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Kinetics of Ion−Molecule Reactions with 2-Chloroethyl Ethyl Sulfide at 298 K: A Search for CIMS Schemes for Mustard Gas

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The rate constants and product ion branching ratios have been measured in a selected ion flow tube (SIFT) at 298 K for a variety of positive and negative ions reacting with 2-chloroethyl ethyl sulfide (2-CEES), a surrogate for mustard gas (HD). This series of experiments is designed to elucidate ion−molecule reactions that have large rate constants and produce unique product ions to guide the development of chemical ionization mass spectrometry (CIMS) detection methods for the chemical weapon agent using the surrogate instead. The negative ions typically used in CIMS instruments are essentially unreactive with 2-CEES, that is, SF_6^-, SF_4^-, CF_3O^-, and CO_3^-. A few negative ions such as NO_2^- and NO_3^- undergo three-body association to give a unique product ion, but the bimolecular rate constants are small in the SIFT. Positive ions typically react at the collisional limit, primarily by charge and proton transfer, some of which is dissociative. For ions with high proton binding energies, association with 2-CEES has also been observed. Many of these reactions produced ions with the 2-CEES intact, including the parent cation, the protonated cation, and clusters. G3(MP2) calculations of the thermochemical properties for 2-CEES and mustard have been performed, along with calculations of the structures for the observed product cations. Reacting a series of protonated neutral molecules with 2-CEES brackets the proton affinity (PA) to between 812 ($(CH_3)_2CO$) and 854 (NH_3) kJ mol^{-1}. G3(MP2) calculations give a PA for 2-CEES of 823 kJ mol^{-1} and a PA for mustard of 796 kJ mol^{-1}, indicating that the present results for 2-CEES should be directly transferable to mustard to design a CIMS detection scheme.

Introduction

The ability to sensitively and accurately detect chemical weapon agents in the gas phase remains an important problem in homeland security, battlefield operations, chemical weapon stockpile handling, and chemical weapon disposal facilities. The quantities needed to cause harm to humans are small; therefore, the analytical requirements are rigorous. Chemical weapons disposal and stockpile facilities represent some of the most strenuous requirements because the live agents are handled regularly. The detection systems currently in use in the demilitarization plants depend on preconcentration of the air, followed by rapid heating of a collection filter with gas chromatographic separation.[1] Different detectors are used depending on the chemical agent. The systems are capable of detecting small concentrations, but they lack real time capability and are susceptible to false positives at the low concentrations that are needed to protect personnel. As the requirements become more stringent, that is, detection at the boundaries of the facilities, the preconcentration time is increased. At best, the current systems have cycles of several minutes and can detect only one agent at a time.

A recent National Academy of Sciences (NAS) report[1] on monitoring air at chemical agent disposal facilities has outlined several scenarios where real time detection would be useful in the plants. Other applications, such as battlefield detection and homeland security, also have obvious needs for real time monitoring. The NAS committee examined several alternative technologies to the ones currently in use at the plants and concluded that the only technology that demonstrated enough promise to pursue in the short term is chemical ionization mass spectrometry (CIMS), in large part because of the success CIMS has had at selectively and sensitively detecting many atmospheric neutrals.[2−10] The key to the CIMS technique is finding readily generated primary ions that react rapidly with the agents and yield product ions with unique mass signatures. The latter goal is usually accomplished by using reactions that keep the reagent intact after ionization.

As chemical weapons cannot be readily studied in most laboratories, the use of surrogates and theoretical calculations are required. In this work, we measure the kinetics for a large number of positive and negative ions reacting with the mustard surrogate 2-chloroethyl ethyl sulfide (2-CEES), given as $C_2H_5SC_2H_4Cl$. Mustard (HD) has a similar formula of $ClC_2H_4SC_2H_4Cl$. Thus, all of the functional groups are present in the surrogate compound. Reactant ions are mostly chosen from those used in the various atmospheric CIMS instruments,[2−10] as well as those ions used in commercial ion reactors.[11] In addition, theoretical calculations of the ionization potentials and proton, oxide, and fluoride affinities of both 2-CEES and mustard have been performed to complement the studies involving the surrogate, including energetics and structures for the fragment ions, only some of which have been studied in the literature.[12−25] The combination of theory and experiment allows facile transfer of the results based on the surrogate study to laboratories that can work with mustard gas.

