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Product channeling in the reactions of $CS^+(X\,^2\Sigma^+)$ with simple carboxylic acids and esters

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Abstract

In the present work, a selected ion flow tube was used to study the reactions of $CS^+(X\,^2\Sigma^+)$ with H_2, CO, and a series of carboxylic acids and esters, RCO_2R' (R, R′ = H, CH_3, C_2H_5), at 296 ± 4 K. The CS^+ ion is expected to be a reasonable ionic analogue of the neutral pseudohalogen, CN, because of its strong chemical bond and isovalency. The reactions of CS^+ with the RCO_2R' series were all fast at greater than 80% of the theoretical upper-limit ion/dipole capture rate coefficient. Numerous binary ion products were observed, the most prevalent being the acylium ion (RCO^+), the radical ion of the neutral reactant, and HCS^+; no ternary association products were observed. Despite the abundance of product channels, these reactions were simple mechanistically, proceeding either by the induction of lone pair electrons on the carboxyl O atoms, or by H-atom transfer, which was chiefly homolytic rather than heterolytic. Induction of an O-atom lone pair by the C-terminus of CS^+ into a molecular orbital of the activated complex is believed to lead to product formation through an oxonium ylide intermediate. The CS^+ was converted, with few exceptions, into the small product molecules OCS, CS, and HCS^+. Except in one instance, rupture of the strong C–S bond did not occur. The reactions of CS^+ with the RCO_2R' series are compared with the analogous reactions of S_2^+, SO^+, S^+, H_3O^+, NO^+, and O_2^+ which have been studied previously. The reactive behavior of CS^+ is discussed with regard to the pseudohalogen character of this ion and its potential role in studies of chemical reaction dynamics. Additionally, the rate coefficients and product distributions for the reactions of S^+ with NO_2 and C_3H_4 (allene) at 296 ± 4 K are presented. (Int J Mass Spectrom 208 (2001) 99–112) © 2001 Elsevier Science B.V.

Keywords: CS^+ ion; CN radical; Pseudohalogen; Ion/molecule reactions; Rate coefficients; Product distributions; Vapor viscosity

1. Introduction

Little is known about the reactivity of singly charged carbon monosulfide (CS^+). Although expected to be present in interstellar molecular clouds (ISC) as an intermediate in the chemical cycle between CS and HCS^+ [1,2], its detection in ISC to date has been only tentative [3]. This is largely because CS^+ reacts rapidly with molecular hydrogen [4]

$$CS^+ + H_2 \rightarrow HCS^+ + H$$

$$k_1^{(2)}\ (300\ \mathrm{K}) = 4.3 \times 10^{-10}\ \mathrm{cm^3\ molec^{-1}\ s^{-1}} \qquad (1)$$

and consequently does not persist in ISC, where H_2 is the most abundant molecular species by several orders of magnitude [5]. Hence, from the standpoint of interstellar chemical kinetics, there has been little motivation to study reactions of CS^+, and only its

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reactions with H_2, CH_4, O_2, OCS, and CH_3NCS have been investigated previously [6].

From a more fundamental standpoint, this lack of attention is not justified. CS^+ is isovalent with the cyano radical (CN), which is often called a "pseudohalogen" due to its electronegativity between F and Cl, and the strength of the C≡N triple bond [7]. Classical studies of chemical dynamics have focused on reactions involving three atoms, viz. A + BC → AB + C, where A, B, and C usually are members of the hydrogen/halogen family (H, F, Cl, Br, I). Such atom/diatom systems are the most tractable experimental and theoretical prototypes for dynamical studies of binary reactions in the gas phase [8]. The substitution of CN for a halogen atom comprises a natural extension of such systems to include polyatomic reactants and products [7]. Amongst ions CS^+, with its strong chemical bond (~148 kcal mol^{-1}) and moderate recombination energy (11.33 eV) [9,10], is perhaps the best representative pseudohalogen. Whereas CO^+, which is isoelectronic with CN, has a relatively large recombination energy of 14.01 eV [10], and reacts substantially by charge transfer with many molecules [6], the analogous reactions of CS^+ better reflect the dynamics of short-range chemical encounters rather than longer-range charge-transfer (i.e. electron-jump) interactions [11].

A comparison of the reactions of CN with the few analogous data available for CS^+ reveals some striking similarities. Note that comparisons between ion/neutral and neutral/neutral reaction kinetics usually are not considered valuable, since the latter reactions often exhibit behaviors governed by potential barriers at the transition state. However, reactions involving neutral radicals often are dominated by long-range intermolecular forces, and do not have discernable effects due to barriers [12,13]; thus, a comparison with ion/neutral reactions can be useful. Only H-atom abstraction, respectively, forming HCN [14,15] and HCS^+ [16], is observed with H_2 and CH_4 (the CSH^+ isomer lies 75.8 kcal mol^{-1} higher in energy than HCS^+ at the G2 level of ab initio theory [17], and is therefore inaccessible to these reactions). For both CN and CS^+, the CH_4 reaction has a positive temperature dependence and is more efficient than the nearly isenthalpic H_2 reaction [14–16]. In its reaction with O_2, CN has three exothermic product channels, viz. OCN + O (0.76), CO + NO (0.22), and N + CO_2 (0.02), where the given product branching fractions were determined at 296 K [18]. In a drift tube mass spectrometer experiment [16], for $T<200$ K, three similar product channels were reported for the analogous CS^+ reaction: OCS^+ + O (0.70), CO + SO^+ (0.20), and O_2^+ + CS (0.10). Note that S^+ and O_2^+ both appear at 32 *u*/*z* (where *u*/*z* represents the units of atomic mass per unit of charge), and thus a minor S^+ + CO_2 channel may occur as well (the authors of this work did not state whether the $^{34}S^+$ isotope was searched for [16]). As the effective temperature was increased to ~3000 K in this latter reaction, the overall rate coefficient remained roughly constant, but the product branching fractions changed, viz. OCS^+ + O (0.40), CO + SO^+ (0.10), O_2^+ + CS (0.50) [16]. Thus, the product channels, excluding charge transfer, exhibit a negative temperature dependence as they do in the CN + O_2 reaction [18,19]. The systematic comparison of kinetic and dynamic behavior for related ionic and radical reactions has received very little attention, although such a field of study could greatly enhance our general understanding of chemically reacting systems [20].

During the course of several reactivity studies in our laboratory [21–23], involving sulfurated ions of potential importance for the chemical evolution of ISC, CS^+ was generated and its ion/molecule reactions studied in the gas phase at room temperature. Here we present its reactions with the abundant interstellar molecules, H_2 and CO, as well as the family of organic acids and esters RCO_2R' (R, R′ = H, CH_3, C_2H_5), excluding propionic acid ($C_2H_5CO_2H$), which has a very low room-temperature vapor pressure. The systematic substitution of these hydrogen and alkyl groups on a carboxyl backbone enables their influence on the mechanism of reaction and the product channel selectivity to be assessed. The reactions of only a handful of other ions, viz. S_2^+ [21], S^+ [23], H_3O^+, NO^+, and O_2^+ [24] have been investigated with the entire RCO_2R' (R, R′ = H, CH_3, C_2H_5) series. A comparison of these studies with the current data set for CS^+ illustrates many of the reactivity trends observed for thermal ion/molecule reactions in general. Additionally, we present the reactions of S^+ with NO_2 and C_3H_4 (allene), which we did not report previously [23].

