Selected ion flow tube studies of S_2^+ reactions with a series of organic molecules

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Abstract

A selected ion flow tube (SIFT) has been used to study the reactions of S_2^+ with a series of organic molecules (as well as H_2, CO, NH_3, NO and NO_2). These include the hydrocarbons, C_2H_4, C_2H_6, CH_2CCH_2, CH_3CHCH_2 and C_3H_8; alcohols and thiols, CH_3OH, C_2H_5OH, CH_3SH and C_2H_5SH; ethers $(CH_3)_2O$ and $(C_2H_5)_2O$; aldehydes and ketones, CH_3CHO, C_2H_5CHO and $(CH_3)_2CO$; and carboxylic acids and esters, HCO_2H, HCO_2CH_3, $HCO_2C_2H_5$, CH_3CO_2H, $CH_3CO_2CH_3$, $CH_3CO_2C_2H_5$, $C_2H_5CO_2H$, $C_2H_5CO_2CH_3$ and $C_2H_5CO_2C_2H_5$. The rate coefficients are generally close to the collisional values, with exceptions among the reactions involving the smaller molecules. Most prevalent are abstraction reactions leading to formation of the thiosulfeno radical, HS_2, or its protonated form; three-body associations; and channels leading to formation of the acetyl and propionyl cations, CH_3CO^+ and $C_2H_5CO^+$, respectively. Only in reactions involving the alkenes is cleavage of the S–S bond of S_2^+ observed. The isomeric molecules in the data set generally react very differently, as would be expected from reactivity controlled by the position and complexity of the functional groups. The data are discussed in terms of reaction mechanisms, thermodynamics, and implications for interstellar chemistry.   © 1997 Elsevier Science B.V.

Keywords: Rate coefficients; Energetics; Ion-molecule reactions; Interstellar chemistry; Sulfur dimer cation
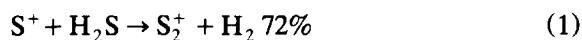
1. Introduction

Although the reactions of S^+ ions have been extensively studied [1–3], very few reactions of S_n^+

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($n \geq 2$) have been investigated [2–5]. The S^+ reactions were studied mainly because of their significance to interstellar molecular synthesis; 15 of the > 100 molecules detected in interstellar clouds contain sulfur (CS, NS, SiS, H_2S, SO_2, OCS, H_2CS, HNCS, CH_3SH, C_2S, C_3S, SO, SO^+, HCS^+ and C_5S (detection uncertain)) [6]. S^+ has been calculated to have a moderately large abundance in dense clouds ($> 10^4$ cm^{-3} H_2 density)

[1] and is particularly significant in diffuse clouds (~ 100 cm^{-3} of H/H$_2$) since S-atoms can be ionized by the starlight which penetrates these regions (wavelengths corresponding to energies less than the ionization potential of H-atoms (IP $= 13.6$ eV)) [7]. Since S$^+$ is unreactive with the two most abundant molecules, H$_2$ and CO (rate coefficients, k, of $< 1(-14)$ and $< 5(-13)$ cm^3 s^{-1} respectively) and also with CO$_2$ and H$_2$O [3,8], it is available to react with other species such as the observed H$_2$S and OCS by the rapid reactions

$$S^+ + H_2S \rightarrow S_2^+ + H_2 \quad 72\% \tag{1}$$

$$\rightarrow HS_2^+ + H \quad 23\% \tag{1b}$$

$$\rightarrow H_2S^+ + S \quad 5\% \tag{1c}$$

and

$$S^+ + OCS \rightarrow S_2^+ + CO \tag{2}$$

with overall rate coefficients $k = 8.2(-10)$ and $9.1(-10)$ cm^3 s^{-1}, respectively [3,8]. A third pathway to the formation of S$_2^+$ from observed interstellar species is

$$SO^+ + H_2S \rightarrow S_2^+ + H_2O \tag{3}$$

with a rate coefficient of $k = 1.3(-9)$ cm^3 s^{-1} [3]. Thus, a reservoir of S$_2^+$ is created, the reactions of which can then contribute to the chemistry. In the relatively few reactions that have been studied previously, S$_2^+$ has been found to be unreactive with H$_2$, N$_2$, O$_2$, H$_2$O, N$_2$O and CH$_4$, although there is some minor reactivity, reported in the literature, with NO, NO$_2$ and NH$_3$ ($k = 7.1(-12)$, $3.5(-10)$ and $1.5(-12)$ cm^3 s^{-1}, respectively) [4,5]. A small number of S$_n^+$ reactions with $n = 3$–8 have also been studied [4,5]. Note that H$_2$S$^+$ and S$_2$ have been discovered in the comet Araki-Alcock [9], and thus photoionization to produce S$_2^+$ is bound to occur in this photon-rich environment.

In the present investigations, a comprehensive study of S$_2^+$ reactions has been made with a series of 28 molecules varying in complexity from diatomics to those containing 17 atoms, representing several of the important functional groups of organic molecules. This series includes hydrocarbons, alcohols and thiols, ethers, aldehydes, the ketone acetone, carboxylic acids and their methyl and ethyl esters. Fourteen of these species, viz. H$_2$, CO, NO, NH$_3$, C$_2$H$_4$, (CH$_3$)$_2$CO, CH$_3$OH, C$_2$H$_5$OH, CH$_3$SH, CH$_3$CHO, (CH$_3$)$_2$O, HCO$_2$H, HCO$_2$CH$_3$ [6,10] and, most recently, CH$_3$CO$_2$H [11], have been detected in the interstellar medium. The ionization potential of S$_2$ has been determined by Liao and Ng to be 9.356 eV and is quite small, with the S$_2^+$ bond energy being 5.376 eV [12]. Thus, in most of the cases considered in the present study, charge transfer is not energetically possible. In these cases, the reactions show a high propensity for association and for hydride abstraction.

2. Experimental

The details of selected ion flow tubes of the type used for these studies have been presented previously [13] and will only be briefly reviewed here. The S$_2^+$ ions were generally produced in a low-pressure electron-impact ion source containing CS$_2$. The details of the mechanism for the production of S$_2^+$ from this molecule have been discussed by several authors [14–16]. S$_2^+$ ions were selected by a quadrupole mass filter from the CS$_2^+$, S$_2^+$, CS$^+$, CS$_2^{2+}$, S$^+$ and C$^+$ ions issuing from the source and focused though a 1-mm hole into the flow tube. The selected S$_2^+$ ions then flowed with the He carrier gas at a pressure of ~ 0.5 torr to a detection quadrupole mass spectrometer/ion counting system at the downstream end of the flow tube. On injection, there was about 2–3% collisional fragmentation to produce S$^+$. Where it was significant, the products of the reactions of this S$^+$, which occurred in parallel with the S$_2^+$ reactions, were determined in a separate study (to be published elsewhere) and their effects were accounted for in the ion product distribution of the S$_2^+$ reaction. In general, no attempt was made to completely discriminate against injected ions containing the ^{33}S and ^{34}S isotopes of ^{32}S since these are only 0.8 and 4.4%

of the major isotope, respectively. Indeed, in some cases the presence of product ions containing these isotopes enabled the elemental composition of a contentious product ion to be unambiguously determined (e.g. $C_2H_4S_2^+$ rather than $C_2H_4SO_2^+$ as a product in the S_2^+ reaction with $HCO_2C_2H_5$).