Experimental Section

The rate constants and product ion branching ratios were measured at 298 K using the selected ion flow tube (SIFT) at

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TABLE 1: Rate Constants for the Reaction of Various Positive Ions with 2-Chloroethyl Ethyl Sulfide (2-CEES) at 298 K Measured in a Selected Ion Flow Tube (SIFT)[a]

ion	products	branching ratio	experimental rate constant × 10^{-9}cm^3 s^{-1}	collision rate constant × 10^{-9} cm^3 s^{-1}
O_2^+	$C_4H_9ClS^+ + O_2$	0.11	3.1	2.8
	$C_3H_6ClS^+ + CH_3 + O_2$	0.02		
	$C_4H_9S^+ + Cl + O_2$	0.07		
	$C_3H_7S^+ + (CH_2Cl + O_2)$	0.70		
	$C_2H_5S^+ + (C_2H_4Cl + O_2)$	0.08		
	$CH_2SH^+ + (C_2H_4 + CH_2Cl + O_2)$	0.02		
$NO+$	$C_4H_9ClS^+ + NO$	0.76	3.2	2.9
	$C_3H_6ClS^+ + (CH_3NO)$	0.01		
	$C_4H_9S^+ + Cl + NO$	0.17		
	$C_3H_7S^+ + (ClCH_2NO)$	0.05		
	$CH_2SH^+ + (C_2H_4 + CH_2ClNO)$	0.01		
CH_3^+	$C_4H_9ClS+ + CH_3$	0.41	4.6	3.8
	$C_4H_9S^+ + (CH_3Cl)$	0.46		
	$C_3H_7S^+ + (C_2H_5Cl)$	0.11		
	$C_2H_5S^+ + (n\text{-}C_3H_7Cl)$	0.02		
H_3O+	$C_4H_{10}ClS^+ + H_2O$	0.53	2.9	3.5
	$C_4H_9S^+ + HCl + H_2O$	0.47		
$H_3O^+ (H_2O)$	$C_4H_{10}ClS^+ + H_2O$	1.00	2.8	2.6
$H_3O^+ (H_2O)_2$	$C_4H_{10}ClS^+ + 2H_2O$	1.00	2.5	2.3
$H_3O^+ (H_2O)_3$	$C_4H_{10}ClS^+ + 3H_2O$	1.00	2.3	2.1
$CH_3OH_2^+$	$C_4H_{10}ClS^+ + CH_3OH$	0.49	3.5	2.8
	$C_4H_9S^+ + HCl + CH_3OH$	0.33		
	$C_3H_7S^+ + (CH_3Cl) + CH_3OH$	0.13		
	$C_2H_5S^+ + (CH_3Cl^+ CH_2) + CH_3OH$	0.06		
$C_2H_5OH_2^+$	$C_4H_{10}ClS^+ + C_2H_5OH$	0.73	3.0	2.4
	$C_4H_9S^+ + HCl + C_2H_5OH$	0.27		
$(CH_3)_2COH^+$	$C_4H_{10}ClS^+ + (CH_3)_2CO$	1.00	3.0	2.2
NH_4^+	$(C_4H_9ClS{\bullet}NH_4)^+$	0.22	1.7	3.5
	$C_4H_{10}ClS^+ + NH_3$	0.33		
	$C_4H_9S^+ + HCl + NH_3$	0.45		
$CH_3NH_3^+$	$(C_4H_9ClS{\bullet}CH_3NH_3)^+$	1.00	0.93	2.8

[a] The experimental rate constants and the corresponding Su-Chesnavich collision rate constants are given in units of $\times 10^{-9}$ cm^3 s^{-1}.

the Air Force Research Laboratory. This instrument was described in detail elsewhere.[26] Therefore, only a brief description follows as pertains to the current measurements.

The reactant ions were generated in a moderate-pressure source using electron impact ionization. Typically, a thoriated iridium filament was used; however, a rhenium metal filament was alternatively used with the halocarbon source chemicals. A single reactant ion was then selected with a quadrupole mass filter and injected into a fast flow of helium buffer gas entering the tube through a Venturi inlet. A dilute mixture of 0.4% 2-CEES in helium was introduced into the reaction region of the flow tube through a stainless steel inlet 59 cm upstream from a sampling nose cone aperture. After sampling, the product ions and any remaining reactant ions were analyzed using a second quadrupole mass analyzer, with subsequent detection by a conversion dynode multiplier.