2. Experimental

These experiments were performed with a selected ion flow tube (SIFT), which has been described previously in detail [25]. Briefly, CS^+ and other ions were generated from CS_2 in a low-pressure (~0.5 mTorr) electron-impact ion source. The CS^+ ions were selected in a quadrupole mass filter and passed through a 1 mm orifice into the higher-pressure (~0.5 Torr) flow tube. High-purity (99.997%) helium, was further purified by passing through a trap containing molecular sieve at 77 K. It was then introduced into the 101 cm long flow tube as the carrier gas at a venturi-type inlet around the region of ion injection. A fast (~100 m s^{-1}) flow of the carrier gas at ~0.5 Torr was established with a Roots-type blower. Since the radial profile of ionization density was close to Bessel function, the CS^+ ions traveled at a higher group velocity of ~150 m s^{-1} [25]. Collisional fragmentation of the CS^+ upon injection produced a minor S^+ contaminant ion with a signal intensity of 0%–5% relative to CS^+. Any contributions to the product spectrum arising from the reactions of S^+ were subtracted from the nascent product distributions using data published previously for these reactions [23].

Complete relaxation to the ground ($X\,^2\Sigma_g^+$) electronic state of CS^+ from the A, B, and C excited states occurred during the ~6 ms of transit time before the ions entered the reaction zone of the flow tube [26]. However, in principle, metastable states of CS^+, e.g. those with quartet spin multiplicity, could also be made during the formation of CS^+ from CS_2 by 70 eV electrons. Kumar et al. [27] showed that CS^+ ions generated from CS_2 in a higher-pressure (50–100 mTorr) electron-impact ion source are relaxed efficiently and emerge in their $X\,^2\Sigma_g^+$ electronic state. Thus, although the more robust low-pressure (~0.5 mTorr) ion source was preferred in most of the present work, checks were made with CS^+ generated in a higher-pressure (200–300 mTorr) source for comparison. Identical CS^+ decays and product branching fractions were obtained with CS^+ generated in the two different sources, implying that the reactivity measured in all of the present experiments was that of CS^+ ions in their $X\,^2\Sigma_g^+$ electronic states. Additional collisional quenching of any residual vibrational and rotational excitation occurred in the ~10^5 collisions with helium experienced by each ion prior to entering the reaction zone.

Neutral reactants were introduced at ring-type inlets [25] positioned to give appropriate reaction lengths. Reactant concentrations were determined from the Poiseuille flow of reactant gas or vapor through a calibrated capillary tube. The carboxylic acids (HCO_2H and CH_3CO_2H) were prepared in dilute (<1.8%) manometric mixtures with helium to facilitate the introduction of these sticky, reactive species. Shifts in the kinetic monomer/dimer equilibria of HCO_2H and CH_3CO_2H upon dilution were accounted for using available equilibrium constants [28,29]. It was justifiably assumed that the carboxylic acid mixture viscosity was equal to that of pure helium within a negligible error at the small mixing ratios employed. Viscosities for the permanent gases were taken from a standard compilation [30], whereas those of the six esters were measured from the rate of pressure drop in a calibrated volume, yielding the following values in micropoise, with ±5% accuracy, at 298 ± 2 K: HCO_2CH_3 (91.2), $CH_3CO_2CH_3$ (81.8), $C_2H_5CO_2CH_3$ (75.8), $HCO_2C_2H_5$ (81.0), $CH_3CO_2C_2H_5$ (75.8), and $C_2H_5CO_2C_2H_5$ (74.8). These values agree within ±5% with estimates based on the Chapman-Enskog method and the Reichenberg equation [31], except that of $C_2H_5CO_2C_2H_5$, for which the estimated viscosity is ~20% greater. Gaseous reactants were used as supplied, and liquid reactants were out-gassed by way of several freeze-pump-thaw cycles before use. Reactants were obtained from commercial sources with the following purities: CS_2 (99.99 wt%), H_2 (99.999 + mol%), CO (99.3 + mol%), HCO_2H (99.4 wt%), CH_3CO_2H (99.8 wt%), HCO_2CH_3 (99.35 wt%), $CH_3CO_2CH_3$ (99.98 wt%), $C_2H_5CO_2CH_3$

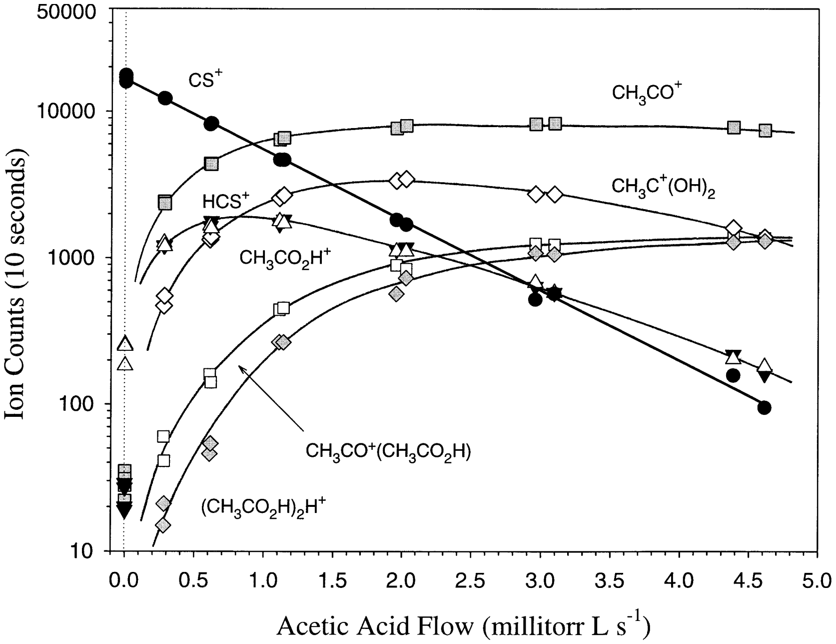


Fig. 1. Representative decay plot showing the variation of CS$^+$ and ion product count rates with CH$_3$CO$_2$H flow. The CS$^+$ decay shows excellent linearity over more than two orders of magnitude. The dominant ion product, CH$_3$CO$^+$, clearly accounts for ~50% of the primary reaction. The other two primary ion products, HCS$^+$ and CH$_3$CO$_2$H$^+$, have nearly identical count rates at all flows; each accounts for ~25% of the primary reaction. The major secondary products are CH$_3$C$^+$(OH)$_2$, arising from proton transfer from HCS$^+$ and CH$_3$CO$_2$H$^+$, and CH$_3$CO$^+$· CH$_3$CO$_2$H, from ternary association of CH$_3$CO$^+$ with CH$_3$CO$_2$H. One tertiary product, the proton cluster (CH$_3$CO$_2$H)$_2$H$^+$, is also shown. The identifications of these ion products and those of the other reactions in the data set are discussed in the text.