The small amount of break-up on injection suggests that there may have been some excitation of the S_2^+. From their collision-induced dissociation study of S_2^+ and CS^+ generated from CS_2, Kumar et al. [15] determined that S_2^+, formed in a high-pressure electron-impact source at 0.05–0.1 torr of CS_2, is effectively collisionally quenched to the ground electronic state. Checks for excitation in the S_2^+ were made in the present work using a high-pressure electron impact source containing CS_2 at ~ 0.2–0.3 torr. No difference in reactivity of S_2^+ generated in the high-pressure source versus the low-pressure source was observed. Some quenching of any vibrational excitation would occur in the ~ 10^5 collisions with He between injection of the S_2^+ and injection of the neutral reactant. All of the decays of S_2^+ were very linear, even for the slower reactions (e.g. $S_2^+ + C_2H_6$), indicating the presence of only one ionic state, presumably the ground vibronic state. Also, no significantly endothermic reaction channel, which would be an indicator of excitation, was observed in this study. As a further check, in some cases N_2 was added upstream as an additional quenchant. No effects due to excitation were detected.

Reactant gases and vapors were added at various points along the flow tube to give appropriate reaction lengths. The flows of these reagents were measured from the pressure drop across a calibrated capillary tube for either the undiluted gases or vapors, or in the cases of HCO_2H, CH_3CO_2H and $C_2H_5CO_2H$, for dilute mixtures of the vapors in He (the pressure of the vapor was kept below its saturation vapor pressure and admixed with He at a pressure of ~ 950 torr). The reaction with CH_3CO_2H was also studied with the undiluted vapor, and identical results were obtained. Viscosities of the permanent gases were taken from the literature [17], and vapor viscosities of the liquid reagents were measured using the pressure drop in a calibrated volume

evacuated through a calibrated capillary; viscosities determined in this manner are accurate to ±5%, and generally show excellent agreement with available literature values [18]. Reactant gases were used without further purification and reactant vapors were further purified by freeze-pump-thaw cycles before use. The reaction rate coefficients and ion product distributions were determined in the usual way [19,20]. The rate coefficients are considered to be accurate to ±20% in general, with the error increasing to ±30% for sticky gases and reactant vapors. For the reagents which exist as mixtures of molecular monomers and dimers in the gas phase (i.e. NO_2, HCO_2H, CH_3CO_2H and $C_2H_5CO_2H$), the true monomer flows were calculated from the measured reagent flows using literature equilibrium constants [21–23]; typical monomer flows were 1.37, 1.77, 1.88, and 1.82 times the measured flows for NO_2, HCO_2H, CH_3CO_2H, and $C_2H_5CO_2H$, respectively. Ion product distributions are accurate to ±5 in the percentage. All measurements were conducted at 298 K ± 4 K.

An example illustrating the quality of the data is given in Fig. 1a and b. Fig. 1a shows that the decay of the S_2^+ count rate with increasing CH_3SH flow has excellent linearity over more than two orders of magnitude change in the count rate. A small charge transfer channel is apparent which is due to the reaction of the small percentage of the fragment ion S^+ [2]. The percentages of the primary and secondary products are plotted as a function of CH_3SH flow in Fig. 1b and the ion product distribution for the primary reaction obtained by extrapolating to zero flow. It can be seen that the $CH_3SH_2^+$ and $C_2H_5S^+$ are products of the secondary reaction of CH_3S^+ with CH_3SH and that the CH_3SH^+ contribution corresponds to the percentage of the S^+ impurity ion. Where mass discrimination in the detection system was significant, it was accounted for in the manner described by Matthews et al. [24]. Thus, the primary product of the S_2^+ reaction is CH_2SH^+/CH_3S^+, i.e.

$$S_2^+ + CH_3SH \rightarrow CH_2SH^+ + HS_2 \qquad (4)$$
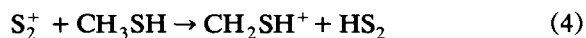
Note the neutral product HS_2 which is very common in these S_2^+ reactions.

3. Results and discussion

Data such as those presented in Fig. 1a and b have been used to construct the list of rate coefficients and ion product distributions in Table 1. The data are arranged by the functional class of the reactant neutral. There is consistent behavior throughout the data set independent of the ionization potential of the reactant. Product channels with HS_2 as the probable neutral product are common, as is association. The rate coefficients quoted where there is an association channel are the binary rate coefficients at a pressure of ~ 0.5 torr. In many of the cases, especially for the more complex reactant neutrals, the rate coefficients are large for association and thus are expected to be pressure-saturated [29]. For the cases where the association is slower (C_2H_4, HCO_2H), determination of the effective binary rate coefficient as a function of pressure should yield the ternary rate coefficient. Where there is competition between binary and ternary channels (e.g. $HCO_2C_2H_5$, CH_2CCH_2), pressure dependence studies may yield the nature of that competition, although again where the reactions are efficient ($HCO_2C_2H_5$, CH_2CCH_2), little change in the product distribution would be expected.

Charge transfer is observed in both cases where it is energetically possible (NO, C_2H_5SH), although it is a very minor product (5%) of the C_2H_5SH reaction. That charge transfer from S_2^+ is not observed in the reactions with CH_3SH and $(C_2H_5)_2O$, which have ionization potentials only slightly higher (9.44 eV and 9.51 eV, respectively [25]) than that of S_2 (9.36 eV [12]), provides additional evidence that the S_2^+ is in its ground vibronic state. In the slow reaction with NH_3, the secondary product NH_4^+ increases as though it were the primary product, indicating rapid proton transfer from the true primary product or products after their formation. Direct charge transfer from S_2^+ to NH_3 is endothermic by 18.5 kcal mol^{-1} (based on thermodynamic data obtained from [25]), and indeed, NH_3^+ is not observed except for a minute fraction which can only be due to the

92% charge transfer channel of the S^+ reaction [3]. The primary products of the reaction of S_2^+ with NH_3 have not been detected, as will be discussed below. In the case of the NO_2 reaction, a small 3% 'charge transfer' channel is observed, 40% of which can be accounted for by the S^+ reaction. The direct charge transfer from S_2^+ to NO_2 is endothermic by 9.1 kcal mol^{-1}. Since the NO_2 reagent is ≥ 99.5 mole% pure (Matheson), the observed channel is unlikely to arise from reactions of S_2^+ with reagent impurities. A possible source of this apparent 'charge transfer' is the direct reaction of S_2^+ with residual dimer N_2O_4, e.g.

