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International Journal of Mass Spectrometry 185/186/187 (1999) 727–743



Gas-phase reactivity of $\text{HS}_2\text{H}^{+\cdot}$ and $\text{S}_2^{+\cdot}$: an investigation of the gas basicity and proton affinity of HS_2^{\cdot}

Brian K. Decker, Nigel G. Adams*, Lucia M. Babcock

Department of Chemistry, The University of Georgia, Athens, GA 30602, USA

Received 9 July 1998; accepted 28 August 1998

Abstract

The reactions of $\text{HS}_2\text{H}^{+\cdot}$ with the series of reference bases: H_2S , CH_2O , $\text{C}_3\text{H}_3\text{F}_3\text{O}$ (1,1,1-trifluoropropanone), $\text{C}_2\text{H}_5\text{I}$, $\text{C}_6\text{H}_4\text{F}_2$ (*o*-difluorobenzene), HCO_2H , C_4H_8 (*trans*-2-butene), *c*- C_3H_6 , *n*- C_3H_6 , CH_3OH , CH_3SH , and $\text{C}_2\text{H}_5\text{OH}$, with proton affinities ranging from 168.5–185.6 kcal/mol, have been investigated with a selected ion flow tube (SIFT) to bracket the gas basicity (GB) and proton affinity (PA) of the hydrothiosulfeno radical (HS_2^{\cdot}). The recently developed thermokinetic method of Bouchoux et al. [Int. J. Mass Spectrom. Ion Processes 153 (1996) 37] applied to the data gives $\text{GB}(\text{HS}_2^{\cdot}) = 169.8 \pm 2.2$ kcal/mol and $\text{PA}(\text{HS}_2^{\cdot}) = 178.0 \pm 2.4$ kcal/mol, consistent with but more accurate than the simple bracketing procedure. The proton affinity is used to calculate the enthalpy of formation of HS_2^{\cdot} , giving $\Delta H_f^{298}(\text{HS}_2^{\cdot}) = 25.0 \pm 2.5$ kcal/mol; this result is compared with the relatively few other reported determinations of this quantity. The HS_2^{\cdot} radical is of potential importance to chemical processes in interstellar clouds (ISC), as well as to fuel refinery and atmospheric chemistry. The $\text{HS}_2\text{H}^{+\cdot}$ reactions and a parallel study of the reactions of $\text{S}_2^{+\cdot}$ are discussed. (Int J Mass Spectrom 185/186/187 (1999) 727–743) © 1999 Elsevier Science B.V.

Keywords: Gas basicity; Proton affinity; Ion/molecule reactions; HS_2^{\cdot} radical; Interstellar chemistry

1. Introduction

The hydrothiosulfeno radical, HS_2^{\cdot} , is the simplest heteronuclear species containing an S–S bond. Recently it was shown in our laboratory that the reactions of the sulfur dimer cation, $\text{S}_2^{+\cdot}$, with hydrogenated organic molecules (designated XH_2) lead in many cases to the formation of HS_2^{\cdot} and/or its protonated form, $\text{HS}_2\text{H}^{+\cdot}$, with a relative branching ratio which depends on the proton affinity (PA) of the

dehydrogenated product, X [1]. In that study we suggested that the HS_2^{\cdot} forms in the $\text{S}_2^{+\cdot}$ reaction by hydride abstraction and initially appears as a proton-bound heterodimer ($\text{HS}_2^{\cdot} \dots \text{H}^+ \dots \text{X}$) which subsequently fragments to HS_2^{\cdot} and HX^+ , or to $\text{HS}_2\text{H}^{+\cdot}$ and X, in proportions governed by the PA of X relative to HS_2^{\cdot} [1]. Such behavior is the basis of the so-called kinetic method pioneered [2] and, more recently, extensively reviewed [3] by Cooks and co-workers for the determination of thermochemical quantities from the fragmentation patterns of activated ion-bound complexes. From our $\text{S}_2^{+\cdot}$ study in a selected-ion flow tube (SIFT), we were able in the spirit of the kinetic method to estimate the PA of HS_2^{\cdot} to be ~ 175 kcal/mol [1].

* Corresponding author.

Dedicated to Professor Michael T. Bowers on the occasion of his 60th birthday.

The present work is intended to refine the determination of PA(HS_2) by means of the well-established bracketing method [4] and by a new “thermo-kinetic” method developed by Bouchoux et al. [5], and to derive therefrom a value for the enthalpy of formation, $\Delta H_f^{\circ 298}(\text{HS}_2)$, from experimentally-determined quantities. Except for our former estimate [1], the proton affinity of HS_2 has not been reported previously. $\Delta H_f^{\circ 298}(\text{HS}_2)$ was estimated to be 22.1 ± 1 kcal/mol by Benson [6] from his principle of group additivity, and Luke and McLean [7], using ab initio methods, calculated $\Delta H_f^{\circ 298}(\text{HS}_2) = 26.7 \pm 3$ kcal/mol. These two determinations do not agree to within their estimated uncertainties, although the ab initio result is certainly to be preferred, it being the more fundamental and detailed of the two approaches. Moran and Ellison [8] measured the electron affinity (EA) of HS_2 by negative-ion photoelectron spectroscopy (PES), and O’Hair et al. [9] determined the gas-phase acidity ($\Delta H_{\text{acid}}^{\circ}$) of neutral HS_2H by bracketing the gas-phase basicity of HS_2^- [9]. O’Hair et al. used these results to deduce a value of 28 ± 3.5 kcal/mol for $\Delta H_f^{\circ 298}(\text{HS}_2)$, in reasonable agreement with the ab initio prediction [7,9]. The present study approaches $\Delta H_f^{\circ 298}(\text{HS}_2)$ from a different and complementary chain of thermochemical relationships.

The HS_2 radical was first detected in a flash photolysis kinetic study of H_2S by Porter in 1950 [10], from an absorption band system in the 315–380 nm range which has not yet been assigned to date. The \tilde{A}^2A' first excited state of HS_2 was first observed and correctly assigned from the $\tilde{A}^2A' \rightarrow \tilde{X}^2A''$ (π^* , n) emission band system in the 950–2100 nm range by Holstein et al. in 1985 [11], guided by a detailed ab initio treatment of the radical by Sannigrahi et al. [12]. In a more recent ab initio study at the self-consistent field (SCF) and unrestricted second-order Møller-Plesset (UMP2) levels of theory, Zhuo et al. [13] calculated molecular parameters for HS_2 which were later used by Yamamoto and Saito as a basis for comparison when they recorded its microwave spectrum in the 140–310 GHz range [14]. The far infrared spectrum of HS_2 has also been recorded, by Ashworth et al. [15] in the 170–305 μm range. These studies have thoroughly characterized the HS_2 radical in its

ground electronic state [15], which is an asymmetric top “ π ” radical with a significant electric dipole moment, on the order of 1.4 Debyes [13].

Comparatively little is known about the disulfane molecular cation, HS_2H^+ , or protonated HS_2 . Because an accurate value for the adiabatic ionization energy (IE) of neutral disulfane (HS_2H) is crucial to the determination of $\Delta H_f^{\circ 298}(\text{HS}_2)$ from the proton affinity of HS_2 , it is fortunate that Cheng et al. recently redetermined this quantity in a careful measurement of the photoionization efficiency (PIE) spectrum of disulfane [16]. From this, they derived a revised value for $\Delta H_f^{\circ 298}(\text{HS}_2\text{H}^+)$ some 5.8 kcal/mol lower than that recommended by Lias et al. [17]. Along with their PIE study, Cheng et al. performed an ab initio study of HS_2H^+ at the UMP2 level of theory and found two stable isomeric forms: A *cis*- HS_2H^+ with a dihedral angle of 0° and a *trans*- HS_2H^+ with a dihedral angle of 180° ; the *trans* isomer has a calculated IE in excellent agreement with the photoionization threshold for HS_2H [16], with the *cis* isomer being some 2.7 kcal/mol higher in energy. No data on the isomerization barrier were presented [16].

The thermochemistry and reactivity of HS_2 and its derivatives are important from the points of view of atmospheric, fuel refinery and interstellar chemistry. The isovalent oxygenated analogues peroxy (HO_2) and thioperoxy (HSO) are known to be important participants in the destruction of stratospheric ozone and the oxidation of reduced forms of anthropogenic sulfur in the atmosphere [e.g. 18–23]. The role of HS_2 in terrestrial atmospheric chemistry is unknown at present, although pathways to its formation in the atmosphere and reaction with atmospheric gases have been suggested [24]. More work clearly needs to be done in this area. HS_2 has been inferred to be a product of H_2S decomposition in a shock tube [25], and also an intermediate in the synthesis of polysulfanes, HS_nH ($n = 2, 3, 4 \dots$), during the oxidation of mercaptans by molecular sulfur [26]. These results suggest that HS_2 as a reactive intermediate is responsible in part for the shortfall in H_2S recovery from sour natural gas in the modified Claus process [27], and, in general, that the chemistry of HS_2 is relevant

to the processing of petroleum and natural gas at elevated temperatures.