(99.94 wt%), HCO$_2$C$_2$H$_5$ (98.6 wt%), CH$_3$CO$_2$C$_2$H$_5$ (99.98 wt%), C$_2$H$_5$CO$_2$C$_2$H$_5$ (99.4 wt%).

Reactant and product ions were sampled downstream through a 0.3 mm orifice isolating the flow tube from a differentially pumped quadrupole mass spectrometer at ~10^{-5} Torr. The ions were detected with a channel electron multiplier in pulse-counting mode, whose signals were amplified and passed to a gated pulse counter and desktop computer for analysis and display. Ion counts were corrected for mass discrimination in the detection system as described previously [32] and for contributions from the ^{13}C, ^{34}S, and other isotopes of neighboring ions, where necessary. Reaction rate coefficients and percentage ion product distributions were determined in the usual way [25,33,34], with estimated accuracies of ±20% and ±5 in the percentage, respectively. For sticky reactants such as the carboxylic acids, the estimated accuracy in the rate coefficient decreases to ±30%. All measurements were made at 296 ± 4 K.

3. Results and discussion

3.1. Reactivity

Fig. 1 illustrates the decay of CS$^+$ in its reaction with CH$_3$CO$_2$H, and the creation of the primary, secondary, and one of the tertiary ion products. The linearity of the logarithmic decay implies that the reactivity of the entire CS$^+$ population is well described by a single rate coefficient, which in turn implies the presence of a single electronic state, doubtless the $X\,^2\Sigma_g^+$ ground electronic state (see Sec. 2). This decay linearity is characteristic of all of the reactions in the present study. Table 1 presents the binary rate coefficients, $k^{(2)}{}_{\rm exp}$, determined for the aforementioned reactions of CS$^+$, and for the reactions of S$^+$ with nitrogen dioxide (NO$_2$) and allene (C$_3$H$_4$), which were not reported previously [23] (these neutral reactants were handled as described in [21]). For the purpose of comparison, the theoretical

Table 1
Experimental and theoretical bimolecular rate coefficients for the reactions of CS^+ and S^+ with the indicated neutral molecules at 296 ± 4 K; product ions are also indicated for the S^+ reactions

Ion	Reactant	$k^{(2)}_{exp}$ (cm^3 $molecule^{-1}$ s^{-1})	$k^{(2)a}_{th}$ (cm^3 $molecule^{-1}$ s^{-1})	Products
CS^+	H_2	4.5 (−10)[b]	1.5 (−9)	$HCS^+ + H$
	CO	≤4 (−13)[c]	8.1 (−10)	$CS^+ \cdot CO$
	HCO_2H	1.8 (−9)	1.7 (−9)	d
	CH_3CO_2H	1.9 (−9)	2.0 (−9)	d
	HCO_2CH_3	1.6 (−9)	2.0 (−9)	d
	$CH_3CO_2CH_3$	1.6 (−9)	2.0 (−9)	d
	$C_2H_5CO_2CH_3$	1.7 (−9)	2.0 (−9)	d
	$HCO_2C_2H_5$	1.9 (−9)	2.2 (−9)	d
	$CH_3CO_2C_2H_5$	1.8 (−9)	2.1 (−9)	d
	$C_2H_5CO_2C_2H_5$	1.9 (−9)	2.1 (−9)	d
S^+	NO_2	2.5 (−10)	1.0 (−9)	(0.80) $NO^+ + SO$ (0.20) $NO_2^+ + S$
	C_3H_4 (allene)[e]	1.2 (−9)	. . .	(0.40) $C_3H_4^+ + S$ (0.25) $C_3H_3^+ + SH$ (0.15) $C_3H_3S^+ + H$ (0.12) $CH_2S^+ + C_2H_2$ (0.06) $HCS^+ + C_2H_3$ (0.02) $C_2H_4^+ + CS$

[a] Theoretical capture rate coefficient, $k^{(2)}_{th}$ was determined from the theoretical model of Su and Chesnavich [35].

[b] In excellent agreement with the value of 4.3 (−10) cm^3 $molecule^{-1}$ s^{-1} reported by Anicich [4].

[c] Presented as an effective binary rate coefficient for a ternary association reaction (see text).

[d] See Table 2.

[e] An unknown fraction (however, see [23]) of the S^+ was in its metastable ^2P and ^2D electronic states for this study, which may have slightly altered the measured product distribution, reported here, from that of the ground-state S^+ (^4S) reaction.

upper-limit binary rate coefficients, $k^{(2)}{}_{th}$, were calculated from the parametrized variational ion/dipole trajectory theory of Su and Chesnavich [35], and are presented in Table 1 alongside the experimental data. The electric dipole moments and electric dipole polarizabilities needed for these calculations were obtained from standard chemical reference compilations [30,36].

The measured rate coefficient for the reaction of CS^+ with H_2 is $(4.5 \pm 0.9) \times 10^{-10}$ cm^3 $molecules^{-1}$ s^{-1}, in excellent agreement with the value of 4.3×10^{-10} cm^3 $molecules^{-1}$ s^{-1} from an evaluation by Anicich [4]. The only product ion observed is HCS^+, as reported previously [4,16,21]. The reaction with CO proceeds entirely by ternary association, with an effective binary rate coefficient of $\leq 4 \times 10^{-13}$ cm^3 $molecules^{-1}$ s^{-1} in 0.5 Torr of helium, corresponding to a ternary rate coefficient of $\leq 2 \times 10^{-29}$ cm^6 $molecules^{-2}$ s^{-1}. In contrast, the reactions of CS^+ with the RCO_2R' (R, R′ = H, CH_3, C_2H_5) series of carboxylic acids and esters are all fast, with measured rate coefficients $\geq 0.8k^{(2)}{}_{th}$ (see Table 1). No ternary association product channels are observed in any of these reactions and, within the experimental accuracy, all proceed at their theoretical binary collisional capture rates [35]. As discussed below, numerous product channels are observed, with the relative branching ratios governed by the type and position of substitution on the carboxyl backbone.