$$S_2^+ + N_2O_4 \rightarrow NO_2^+ + NO + S_2O$$

$$\Delta H^\circ_{rxn} = -6 \text{ kcal mol}^{-1} \tag{5}$$
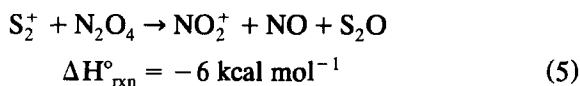
The equilibrium concentration of N_2O_4 required to account for the remaining NO_2^+ signal is about 0.2 mole% of the total NO_2/N_2O_4 concentration. Although the equilibrium concentration of N_2O_4 in the flow tube at the highest NO_2 flows employed is calculated to be less than 0.001 mole% of the total NO_2/N_2O_4 concentration, the N_2O_4 concentration in the inlet flow line is much higher, of the order of 20 mole%. Thus, a sufficient non-equilibrium concentration of N_2O_4 could be available in the vicinity of the inlet ring port for reaction (5) to produce the small observed NO_2^+ signal. Alternatively, it is known that NO_2 undergoes efficient dissociative adsorption onto stainless steel surfaces [30,31], producing NO(gas) and adsorbed atomic oxygen. NO_2 reacts with the adsorbed O to form NO_3, which could then desorb and react with S_2^+:

$$S_2^+ + NO_3 \rightarrow NO_2^+ + S_2O$$

$$\Delta H^\circ_{rxn} \sim -41 \text{ kcal mol}^{-1} \tag{6}$$
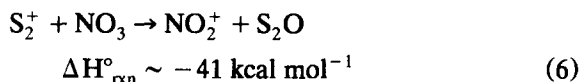
where the reaction enthalpy has been calculated from data in references [25] and [32]. Neither reaction (5) nor reaction (6) has been studied experimentally.

The production of neutral HS_2, or thiosulfeno, is an interesting feature of the data; in many of the reactions (with CH_3CHCH_2, C_3H_8, CH_3OH, C_2H_5OH, CH_3SH, C_2H_5SH, $(CH_3)_2O$,

Table 1
Reaction rate coefficients and fractional ion distributions for the reactions of S_2^+ with the indicated neutral reactants at 298 K ± 4 K

Reactants	IP[a] (eV)	$k_{exp}^{(2)}$[b] ($cm^3 \cdot s^{-1}$)	$k_{TST}^{(2)}$[d] ($cm^3 \cdot s^{-1}$)	Ion product distribution	Ion product[e]	Neutral product(s)[e]	ΔH_{rxn}^a (kcal/mol)
Inorganic gases							
H_2	15.43	< 1(−13)	1.5(−9)	—	—	—	—
CO	14.01	< 1(−13)	7.6(−10)	—	—	—	—
NH_3	10.16	1.6(−11)	2.2(−9)	?	?	?	—
NO	9.26	5.1(−10)	7.1(−10)	1.00	NO^+	S_2	−2.3
NO_2	9.75	1.3(−10)	8.6(−10)	0.98	NO^+	S_2O	−31
				< 0.02	NO_2^+	?	—
Hydrocarbons							
C_2H_4	10.51	6.4(−11)	1.1(−9)	1.00	$S_2^+ \cdot C_2H_4$	—	—
C_2H_6	11.52	3.2(−11)	1.1(−9)	1.00	$H_2S_2^+$	C_2H_4	+4
CH_2CCH_2	9.69	1.0(−9)	—	0.65	$S_2^+ \cdot C_3H_4$	—	—
				0.20	CS_2^+	C_2H_4	−20
				0.05	$C_3H_3S^+$	HS^f	—
				0.05	$C_2H_2S^+$	CH_2S	−25
				0.05	$C_2H_3S^+$	CHS	−15
CH_3CHCH_2	9.73	1.2(−9)	1.2(−9)	0.60	$S_2^+ \cdot C_3H_6$	—	—
				0.15	$CH_2S_2^+$	$C_2H_4^f$	—
				0.10	$C_3H_4S^+$	H_2S	≤ −9
				0.05	$C_2H_3S^+$	CH_3S	−18
				0.05	$C_3H_5^+$	HS_2	−3 est.
				0.05	$C_3H_5S^+$	HS^f	—
C_3H_8	10.95	9.9(−10)	1.2(−9)	0.90	$C_3H_7^+$	HS_2	≤ −1 est.
				0.10	$H_2S_2^+$	$n\text{-}C_3H_6$	+1
Alcohols and thiols							
CH_3OH	10.85	8.7(−10)	2.0(−9)	0.90	$H_2S_2^+$	CH_2O^f	≤ −6
				0.10	CH_2OH^+	HS_2	−8 est.
C_2H_5OH	10.47	1.7(−9)	1.9(−9)	0.95	$C_2H_5O^+$	HS_2	−29 est.
				0.05	$H_2S_2^+$	$C_2H_4O^f$	≤ −2
CH_3SH	9.44	1.2(−9)	—	1.00	CH_3S^+	HS_2	−13 est.
C_2H_5SH	9.29	1.8(−9)	1.8(−9)	0.95	$C_2H_5S^+$	HS_2	−16 est.
				0.05	$C_2H_5SH^+$	S_2	−1.6
Ethers							
$(CH_3)_2O$	10.03	1.6(−9)	1.6(−9)	1.00	$C_2H_5O^+$	HS_2	−23 est.
$(C_2H_5)_2O$	9.51	1.7(−9)	1.6(−9)	1.00	$C_4H_9O^+$	HS_2	−39 est.
Aldehydes and ketones							
CH_3CHO	10.23	2.2(−9)	2.6(−9)	1.00	CH_3CO^+	HS_2	−29 est.
C_2H_5CHO	9.95	1.9(−9)	2.4(−9)	1.00	$C_3H_5O^+$	HS_2	−39 est.
$(CH_3)_2CO$	9.71	1.4(−9)	2.7(−9)	1.00	$S_2^+ \cdot C_4H_6O$	—	—
Carboxylic acids and esters							
HCO_2H	11.33	∼ 5(−11)[c]	1.6(−9)	1.00	$S_2^+ \cdot CH_2O_2$	—	—
HCO_2CH_3	10.82	3.9(−10)	—	1.00	$S_2^+ \cdot C_2H_4O_2$	—	—
$HCO_2C_2H_5$	10.61	1.5(−9)	2.0(−9)	0.50	$S_2^+ \cdot C_3H_6O_2$	—	—
				0.30	$C_3H_5O_2^+$	HS_2^f	—
				0.15	$C_2H_5O^+$	$CO + HS_2^f$	−20 est.
				0.05	$C_2H_4S_2^+$	$CH_2O_2^f$	≤ −2 est.