The rate constants were obtained by measuring the pseudo-first-order decay of the reactant ion as a function of 2-CEES concentration over a previously measured time. The rate constants have relative uncertainties of ±15% and absolute uncertainties of ±25%.[26] Product ion branching ratios were obtained by plotting the fraction of each product ion versus 2-CEES concentration, then extrapolating to zero concentration. The extrapolation minimized the contributions from secondary reactions of the product ions with the 2-CEES in the flow tube. Product branching ratios for the major product ions typically had better than ±10% uncertainties.[27] Minor channels are reported in the tables, particularly for product ions that were observed with more than one type of reactant ion. While contributions from trace impurities can not be completely ruled out, the major product ions would be of the greatest interest in finding an ion chemistry signature for uniquely detecting the chemical weapon agent simulant.

Materials

The following reagents were used in the measurements: 2-chloroethyl ethyl sulfide (Aldrich, 98%), helium (AGA, 99.997%), oxygen (AGA, 99.999%), nitrogen (Middlesex Gases, 99.999%), nitric oxide (Matheson, 99.5%), nitrogen dioxide (AGA, 99.5%), sulfur dioxide (Matheson, 99%), hexafluoropropylene oxide (Aldrich, 99.5%), carbon dioxide (Middlesex Gases, 99.999%), sulfur hexafluoride (Matheson, 99.8%), ammonia (Matheson, 99.99%), methanol (Baker, 99.7%), ethanol (EM Science, Anhydrous, Denatured), monomethylamine (Matheson, 99.5%), acetone (Baker, HPLC grade), chlorine (Aldrich, 99.5+%), nitric acid (Fisher, 70% w/w), and distilled water. All of the reactant ions listed in Tables 1 and 2 were produced using the pure source gases listed above, except for FSO_2^- and CF_3O^-, which were generated by adding sulfur dioxide and a 20% hexafluoropropylene oxide/helium mixture together in the ion source. The materials were used as obtained from the manufacturer, except for performing freeze−pump−thaw treatments on all of the liquid samples, including the 2-CEES, in order to remove trapped gases.

Results

Tables 1 and 2 show the experimental results for the kinetics survey of positive and negative ions, respectively. The measured rate constants are given along with the collision rate constant determined using the Su-Chesnavich parametrized form.[28,29] The

TABLE 2: Rate Constants for the Reaction of Various Negative Ions with 2-Chloroethyl Ethyl Sulfide (2-CEES) at 298 K Measured in a Selected Ion Flow Tube (SIFT)[a]

ion	products	experimental rate constant × 10^{-9} cm^3 s^{-1}	collision rate constant × 10^{-9} cm^3 s^{-1}
SF_5^-	No Reaction	<0.001	1.8
SF_6^-	No Reaction	<0.001	1.7
F^-	$Cl^- + (C_4H_9FS)$	4.0	3.5
CO_3^-	No Reaction	<0.001	2.2
O^-	$Cl^- + (C_4H_9SO)$	4.3	3.7
O_2^-	$Cl^- + (C_4H_9SO_2)$	2.7	2.8
CF_3O^-	No Reaction	<0.001	2.0
FSO_2^-	$(C_4H_9ClS{\bullet}FSO_2)^-$	0.030	2.0
SO_2^-	$(C_4H_9ClS{\bullet}SO_2)^-$	0.016	2.2
NO_2^-	$(C_4H_9ClS{\bullet}NO_2)^-$	0.13	2.4
NO_3^-	$(C_4H_9ClS{\bullet}NO_3)^-$	0.021	2.2
NO_3^- (HNO_3)	$(C_4H_9ClS{\bullet}NO_3)^- +$ HNO_3 (>97%) $(C_4H_9S{\bullet}NO_2)^- +$ $ClO + HNO_3$ (<3%)	0.026	1.8
Cl^-	$(C_4H_9ClS{\bullet}Cl)^-$	0.23	2.7

[a] The experimental rate constants and the corresponding Su-Chesnavich collision rate constants are given in units of $\times 10^{-9}$ cm^3 s^{-1}. Product ion branching ratios are given in parenthesis where more than a single product has been observed.