3.2. Product distributions with RCO_2R' (R, R′ = H, CH_3, C_2H_5)

The percentage product distributions for the reactions of $CS^+(X\,^2\Sigma^+)$ with the RCO_2R' (R, R′ = H, CH_3, C_2H_5) series of carboxylic acids and esters are presented in Table 2. Although the estimated accuracy of ±5 in the percentage casts doubt on the existence

Table 2
Percentage (%) primary ion product distributions for the reactions of CS^+ ($X\ ^2\Sigma^+$) with a series, RCO_2R' (R, R′ = H, CH_3, C_2H_5), of carboxylic acids and esters at 296 ± 4 K; first ionization energies (in eV) of the neutral reactants are indicated in parentheses; "Me" is equivalent to CH_3, C_2H_5; the recombination energy of CS^+ ($X\ ^2\Sigma^+$) is 11.33 eV for comparison [9, 10].

m/z (*u/z*)	Product Ion	HCO_2H (11.33)	$MeCO_2H$ (10.65)	HCO_2Me (10.84)	$MeCO_2Me$ (10.25)	$EtCO_2Me$ (10.15)	HCO_2Et (10.61)	$MeCO_2Et$ (10.01)	$EtCO_2Et$ (10.00)
. . .	RCO^+	15	50	55	75	65	$40 - X^a$	35	35
. . .	M^{+b}	5[a]	25[a]	18[a]	25	20	6	5	12
45	HCS^+	20	25	15		5	$18 - Y^a$	13	7
. . .	$(M^b\text{–}H)^+$			3			2	1	1
28	$C_2H_4^+$						25	1	1
29	$C_2H_5^+$					10	X^a	2	8
30	CH_2O^+	45					6		
31	CH_2OH^+			5					
34	H_2S^+	3							
43	CH_3CO^+			4					
45	$C_2H_5O^+$						Y^a		
57	$C_2H_5CO^+$						3		
59	$C_2H_3O_2^+$							2	
61	$C_2H_5O_2^+$							30	
61	$HOCS^+$	10							
62	$HOCSH^+$	2							
70	$C_4H_{6}O^+$							8	
73	$C_3H_5O_2^+$							3	4
74	$C_3H_6O_2^+$								12
75	$C_3H_7O_2^+$								16
84	$C_5H_{8}O^+$								2
87	$C_4H_{7}O_2^+$								2

[a] Two possible product ions appear at the same *m/z* (see text).
[b] The parent neutral molecule, RCO_2R', is here represented by "M."

of some of the minor products reported, the reproducible detection of ion counts at these *m/z* values, and the high purities of the reagent and carrier gases (see Sec. 2), argue for their inclusion in the reported distributions. Ion products contributing <1% to the distribution, and therefore possibly originating from reagent impurities, are not reported. Because of their prevalence, three product channels are listed at the top of Table 2: formation of an acylium ion, RCO^+ (R = H, CH_3, C_2H_5), charge (i.e. electron) transfer, and H-atom transfer forming either HCS^+ or HCS. The acylium ion, because of its high stability in general [37], is observed as a primary product in all of these reactions, representing in most cases the dominant product channel, if not the majority reaction product.

Also observed in every case is the molecular ion of the neutral reactant. The recombination energy (RE) of $CS^+(X\ ^2\Sigma^+)$, 11.33 eV [9,10], is approximately equal to the ionization energy (IE) of HCO_2H, and is greater than those of the other neutrals (see Table 2) [10]. The branching percentage for electron transfer apparently does not correlate with $RE(CS^+) - IE(RCO_2R')$, unlike the situation for $S^+(^4S)$, where a strong correlation is observed [11,23]. When alternative product channels are present, which involve changes in chemical bonding, the prominence of electron transfer reflects its competitiveness with such chemical channels. Note that these chemical channels by their nature require impact parameters on the order of chemical bonding distances, whereas electron transfer often occurs at much longer ranges, hence with much larger impact parameters [11]. In part, the difference in electron transfer behavior between molecular CS^+ and atomic S^+ may be explained by the overlap between wave functions representing the ion and its corresponding neutral species, which influences the efficiency of long-range electron transfer. Molecules, unlike atoms, may have different equilibrium nuclear geometries in their ionized and neutral states, such that the Franck-Condon overlap between these states is improved by geometric distortion in the ion/molecule interaction field (e.g. $CS^+(X\,^2\Sigma^+)$ has an equilibrium bond length ~5% shorter than that of $CS(X\,^2\Sigma^+)$ in the absence of an external field [38]). Thus, *efficient* electron transfer with molecular ions may require smaller impact parameters than with atomic ions. At these smaller impact parameters, the electron transfer process could thus compete directly with the chemical product channels [11]. Note that if the electron transfer dissociates a fraction of the molecular ions (M^+), the branching percentage corresponding to M^+ will not represent the electron transfer channel in its entirety, and any correlation between that branching percentage and RE(ion) − IE(M) will be obscured. This situation occurs in the reactions of CS^+ with $RCO_2C_2H_5$ ($R = H, CH_3, C_2H_5$) (see Sec. 3.5), and explains in part the relatively small contribution from M^+ in their product distributions (see Table 2).

The third prevalent type of product channel is H-atom transfer, which is observed with every reactant except $CH_3CO_2CH_3$. The strength of the H–CS^+ bond, as deduced from the enthalpies of formation of HCS^+, CS^+, and H [10] in the process $HCS^+ \rightarrow CS^+ + H$, is ~135 kcal mol^{-1}, much greater than a typical C–H bond (~100 kcal mol^{-1}). H-atom transfer must therefore be kinetically inhibited with the methyl H atoms of $CH_3CO_2CH_3$, proceeding through a potential barrier which renders it noncompetitive with the observed product channels. Hydride ion (H^-) transfer is observed only as a very minor product channel in a few cases, which reflects the low ionization energy of HCS (≤7.5 eV [39]) and hence, the low recombination energy of HCS^+. Because H-atom and H^--ion transfers represent homolytic and heterolytic cleavage of the same bond type, respectively, they are listed together in the top portion of Table 2. The remaining products of the CS^+ reactions with RCO_2R' series are listed in order of increasing *m/z* in the bottom portion of Table 2, and discussed for each reactant in the following sections. Two prominent features of the data are the ion products at 28 *u/z* and 29 *u/z*, corresponding to $C_2H_4^+$ and $C_2H_5^+$ (which are likely to occur only for the neutrals having a C_2H_5 group), and the series of related (A, $A + 14$) *u/z* ion products (where A is the *m/z* value of a particular ion product, in units of *u/z*) with $CH_3CO_2C_2H_5$ and $C_2H_5CO_2C_2H_5$. One or two products with HCO_2CH_3 and $HCO_2C_2H_5$ also bear an (A, $A + 14$) *m/z* relationship. Potential ambiguities in the assignment of product identity are discussed below, on a case-by-case basis.

3.3. Product distributions with the carboxylic acids

The acylium ion (i.e. the formyl ion, HCO^+) is a minor product with HCO_2H, which is anomalous for the reaction set as a whole (see Table 2). The dominant ion product, CH_2O^+ and/or its isomer, $HCOH^+$, is represented generically as CH_2O^+ in Table 2. This product may be formed either by abstraction of the carbonyl O-atom forming $HCOH^+$ + OCS, or alternatively by homolytic transfer of the hydroxyl group to CS^+ (α-cleavage) followed by internal proton transfer to the HCO leaving group. Without internal proton transfer, the α-cleavage forms $HOCS^+$ + HCO (or H + CO). Note that the proton affinities and gas basicities of HCO and OCS are comparable [40]. Heterolytic cleavage of the hydroxyl group forms HCO^+ + HOCS (or H + OCS). Rice et al. have calculated numerous stationary points on the [H, O, C, S] potential-energy surface (PES), using density functional theory at the QCISD(T)//UMP2 level with aug-cc-pVTZ and 6-311+G(2*df*, 2*p*) basis sets [41]. The recombination energy (RE) of $HOCS^+$, based on estimates of $\Delta H_f°(HOCS^+)$ and $\Delta H_f°(HOCS)$ from the known proton affinity of OCS [40], $\Delta H_f°(H^+)$, $\Delta H_f°(OCS)$ [10], and the study of Rice et al. [41], is ~7 eV, substantially smaller than IE(HCO) (= 8.12 ± 0.04 eV [10]). Therefore, the net transfer of an electron from HCO to $HOCS^+$ is unlikely, and the neutral products of the channel forming HCO^+ probably are H + OCS rather than HOCS.