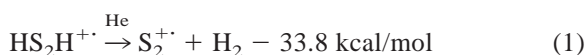
Our initial S_2^+ study [1] was motivated by consideration of the chemistry of sulfur in interstellar clouds (ISC). No molecule containing two sulfur atoms has yet been detected in ISC, although the neutral sulfur dimer, S_2 , has been observed in the comet Araki-Alcock [28] and has been searched for in several interstellar sources [29]. Because of its relatively low IE of 9.356 eV [30], S_2 can be either photoionized or chemi-ionized to form S_2^+ in ISC. Several ion-molecule reaction pathways to form S_2^+ have also been discussed [1]. Because S_2^+ is unreactive with H_2 and CO, the primary molecular constituents of ISC, this ion may accumulate and be present to react with interstellar organic molecules [1]. It has been shown that HS_2 is a very frequent product of such reactions [1]. S_2 has been predicted to be particularly abundant in the interstellar objects known as hot molecular cores [31], and S_2 along with its derivatives (S_2^+ , HS_2 , HS_2H , etc.) have been considered in models of interstellar gas [e.g. 31–33] and grain [34] chemistry.

In this study, we present the reactions of both HS_2H^+ and S_2^+ with the following set of 12 bases, with the corresponding PA in kcal/mol (taken from the National Institute of Standards and Technology (NIST) database of Hunter and Lias [35]) indicated in parentheses: H_2S (168.5), H_2CO (170.4), $CH_3C(O)CF_3$ (173.0), C_2H_5I (173.2), *o*- $C_6H_4F_2$ (174.8), HCO_2H (177.3), *trans*-2- C_4H_8 (178.5), *c*- C_3H_6 (179.3), *n*- C_3H_6 (179.6), CH_3OH (180.3), CH_3SH (184.8) and C_2H_5OH (185.6). Additionally, we present the reactions of S_2^+ with NH_3 , for which we have now detected the primary reaction product which was not observed in the former study [1]; with $(CH_3)_2CHOH$, to further characterize the reactivity of S_2^+ with alcohols; and to make a slight correction to the reaction of S_2^+ with ethanol as presented in the former study [1].

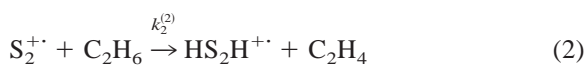
2. Experimental

The selected ion flow tube (SIFT) technique has been described in detail elsewhere [36], and will be treated here only in outline, except in such particulars

as are specific to the present study. HS_2H^+ was generated by electron impact (EI) on diethyl disulfide, $C_2H_5S_2C_2H_5$ [37], in a low-pressure EI ion source operated at 70 eV electron energy. The ion injection energy was kept as low as possible, commensurate with a usable flux of HS_2H^+ ions, because the threshold for collision-induced dissociation (CID) by the process:



occurs at about 25.7 eV of translational kinetic energy for HS_2H^+ in the laboratory frame of reference. To obtain usable ion signals, an injection energy of at least 30 eV was required, and thus an S_2^+ fragment was observed, whose peak intensity increased relative to HS_2H^+ as the ion lenses and quadrupole surfaces became gradually corrupted with sulfuretted deposits, necessitating higher injection energies. The S_2^+ peak intensity was minor under optimal operating conditions; about 5%–10% that of HS_2H^+ . Alternatively in some runs HS_2H^+ was created by the reaction of injected S_2^+ with ethane:



with a bimolecular rate coefficient $k_2^{(2)} = 3.2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ [1]. Ethane has a relatively low proton affinity (PA = 142.5 kcal/mol [35]) and is unreactive with HS_2H^+ , and thus did not complicate the primary product spectrum when it was used to generate HS_2H^+ . However, a contaminant peak, $C_4H_9^+$ did appear when ethane was added, at a peak intensity of ~20 % of the HS_2H^+ . A number of chemical pathways are possible to form $C_2H_5^+$, which then reacted with the abundant ethane to form the observed $C_4H_9^+$ impurity ion [38]. For example, S^+ , a minor fragmentation ion when S_2^+ is injected (see below), reacts with ethane to give $C_2H_5^+$ as a 70 % reaction channel [39]; and ethylene, which can be protonated by an impurity ion such as SH^+ , is the major impurity (typically at 3000 ppm) in ethane (Matheson CP Grade). In any event, the presence of $C_4H_9^+$ did not affect the analysis in the cases where HS_2H^+ reacted only by rapid proton transfer, and in all other cases the

experiment was also conducted with $\text{HS}_2\text{H}^{+\cdot}$ injected directly from a clean SIFT for comparison.

Because $\text{S}_2^{+\cdot}$ was a small but persistent impurity ion in the $\text{HS}_2\text{H}^{+\cdot}$ experiments, its reactions were investigated in a parallel study. The $\text{S}_2^{+\cdot}$ was produced from CS_2 as in our former study [1]. In order to eliminate the small S^+ impurity ion from the CID of $\text{S}_2^{+\cdot}$ on injection, in some runs the $\text{S}_2^{+\cdot}$ was alternatively generated in the flow tube by the reaction sequence:



for which $k_{3b}^{(2)} = 9.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ [40]. The N_2 was used to collisionally quench the $\sim 20\%$ of S^+ ions formed in metastable electronic states (${}^2\text{D}$ and ${}^2\text{P}$) to the ground ${}^4\text{S}$ state [39], because the metastable $\text{S}^{+\cdot}$ transfers its charge to OCS. With quenching by N_2 , the $\text{OCS}^{+\cdot}$ impurity was minor, on the order of 5%–7% of the $\text{S}_2^{+\cdot}$ peak intensity, and the reactions of $\text{S}_2^{+\cdot}$ were easy to distinguish from the side reactions of $\text{OCS}^{+\cdot}$. Although $\text{S}_2^{+\cdot}$ could in principle have interfered with product identification in the $\text{HS}_2\text{H}^{+\cdot}$ reactions, the $\text{S}_2^{+\cdot}$ ion clearly cannot participate in proton transfer reactions, and in fact did not interfere with the primary product ion spectrum from $\text{HS}_2\text{H}^{+\cdot}$, except in the cases (*trans*-2-butene, *o*-difluorobenzene, and iodoethane) where charge transfer is possible for both ions.

Parent ions and parent-precursor ions were selected in the SIFT quadrupole mass filter and focused through a 1-mm hole into the flow tube. The precursor ions were reacted upstream in the flow tube to form the parent ions as discussed above, and the neutral reactants were added at various fixed ring inlets to establish appropriate reaction lengths. Neutral reactant flows were determined by their pressure drop across a calibrated capillary tube, which requires a knowledge of their gas-phase viscosities. These were taken from literature sources [41,42] or, where unavailable, measured by the pressure drop in a calibrated volume filled with reactant vapor below its saturation vapor pressure, as the vapor was allowed to

leak through the calibrated capillary tube. Viscosities measured this way are accurate to $\pm 5\%$. In the case of formic acid, the vapor was used neat and also in a dilute 0.75% manometric mixture with helium; in both cases, the measured flow was corrected to account for the monomer-dimer equilibrium of formic acid using the data of Taylor and Bruton [43]. Formaldehyde was introduced by sublimation from solid paraformaldehyde maintained at $\sim 80^\circ\text{C}$. Liquid reagents were purified by several freeze-pump-thaw cycles before use, and gaseous reagents and paraformaldehyde were used without further purification. Liquid reagents such as iodoethane and formic acid, which undergo thermal decomposition, were refrigerated at 9°C until use. The reagents were obtained from commercial sources with the following purities: ethanol (200 proof); methanethiol (99.5+ %); methanol (99.9 wt. %); propene (99+ mol. %); cyclopropane (99.0+ %); *trans*-2-butene (99.7 wt. %); formic acid (99.4 wt. %); *o*-difluorobenzene (99.7 wt. %); iodoethane (98.8 wt. %); 1,1,1-trifluoropropanone (99.9 wt. %); paraformaldehyde (95 wt. %); hydrogen sulfide (99.5+ %); ammonia (99.99+ %); 2-propanol (99.98 wt. %); ethane (99.0+ mol. %); carbonyl sulfide (97.5 mol. %); carbon disulfide (99.99 wt. %); diethyl disulfide (99.8 wt. %).