Table 1 (continued)

Reactants	IP^a (eV)	$k_{exp}^{(2)b}$ (cm^3·s^{-1})	$k_{TST}^{(2)d}$ (cm^3·s^{-1})	Ion product distribution	Ion product^e	Neutral product(s)^e	ΔH_{rxn}^a (kcal/mol)
CH_3CO_2H	10.66	1.3($-$9)	1.8($-$9)	0.90	CH_3CO^+	HS_2O^f	—
				0.10	$S_2^+ \cdot C_2H_4O_2$	—	—
$CH_3CO_2CH_3$	10.27	1.5($-$9)	1.8($-$9)	0.75	CH_3CO^+	$CH_2O + HS_2^f$	$\leq$ +4 est.
				0.20	$S_2^+ \cdot C_3H_6O_2$	—	—
				0.05	$C_3H_5O_2^+$	HS_2^f	—
$CH_3CO_2C_2H_5$	10.01	1.6($-$9)	1.9($-$9)	0.50	$C_4H_7O_2^+$	HS_2^f	—
				0.25	$S_2^+ \cdot C_4H_8O_2$	—	—
				0.25	CH_3CO^+	$C_2H_4O + HS_2^f$	$\leq$ $-$2 est.
$C_2H_5CO_2H$	10.53	$\sim$ 1.5($-$9)^c	1.8($-$9)	1.00	$C_3H_5O^+$	HS_2O^f	—
$C_2H_5CO_2CH_3$	10.15	1.6($-$9)	—	1.00	$C_3H_5O^+$	$CH_2O + HS_2^f$	$\leq$ $-$6 est.
$C_2H_5CO_2C_2H_5$	10.00	1.8($-$9)	—	0.85	$C_3H_5O^+$	$C_2H_4O + HS_2^f$	$\leq$ $-$2.4 est.
				0.15	$C_5H_9O_2^+$	HS_2^f	—

The ionization potential (IP) of S_2 is 9.36 eV for comparison [12].

^{a} Thermodynamic values are generally based on data from the compilation of Lias et al. [25]. Exceptions are $\Delta H_f^{\circ 298}(HS_2)$, which is assumed to be approximately 22.1 $\pm$ 1 kcal mol^{-1}, after the estimate of Benson [26]; and ΔH_f ($C_2H_4S_2^+$), which has been obtained from the ab initio calculations of Ekern et al. [27]; heats of reaction based on these values are labeled 'est.'. In cases where the product identities are ambiguous, the given heats of reaction are for the least energetically favorable isomeric combinations among the suggested products, as indicated by the $\leq$ sign.

^{b} Effective binary rate coefficients are given for ternary reactions at $\sim$ 0.5 torr carrier pressure (see text).

^{c} Rate coefficients given for the reactions of S_2^+ with HCO_2H and $C_2H_5CO_2H$ are approximate values (see text).

^{d} Collisional rate coefficients are calculated from the variational transition state theory of Su and Chesnavich [28].

^{e} Products of binary reactions are written in empirical form, except where reaction energetics renders the structure of the product unequivocal. Association products are written as loosely-bound complexes of the reactant with S_2^+, to distinguish them visually from the binary products. Unless otherwise indicated (footnote^f), neutral products are unequivocal from the reaction energetics.

^{f} Suggested neutral product(s); others may be possible.

($C_2H_5)_2O$, CH_3CHO, and C_2H_5CHO), it is unequivocally the only energetically possible neutral product of its respective channel. In three of these reactions (with C_3H_8, CH_3OH, and C_2H_5OH), $H_2S_2^+$, i.e. protonated HS_2, is produced in parallel with HS_2 as the only competing channel; thus, there are channels with the proton residing on either of the product fragments. Only in the case of C_2H_6 is the $H_2S_2^+$ product seen alone. These situations can be rationalized by considering that the reaction proceeds through an initial hydride abstraction

$$S_2^+ + XH_2 \rightarrow (XH^+ + HS_2) \qquad (7)$$

with the intermediate having the form of the proton bound complex (X...H$^+$...HS$_2$). Whether this fragments to XH$^+$ or $H_2S_2^+$ then depends on which neutral fragment has the larger proton affinity. Unfortunately, the proton affinity of HS_2 is not known. However, from a study of Table 2, it can be seen that for X with proton affinities greater than $\sim$ 180 kcal mol^{-1}, the proton mostly

resides with X, and thus neutral HS_2 is produced. For the CH_3OH and C_3H_8 reactions, the proton affinity of X (CH_2O and CH_3CHCH_2) is 170.4 and 179.6 kcal mol^{-1}, respectively, and since both XH$^+$ and $H_2S_2^+$ are observed, with $H_2S_2^+$ being dominant in the former reaction and minor in the latter reaction, this implies that the proton affinity of HS_2 is roughly 175 kcal mol^{-1}, which is simply the average of these neighboring proton affinities; a more refined estimate would require the calculation of the accessible state densities of the competing exit channels in the proton-bound complex. Now, since C_2H_4 (X in the C_2H_6 reaction) has a proton affinity of 162.6 kcal mol^{-1}, the proton will reside with the HS_2, as is observed. In the reaction with CH_3SH, X is most probably CH_2S (thioformaldehyde). CH_3S^+/CH_2SH^+ is the 100% reaction product (see Eq. (4)), i.e. no $H_2S_2^+$ is observed, as expected from the proton affinity of thioformaldehyde (181.6 kcal mol^{-1}).

Additional understanding of the reactivity of S_2^+ ions can be obtained by comparing the reac-
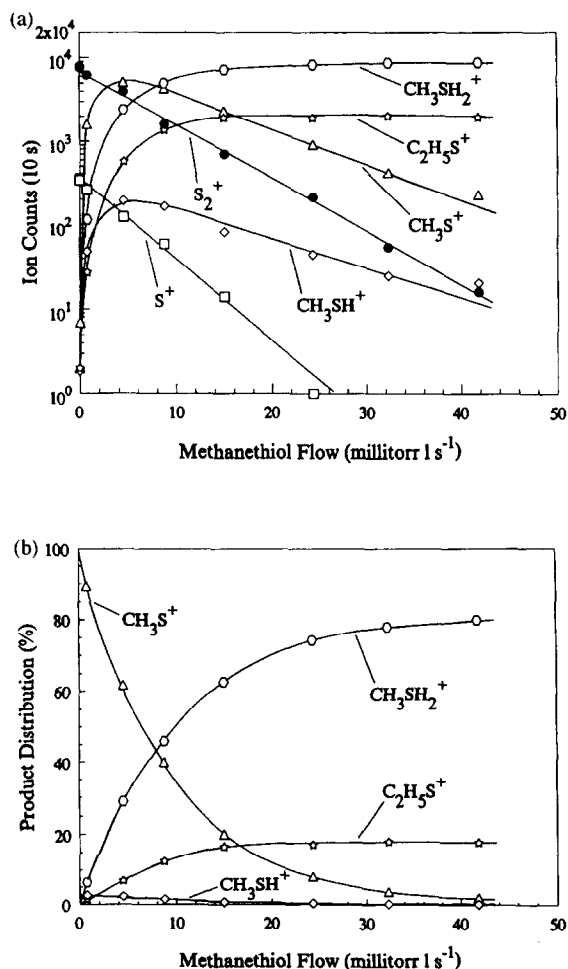
Fig. 1. (a) Variation of the S_2^+ and ion product count rates with CH_3SH flow and (b) percentages of the ion products as a function of CH_3SH flow. In (a), the S_2^+ decline is linear over more than two orders of magnitude. The reaction of the small S^+ impurity, which is due to collisional break-up of S_2^+ on injection into the flow tube, is the source of the small charge transfer channel shown in the figure. From (b), it can be seen that CH_3S^+/CH_2SH^+ is the only primary product and this reacts further to give both $CH_3SH_2^+$ $(+CH_2S)$ and $C_2H_5S^+$ $(+H_2S)$. The data are not corrected for mass discrimination in the detection system. The rate coefficient and ion product distribution from these and the other data are listed in Table 1.