An interesting product is observed at 62 *u/z*, which must be an isomer of the $[2H, O, C, S]^+$ system. Le et al. [42] have constructed a stationary-point PES of this system using the same ab initio method employed by Rice et al. [41] (see previous discussion), but with smaller 6-311++G(*d*,*p*) and 6-31(*d*,*p*) basis sets. Singly ionized thioformic acid, $(HC(=S)OH)^+$, in its *anti*-conformation was found to be the global energy minimum on this surface [42]. Connectivity in the $CS^+ + HCO_2H$ reaction prescribes that either $(HC(=S)OH)^+$ or the thiohydroxycarbene radical ion, $(HS–C–OH)^+$, is formed initially. Enough energy is released in this reaction to drive the isomerization of either ion to the ion–molecule complex $H_2S^+ \cdot CO$, which dissociates into $H_2S^+ + CO$ [42]. Ion products are observed at 62 *u*/*z* and 34 *u*/*z*, contributing ~2% and ~3%, respectively, to the total product distribution for the $CS^+ + HCO_2H$ reaction. Lahem et al. also have observed spontaneous decomposition of the 62 *u*/*z* ion (generated by electron impact on S-ethyl thioformate) to $H_2S^+ + CO$ [43]. Thus, the observed H_2S^+ is considered to originate from the ion product at 62 *u*/*z*. Decomposition of the nascent ion at 62 *u*/*z* may also contribute in part to the observed HCO^+, HCS^+, and $HOCS^+$ [43].

The empirical identities (i.e. the atomic compositions) of the ion products discussed above are unambiguous. The two remaining products with HCO_2H, indicated in Table 2 as HCS^+ $(+CO_2H)$ at 45 *u*/*z* and HCO_2H^+ $(+CS)$ at 46 *u*/*z*, coincide with possible alternatives, viz. CO_2H^+ $(+HCS)$ at 45 *u*/*z*, and CH_2S^+ $(+CO_2)$ at 46 *u*/*z*. However, the true identity of the 45 *u*/*z* ion is abundantly clear from its slow secondary reaction with HCO_2H: CO_2H^+ would react rapidly due to the large difference in proton affinity between CO_2 and HCO_2H [40,44], and thus the slowly reacting ion at 45 *u*/*z* must be mostly or entirely HCS^+. This also makes sense from a thermochemical point of view, since IE(HCS) (~7.5 eV [39])<IE(HOCO) (~8.2 eV [45]). The identity of the 46 *u*/*z* ion is less certain; since $RE(CS^+) \approx IE(HCO_2H)$ [10], it might seem surprising that even as much as 5% of the product is due to electron transfer (see Table 2). Sumathi et al. [46], using ab initio methods very similar to those described previously [41,42], calculated stationary-point PESs for the $[nH, C, S]^+$ ($n = 1–4$) systems, and found that the reaction $HCS^+ + H_2 \rightarrow CH_2S^+ + H$ proceeds through a very low barrier of ~0.9 kcal mol^{-1} on the triplet surface, with an exothermicity of ~30 kcal mol^{-1} [46]. Therefore some CH_2S^+ might possibly be formed in a two-step process, although this should not compete effectively with simple H-atom transfer forming HCS^+.

Only the three most prevalent product ions are observed with CH_3CO_2H, viz. the acylium ion (i.e. the acetyl ion, CH_3CO^+), HCS^+, and the electron transfer molecular ion. Heterolytic cleavage of the hydroxyl group to form CH_3CO^+ is exothermic enough to dissociate the neutral fragment to H + OCS [41]. Similarly, abstraction of the carbonyl O atom forms $CH_3CO^+ + (H+OCS)$ rather than CH_3COH^+ $(+OCS)$. The H-atom transfer forming HCS^+ presumably occurs only with the hydroxyl H atom, since the process is kinetically inhibited with the methyl H atoms of $CH_3CO_2CH_3$ (see Section 3.2 and Table 2). The resulting acetyloxyl radical, CH_3CO_2, has a low barrier for dissociation to $CH_3 + CO_2$ [47], and therefore probably does so. A possible alternative to electron transfer at 60 *u*/*z* is the formation of OCS^+ if the neutral products are $CH_4 + CO$, both of which have higher IEs than OCS [10]. However, an ion product at 60 *u*/*z* is observed only with the two 60 u reactants, CH_3CO_2H and HCO_2CH_3, both of whose IEs are smaller than $RE(CS^+)$ (see Table 2), so that some electron transfer is expected. Moreover, inspection of Fig. 1 shows that both HCS^+ and the 60 *u*/*z* ion (labeled as $CH_3CO_2H^+$ in Fig. 1) react with CH_3CO_2H, forming secondary ions entirely at 61 *u*/*z* (labeled as the proton-transfer product, $CH_3C^+(OH)_2$, in Fig. 1). If the 60 *u*/*z* ions were mostly OCS^+, its reaction with CH_3CO_2H would have to form $HOCS^+$, the only possible primary ion product for this reaction at 61 *u*/*z*, with a branching fraction near unity. Although this reaction has not been studied previously, such a product distribution seems unlikely, since CH_3CO^+ normally is a major product in reactions of CH_3CO_2H with unsaturated ions [6,21,23,24, and this work].

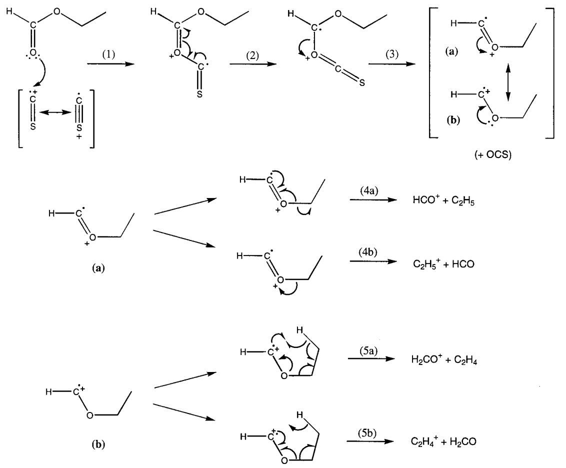
3.4. Product distributions with the methyl esters

The acylium ion is most prominent with the methyl esters (see Table 2). Heterolytic transfer of the ester group forms RCO^+ (R = H, CH_3, C_2H_5), with CH_3 and OCS for the neutral fragments, CH_3OCS probably being kinetically unstable or nearly so. Electron transfer is the only other active product channel with $CH_3CO_2CH_3$, whereas $C_2H_5^+$ and a small (5%) H-atom transfer channel are observed with $C_2H_5CO_2CH_3$. The $C_2H_5^+$, which is observed at a comparable level in the reaction with $C_2H_5CO_2C_2H_5$, may result from the decarbonylation of metastable $C_2H_5CO^{+}*$. H-atom transfer occurs only with hydrogen atoms on the ethyl group of $C_2H_5CO_2CH_3$, since this product channel is not active with $CH_3CO_2CH_3$; the resulting $C_2H_4CO_2CH_3$ radical then might be expected to decompose into $C_2H_4 + CH_3OCO$ or $C_2H_4 + CO_2 + CH_3$.