The ion swarm and neutral reactants were entrained in a flow of He carrier gas at a pressure of ~ 0.5 Torr and a plug flow velocity of $\sim 8000 \text{ cm s}^{-1}$. All experiments were conducted at $296 \pm 3 \text{ K}$. Ions were sampled by a detection orifice leading to a differentially-pumped quadrupole mass spectrometer/ion counting system located downstream. Ion currents collected by an on-axis channel multiplier were amplified and then passed to a gated pulse counter and a desktop computer for processing. Reaction rate coefficients and product distributions were determined in the usual way [44,45]. Rate coefficients are accurate to $\pm 20\%$ for permanent gases, and to $\pm 30\%$ for sticky gases and vapors from liquid reagents (and formaldehyde); reproducibility is generally better than $\pm 10\%$. For the determination of correct product channel branching ratios, mass discrimination in the detection system was accounted for by summing the parent (A^+) and product (C_j^+) ion signals, including

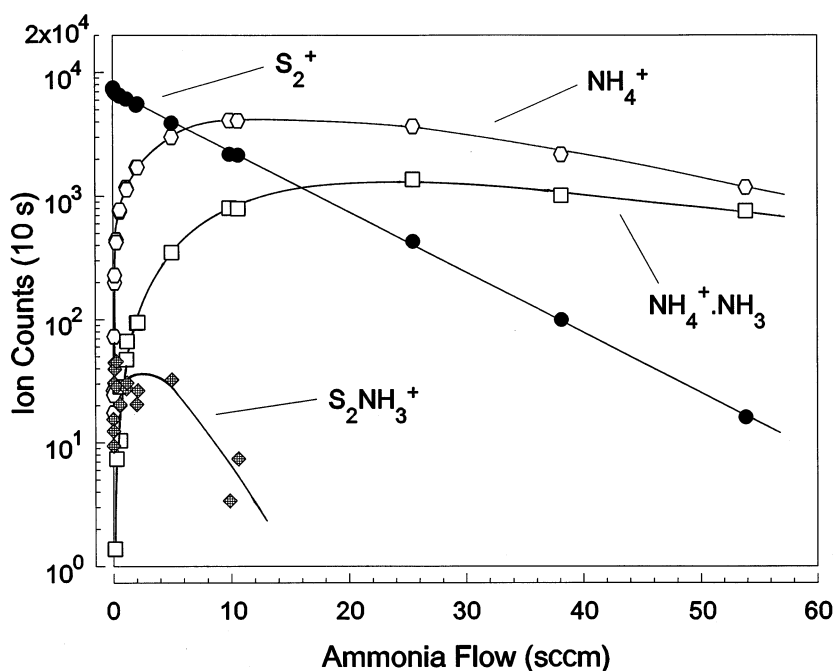


Fig. 1. Variation of S_2^+ and ion product count rates with NH_3 flow. The S_2^+ decay is linear over nearly three orders of magnitude. The primary product of this slow reaction is the cluster ion, $S_2NH_3^+$, which in turn rapidly proton transfers to ammonia. The resulting NH_4^+ proceeds to cluster successively with NH_3 (ammonia clusters higher than $NH_4^+ \cdot NH_3$ are omitted for clarity). The rate coefficient and ion product distribution for this and the other reactions in this study are presented in Table 1.

mass discrimination factors for the latter (f_j), and equating to the initial parent ion signal (A_0^+) as follows:

$$A_0^+ = A^+(B_k) + \sum_j f_j C_j^+(B_k) \quad (4)$$

where B_k is the k th concentration or flow of neutral reactant. When $k > j$, this system of equations overdetermines the mass discrimination factors f_j , and a multiple linear regression analysis can be performed to obtain these factors. In practice, consistent and reliable factors can only be obtained for systems in which the C_j^+ all vary with respect to each other as a function of neutral reactant flow. Furthermore, it is essential to monitor all significant product ions, primary, secondary, tertiary, etc. This method works better for systems in which there are fewer than four product ions. Note that it assumes that there is no significant relative diffusive loss among the various ions A^+ and C_j^+ in the flow tube (see [46]). The ion product distributions obtained are considered to be accurate to ± 5 in the percentage.

Fig. 1 and Fig. 2(a) and (b) demonstrate the quality of the data collected in this study. Fig. 1 is a rate plot showing the excellent linearity of the S_2^+ decay over nearly three orders of magnitude in its reaction with NH_3 . The NH_4^+ which is produced as a secondary product of the reaction proceeds to cluster with the neutral ammonia in the flow tube; for clarity only the first cluster is shown in the plot. Also indicated is the primary product of the reaction, $S_2NH_3^+$, which was not detected in our former study [1] because of its rapid proton transfer to ammonia. Fig. 2(a) shows the reaction of HS_2H^+ with $n-C_3H_6$ (propene), with a side reaction of the S_2^+ impurity illustrated. The decays of both the HS_2H^+ and the S_2^+ are linear over two orders of magnitude. The primary products of the HS_2H^+ reaction are proton transfer and ternary association. Only the major (60%) channel of the S_2^+ reaction, i.e. ternary association, is shown on the plot, again for clarity. The percentages of products originating from the HS_2H^+ reaction alone are plotted as a function of propene flow in Fig. 2(b). The ternary

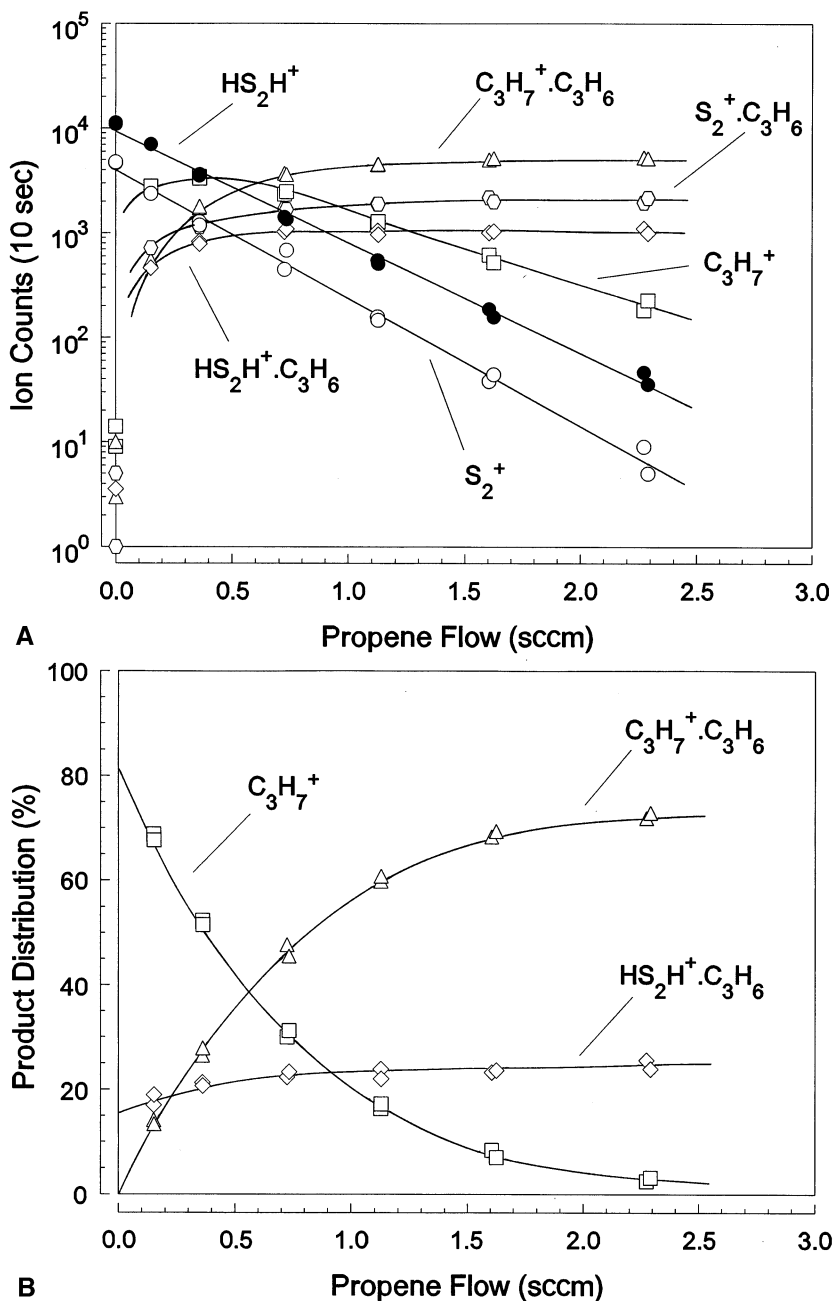


Fig. 2. (A) Variation of the HS_2H^+ and product ion count rates with n - C_3H_6 (propene) flow and (b) Percentages of the ion products of the HS_2H^+ reaction as a function of n - C_3H_6 flow. In (A), a side reaction because of the impurity ion S_2^+ (see text) is shown. The decays of HS_2H^+ and S_2^+ are linear over two orders of magnitude. The major product (60%) of the S_2^+ reaction is the cluster ion, $S_2^+ \cdot C_3H_6$; for clarity, its minor products are not illustrated. From (B), it can be seen that HS_2H^+ proton transfers (85%) to form $C_3H_7^+$ and associates (15%) to form $HS_2H^+ \cdot C_3H_6$ at ~ 0.5 Torr He pressure. The rate coefficients and ion product distributions for these and the other reactions in this study are presented in Table 1.

association to form $C_6H_{13}^+$ is evidently a secondary reaction, as expected, and the branching ratio between proton transfer and ternary association at the pressure employed (~ 0.5 Torr) is obtained by extrapolation to zero flow to eliminate the effects of the secondary reaction.

3. Results and discussion

The rate coefficients ($k_{\text{exp}}^{(2)}$) and fractional ion product distributions for the reactions of HS_2H^+ and S_2^+ are presented in Table 1, with the neutral reactants arranged in order of decreasing proton affinity. The collisional capture rate coefficients ($k_{\text{TST}}^{(2)}$), as calculated from the variational transition state theory of Su and Chesnavich [51], are included for comparison with the experimental values. Rate coefficients for reactions leading to ternary association channels are presented as effective binary rate coefficients at ~ 0.5 Torr. When close to the collisional value, these indicate that the association is pressure-saturated [52]. When the ternary association is inefficient, i.e. not pressure-saturated, the ternary rate coefficient can be determined as $k_{\text{exp}}^{(2)}/[\text{He}]$.