tivities and ion product distributions for the different classes of organic compounds in Table 1.

3.1. Inorganic

The reactions are simple for these species and

most have been studied previously [4,5]. Niedner-Schatteburg et al. [4], using an FT-ICR, also found H_2 to be unreactive with S_2^+ and, in a later paper [5] obtained rate coefficients of $7.1(-12)$, $3.5(-10)$ and $1.5(-12)$ cm^3 s^{-1} for NO, NO_2 and NH_3, respectively. The NO and NH_3 values are very different from the present values (by at least an order of magnitude; see Table 1). That the rate coefficient for NO_2 was only about a factor of 3 different is not unreasonable, considering the difficulties with these gases in the ICR study. We have no explanation for the other differences. Since none of the other reactions in the present study have been investigated previously, the rate coefficient of the straightforward reaction

$$CS^+ + H_2 \rightarrow HCS^+ + H \ 100\% \tag{8}$$
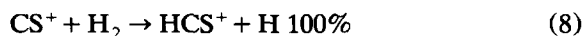
which had been determined previously [3], was measured as a reproducibility check, under experimental conditions identical to those for the S_2^+ studies, except that CS^+ was selected from the ion source instead of S_2^+. A value of $4.5(-10)$ cm^3 s^{-1} was obtained for the rate coefficient, in excellent agreement with the literature value of $4.3(-10)$ cm^3 s^{-1} [3].

For the reaction of S_2^+ with NH_3, Schindler et al. [5] report the endothermic charge-transfer product NH_3^+, which we do not observe, as was discussed above. These authors report the same products as the present study for the NO_2 reaction, but they do not give a product distribution, nor any explanation for the apparent endothermic charge-transfer from S_2^+ to NO_2; we have discussed possible sources of this apparent 'charge transfer' channel for our experimental situation above.

The source of the NH_4^+ which behaves as though it were the primary product of the NH_3 reaction remains elusive. Better than unit mass resolution was employed in this particular study, both in the SIFT quadrupole mass filter and in the detection mass spectrometer, so that neighboring mass peaks, such as NH_3^+ and NH_4^+, were well resolved, and no isotopes of the parent ion other than $^{32}S_2^+$ were permitted into the flow tube. Thus, if possible primary products such as

Table 2

Proton affinities of the suggested neutral products and product distributions for the reactions of S_2^+ leading to the probable formation of HS_2 or $H_2S_2^+$ [a]

Reactant, H_2X	Identity of X	Proton affinity of X (kcal mol^{-1})	Product distribution (%)	
			$H_2S_2^+$	HX^+
C_2H_6	C_2H_4	162.6	100	0
CH_3OH	CH_2O	170.4	90	10
C_3H_8	CH_3CHCH_2	179.6	10	90
C_2H_5OH	CH_3CHO	183.8	5	95
CH_3CHCH_2	C_3H_4[b]	178.8, 185.3, 197.3	0	5
CH_3SH	CH_2S	181.6	0	100
C_2H_5SH	CH_3CHS[c]	?	0	100
$(CH_3)_2O$	C_2H_4O[d]	184.9	0	100
$(C_2H_5)_2O$	$C_2H_5OCHCH_2$	207.9	0	100
CH_3CHO	CH_2CO	197.3	0	100
C_2H_5CHO	C_3H_4O[e]	190.5, 199.4	0	100
$HCO_2C_2H_5$	$C_3H_4O_2$	?	0	30
	CH_3CHO[f]	183.8	0	15
$CH_3CO_2CH_3$	$C_3H_4O_2$	?	0	5
	CH_2CO[f]	197.3	0	75
$CH_3CO_2C_2H_5$	$C_4H_6O_2$	?	0	50
	CH_2CO[f]	197.3	0	25
$C_2H_5CO_2CH_3$	C_3H_4O[e,f]	190.5, 199.4	0	100
$C_2H_5CO_2C_2H_5$	$C_5H_8O_2$[f]	?	0	15
	C_3H_4O[e,f]	190.5, 199.4	0	85

The proton affinity of HS_2 is estimated to be ~ 175 kcal mol^{-1} (see text).

[a] Proton affinity values are taken from the NIST database of Hunter and Lias [33].

[b] Proton affinities for propyne, allene, and cyclopropene, respectively.

[c] Proton affinity unavailable.

[d] Oxirane.

[e] Proton affinities for 2-propenal and methylketene, respectively.

[f] Plausible neutral products formed along with HS_2 in these channels are among H_2, CO, CH_4, CH_2O, CH_3CHO, and CH_2CHOH, with respective proton affinities in kcal mol^{-1} of 100.9, 141.7, 129.9, 170.4, 183.8, and not available [33] (see text and Table 1).

HS_2^+ or NH_2^+ were present, they would not have been masked by S_2^+ or NH_3^+ counts, respectively, in the mass spectral scan. Moreover, reactions of S_2^+ with NH_3 to form NH_2^+, HS_2^+, or $H_2S_2^+$ are all highly endothermic (> 50 kcal mol^{-1}) from consideration of the reaction energetics (a lower limit of $\Delta H_f^\circ(HS_2^+)$ was estimated to be ~ 246 kcal mol^{-1} from the observation, made in a separate study in this laboratory, that HS_2^+ transfers a proton to OCS (proton affinity $= 150.2$ kcal mol^{-1}); $\Delta H^\circ_f(HS_2)$ was taken to be ~ 22.1 kcal mol^{-1} [26]). Reaction to form H_3S^+ is also endothermic, by nearly as much as the direct charge transfer from S_2^+ to NH_3. Thus, a likely candidate for the primary product is not immediately apparent. The primary reaction is slow ($k^{(2)} = 1.6(-11)$ cm^3 s^{-1}; see Table 1). If, as seems likely, the

secondary reaction to form NH_4^+ is a rapid proton-transfer to NH_3 near the gas-kinetic limit, the maximum signal of the primary ion is certainly less than 1% of the parent ion signal, and therefore difficult to detect at the high resolution necessary to study this reaction.