With HCO_2CH_3, the ion product at 60 *u/z* possibly includes some OCS^+ as well as the electron transfer molecular ion, as discussed in Sec. 3.3 for CH_3CO_2H. Note that 10% of the $S^+ + HCO_2CH_3$ reaction forms the analogous product channel, $SO^+ + (CH_4{+}CO)$ [23]. H-atom transfer probably proceeds only with the formyl H atom, forming $HCS^+ + CH_3OCO$ (or $CH_3 + CO_2$) and CH_3OCO^+ ("$(M - H)^+$" in Table 2) + HCS. At the Gaussian-2 level of ab initio theory, Ruttink et al. [48] have determined that $IE(CH_3OCO) = 7.32$ eV, which is close to IE(HCS) ($\leq 7.499 \pm 0.005$ eV [39]); thus, competition for the charge might be expected to occur between the HCS and CH_3OCO leaving groups, in accordance with Stevenson's rule [37]. The observed CH_2OH^+ arises from the H^- transfer, possibly through a metastable $CH_3OCO^{+}*$ intermediate. Hydride ion transfer, forming $(M - H)^+$, is observed as a very minor product with the ethyl esters as well (see Table 2). Abstraction of the carbonyl O atom (formally, O^-) generates OCS and $[HCOCH_3]^{+\cdot}$, which decomposes to form $CH_3CO^+ + H$ at least in part. This unusual product channel is also observed with $HCO_2C_2H_5$ (see Table 2).

3.5. Product distributions with the ethyl esters

With $HCO_2C_2H_5$, two pairs of ion products representing competing channels are formed, viz. HCO^+ and $C_2H_5^+$, both at 29 *u/z*, and CH_2O^+ (or $HCOH^+$) and $C_2H_4^+$, at 30 *u/z* and 28 *u/z*, respectively (see Table 2). Together, HCO^+ and $C_2H_5^+$ account for 40% of the reaction product; unfortunately, they could not be differentiated in these experiments, either by their *m/z* values or their reactivities, since both react by proton transfer with $HCO_2C_2H_5$ at the gas-kinetic rate [40,44]. A similar ambiguity exists for HCS^+ and $C_2H_5O^+$, both at 45 *u/z*. Thus in Table 2, these product percentages are expressed as "$40-X$" and "X" for HCO^+ and $C_2H_5^+$, and "$18 - Y$" and "Y" for HCS^+ and $C_2H_5O^+$, respectively. For the other product channels, viz. electron transfer, H^- transfer, and the channels forming $C_2H_4^+$, CH_2O^+, and $C_2H_5CO^+$, the atomic compositions of the ions are unambiguous.



Scheme 1. Probable mechanism for the product channels forming HCO^+, $C_2H_5^+$, H_2CO^+, and $C_2H_4^+$ in the reaction of CS^+ with $HCO_2C_2H_5$. See the text (Sec. 3.5) for details.

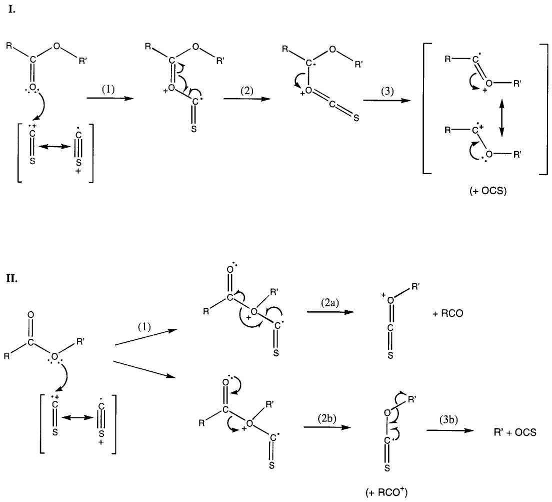
Scheme 1 depicts a probable mechanism forming HCO^+ and $C_2H_5^+$ on the one hand, and CH_2O^+ and $C_2H_4^+$ on the other, in the reaction with $HCO_2C_2H_5$. In step (1), CS^+ (in its carbene resonance structure) interacts with the carbonyl O atom, promoting a lone pair inductively into a molecular orbital of the activated ion complex. The resulting oxonium ylide ion undergoes a rearrangement in step (2), in which the radical site migrates to the more acidic carboxyl carbon atom. Inductive cleavage in step (3) releases carbonyl sulfide (OCS), and the resulting radical ion inter-converts between its oxonium ylide and carbene resonance structures [(a) and (b), respectively, in Scheme 1]. The ylide ion (a) decomposes by heterolytic and/or homolytic cleavage, forming $HCO^+ + C_2H_5$ [step (4a)] and/or $C_2H_5^+ + HCO$ [step 4(b)] respectively, in relative proportions governed by Stevenson's rule [37]. The HCO^+ and $C_2H_5^+$ both should be formed in appreciable abundance, since IE(C_2H_5) (=8.117 ± 0.008 eV [49]) is comparable to IE(HCO) (=8.12 ± 0.04 eV [10]). The carbene radical ion (b) undergoes H-atom (McLafferty) rearrangement [37] [step 5(a)] and internal hydride transfer [step 5(b)], both of which proceed through a five-membered ring transition state. The decomposition products are $H_2CO^+ + C_2H_4$ and $C_2H_4^+ + H_2CO$, respectively. That Stevenson's rule qualitatively predicts the proportions of these product channels is suggested by the ion product percentages for H_2CO^+ (6%) and $C_2H_4^+$ (25%), given that IE(H_2CO) (=10.88 ± 0.01 eV)>IE(C_2H_4) (=10.514 ± 0.001 eV) [10].

The general mechanism of Scheme 1 should also apply to the reactions with $CH_3CO_2C_2H_5$ and $C_2H_5CO_2C_2H_5$. With these, the acylium ion is much more prominent than $C_2H_5^+$, because CH_3CO and C_2H_5CO have much smaller IEs than C_2H_5 [10] (the $C_2H_5^+$ product in the reaction with $C_2H_5CO_2C_2H_5$ is likely enhanced by the decarbonylation of metastable $C_2H_5CO^{+}*$; see Sec. 3.4). Only very small contributions from $C_2H_4^+$ (1%) are observed, possibly corresponding to step (5b) of Scheme 1. However, the aldehyde radical ions corresponding to step (5a) are not observed. Although signal interferences occur at 44 *u/z* due to CS^+ and ^{13}C isotopes of CH_3CO^+, and at 58 *u/z* due to ^{13}C isotopes of $C_2H_5CO^+$, the signals observed at these *m/z* values are not enhanced relative to the expected background from these interferences, and thus any contribution from the aldehyde radical ions is quite small. Thus, the observed $C_2H_4^+$ more likely arises from unimolecular decomposition of the molecular ion following electron transfer, as discussed immediately below.