Apart from the proton-transfer reactivity of HS_2H^+ which permits the bracketing method, several other features of the S_2^+ and HS_2H^+ reactions are intrinsically interesting, and quite distinct for the two ions. The reactions of S_2^+ in the present study amplify and complement our former results [1], with which they are compared in Sec. 3.1. The reactions of HS_2H^+ are considered in Sec. 3.2, which leads naturally into a discussion of methods for determining the gas basicity and the proton affinity of HS_2 in Sec. 3.3.

3.1. Reactions of S_2^+

S_2^+ reacts slowly at 0.5 Torr with H_2S and with NH_3 by ternary association. In the latter case, the reaction is followed by a rapid proton transfer to ammonia, which makes the product $S_2NH_3^+$ difficult to detect (see Experimental and Fig. 1). Schindler et al. [53] observed the $S_2NH_3^+$ ion as a product of the

binary reaction of S_4^+ with ammonia in Fourier transform ion cyclotron resonance (FTICR); however, they attributed the S_2^+ reaction to a charge transfer forming NH_3^+ , a process which is 18.5 kcal/mol endothermic [1]. We do not observe this endothermic charge transfer; the sole primary product of the reaction is the cluster ion, $S_2NH_3^+$. For the reaction of S_2^+ with hydrogen sulfide, the measured (raw) rate coefficient is $3.4 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$; however, the H_2S (Matheson CP grade) typically has impurities, by weight, of 2700 ppm propene and 810 ppm propane, both of which react with S_2^+ near the collisional rate [1], some three orders of magnitude faster than the reaction with H_2S . No other contaminant of the H_2S contributes significantly to the raw rate coefficient, which may therefore be simply expressed as:

$$k_{\text{raw}}^{(2)} = k_{\text{exp}}^{(2)} + k_{\text{imp}}^{(2)} \quad (5a)$$

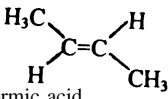
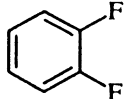
$$k_{\text{imp}}^{(2)} = x_{\text{propene}} k_{\text{propene}}^{(2)} + x_{\text{propane}} k_{\text{propane}}^{(2)} \quad (5b)$$

where $k_{\text{exp}}^{(2)}$ is the true effective binary rate coefficient for the ternary association of S_2^+ with H_2S , and $k_{\text{imp}}^{(2)}$ is the effective rate coefficient for the reactions of the impurity species with S_2^+ . Note in Eq. (5b) that $k_{\text{imp}}^{(2)}$ includes the mole fractions (x) of the propene and propane contaminants and their bimolecular rate coefficients for reaction with S_2^+ , which are known [1]. A plot of the product distribution for the overall reaction yields branching ratios of 0.55 ± 0.15 for $H_2S_3^+$ and 0.45 ± 0.15 for all impurity products. A simple kinetic analysis then gives $k_{\text{exp}}^{(2)} = 1.9 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$, as reported in Table 1, with a somewhat larger than usual uncertainty ($\pm 30\%$). From $k_{\text{exp}}^{(2)}$ and Eqs. (5a) and (5b), the impurity levels of propene and propane in our H_2S sample are respectively ~ 1250 ppm and ~ 370 ppm, assuming the same relative proportion as for the manufacturer's typical values (see above). These lower-than-rated impurity levels are further substantiated by the results of the HS_2H^+ reaction with H_2S discussed in the following section.

It is of interest to consider the possible isomeric forms of the associated complexes arising from the reactions of S_2^+ with H_2S and NH_3 , particularly because the $S_2NH_3^+$ product of the latter proton transfers to ammonia, and hence forms the neutral

Table 1

Reaction rate coefficients and fractional product ion distributions for the reactions of HS_2H^{++} and S_2^{++} with the indicated neutral reactants at $296 \text{ K} \pm 3 \text{ K}$

Reactants	PA ^a	GB ^a	HS_2H^{++}		Ion product distribution	Ion product ^e	S_2^{++}		Ion product distribution	Ion product ^{e,g}		
	IE ^a (eV)	(kcal/mol)	(kcal/mol)	$k_{\text{exp}}^{(2),b}$ ($\text{cm}^3 \cdot \text{s}^{-1}$)			$k_{\text{TST}}^{(2),d}$ ($\text{cm}^3 \cdot \text{s}^{-1}$)	$k_{\text{exp}}^{(2),b}$ ($\text{cm}^3 \cdot \text{s}^{-1}$)			$k_{\text{TST}}^{(2),d}$ ($\text{cm}^3 \cdot \text{s}^{-1}$)	
Ammonia NH_3	10.16	204.0	195.7	1.5 (–11)	2.2 (–9)	1.00	AS		
2-propanol $(\text{CH}_3)_2\text{CHOH}$	10.17	189.5	182.3	1.6 (–11) ^f	1.8 (–9)	0.50	HA		
Ethanol $\text{C}_2\text{H}_5\text{OH}$	10.47	185.6	178	2.3 (–9)	1.9 (–9)	1.00	PT	2.2 (–9)	1.00	HA		
Methanethiol CH_3SH	9.44	184.8	177	2.0 (–9)	1.8 (–9)	1.00	PT	1.7 (–9) ^f	1.8 (–9)	1.00	HA	
Methanol CH_3OH	10.84	180.3	173.2	1.6 (–9)	2.0 (–9)	1.00	PT	1.2 (–9) ^f	2.0 (–9)	0.90	H2A	
Propene $n\text{-C}_3\text{H}_6$	9.73	179.6	172.7	1.0 (–9)	1.2 (–9)	0.85	PT	8.7 (–10) ^f	0.08	HA		
Cyclopropane $c\text{-C}_3\text{H}_6$	9.86	179.3	172.6	7.0 (–10)	1.1 (–9)	0.95	PT	0.02	0.60	AS		
<i>trans</i> -2-butene 	9.10	178.5	171.6	1.5 (–9)	1.2 (–9)	0.85	PT	0.15	0.15	CH ₂ S ₂ ⁺		
Formic acid HCO_2H	11.33	177.3	169.7	4.2 (–10)	1.6 (–9)	1.00	PT	1.2 (–9)	0.85	HA		
<i>o</i> -difluorobenzene 	9.29	174.8	168.0	4.0 (–11)	2.2 (–9)	0.45	C ₃ H ₃ FH ⁺	5.0 (–11)	1.6 (–9)	1.00	AS	
Iodoethane $\text{C}_2\text{H}_5\text{I}$	9.35	173.2	167	<2 (–11) ^c	1.8 (–9)	>0.90	CT	~5 (–11) ^f	2.0 (–9)	2.2 (–9)	0.60	CT
						0.30	CT				0.40	AS
						0.15	PT					
						0.05	C ₃ H ₂ S ₂ FH ⁺					
						0.05	AS					
						<0.10	products	1.7 (–9)	1.8 (–9)	0.35	AS	
										0.30	IS ₂ H ⁺	
										0.20	CT	
										0.10	C ₂ H ₄ S ₂ ⁺	
										0.05	C ₂ H ₃ S ₂ ⁺	

(continued)

radical S_2NH_2 (dissociative proton transfer is almost certainly endothermic at $296 \pm 3 \text{ K}$ for all of the possible channels). Zhuo et al.'s ab initio study of XS_2 radicals ($X = \text{H}, \text{F}, \text{Cl}$) at the UMP2 level of theory shows these species in their ground electronic states to have substantial double-bond character between the

sulfur atoms, with an X–S single bond and the unpaired electron localized on the S=S moiety [13]. The halogen substituents ($X = \text{F}, \text{Cl}$), with their high electronegativities, increase the delocalization of the unpaired electron between the sulfur atoms, and thus shorten the S=S bond in the radical [13]. The S_2NH_2

Table 1 (continued)

Reactants	IE ^a (eV)	PA ^a (kcal/ mol)	GB ^a (kcal/ mol)	HS ₂ H ⁺ <i>k</i> _{exp} ^{(2) b} (cm ³ · s ⁻¹)	<i>k</i> _{TST} ^{(2) d} (cm ³ · s ⁻¹)	Ion		<i>S</i> ₂ ⁺ <i>k</i> _{exp} ^{(2) b} (cm ³ · s ⁻¹)	<i>k</i> _{TST} ^{(2) d} (cm ³ · s ⁻¹)	Ion	
						distrib- ution	Ion product ^e			distrib- ution	Ion product ^{e,g}
1,1,1-trifluoropropanone CH ₃ C(O)CF ₃	10.67	173.0	165.4	1.2 (-10)	2.4 (-9)	1.00	AS	2.7 (-10)	2.4 (-9)	0.50	AS
Formaldehyde CH ₂ O	10.88	170.4	163.3	4.0 (-11)	2.5 (-9)	1.00	CH ₂ S ₂ ⁺	1.1 (-10)	2.5 (-9)	0.50	CH ₃ CO ⁺
Hydrogen sulfide H ₂ S	10.46	168.5	161.0	<1 (-13) ^c	1.4 (-9)	...	NR	1.9 (-12) ^c	1.4 (-9)	1.00	H2A

For comparison, IE(S₂) = 9.36 eV [30] and IE(HS₂H) = 9.06 eV [16].