TABLE 3: Proton Affinities (PA) of Various Neutrals Used to Bracket the PA of 2-Chloroethyl Ethyl Sulfide (2-CEES)[a]

ion	neutral	proton affinity kJ mol^{-1}	proton affinity kcal mol^{-1}
H_3O^+	H_2O	691	165
$CH_3OH_2^+$	CH_3OH	754	180
$C_2H_5OH_2^+$	C_2H_5OH	776	185
$(CH_3)_2COH^+$	$(CH_3)_2C{=}O$	812	194
NH_4^+	NH_3	854	204
$CH_3NH_3^+$	CH_3NH_2	899	215
$C_4H_{10}ClS^+$	C_4H_9ClS	823[b]	197[b]
$C_4H_9Cl_2S^+$	$C_4H_8Cl_2S$	796[b]	190[b]

[a] The PA of protonated mustard is also given for comparision. PA values have been taken from the NIST Webbook. [b] Calculated using G3(MP2) theory. See text for details.

collisional values have been determined using a polarizability for 2-CEES of 13 Å^3 calculated using the additivity methods of both Miller[30] and Bosque and Sales,[31] along with a dipole moment of 2.27 D from G3(MP2) calculations.

(a) Positive Ion Reactions. Charge and proton transfer reactions are frequently used in positive ion CIMS schemes. The positive ion studies focus on those classes of reactions, particularly the O_2^+, NO^+, and $H_3O^+(H_2O)_n$ ions used in commercial field instruments by SYFT Technologies and Trans Spectra and H_3O^+ used in the Ionicon Analytik model.[11] The rate constants and product ion branching ratios for a wide variety of cations reacting with 2-CEES are listed in Table 1. O_2^+, NO^+, and CH_3^+ all undergo exothermic charge transfer with 2-CEES with rate constants at the collision limit. As expected, the higher the recombination energy of the ion, the more dissociative charge transfer is found. For instance, NO^+ mainly forms the parent 2-CEES cation (76%), while only 11% of the parent ion is formed with O_2^+. In addition to charge transfer, CH_3^+ reacts to form alkyl chlorides. At least four different product ions are formed in each of these reactions, and each product ion includes the S atom.

Many of the positive ion reactions, including the charge transfer reactions, dissociate into common fragment ions at m/z = 109 ($C_3H_6ClS^+$), 89 ($C_4H_9S^+$), 75 ($C_3H_7S^+$), 61 ($C_2H_5CS^+$), and 47 (CH_3S^+) amu. The fragment ions observed with O_2^+ and NO^+ are consistent with the product ions seen in the reaction of these two ions with 2-CEES by Cordell et al. using a drift tube method (chemical–ionization–reaction time-of-flight mass spectrometry, or CIR-TOF-MS).[32] In the NO^+ reaction, Cordell et al. observed the $C_3H_7S^+$ ion as the dominant product, whereas the present SIFT measurements find that nondissociative charge transfer ($C_4H_9ClS^+$) accounts for ~75% of the product ions. $C_3H_7S^+$ has also been seen in the present SIFT study, albeit as a 5% product. The $C_3H_7S^+$ fragment ion has also been found to be the dominant product ion in the CIR-TOF-MS measurements with O_2^+ reactant, with none of the nondissociative charge transfer product in the mass spectrum. The current SIFT data for O_2^+ agree with these results for the major product ion; however, a noticeable fraction of the parent $C_4H_9ClS^+$ product (0.11) has been observed. The differences in the product ion fractions between the two methods is not surprising because the CIR-TOF-MS instrument uses a drift tube with an applied electric field inside the flow reactor to remove the clusters that form at the higher operating pressure of 4.5 Torr.[33] This field raises the energy of the ions; thus, the differences between the two experiments reflect increased dissociation with the increased ion energy and the higher operating pressure, consistent with increases in the recombination energy.

The protonated neutrals react with 2-CEES by mainly three mechanisms: dissociative proton transfer, nondissociative proton transfer, and association. H_3O^+ and the proton hydrates, $H_3O^+(H_2O)_{1-3}$, are common CIMS reagents. Other protonated neutrals have been chosen, in part, to help confirm the calculated proton affinity of 2-CEES. Table 3 lists the proton affinities (PAs) for the corresponding neutrals including the G3(MP2) calculated values for 2-CEES and mustard. Essentially all of the ions react at the collision rate with 2-CEES to produce the protonated species, $C_4H_{10}ClS^+$. H_3O^+ also undergoes dissociative proton transfer to give $C_4H_9S^+$ accompanied by loss of HCl. Each channel accounts for roughly half of the reactivity with H_3O^+. These observations are consistent with the results of Cordell et al. for H_3O^+ and H_3O^+ mixed with humid air leading to the proton hydrate product ions in their instrument.[32]

While the clusters appear to react by proton transfer, an alternative mechanism is possible. In previous studies with cluster ions, we have found that a two step mechanism is common involving ligand exchange, followed by thermal evaporation in the He buffer of the remaining H_2O ligands.[34] Thermal dissociation at 300 K and 0.5 Torr of He can occur in the SIFT when the ligand bond strength is less than about 60 kJ mol^{-1}. This mechanism usually becomes obvious during more detailed studies involving temperature dependences. However, for trace detection of chemical weapons agents, the precise mechanism is irrelevant.