The remaining ion products with $CH_3CO_2C_2H_5$ and $C_2H_5CO_2C_2H_5$ arise either from H-transfer or electron transfer and, except for HCS^+, exhibit an (A, $A + 14$) *u/z* relationship between the esters. The $(M - H)^+$ ion product from H^- transfer contributes very little (1%) to these product distributions. The ion S_2^+, from the evidence of its general reactivity [21], has a greater hydride affinity than CS^+, and thus its H^- transfers with $CH_3CO_2C_2H_5$ and $C_2H_5CO_2C_2H_5$ are more exothermic. Conversely, electron transfer is substantially endothermic for S_2^+ (RE = 9.36 eV [10]) with these esters, whereas electron transfer with CS^+ (RE = 11.33 eV [10]) can deposit 30–31 kcal mol^{-1} of reaction energy into M^+. Electron transfer with O_2^+ (RE = 12.07 eV [10]) is even more exothermic, depositing up to 47–48 kcal mol^{-1} into M^+. The fact that no ion products in the 59–73 *u/z* range for $CH_3CO_2C_2H_5$, and the corresponding 73–87 *u/z* range for $C_2H_5CO_2C_2H_5$, are observed in their reactions with S_2^+ [21], whereas two of these products appear in the corresponding reactions with O_2^+ [24], implies strongly that most or all of these products observed with CS^+ arise from electron transfer followed by various unimolecular decompositions of M^+. This conclusion is further supported by the appearance of nearly all of these ions in the 70 eV electron-impact mass spectra for $CH_3CO_2C_2H_5$ and $C_2H_5CO_2C_2H_5$ [10]. The ion products at 59–61 *u/z* with $CH_3CO_2C_2H_5$ and 73–75 *u/z* with $C_2H_5CO_2C_2H_5$ correspond to loss of an ethyl, ethylene, or vinyl group, respectively, the last forming the very stable protonated carboxylic acid, $RC^+(OH)_2$ ($R = CH_3$, C_2H_5), by a McLafferty rearrangement plus a 1,2-β-hydrogen transfer. Since IE(C_2H_4) = 10.51 eV, IE(CH_3CO_2H) = 10.61 eV, and IE($C_2H_5CO_2H$) = 10.44 eV [10], the observed $C_2H_4^+$ probably arises from charge competition with its carboxylic acid leaving partners rather than the mechanism of Scheme 1. The ion products at 70 *u/z* and 84 *u/z* correspond to loss of H_2O, forming either a vinyl ketone radical ion, $RC({=}O^{+\cdot})CH{=}CH_2$, or an oxonium ylide, $R\dot{C}{=}O^+CH{=}CH_2$, both of which are resonance-stabilized by their 1,3-diene structures. Finally, the ion products at 73 *u/z* and 87 *u/z*, respectively, for the two esters correspond to loss of CH_3, forming the resonance-stabilized oxonium ion, $RC({=}O)O^+{=}CH_2$, which also has a 1,3-diene structure.

4. Further discussion

In the mechanism of Scheme 1, it was presumed that CS^+ attacks the electron lone pairs of the carbonyl O atom initially, which is reasonable from the perspective that these are more nucleophilic than the lone pairs on the ester O atom, as indicated by the preferred site of protonation for esters and carboxylic acids [50]. Nevertheless, both of these O atoms are good electrophores, and it is clear from their reactivity with CS^+ and other ions [21–24] that both provide sites for the formation of a reaction intermediate via induction of a lone pair into a molecular orbital of the activated complex. Scheme 2 depicts a generalized extension of Scheme 1 describing the chemical bonding interactions of CS^+ with either of the carboxyl O atoms of RCO_2R' (R, R′ = H, CH_3, C_2H_5). The relative contributions to the product distributions from CS^+ interactions with the carbonyl O-atom [Scheme 2(I)] and the hydroxyl or ester O atom [Scheme 2(II)] could not be determined in these studies, although such data would be extremely interesting from a dynamical point of view, and could be obtained in principle from a study using ^{18}O-labeled RCO_2R'. Electron transfer also involves the carboxyl O atoms, whose lone pair electrons are localized and occupy the highest occupied molecular orbitals in these molecules. From the product distributions in Table 2 and the discussions in Sec. 3, it appears that 75%–100% of the reactivity of CS^+ with RCO_2R' (R, R′ = H, CH_3, C_2H_5) is initiated by the O-atom lone pairs. The remaining reactivity is represented by H-atom transfer, which is chiefly homolytic, forming HCS^+.



Scheme 2. General mechanisms for chemical bonding interactions of CS^+ with the carboxyl oxygen atoms of RCO_2R' (R, R′=H, CH_3, C_2H_5). In mechanism (I), the reaction proceeds by way of induction of a lone pair of electrons on the carbonyl O atom into a molecular orbital of the activated complex. In mechanism (II), a similar induction occurs with a lone pair on the hydroxyl or ester O atom. Step II(2a) occurs only with HCO_2H in the present study. Note that reaction proceeds through an oxonium ylide intermediate in all cases, and that steps I(2), II(2a), and II(3b) are homolytic processes resulting in migration of the radical site away from the CS group. Mechanisms I and II do not include further reactive steps, e.g. internal proton transfer, which are observed in some of the $CS^+ + RCO_2R'$ reactions (see text and Table 2).

In addition to the reactions of CS^+ presented here, those of S_2^+ [21], S^+ [23], H_3O^+, NO^+, and O_2^+ [24] with the entire RCO_2R' series (including $C_2H_5CO_2H$), and of SO^+ with HCO_2H and HCO_2CH_3, also have been studied [22]. The behaviors of these ions are highly varied, reflecting fundamental differences in their electronic structures. For example, H_3O^+ is an even-electron (EE^+), ion in its singlet ground electronic state, and the protonated form of a highly stable neutral molecule (i.e. water), which has a proton affinity much lower than any of the molecules in the RCO_2R' series [40]. The neutral species formed upon electron transfer to H_3O^+, H_3O, is hypervalent and unstable. Thus, proton transfer dominates these reactions of H_3O^+ [24]. Likewise, NO^+ is an EE^+ singlet ion in its ground state, with a recombination energy (RE = 9.26 eV [10]) smaller than any of the IEs of the RCO_2R' series (see Table 2); however, it lacks a proton. Consequently, NO^+ has few available exothermic binary reaction pathways and reacts chiefly by ternary association [24]. The remaining ions, $S_2^+(^2\Pi)$, $SO^+(^2\Pi)$, $S^+(^4S)$, $CS^+(^2\Sigma)$, and $O_2^+(^2\Pi)$, are odd-electron ($OE^{+\cdot}$) radical ions, with REs of 9.36, 10.29, 10.36, 11.33, and 12.07 eV, respectively, in their ground electronic states [10]. The prevalence of charge transfer increases with increasing RE in this series, and ternary association is important only with S_2^+ [21–24]. The reactivities of the isovalent S_2^+, SO^+, and O_2^+ have been compared previously [22], as well as those of S^+ and SO^+ [23]. Heterolytic transfer of H^-, OH^-, and CH_3O^- and other formally EE^- groups are prevalent in the reactions of these ions, and hence, except in the case of electron transfer, the radical site rarely migrates to the other leaving fragment. Conversely with CS^+, net abstractions of $H^{\cdot}$ and O^-, which formally speaking are $OE^{\cdot}$ and $OE^{-\cdot}$ groups, respectively, are more typical; thus, the radical site usually migrates (cf. Scheme 2). Formal O^- transfer is much less common with S_2^+, SO^+, S^+, and O_2^+, and homolytic H-atom transfer does not occur [21–24].