^aThe ionization energies (IE), proton affinities (PA) and gas basicities (GB, 298 K) of the bases were obtained from the most recent NIST database (see [35]).

^bEffective binary rate coefficients are given for ternary reactions at ~0.5 Torr carrier pressure (see text).

^cSee the text for discussions of these determinations.

^dCollisional rate coefficients were calculated from the variational transition state theory of Su and Chesnavich [47]. For these calculations, average electric dipole polarizabilities (α) and electric dipole moments (μ_D) of the bases were obtained from references [48,49] except for: α (CH₃SH) [50]; α (CH₃C(O)CF₃), which was estimated to be 7.8×10^{-24} cm³ from a comparison of the bond polarizabilities [51] of several fluorinated molecules [48]; and μ_D (CH₃C(O)CF₃), which was calculated from ab initio methods to be 2.896 Debyes in its C_s symmetry conformation (see Acknowledgements).

^eIon products are classified by reaction type as follows: PT = proton transfer; AS = ternary association; CT = charge transfer; HA = hydride abstraction; H2A = H₂ abstraction; NR = no reaction; for other modes of reaction the ion product is given explicitly.

^fRate coefficients measured in our previous study [1], presented here for comparison; note that the rate coefficient for the reaction of S₂⁺ with CH₃SH was not redetermined.

^gThe product distributions for the reactions of S₂⁺ with CH₃SH, *n*-C₃H₆, and HCO₂H are reproduced here from the results of our previous study [1].

radical should by analogy have the structure of an amino-substituted thiosulfeno radical; as will be seen, S₂⁺ has a propensity for forming bent S₂X⁺ radicals of this sort. In the case of the H₂S₃⁺ product of the H₂S reaction, it is unclear whether a hydrogen migration occurs in the associated complex to form the trisulfane molecular cation, HS₃H⁺, or whether the complex retains the loosely-bound H₂S...S₂⁺ structure.

In the reactions of S₂⁺ with alcohols and thiols, we have shown previously that H₂ and/or H⁻ abstraction is the dominant process, leading to HS₂H⁺ and/or HS₂ [1]. We have presently reevaluated the reactions with CH₃OH and C₂H₅OH and included (CH₃)₂CHOH, in part because the ethanol (Aldrich) used in the former study [1] was denatured with 3.1 % methanol and 5.5 % 2-propanol by weight. With 200 proof ethanol (AAPER) we do not observe the 5 % H₂ abstraction channel which was reported previously [1], and we therefore attribute that channel entirely to the reaction of S₂⁺ with the methanol impurity. Note also that the rate coefficient for the reaction of S₂⁺

with C₂H₅OH is somewhat higher than previously reported [1] (see Table 1). The present value is preferred, as it includes an additional determination and a reevaluation of the former measurements. The rate coefficients for other S₂⁺ reactions which have been remeasured in the present study all show excellent agreement with the values determined previously (see Table 1). In the reaction with CH₃OH, a small product channel (2 %) leading by H₂O loss to the interesting ionic radical, CH₂S₂⁺, was not reported previously [1]. CH₂S₂⁺ is a recurrent product ion which is discussed further in Sec. 3.2. S₂⁺ reacts rapidly with (CH₃)₂CHOH by H⁻ abstraction to form protonated acetone, (CH₃)₂C⁺OH, and HS₂ (50 %); by OH⁻ abstraction to form C₃H₇⁺ and S₂OH (25 %); by CH₃⁻ abstraction to form protonated acetaldehyde, CH₃C⁺(H)OH, and CH₃S₂ (10 %); and by an H₂O loss analogous to the one for the methanol reaction, forming C₃H₆S₂⁺ (10 %). A small (5 %) channel complementary to the OH⁻ abstraction and forming H₂S₂O⁺ and C₃H₆ also occurs. The neutral products

are inferred here with confidence, because further fragmentation is unlikely on energetic grounds, and because of the resulting internal consistency of the various reaction channels. The S_2OH^\cdot radical is also the inferred neutral product of the OH^- abstraction by S_2^{++} from CH_3CO_2H and $C_2H_5CO_2H$ [1], and likely has the hydroxy-substituted thiosulfeno structure, in analogy with the discussion above. Note that an H_2 abstraction channel is not observed in the $(CH_3)_2CHOH$ reaction, which is not surprising, as HS_2 must compete with acetone (PA = 194 kcal/mol [35]) for the proton. Also note that H^- , OH^- , and CH_3^- abstractions are all observed with $(CH_3)_2CHOH$, indicating the stabilization of the carbocation by the additional methyl group as compared with C_2H_5OH , for which only the H^- abstraction is observed. Oddly, the H_2O loss channel to form $C_2H_4S_2^{++}$ is not observed in the ethanol reaction, although the analogous channel occurs with both methanol and 2-propanol, and $C_2H_4S_2^{++}$ appears elsewhere as a product in this and in our previous study (see below and reference [1]).

The hydrocarbon chemistry of S_2^{++} has been further characterized by its reactions with cyclopropane and *trans*-2-butene. S_2^{++} reacts with cyclopropane principally by H^- abstraction (85 %), with a C_2H_4 loss channel forming $CH_2S_2^{++}$ (10 %), and a small S–S cleavage channel forming $C_3H_5S^+$ (+ HS^\cdot) (5 %). These channels also appear in the S_2^{++} reaction with the structural isomer propene, for which however association (60 %) rather than H^- abstraction (5 %) is the dominant channel; propene additionally gives more S–S cleavage channels (see Table 1). Association does not occur with cyclopropane, which because of its hybridization lacks a π -donor effect; π -bonds have been noted to facilitate the stabilization of S_2^{++} ion/molecule complexes [1]. It is somewhat surprising in this light that S_2^{++} undergoes rapid H^- abstraction with *trans*-2-butene, with no association detected at ~ 0.5 Torr. The explanation lies with the reaction enthalpy: The $CH_2=CHCH_2^+$ carbocation has a hydride affinity some 19 kcal/mol greater than that of $CH_2=CHC^+(H)CH_3$ [54], and thus, the H^- transfer from *trans*-2-butene is too exothermic for collisional stabilization to occur, whereas such stabilization is

highly competitive with the binary channels in the propene reaction. Note that charge transfer, which is ~ 6 kcal mol $^{-1}$ exothermic, is a relatively minor channel (15% as compared to 85% for H^- abstraction) with *trans*-2-butene.

With *o*-difluorobenzene, S_2^{++} reacts simply by charge transfer (60 %) and association (40 %). No H^- abstraction is observed, which is consistent with the high stability of benzene against H^- loss [54]. Here again we see a rapid collisional stabilization in the interaction of S_2^{++} with a π -donor molecule. By analogy with the difference in reactivity between propene and *trans*-2-butene discussed above, in the case of toluene we would predict a facile H^- abstraction by S_2^{++} , due to the additional stability conferred on the benzyl cation by its resonance forms; the hydride affinity of $\phi-CH_2^+$ is comparable to that of $CH_2=CHC^+(H)CH_3$ (see above) [54]. In the case of C_2H_5I , the reaction is more complex, and association (35 %) is the dominant channel, although abstraction of HI (i.e. C_2H_4 loss) (30 %) occurs at a comparable level. Near-resonant charge transfer (20 %), loss of HI forming $C_2H_4S_2^{++}$ (10 %), and loss of I forming $C_2H_5S_2^{++}$ (5 %) also occur. S_2^{++} is much more reactive with iodoethane than with ethane (see Experimental and [1]). By analogy, we would predict that S_2^{++} , although unreactive with CH_4 [53], would react with CH_3I by methylene abstraction to form the commonly observed $CH_2S_2^{++}$ (+HI). In the reaction with C_2H_5I , products from the impurity C_2H_5OH are also observed; this is not surprising, as ethanol is the precursor in the manufacture of iodoethane [55,56], and the two compounds form a binary azeotrope [57]. The approximate level of the impurity (~ 1 %; see Experimental) is too low to affect the determination of the rate coefficient for the rapid reaction of S_2^{++} with C_2H_5I (see Table 1).

We have previously shown that S_2^{++} undergoes rapid H^- abstraction with acetaldehyde (CH_3CHO) and propionaldehyde (C_2H_5CHO) [1]; for these molecules, the X fragments in the proton-bound ion complex ($HS_2 \dots H^+ \dots X$) are ketene and methylketene, respectively, with proton affinities substantially higher than HS_2 [1,35]. Thus, the XH^+ fragment is observed, and HS_2H^+ is not [1]. Conversely for

formaldehyde (H_2CO), the X fragment is CO, with a substantially lower proton affinity than HS_2^+ [1,35], and HS_2H^{++} is observed to the exclusion of HCO^+ . Such results provide additional evidence for the essential soundness of the kinetic method of Cooks and co-workers [2,3]. With the ketone acetone, S_2^{++} has been shown to associate (100 %) at about half the collisional rate [1]; association is also a product channel (50 %) with 1,1,1-trifluoropropanone ($\text{CH}_3\text{C}(\text{O})\text{CF}_3$), although the trifluoromethyl substituent weakens the C–C bond enough for α -cleavage to occur, forming CH_3CO^+ and CF_3S_2^+ (50 %). Formation of separated CF_3^+ and S_2 in this reaction is energetically impossible at 296 ± 3 K.