Increasing the proton binding energy in the reagent ion is found to generally increase the amount of nondissociative proton transfer, as expected. An exception is noted for the reagent ions $H_3O^+(H_2O)_{0-3}$ and $CH_3OH_2^+$, where the dissociative to nondissociative fractions are about the same, even though the energy available changes by 63 kJ mol^{-1}. For protonated acetone, $H^+(CH_3COCH_3)$, only nondissociative proton transfer has been found. NH_4^+ is the ion with the smallest proton binding energy to undergo association with 2-CEES and to proceed at a rate lower than the collisional value. For this ion, both dissociative and nondissociative proton transfer have also been observed, the former driven by the formation of HCl or NH_4Cl. The reagent ion $CH_3NH_3^+$ only produces the association product

TABLE 4: Summary of the Energetics Results from G3(MP2) Calculations for 2-Chloroethyl Ethyl Sulfide (2-CEES) and Mustard (HD)

G3(MP2)	2-CEES C_4H_9SCl	mustard (HD) $C_4H_8SCl_2$
Ionization Potential (IP) eV	8.59	8.74
Fluoride Affinity (FA) kJ mol^{-1}	64	104
Proton Affinity (PA) kJ mol^{-1}	823	796

ion at about a third of the collisional value. The present results are consistent with the proton affinity (PA) calculation for 2-CEES, which shows a PA between that of acetone and ammonia.

(b) Negative Ion Reactions. Table 2 shows the rate constants and product ion branching ratios for the reactions of various negative ions with 2-CEES. Several of the typical negative ion CIMS reactant ions do not react with 2-CEES, that is, SF_5^-, SF_6^-, CO_3^-, and CF_3O^-. Given that no product ions have been observed, an upper limit of 1×10^{-12} cm^3 s^{-1} is placed on the rate constants for these reactions. O^-, O_2^-, and F^- react with 2-CEES at the collision rate constant. However, they all react to produce only a Cl^- product ion, which is so common that it will not be useful for 2-CEES detection using a CIMS reactor. FSO_2^-, SO_2^-, NO_2^-, NO_3^-, and Cl^- react relatively slowly to give an association product ion with bimolecular rate constants in the 10^{-10} to 10^{-11} cm^3 s^{-1} range at 0.4 Torr He buffer gas. No fluoride (F^-) or oxide (O^-) transfer product ions have been observed with any of the reactant ions. The $NO_3^-(HNO_3)$ reaction proceeds by slow ligand exchange to yield the same product ion as found in the bare NO_3^- reaction. The $NO_3^-(HNO_3)$ reaction is about 1% efficient, which is too slow to be useful for 2-CEES detection.

(c) Structure and Energetics Calculations. Information is available in the literature on the energetics and structures of the CH_3S^+, $C_2H_5S^+$, and $C_3H_7S^+$ product ions.[12−25] However, little is known about the other fragment ions observed in the positive ion survey, and little is known about the thermochemistry and various ion affinities of neutral 2-CEES and mustard. Consequently, we have performed theoretical calculations of minimum energy structures and energetics for the observed product cations. In addition, we have calculated ionization potentials as well as proton, fluoride, electron, and oxide affinities of 2-CEES and mustard have also been calculated. The 0 K energies, 298 K enthalpies, and 298 K free energies determined are given in Table S1 of Supporting Information as calculated using Gaussian 03[35] at the G3(MP2) level of theory[36] for the minimum energy structures listed. Table 4 summarizes the various affinities and ionization potentials for 2-CEES and mustard. The G3(MP2) method is computationally less expensive than G3 theory[37] while retaining much of the accuracy, and it is better than the lower level G2 theory.[38] An average absolute deviation of ±5.4 kJ mol^{-1} is found for energies calculated by G3(MP2) versus the ±4.2 kJ mol^{-1} deviation with G3. The wave function stability has been verified for all of the minimum energy structures at the HF/6−31G(d) level. The geometries calculated are shown in Figures S1−S7 of Supporting Information and have been optimized at the MP2(Full)/6−31G(d) level.

