbon beam at $m/e=45$, i.e., HC$_3$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 and are closed. The LAB distribution of the HCS product peaks at 47° near the center-of-mass angle of 45.8° 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.

III. RESULTS

Reactive scattering signal was only observed at $m/e=45$, i.e., HC$_3$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° ±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 $P(E_T)$ 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 220–320 kJ mol$^{-1}$, whereas the sum of...
the reaction exothermicity of reaction (1) and relative collision energy gives 210±30 kJ mol\(^{-1}\) (Refs. 23–25). Even within the error limits, the 165±5 kJ mol\(^{-1}\) less stable HSC\((X^2\!\!\!\!\!\!A)\) 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\(_2\)SC 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 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\(_2\)SC 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 \(\mathbf{L}'\), 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\(^{(1P)}\) to the nonbonding electrons forming triplet 1,1-dihydrothiocarbonyl \{1\} or insertion in the S-H-bond to triplet \(\text{trans/cis}\) thiohydroxycarbene \{3\} (\(C_1\) point group; \(^3\!\!\!\!\!\!A\) electronic state) or \{4\}. \{1\} can undergo hydrogen migration to \{3\}, intersystem crossing (ISC) to singlet 1,1-dihydrothiocarbonyl \{2\} followed by H-migration to singlet \(\text{trans/cis}\) thiohydroxycarbene \{5\} \((C_1;{^-1}\!\!\!\!\!\!A')/\{6\} (C_1;{^1\!\!\!\!\!\!A'})\), or decomposes to HSC\((X^2\!\!\!\!\!\!A')\)+H. The final fate of the thiohydroxycarbenes results in C–H and/or S–H bond rupture to HSC\((X^2\!\!\!\!\!\!A')\) and/or HCS\((X^2\!\!\!\!\!\!A')\) and H\((\!\!\!\!\!\!^2S_{1/2})\) or a hydrogen migration to singlet/triplet thioformaldehyde \{8\} \((C_2\nu;\!\!\!\!\!\!X^1\!\!\!\!\!\!A_1)\) and \{7\} \((C_2;\!\!\!\!\!\!^3\!\!\!\!\!\!A')\). A final C–H-bond rupture in \{7/8\} could yield HCS\((X^2\!\!\!\!\!\!A')\) and H\((\!\!\!\!\!\!^2S_{1/2})\) as well.

Since the thioformyl isomer HCS\((X^2\!\!\!\!\!\!A')\) was identified, H-loss of \{1\}/\{2\} yielding HSC\((X^2\!\!\!\!\!\!A')\) 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\((X^2\!\!\!\!\!\!A')\) is about 50 kJ mol\(^{-1}\), decomposing complexes \{7\} and \{8\} must be ruled out as well. Therefore, none of the four remaining H\(_2\)CS 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\((X^2\!\!\!\!\!\!A')\)+H instead of a C–H-cleavage forming HSC\((X^2\!\!\!\!\!\!A')\)+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\((X^2\!\!\!\!\!\!A')\) 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$_2$SC surfaces will be used to quantify the entrance and exit barriers as well as the nature of the initially formed H$_2$SC 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$_2$S, 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, 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$^{-10}$ cm$^3$ s$^{-1}$, possibly transforming HCS into in OCS detected in combustion processes. Hence, the role of the reaction chain (5)--(6)

\begin{align*}
C(3P_j) + H_2S(X^1A_1) &\rightarrow H_2SC \rightarrow HCS(X^2A') + H(2S_{1/2}), \quad (5) \\
HCS(X^2A') &\rightarrow CS(X^1\Sigma^+) + H(2S_{1/2}), \quad (6) \\
HCS(X^2A') + O(3P_j) &\rightarrow OCS(X^1\Sigma^+) + H(2S_{1/2}) \quad (7)
\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 from (CH$_3$)$_2$S (Ref. 30) and CH$_3$SH (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$_2$/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$_3$→HCS+H$^{32,33}$ or C$_2$H$_3$+S→HCS+H$_2$S in the gas phase or CH$^+$+SH$^-\rightarrow$HCS+H on interstellar grains. 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$_2$S on interstellar grains might resolve the anticorrelation of HCS and H$_2$S in carbon rich dark clouds TMC-1. Since H$_2$S 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.

---