3.2. Hydrocarbons

The reactions of S_2^+ with the hydrocarbons in this study show two strikingly different general types of reactivity, depending on whether the hydrocarbon is saturated or unsaturated. In reactions with the alkanes (C_2H_6 and C_3H_8), S_2^+ abstracts either H^- or H_2, and does not associate. In reactions with the alkenes (C_2H_4, CH_2CCH_2, and CH_3CHCH_2), association is the

dominant channel (100%, 65%, and 60%, respectively), and for allene and propylene, the binary channel products all indicate extensive structural rearrangement in the activated complex. For example, the second largest channel (20%) for allene leads to the interesting product CS_2^+, indicating the abstraction of atomic carbon from allene to leave ethylene. Similarly, the second largest channel (15%) for propylene leads to $CH_2S_2^+$, also leaving ethylene as the neutral fragment; thus, these two channels appear to be analogous. All of the remaining channels of both the allene and the propylene reactions are minor (about 5% each), and all lead to the formation of ion products containing only one sulfur atom, thereby indicating cleavage of the 5.38 eV (124 kcal mol^{-1}) S–S bond of S_2^+ [12]. These are the only reactions in this study for which such cleavage occurs. Since association is an important product of the rapid reactions of S_2^+ with the alkenes, the intermediate complex is probably long-lived and thus tightly-bonded, allowing time for collisional stabilization. That the binary channels leading to extensive molecular reorganization occur in parallel with association indicates that, although they are efficient, the binary processes do not occur on a short time scale, but rather require substantial exploration of the potential surface of the intermediate complex to locate the exit channels. The association of S_2^+ with pi-bonded systems such as alkenes and carbonyls is a very persistent feature of its chemistry, and will be noted where it occurs in the discussions that follow.

Except for C_2H_4 and C_2H_6, the hydrocarbons react with S_2^+ at or near the collisional rate. The reaction with C_2H_6 to form $H_2S_2^+$ is apparently endothermic by about 4 kcal mol^{-1}, but its reactivity cannot be explained simply by the high-energy tail of the thermal Boltzmann distribution. The measured rate coefficient, $k_{exp}^{(2)}$, is 3.2(−11) cm^3 s^{-1}, which when compared to the collisional rate coefficient, $k_{TST}^{(2)}$, of 1.1(−9) cm^3 s^{-1} calculated from the variational transition state theory of Su and Chesnavich [28], could imply an endothermicity as large as 2.1 kcal mol^{-1} (determined using the Arrhenius-type expression $k_{exp}^{(2)} = k_{TST}^{(2)} \exp(-\Delta H_{rxn}^\circ / RT)$). Although the discrepancy could be explained if the thermal energy

contained in the 18 vibrational modes of ethane is utilized, the reaction complex is unlikely to have access to much of this energy, particularly since S_2^+ and ethane are not observed to associate, and therefore are not strongly bonded in the intermediate complex. A more likely explanation is an inaccuracy in the literature value for the heat of formation of $H_2S_2^+$, which is given as 218 kcal mol^{-1} in the Lias et al. compilation [25]. This value is based on the vertical ionization potential of neutral H_2S_2, which was deduced to be 9.3 eV (214 kcal mol^{-1}) from the photoelectron spectrum of H_2S_2 recorded by Wagner and Bock [34]. A small error in the extrapolation of the lowest-energy photoelectron peak to the energy axis can lead to a slight inaccuracy in the determination of the first ionization potential; indeed, a mere 1% adjustment of the ionization potential of H_2S_2 to 9.2 eV (212 kcal mol^{-1}) completely accounts for the apparent discrepancy. Thus, the current literature value for the heat of formation of $H_2S_2^+$ appears to be slightly too high (by at least 2 kcal mol^{-1}).

Where HS_2 appears as a neutral product, in the hydrocarbon reactions and in the others discussed below, reaction enthalpies are calculated using the estimate for the heat of formation, $\Delta H_f^{\circ 298}(HS_2)$, of 22.1 ± 1 kcal mol^{-1} made by Benson [26]. This value generally gives negative enthalpies of reaction for the channels leading presumably to HS_2 in the present study. Aside from several spectroscopic studies, very little is known about the thiosulfeno radical and its chemistry [35–37].

3.3. Alcohols, thiols, ethers and aldehydes

Except for the small exothermic charge transfer channel with C_2H_5SH, all of the reactions studied with these classes of compound proceed by hydride abstraction or H_2 abstraction to form HS_2 or its protonated form, $H_2S_2^+$, respectively. These are the reactions involving the almost energy-resonant proton-bound complexes discussed above. Note that the proton affinities of the X fragments of the hydride abstractions (see the mechanism in Eq. (5) and Table 2) other than the methanol reaction are greater than 181 kcal mol^{-1}

where they can be determined, and that in all of these reactions, except with ethanol, the products are always HX^+ and HS_2 (see Table 2). That the HX^+ fragments are the protonated forms of stable neutral molecules is supported by the fact that the ion product of hydride abstraction with CH_3OH must be protonated formaldehyde, CH_2OH^+, and not the methoxy cation, CH_3O^+, by reason of the reaction energetics; and thus, in the channel of this reaction leading to $H_2S_2^+$, the neutral fragment is likely to be CH_2O and not $CO + H_2$, which is also energetically possible. Presumably, reaction mechanisms are analogous for the chemically similar species, e.g. the alcohols and thiols, and the protonated aldehydes and thioaldehydes respectively are formed where they are not necessarily dictated by reaction energetics.

The reactions are all fast, generally at or near the collisional rate. That the reactions with the smaller reactants (CH_3OH, CH_3SH) are less rapid may be a feature of the shorter lifetime of the intermediate complex in these cases, due to the smaller number of vibrational modes in which the energy of the association can be dissipated. Thus, there may not be time for the hydride ion abstraction step of the mechanism (Eq. (5)) to occur for every collision event.

3.4. Acetone

Acetone is the only ketone reacted with S_2^+ in the current study. It rapidly associates, with a rate coefficient of $1.4(-9)$ cm^3 s^{-1}, about half of the collisional rate. More reactions of S_2^+ with ketones need to be performed before any trends in their reactivity can be assessed. However, the fact that S_2^+ associates with acetone provides additional evidence for the strong interaction of this ion with pi-bonded systems. In every case in which S_2^+ associates, it is with compounds that have either a carbonyl or an alkene functional group. Among such compounds, S_2^+ only fails to associate with the aldehydes and the largest esters, i.e. the propionates (see below and also Table 1).