3.2. Reactions of HS_2H^{++}

As Eq. (1) indicates, HS_2H^{++} is structurally lower in energy than $\text{S}_2^{++} + \text{H}_2$ by 33.8 kcal/mol; this fact is reflected in its somewhat lower reactivity compared to S_2^{++} (see Table 1). The *modes* of reactivity of the two ions are quite different, as governed by their relative degrees of saturation. Hydride abstraction dominates the chemistry of S_2^{++} as we have seen, just as proton transfer dominates that of HS_2H^{++} ; HS_2^+ is therefore a common product in the reactions of both ions.

Referring to Table 1, we note that HS_2H^{++} transfers a proton at the gas-kinetic rate (within experimental accuracy) to $\text{C}_2\text{H}_5\text{OH}$, CH_3SH , and CH_3OH ; for these bases, the proton transfer is a 100% channel. With *n*- C_3H_6 , *c*- C_3H_6 , and $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)\text{H}$ (*trans*-2-butene), proton transfer is also rapid, although it is somewhat slower than gas-kinetic with cyclopropane. For these bases, a minor ternary association channel also appears, implying that the proton transfer is close enough to thermoneutral that the ion complex persists long enough for collisional stabilization to occur. A small (5 %) charge transfer channel is also observed with *trans*-2-butene, which is nearly thermoneutral for the *trans* isomer of HS_2H^{++} (see Introduction and Table 1). Formic acid is the base with the lowest proton affinity (PA = 177.3 kcal/mol [35]) for which a 100 % proton transfer channel is observed; its reaction is relatively slow, occurring at only 27 % of

the gas-kinetic rate, and thus is probably endothermic or nearly thermoneutral.

Below formic acid on the proton affinity scale, the reactions of HS_2H^{++} are quite slow and do not generally proceed by proton transfer. For example, with *o*-difluorobenzene the major product channel (45 %) is an interesting ring opening to form $\text{C}_3\text{H}_3\text{FH}^+$ (and presumably $\text{C}_3\text{H}_2\text{S}_2\text{F}$); the product identities are substantiated by the isotope ratio of the ionic product and by the appearance of a minor (5 %) complementary channel in which $\text{C}_3\text{H}_2\text{S}_2\text{FH}^{++}$ (and presumably $\text{C}_3\text{H}_3\text{F}$) is formed. Honjou [58] has investigated the structural isomers of $\text{C}_3\text{H}_3\text{F}$ by ab initio SCF and MP4 methods and found 3-fluoropropyne and fluoroallene to be the most stable forms. However, 3-fluorocyclopropene is mechanistically a more likely candidate for this product because it preserves the H–C bonding arrangement on the carbon skeleton, and is significantly more stable than 1-fluorocyclopropene [58]. The structure of the $\text{C}_3\text{H}_2\text{S}_2\text{F}$ radical merits theoretical investigation; it could be an S_2 -substituted version of the $\text{C}_3\text{H}_3\text{F}$ fragment, or indeed it could have the structure of a five-membered heterocycle, incorporating the S–S group into the ring. Endothermic charge transfer is also a product channel (30 %) of the slow HS_2H^{++} with *o*-difluorobenzene, as well as endothermic proton transfer (15 %) and association (5 %).

The reaction of HS_2H^{++} with $\text{C}_2\text{H}_5\text{I}$ is complicated by the presence of the small but critical $\text{C}_2\text{H}_5\text{OH}$ impurity discussed in Sec. 3.1. Because the rate coefficient for the HS_2H^{++} reaction with ethanol has been measured (see Table 1), in principle we can use Eq. (5a) to derive $k_{\text{exp}}^{(2)}$ from $k_{\text{raw}}^{(2)}$ if we know the exact level of the $\text{C}_2\text{H}_5\text{OH}$ impurity in the iodoethane; unfortunately, this is not known. The $\text{C}_2\text{H}_5\text{I}$ is 98.8 % pure by weight (see Experimental), and the raw rate coefficient obtained from the exponential fit of the HS_2H^{++} decay is $7.8 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$. Assuming the remaining 1.2 % of the sample to be $\text{C}_2\text{H}_5\text{OH}$, this reactivity is entirely accounted for, within experimental error, by the ethanol impurity. Most of the 1.2 % impurity is expected to be ethanol (see Sec. 3.1), and therefore the reaction with $\text{C}_2\text{H}_5\text{I}$ is much slower than the raw rate coefficient indicates. Making the conser-

vative assumption that the C₂H₅OH impurity is at least ~0.8 % by weight, with the remainder being a component such as H₂O (which is unreactive with HS₂H⁺ [59]), Eq. (5a) gives an upper limit of $\sim 2 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ for $k_{\text{exp}}^{(2)}$ as indicated in Table 1; this is obviously a rough estimate. The ethanol impurity also complicates the product analysis for this slow reaction although endothermic charge transfer appears to be the dominant channel (>90 %) as indicated in Table 1.

HS₂H⁺ reacts with 1,1,1-trifluoropropanone by ternary association, which is not pressure saturated at ~0.5 Torr (see Table 1). Interestingly, the HS₂H⁺ · CF₃C(O)CH₃ undergoes a ligand switch to form the proton-bound homodimer, (CH₃C(O)CF₃)₂H⁺ and free HS₂. With formaldehyde, an unusual binary channel is observed: HS₂H⁺ abstracts C (with H₂O loss) to form CH₂S₂⁺, which is a recurrent product in the reactions of S₂⁺, as we have noted in Sec. 3.1. That this binary channel, in which the strong C=O bond of formaldehyde is broken, occurs in preference to proton transfer indicates that the latter process is quite endothermic. The CH₂S₂⁺ ion is expected to be a bent chain radical, essentially an S₂-substituted methyl cation, in which the π-donor effect confers substantial stability [60]. Although there have apparently been no ab initio studies of CH₂S₂⁺, the corresponding neutral molecule is thioformaldehyde S-sulfide (CH₂=S=S), or thiosulfine, which has been theoretically investigated by Fabian [61]. Thiosulfine is characterized by a bent, planar geometry and a charge-separated, diradicaloid electronic structure, with negative charge density localized on the terminal sulfur [61].

In the reaction of HS₂H⁺ with H₂S, only products arising from the propene and propane impurities (discussed in Sec. 3.1 above) are observed. C₃H₇⁺ is formed, and proceeds to cluster with H₂S. The raw rate coefficient measured for the reaction is $5.3 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$; this is entirely accounted for by the reactivity of HS₂H⁺ with the impurities at the levels derived above from the S₂⁺ reaction (see Sec. 3.1). Thus, we set an upper limit of $\sim 1 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ for the true rate coefficient of the reaction of HS₂H⁺ with H₂S; i.e., within our limits of sensitivity, there is no reaction.

3.3. Determination of thermodynamic properties of HS₂

One of the virtues of the SIFT technique is that the concentration of a stable neutral reference or reactant gas is well-determined, thereby allowing accurate kinetic studies of ion/molecule reactions with that gas; unfortunately, this facility does not extend to the case of a transient species such as HS₂, which cannot be easily produced in accurately-known quantities in the reaction vessel. It is therefore impossible to study the equilibrium:



in both the forward and reverse directions, and thereby obtain the equilibrium constant (K_{eq}) which gives the Gibbs free energy of the reaction (ΔG_{rxn}^0) and hence, the gas basicity (GB) of HS₂ relative to B by Eq. (7):

$$\Delta G_{\text{rxn}}^0 = \text{GB}(\text{HS}_2, T) - \text{GB}(\text{B}, T) = -R_g T \ln K_{\text{eq}} \quad (7)$$

where R_g is the gas constant. However, the bracketing method allows us to set upper and lower limits on GB(HS₂, 296 ± 3 K) by noting the occurrence and nonoccurrence of proton transfer in the reactions of HS₂H⁺ and applying the criterion for spontaneity, viz.,

$$\Delta G_{\text{rxn}}^0 \leq 0 \Rightarrow \text{GB}(\text{HS}_2, T) \leq \text{GB}(\text{B}, T) \quad (8a)$$

rapid proton transfer observed

$$\Delta G_{\text{rxn}}^0 \geq 0 \Rightarrow \text{GB}(\text{HS}_2, T) \geq \text{GB}(\text{B}, T) \quad (8b)$$

slow or no proton transfer observed

Thus, referring to Table 1, a fairly rapid proton transfer is observed with formic acid, which has a gas basicity GB(HCO₂H, 298 K) = 169.7 ± 2 kcal/mol [35]. Conversely, the proton transfer to *o*-difluorobenzene is a minor channel of a slow reaction; GB(1,2-C₆H₄F₂, 298 K) = 168.0 ± 2 kcal/mol [35]. The bracketing method therefore gives GB(HS₂, 298 K) = 169 ± 3 kcal/mol; the difference between the experimental temperature of 296 ± 3 K and the standard 298.15 K is negligible for this determination.