In the S^+ reaction with HCO_2CH_3 [23], ion products at 62 *u/z* and 34 *u/z* were observed, corresponding to $[2H, O, C, S]^+$ and H_2S^+, respectively, as discussed in Sec. 3.3 for the $CS^+ + HCO_2H$ reaction. The percentages of the nascent product distribution were determined to be 8% for the 62 *u/z* ion and 9% for H_2S^+ [23], although it was not appreciated at the time that the H_2S^+ originated from the unimolecular decomposition of a metastable fraction of the 62 *u/z* ions. The reaction with HCO_2CH_3 was the only one for S^+ in which $[2H, O, C, S]^+$ was observed, and in which H_2S^+ consequently appeared as a significant ion product [23]. In the reaction of S^+ with $HCO_2C_2H_5$, all of the 29 *u/z* product ion was attributed to $C_2H_5^+$, although from the evidence of the discussion in Sec. 3.5 and the mechanism of Scheme 1, competition between HCO^+ and $C_2H_5^+$ might occur. Nevertheless, $C_2H_5^+$ is more likely the dominant product because S^+ reacts principally by formal OH^- rather than O^- transfer [23].

Pascoli and Lavendy [51] have studied CS^+ and other cationic sulfur carbide cluster ions using BL3LYP density functional theory. According to their calculations, $CS^+(^2\Sigma^+)$ has a permanent electric dipole moment, μ_D, of only 0.58 D, presumably positive toward the S-atom (although these authors did not specify the direction of μ_D). Their calculations also indicate Mulliken atomic charges of 0.78 and 0.22, respectively, for the S atom and the C atom of CS^+, and thus, the charge is principally associated with the S atom in the absence of an external field. The same is true for SO^+, which has Mulliken charges of 0.69 and 0.31, respectively, for S and O [22]. However, μ_D is much larger for SO^+, 2.2–2.3 D, and is definitely positive towards the S atom [22]. These results imply that the charge distribution is more diffuse, and hence, more polarizable, with $CS^+(^2\Sigma)$ than with $SO^+(^2\Pi)$, and consequently that reactive input trajectories in which the C-terminus of CS^+ is directed toward the nucleophilic regions of the neutral molecule are attractive as well as the input trajectories with approach by the S-terminus. Such is not the case with SO^+, for which the S-terminus reactive approaches are strongly favored [22]. In the prior discussions, a C-terminus approach in the reactions of CS^+ was tacitly assumed, because of the high stabilities of HCS^+ and OCS relative to CSH^+ and CSO^+. For electron transfer, approach by either end of the CS^+ molecule is feasible.

Despite the diversity of ion products and product distributions in the reactions of CS^+ with the RCO_2R' series, their underlying mechanistic simplicity is characteristic of a pseudohalogen. Nearly all of the CS^+ reactions include a homolytic step (cf. Scheme 2), permitting the completion of a closed-shell configuration by transferring the radical site to a different leaving group. The CS^+ preferentially abstracts monovalent groups such as H, OH, and O^-. Abstraction of alkyl groups is strongly disfavored, whereas conversely, products such as CH_3S^+ and CH_3SO^+ are observed in the reactions of S^+ [23] and SO^+ [22]. Much of the apparent complexity arises from electron-transfer-initiated unimolecular decompositions, which are particularly evident in the reactions with $CH_3CO_2C_2H_5$ and $C_2H_5CO_2C_2H_5$. Apart from the electron-transfer product channels, which are inaccessible to neutral species, the reactivity of CS^+ is expected to be analogous mechanistically to that of CN. Therefore the comparative study of the chemical reaction dynamics (i.e. calculation of the reaction PESs and state-resolved measurement of the reaction energy disposal) of related ionic (CS^+) and neutral (CN) pseudohalogen reactions should enhance our fundamental understanding of both ion/neutral and radical/neutral chemistry.

5. Summary and conclusions

The reactions of $CS^+(X\,^2\Sigma^+)$ with H_2, CO, and the series RCO_2R' (R, R$' = $ H, CH_3, C_2H_5) of carboxylic acids and esters (excluding $C_2H_5CO_2H$), and additionally two reactions of S^+, were studied in the gas phase at 296 ± 4 K with a SIFT. The reactions of CS^+ with the RCO_2R' series were all fast, with binary rate coefficients $\geq 0.8k^{(2)}_{th}$, where $k^{(2)}_{th}$ is the theoretical upper-limit capture rate coefficient [35]. No ternary stabilization products were observed, and therefore all of these reactions proceeded rapidly relative to the ~300 ns timescale between hard-sphere collisions with the He carrier gas. Among the numerous product ions observed, the three most prevalent were the acylium ion, RCO^+, the molecular ion of the neutral reactant, and HCS^+. All of the product channels could be explained by the induction of lone pair electrons from either of the carboxyl O atoms, forming an oxonium ylide intermediate prior to chemical bonding rearrangements, or by H-atom transfer, which was chiefly homolytic (forming HCS^+ rather than HCS). With few exceptions, the CS^+ was converted into the small product molecules OCS, CS, and HCS^+. It was deduced from the reaction energetics and mechanisms that the other neutral products generally were also of low atomicity (e.g. H, CO, CO_2, HCO, HCS, CH_3, C_2H_3, C_2H_4, and C_2H_5).

The reactions of CS^+ with the RCO_2R' (R, $R' = H, CH_3, C_2H_5$) series were compared with the corresponding reactions of S_2^+, SO^+, S^+, H_3O^+, NO^+, and O_2^+ for which data are available [21–24]. Due to their diverse natures, the reactive behaviors of these ions are representative of many important classes of ion/molecule reactions; e.g. charge transfer, proton transfer, atom abstraction, and ternary association. In comparison with that of the other ions, the CS^+ reactions were mechanistically distinct in that a homolytic step usually occurred, resulting in the migration of the radical site to a different leaving group. Such behavior is expected with a pseudohalogen, for which a single bonding electron is required to complete a molecular "octet." The experimental evidence presented here suggests that CS^+ is an appropriate model ion for comparative dynamical studies of ionic and neutral diatomic pseudohalogen reactions, and particularly for comparison with the reactions of the neutral cyano radical, CN.

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