3.5. Carboxylic acids and esters; (R-CO_2-R'; see Table 1)

With the carboxylic acids and esters, the most

complex and most highly-oxidized reactants considered in the present study, the prevalent themes of association and hydride abstraction by S_2^+ are again observed, with patterns of reactivity governed in a discernible fashion by the extent of alkyl substitution of the R and R' moieties. Tendency to associate decreases dramatically with increasing substitution of the carbon-bonded moiety, R, in the ~ 0.5 torr carrier gas environment employed in these studies. Association is the only channel for the smallest formates, HCO_2H and HCO_2CH_3, and although $HCO_2C_2H_5$ has three binary reaction channels, association accounts for 50% of its reactivity with S_2^+. Association accounts for 10% to 25% of the reactivity of the acetates ($R = CH_3$), and is negligible for the propionates ($R = C_2H_5$) at the carrier pressures employed, although trace amounts of the associated product are indicated in the mass spectra of the propionate reactions. The reverse trend occurs for increasing substitution of the oxygen-bonded moiety, R'. The effective bimolecular rate coefficients of the association channels for HCO_2H, HCO_2CH_3, and $HCO_2C_2H_5$, respectively, are $\sim 5(-11)$, $3.9(-10)$, and $7.5(-10)$ cm^3 s^{-1} (see Table 1). Similarly, the effective rates of association for the acetates with increasing R' substitution are $1.3(-10)$, $3.0(-10)$, and $4.0(-10)$ cm^3 s^{-1}, respectively. The increase in association with increase in the complexity of the intermediate complex is consistent with the increase in the number of vibrational degrees of freedom in which the energy of association can be dissipated. This increases the lifetime against unimolecular decomposition, and therefore, the probability of collisional stabilization. Note that the rate coefficient for the reaction with HCO_2H is given as an approximate value, due to the difficulty of measuring a small rate coefficient with a dilute mixture of 2% formic acid in helium. The rate coefficient for the reaction with $C_2H_5CO_2H$ is also given as approximate, due to difficulties in the preparation of propionic acid/helium mixtures, because of the low vapor pressure of propionic acid at 298 K.

The trend of decreasing association with increasing substitution of the R moiety could be explained, at least in part, by the occurrence of binary channels resulting in the formation of the

highly stable acetyl cation (CH_3CO^+) and propionyl cation ($C_2H_5CO^+$) in the acetate and propionate reactions, respectively. These species, which can be considered the protonated forms of ketene and methylketene, respectively, are ubiquitous products of the reactions with the acetates and propionates, and in five of the six reactions considered, they are the dominant products by a large margin (75–100% of the reaction products — see Table 1). Thus, where they can proceed, binary channels leading to CH_3CO^+ or $C_2H_5CO^+$ might simply occur on a time scale shorter than the ternary association. Note that in the reactions with CH_3CO_2H and $C_2H_5CO_2H$, the respective product channels leading to CH_3CO^+ and $C_2H_5CO^+$ demand by reason of reaction energetics that the neutral fragment be some form of the molecule HS_2O, and that this molecule must have a heat of formation of -13 kcal mol^{-1} for the reaction with CH_3COOH to be thermoneutral, using currently available heats of formation for the reactants and products [25]. HS_2O could be a sulfur analogue of HSO_2, which has a heat of formation of -53 kcal mol^{-1} at 298 K, according to an ab initio study by Boyd et al. [38]. Thus, although thermodynamic information on the HS_2O molecule is not available, it seems plausible that its heat of formation is low enough to satisfy the energetics in the CH_3CO_2H and $C_2H_5CO_2H$ reactions.

In the other reactions leading to protonated ketene (CH_3CO^+) or protonated methylketene ($C_2H_5CO^+$) channels, HS_2 is a likely neutral product in every case, although insufficient thermodynamic information, and the multiplicity of possible neutral products, have prevented the definite determination of the neutral products for these channels. If HS_2 is indeed formed, then the remaining plausible neutral products for these channels include H_2, CO, CH_4, CH_2O, CH_3CHO, and CH_2CHOH, all of whose proton affinities (except for vinyl alcohol, for which the proton affinity is unavailable) are significantly lower than those of ketene and methylketene (see Table 2). Thus, as is observed, the proton should reside with the product that has the highest proton affinity in these reaction channels, in accordance with the mechanism of Eq. (5). Hydride

abstraction is also observed in the reactions of every ethyl ester ($RCO_2C_2H_5$), presumably leading to the protonated vinyl ester in these cases. Although again it seems certain that the neutral product is HS_2, insufficient thermodynamic information about the ion prevents the unambiguous determination of the neutral product in these cases.

Ethyl formate ($HCO_2C_2H_5$) is the only reactant among the carboxylic acids and esters which shows additional product channels other than those discussed above. A 15% channel, leading to $C_2H_5O^+$ and the presumptive neutral products CO and HS_2, is observed; the ion product was distinguished from the three possible ion products of the reaction at $m/z = 45$ by careful inspection of the isotope ratio. Note that the $C_2H_5O^+$ product of this channel is possibly of the same isomeric form as the $C_2H_5O^+$ product of the ethanol reaction. Additionally, an interesting 5% channel is observed with $HCO_2C_2H_5$ leading to $C_2H_4S_2^+$, which has the same empirical formula as the association product of ethylene with S_2^+. The occurrence of this product with $HCO_2C_2H_5$ implies that the ethyl moiety has some of the qualities of a vinyl group in the resonance structures of $HCO_2C_2H_5$, so that S_2^+ interacts with the moiety in a way similar to its association with ethylene. Possible structures for the $C_2H_4S_2^+$ cation and their relative energies have been investigated in an experimental and ab initio study of the reactions of thiirane radical cation with thiirane by Ekern et al. [27].

It is interesting to compare the reactivity of S_2^+ with that of the analogous oxygenated ions SO^+ and O_2^+ as given in the literature [2,3]. Very few data are available for SO^+ with the molecules in the present study (only for H_2, CO and NH_3). Both SO^+ and O_2^+ are unreactive with CO ($< 1(-12)$ cm^3 s^{-1} and no reaction, respectively), as is S_2^+. With NH_3, both react similarly by rapid charge transfer, which is endothermic for S_2^+. In all of the other reactions that have previously been studied (with NO, NO_2, C_2H_4, C_2H_6, CH_3OH and HCO_2H), O_2^+, unlike S_2^+, generally reacts rapidly by charge transfer by virtue of the larger ionization potential of O_2 (12.07 eV relative to 9.36 eV for S_2 [25]). Only in the cases of

CH_3OH and HCO_2H is there another reaction channel, hydride abstraction, yielding the neutral product HO_2 analogous to the common product HS_2 in the present studies, although this does not occur in the HCO_2H reaction with S_2^+.