Note that the bracketing method directly measures the relative *gas basicity* of a species, and not its relative proton affinity [4,5,35,62]; the latter quantity must be derived from the gas basicity from a knowledge of the change in the entropy on protonation of the species, viz. for HS_2^- ,



For the half-reaction (9), the proton affinity is related to the gas basicity through the entropy change by [35]:

$$\text{PA}(\text{HS}_2^-, T) = \text{GB}(\text{HS}_2^-, T) + TS^0(\text{H}^+, T) - T\Delta S_p(\text{HS}_2^-, T), \quad (10)$$

where $S^0(\text{H}^+, T)$ is the classical molar entropy of the proton determined from the Sackur-Tetrode equation (e.g. [63]). $\Delta S_p(\text{HS}_2^-, T)$ is the entropy of protonation of HS_2^- at temperature T , defined as [35]:

$$\Delta S_p(\text{HS}_2^-, T) = S^0(\text{HS}_2\text{H}^+, T) - S^0(\text{HS}_2^-, T) \quad (11)$$

Because the van't Hoff method cannot be used here to obtain the entropy change in Eq. (11) [35], it must be calculated, preferably [64] from the full partition function [63]; however, many of the parameters necessary for the full calculation are not available for both HS_2^- and HS_2H^+ . We assume that the change in rotational symmetry number (σ) in going from HS_2^- to HS_2H^+ gives a reasonable estimate of $\Delta S_p(\text{HS}_2^-, 298 \text{ K})$ [35]; this quantity is then calculated from [35]:

$$\Delta S_p(\text{HS}_2^-, 298 \text{ K}) = R_g \ln [\sigma(\text{HS}_2^-)/\sigma(\text{HS}_2\text{H}^+)] \quad (12)$$

which gives $\Delta S_p(\text{HS}_2^-, 298 \text{ K}) = -1.38 \text{ cal/mol/K}$. Taken together with $S^0(\text{H}^+, 298 \text{ K}) = 25.96 \text{ cal/mol/K}$, the proton affinity of HS_2^- is calculated to be $\text{PA}(\text{HS}_2^-, 298 \text{ K}) = 177 \pm 3 \text{ kcal/mol}$ (the estimated error of $TS^0(\text{H}^+, 298 \text{ K}) - T\Delta S_p(\text{HS}_2^-, 298 \text{ K})$ is $\pm 1 \text{ kcal/mol}$).

Recently, the so-called thermokinetic method has been developed by Bouchoux et al. to extract the relative gas basicity of a species from its reaction efficiency with a series of reference bases of known GB [5,35,62]. This method makes use of more of the kinetic information obtained in a bracketing study, and should thus provide a more accurate determina-

tion of the GB than simple bracketing; it is particularly useful with species such as HS_2^- , for which the protonated form can be prepared and reacted with a series of neutral molecules, but for which study of the reverse reactions is difficult or impossible [35]. The reaction efficiency (RE), which is simply the ratio of the experimentally-determined rate coefficient, $k_{\text{exp}}^{(2)}$, to the collisional rate coefficient, $k_{\text{TST}}^{(2)}$, calculated from theory [51], can be related to the gas basicity of the species under study by [5,62]:

$$\begin{aligned} \text{RE} &= \frac{k_{\text{exp}}^{(2)}}{k_{\text{TST}}^{(2)}} = \frac{1}{1 + e^{(\Delta G_{\text{Eq.}(6)}^0 + \Delta G_a^0)/R_g T}} \\ &= \frac{a}{1 + e^{[b(-\text{GB}(\text{B})+c)]}} \end{aligned} \quad (13)$$

where ΔG_a^0 is an apparent energy barrier for the reaction in Eq. (6) [5,62]. From Eq. (13) an iterative fit was made with the three parameters (a , b , c) shown, which relate the experimental RE to the $\text{GB}(\text{B})$ taken from reference [35] (also see Table 1). From the fit, $\text{GB}(\text{HS}_2^-) \approx c - 1/b$ [5,62].

Fig. 3 shows the data from the reactions of HS_2H^+ fitted with the expression for RE in Eq. (13). From the fit we obtain the parameters: $a = 0.99 \pm 0.31$; $b = 0.58 \pm 0.32$ (in mol/kcal); and $c = 171.55 \pm 0.02$ (in kcal/mol), where the given uncertainties are 95% confidence intervals in the fit parameters. Accounting for the uncertainty of $\pm 2 \text{ kcal/mol}$ in the gas basicities of the reference bases [35], parameters b and c give a calculated $\text{GB}(\text{HS}_2^-, 298 \text{ K}) = 169.8 \pm 2.2 \text{ kcal/mol}$, from which we obtain $\text{PA}(\text{HS}_2^-, 298 \text{ K}) = 178.0 \pm 2.4 \text{ kcal/mol}$ by using Eq. (10) and the entropy values given above. The $\text{GB}(\text{HS}_2^-, 298 \text{ K})$ and $\text{PA}(\text{HS}_2^-, 298 \text{ K})$ obtained from the simple bracketing and thermokinetic methods are in good agreement, within experimental uncertainty. We recommend the values obtained from the thermokinetic method, as they incorporate more of the information about the reactivity of HS_2H^+ with the reference bases.

The thermokinetic method as developed by Bouchoux et al. assumes a simple kinetic situation in which the protonated base, BH^+ , is the only possible product of the forward reaction, as implied by Eq. (6)

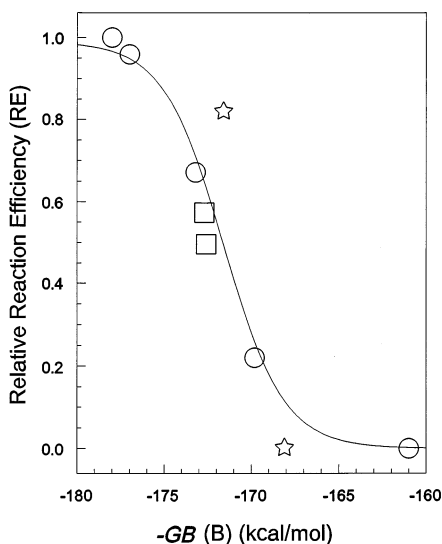


Fig. 3. Plot of the relative reaction efficiency (RE) vs the negative of the gas basicity of the reference base, $-GB(B)$, for the reactions of HS_2H^+ with the series of bases, B, employed in the present study (see text). Reactions for which competing binary channels occur to the exclusion of proton transfer are not included in the plot (see Table 1). The RE values are normalized to the RE of C_2H_5OH , assuming that substantially exothermic proton transfer generally proceeds at the collisional rate [62,65]. The data are fit to the three parameter thermokinetic model of Bouchoux et al. [5] shown in Eq. (13) in the text. Circles indicate reactions for which proton transfer is the only observed product (except in the case of H_2S , where no reaction is observed—see Table 1). Squares indicate reactions for which association occurs in addition to proton transfer. Stars indicate reactions for which competing binary channels occur in addition to association and proton transfer. Reactions having additional channels are treated as discussed in the text.

[5]. In our analysis, we have assumed that the experimental rate coefficient for proton transfer ($k_{PT}^{(2)}$) can be expressed as the product of the branching fraction for proton transfer and the overall experimental rate coefficient. For example, in the case of propene, there is an 85% proton transfer channel, and we have used $k_{PT}^{(2)} = 0.85k_{exp}^{(2)}$ to determine RE for the thermokinetic analysis. Thus, any channels in parallel with the proton transfer are essentially lumped together with the back reaction leading to the reactant species. When the parallel channel is ternary association, this assumption is justified, because the appearance of an association product implies that the particular ion/molecule complex has a sufficiently low energy and thus is sufficiently long-lived ($\geq 10^{-7}$ s) to be stabi-

lized by the carrier gas at ~ 0.5 Torr. Such stabilization would not be expected in higher energy ion/molecule encounters where proton transfer was energetically accessible [65], and thus, the two processes are independent and do not compete. In a low-pressure environment, for which the analysis was originally developed [5], the contribution to the reactivity arising from the ternary association channel would be expected to disappear; i.e. the complex would not be stabilized, and would instead revert back to the reactant species by unimolecular dissociation. In the case of competing binary channels, such as the 5% charge transfer channel with *trans*-2-butene (see Table 1), this assumption is dangerous, and its validity rests on the level of independence of the various binary channels. The situation is not clear, but fortunately the charge transfer channel with *trans*-2-butene is not highly competitive with the proton transfer, and does not affect the value of RE significantly (within experimental error). The only other reaction actually used in the determination of the GB and PA of HS_2^+ for which binary channel competition occurs is that with *o*-difluorobenzene. Fortunately in this case the overall reactivity is so low ($RE = 0.015$; see Fig. 3 caption) that the reaction is clearly in the regime of endoergic proton transfer. In light of these statements, it is important to note that the iterative fitting procedure for Eq. (13) yields exactly the same value for $GB(HS_2^+)$ (169.8 kcal/mol) when the data from the *trans*-2-butene and *o*-difluorobenzene reactions are excluded.

Finally, we consider the enthalpy of formation of HS_2^+ , which can be determined from its proton affinity. Fig. 4 shows the thermodynamic relationships among HS_2^+ and related species. $\Delta H_f^{298}(HS_2^+)$ is obtained from the relation:

$$\Delta H_f^{298}(HS_2^+) = \Delta H_f^{298}[HS_2H(gas)] + IE(HS_2H) + PA(HS_2) - \Delta H_f^{298}(H^+) \quad (14)$$

Cheng et al. [16] combined the known $\Delta H_f^{298}[HS_2H(gas)] = 3.8$ kcal/mol from bomb calorimetry [6,66] and their own value for $IE(HS_2H) = 208.9$ kcal/mol from PIE spectroscopy to obtain $\Delta H_f^{298}(HS_2H^+) = 212.7 \pm 0.5$ kcal/mol [16]; taking

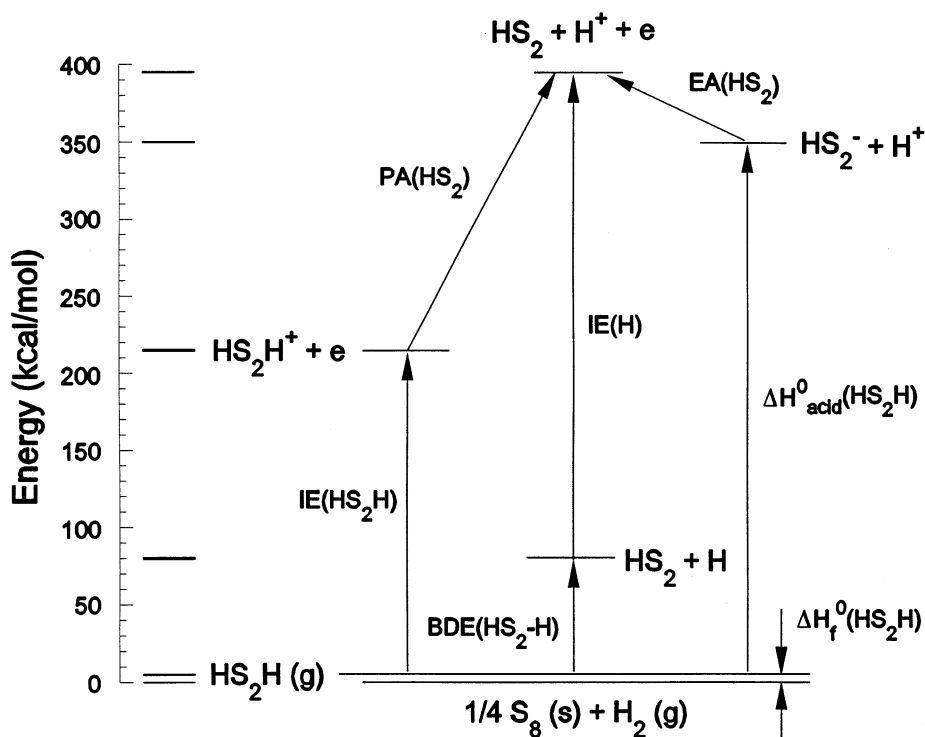


Fig. 4. Thermodynamic and thermochemical relationships among HS_2H , HS_2^- and related species, taken from references [6,8,9,16,35] and the present work. Key: BDE = bond dissociation energy, ΔH_{acid}^0 = gas-phase acidity; ΔH_f^0 = enthalpy of formation; EA = electron affinity; IE = ionization energy; PA = proton affinity. The energy scale is accurate to within a few kcal/mol.

this together with our value of $\text{PA}(\text{HS}_2^-)$, 298 K = 178.0 ± 2.4 kcal/mol and the known $\Delta H_f^{\circ 298}(\text{H}^+) = 365.7$ kcal/mol (with negligible error for the present determination), we obtain $\Delta H_f^{\circ 298}(\text{HS}_2^-) = 25.0 \pm 2.5$ kcal/mol.

Table 2 summarizes the reported determinations of $\Delta H_f^{\circ 298}(\text{HS}_2^-)$, which have been made by four rather distinct approaches. The first estimate, reported by Benson in 1978 [6] and based on his group additivity

Table 2
Summary of the determinations of $\Delta H_f^{\circ 298}(\text{HS}_2^-)$

$\Delta H_f^{\circ 298}(\text{HS}_2^-)$ (kcal/mol)	Method	Reference
22.1 ± 1	Group additivity	Benson [6]
26.7 ± 3	ab initio (Møller-Plesset)	Luke and McLean [7]
$28. \pm 3.5$	Combined $\text{EA}(\text{HS}_2^-)$ and $\Delta H_{\text{acid}}^0(\text{HS}_2\text{H})$	O'Hair et al. [9]
25.0 ± 2.5	Combined $\text{PA}(\text{HS}_2^-)$ and $\text{IE}(\text{HS}_2\text{H})$	This work

scheme, gives $\Delta H_f^{\circ 298}(\text{HS}_2^-) = 22.1 \pm 1$ kcal/mol. Benson's estimate is based on his deduced value of 17.3 ± 1 kcal/mol for $\Delta H_f^{\circ 298}(\text{CH}_3\text{S}_2^-)$, which is in good agreement with a recent calculation based on a photofragment time-of-flight experiment by Ma et al. [67], giving 17.8 ± 1.5 kcal/mol. Ma et al. also report a determination of this quantity from a Gaussian-2 ab initio calculation, giving $\Delta H_f^{\circ 298}(\text{CH}_3\text{S}_2^-) = 21.8$ kcal/mol, some 4.5 kcal/mol higher than Benson's value. Interestingly, this is nearly the same discrepancy as between Benson's $\Delta H_f^{\circ 298}(\text{HS}_2^-) = 22.1 \pm 1$ kcal/mol and the ab initio calculation of Luke and McLean [7], using Møller-Plesset perturbation theory extrapolated to infinite order after a method by Pople et al. [68], and giving $\Delta H_f^{\circ 298}(\text{HS}_2^-) = 26.7 \pm 3$ kcal/mol. The only experimental determination of $\Delta H_f^{\circ 298}(\text{HS}_2^-)$ other than the present one is that of O'Hair et al. [9], who calculate this quantity from their determination of the gas-phase acidity of HS_2H

[9] and Moran and Ellison's measurement of the electron affinity of HS_2^- [8] (see Fig. 4); their result, $\Delta H_f^{\circ 298}(\text{HS}_2^-) = 28 \pm 3.5$ kcal/mol, is somewhat higher than the present determination, although the two values agree to within their estimated uncertainties.

4. Summary and conclusions

The selected ion flow tube (SIFT) technique provides kinetic data from ion/molecule reactions at well-defined temperatures, pressures, and reactant concentrations. These data in turn can be used to determine thermodynamic relationships among the reacting species, which has been done in the present work to obtain the gas basicity (GB, 298 K), proton affinity (PA) and enthalpy of formation ($\Delta H_f^{\circ 298}$) of the hydrothiosulfeno radical (HS_2^-) by means of the thermokinetic method of Bouchoux et al. [5]. The value for $\Delta H_f^{\circ 298}(\text{HS}_2^-)$ obtained, 25.0 ± 2.5 kcal/mol, barely agrees with the value 28 ± 3.5 kcal/mol obtained by O'Hair et al. [9]. The primary source of error in both determinations is the ± 2 kcal/mol uncertainty in the relevant thermochemical quantities of the reference molecules used to bracket GB(HS_2^-) in the present study and the gas-phase acidity, $\Delta G_{\text{acid}}^0(\text{HS}_2\text{H})$, in the study of O'Hair et al. [9]. There have been no significant changes between the thermochemical values used by O'Hair et al. from the 1988 Lias et al. database [69] and the 1997 Hunter and Lias database used in the present study [35]. Thus, this is not the cause of the difference. Discrepancies persist among values in the NIST gas basicity/proton affinity ladder and other current thermochemical ladders, although agreement is generally good in the present range of interest [70]. The thermokinetic method [5] is observed to provide thermochemical quantities with accuracy superior to the simple bracketing procedure.

In addition to determining thermochemical data for HS_2^- , the present study has further explored the reactivity of the $\text{S}_2^{+\cdot}$ radical cation, which is now well-characterized by this and our previous study [1]; $\text{S}_2^{+\cdot}$ chemistry is seen to be dominated by the abstraction of functional groups, particularly H^- , and by π -donor-

stabilized association. Systematic studies of ion/molecule reactions such as these aid in predicting the occurrence of molecular and radical species in interstellar clouds (ISC). Although a search for neutral S_2 in several ISC proved unsuccessful twenty years ago [29], the recent discovery of interstellar acetic acid ($\text{CH}_3\text{CO}_2\text{H}$) [71], marking the first discovery of a new interstellar species by means of an interferometric array radio telescope, gives hope that more spatially-localized and difficult-to-detect interstellar species will be discovered by this new technique in the near future.

Acknowledgements

We gratefully acknowledge the National Science Foundation, Division of Astronomical Sciences, which funded this work under grant no. AST-9415485. We also thank T. Daniel Crawford of the Center for Computational Quantum Chemistry at The University of Georgia for his Double Zeta Plus/Self Consistent Field (DZP/SCF) calculation of the dipole moment of 1,1,1-trifluoropropanone, which enabled us to determine the collisional capture rate constants for the $\text{HS}_2\text{H}^{+\cdot}$ and $\text{S}_2^{+\cdot}$ reactions with that molecule.

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