4. Conclusions

The present study of the reactions of S_2^+ with a series of hydrocarbons, alcohols, thiols, aldehydes, ethers, carboxylic acids and esters has shown the general features of association and the production of neutral HS_2, the latter of which is believed to result from the fragmentation of proton-bound complexes, $(X...H^+...HS_2)$. S-atom insertion is observed only with the alkenes, in contrast to S^+ reactions with similar species [1–3], for which insertion channels are common; this is probably a result of the strength of the S_2^+ bond. However, the association reactions result in the incorporation of S_2 and this could be a route to S_2-containing species in the interstellar medium (ism). Note that the weakly-bonded association complexes may only be able to isomerize to specific more strongly bonded forms, so that all possible isomers should not be assumed to exist in the ism. This has recently been discussed with respect to the isomeric forms of $CH_3O_2^+$, CH_5O^+ and $C_2H_7O^+$ [24,39]. No species containing S_2 have yet been detected in the ism and these should be searched for. In particular, interstellar thiosulfeno (HS_2) should be searched for, since it is a common product in the S_2^+ reactions. In addition, where fragmentation of the proton-bound complex results in $H_2S_2^+$ production, more HS_2 is likely to be produced following dissociative recombination with electrons,

$$H_2S_2^+ + e \rightarrow H + HS_2 \tag{9}$$

(this is not the only energetically possible channel). Note that a recent study of the dissociative recombination of H_3O^+ has shown that only a small proportion of the recombinations result in $H + H_2O$ (5%) with further fragmentation to two atoms and a diatomic molecule in 60% of the cases [40]. Thus, by analogy, other dissociative channels might be expected in the case of $H_2S_2^+$.

References

[1] D. Smith, N.G. Adams, E. Herbst. Astron. Astrophys. 200 (1988) 191.
[2] Y. Ikezoe, S. Matsuoka, M. Takebe, A. Viggiano. Gas Phase Ion Molecule Reaction Rate Constants through 1986, Maruzen, Tokyo, 1987.
[3] V. Anicich. J. Phys. Chem. Ref. Data 22 (1993) 1469.
[4] G. Niedner-Schatteburg, J. Silha, T. Schindler, V.E. Bondybey. Chem. Phys. Lett. 187 (1991) 60.
[5] T. Schindler, C. Berg, G. Niedner-Schatteburg, V.E. Bondybey. Ber. Bunsenges. Phys. Chem. 96 (1992) 1114.
[6] M. Guelin. In: A.J. Sauval, R. Blomme, N. Grevesse (Eds.), Laboratory and Astronomical High Resolution Spectra, vol. 81, APS Conference Series, 1995, p. 438.
[7] D. Smith, N.G. Adams. Int. Revs. Phys. Chem. 1 (1981) 271.
[8] D. Smith, N.G. Adams, W. Lindinger. J. Chem. Phys. 75 (1981) 3365.
[9] C.B. Cosmovici, S. Ortolani. Nature 310 (1984) 122.
[10] T.J. Millar, D.A. Williams. In: T.J. Millar, D.A. Williams (Eds.), Dust and Chemistry in Astronomy, Institute of Physics Publishing, Bristol, 1993, p. 1.
[11] D.M. Mehringer, L.E. Snyder, Y. Miao. Astrophys. J. 480 (1997) L71.
[12] C.L. Liao, C.Y. Ng. J. Chem. Phys. 84 (1986) 778.
[13] N.G. Adams, D. Smith. In: J.M. Farrar, W.H. Saunders (Eds.), Techniques for the Study of Ion-Molecule Reactions, Wiley, New York, 1988, p. 165.
[14] K. Nagesha, B. Bapat, V.R. Marathe, E. Krishnakumar. Chem. Phys. Lett. 230 (1994) 283.
[15] G.R. Kumar, L. Menon, D. Mathur. Phys. Rev. A 48 (1993) 1257.
[16] S. Mazumdar, S.V.K. Kumar, V.R. Marathe, D. Mathur. Rapid Commun. Mass Spectrom. 3 (1989) 24.
[17] W. Braker, A.L. Mossman. Matheson Gas Data Book, 6th Ed., Matheson, 1980.
[18] C.L. Yaws. Handbook of Viscosity, Library of Physico-Chemical Property Data, Gulf Publishing Company, Houston, 1995.
[19] N.G. Adams, D. Smith. Int. J. Mass Spectrom. Ion Phys. 21 (1976) 349.
[20] N.G. Adams, D. Smith. J. Phys. B 9 (1976) 1439.
[21] J. Chao, R.C. Wilhoit, B.J. Zwolinski. Thermochim. Acta 10 (1974) 359.
[22] M.D. Taylor, J. Bruton. J. Am. Chem. Soc. 74 (1952) 4151.
[23] M.D. Taylor. J. Am. Chem. Soc. 73 (1951) 315.

[24] K.K. Matthews, N.G. Adams, N.D. Fisher. J. Phys. Chem. 101 (1997) 2841.

[25] S.G. Lias, J.E. Bartmess, J.F. Liebman, J.L. Holmes, R.D. Levin, W.G. Mallard. J. Phys. Chem. Ref. Data, 17 (Suppl. 1) (1988).

[26] S.W. Benson. Chem. Rev. 78 (1978) 23.

[27] S. Ekern, A. Illies, M.L. McKee, M. Peschke. J. Am. Chem. Soc. 115 (1993) 12510.

[28] T. Su, W.J. Chesnavich. J. Chem. Phys. 76 (1982) 5183.

[29] D. Smith, N.G. Adams. Chem. Phys. Lett. 54 (1978) 535.

[30] W.A. Brown, P. Gardner, D.A. King. Surf. Sci. 330 (1995) 41.

[31] D.A. Outka, R.J. Madix. Surf. Sci. 179 (1987) 1.

[32] R. Atkinson, D.L. Baulch, R.A. Cox, R.F. Hampson, Jr., J.A. Kerr, J. Troe. J. Phys. Chem. Ref. Data 21 (1992) 1125.

[33] E.P. Hunter, S.G. Lias. J. Phys. Chem. Ref. Data (1997) (in press); Web Site: http://webbook.nist.gov/paser.htm.

[34] G. Wagner, H. Bock. Chem. Ber. 107 (1974) 68.

[35] S.H. Ashworth, K.M. Evenson, J.M. Brown. J. Mol. Spec. 172 (1995) 282.

[36] S. Yamamoto, S. Saito. Can. J. Phys. 72 (1994) 955.

[37] Q. Zhuo, D.J. Clouthier. J. Chem. Phys. 100 (1994) 2924.

[38] R.J. Boyd, A. Gupta, R.F. Langler, S.P. Lownie, J.A. Pincock. Can. J. Chem. 58 (1980) 331.

[39] N.G. Adams, N.D. Fisher. In: N.G. Adams, L.M. Babcock, Advances in Gas Phase Ion Chemistry, JAI Press, Greenwich, CT, 1998, in press.

[40] T.L. Williams, N.G. Adams, L.M. Babcock, C.R. Herd, M. Geoghegan. Mon. Not. R. Astron. Soc. 282 (1996) 413.