The goal of the experiments is to find fingerprint product ions for the reaction of various types of ions with the 2-CEES surrogate in order to extrapolate to reactions with mustard gas. As indicated previously, the structure calculations are intended to relate the observed product ions to minimum energy structures to gain some insight into the possible reaction pathways. Barriers on the potential surfaces will influence the observed product ion branching ratios. However, a complete understanding of the reaction dynamics is beyond the scope of the current work.

1. Negative Ion Structures. No stable anion structure for $C_4H_9SCl^-$ was found for the 2-CEES arrangement, nor could a stable geometry be found for the $C_4H_8Cl_2S^-$ mustard anion, indicating that the electron affinities are negative. Attempts to determine a stable geometry for adding an O^- to either 2-CEES or mustard also failed, as the molecular structures simply moved toward dissociation during the optimization process. An F^- can be added to the central S atom in both mustard and the 2-CEES surrogate. However, the fluoride affinity (FA) is small, with long S−F distances of 2.24 and 2.28 Å in binding to 2-CEES and mustard, respectively. These structures are shown in Figure S1. The respective fluoride affinities (FAs) for 2-CEES and mustard are 64 and 104 kJ mol^{-1}. These small fluoride affinities explain the lack of reactivity with the fluoride transfer agents attempted in the present work, all of which have higher $X-F^-$ bond strengths.

2. $C_4H_9SCl^+$, $C_4H_{10}SCl^+$ (m/z = 124, 125). The minimum energy structures for neutral 2-CEES, the 2-CEES cation, and protonated 2-CEES are shown in Figure S2a−c. The electron is removed from the central S atom in the cation and the terminal Cl is bent back toward the positive charge center. Neutral 2-CEES has a substantial negative charge on the central S atom, which is consistent with favoring the addition of a proton to the S center. Neutral 2-CEES has a staggered arrangement for the terminal Cl as expected for a straight chain alkyl thioether.

3. $C_3H_6SCl^+$ (m/z = 109). The $C_3H_6SCl^+$ ion shown in Figure S3b results from CH_3 cleavage from ionized 2-CEES. However, the ion formed by hydrogen migration in Figure S3a is 31.7 kJ mol^{-1} (0.33 eV) lower in energy. This rearrangement results in terminal methyl groups on both sides of the molecule.

4. $C_4H_9S^+$ (m/z = 89). As with $C_3H_6SCl^+$, the minimum energy structure for $C_4H_9S^+$ also includes a hydrogen migration to leave terminal methyl groups on both sides after loss of Cl. The CH_3 group on the ethyl chain is bent back toward the central S atom; however, the cis-type structure (Figure S4b) is only 2.6 kJ mol^{-1} (0.027 eV) higher in energy, also having CH_3 groups on the ends. No structure could be found having a $C_2H_4SC_2H_5^+$ arrangement similar to the initial 2-CEES structure with the C−Cl bond simply clipped. There is a stable structure involving terminal $-CH_2$ rotation to form a triangular CH_2-S-CH_2 structure (not shown). This triangular isomer lies 12.1 kJ mol^{-1} (0.13 eV) higher in energy than the minimum energy structure and would require more substantial rearrangement than the H migration pathway.

5. $C_3H_7S^+$ (m/z = 75). The 75 amu ion is analogous to the 109 amu ion, except that the parent ion has lost the $-CH_2Cl$ terminal group instead of a CH_3. The minimum energy structure in (Figure S5a) has undergone a H migration to leave a pair of terminal methyl groups as with all of the ions discussed above. The isomer with a terminal CH_2 from cleaving the $-CH_2Cl$ group (Figure S5b), prefers to have the terminal $-CH_3$ on the ethyl chain bent back toward the more positively charged sulfur center. This isomer is 41.0 kJ mol^{-1} (0.42 eV) higher in energy than the minimum energy structure. These results are in excellent agreement with the calculations of Chalk et al. of the potential energy surface of the rearrangement and fragmentation pathways of $C_3H_7S^+$ ions at the G2 level of theory, where the energy difference is 40.1 kJ mol^{-1}. They have also found that a 172 kJ mol^{-1} (1.8 eV) barrier exists for isomerization from isomer (S5b) to the global minimum structure (S5a).[14]

6. $C_2H_5S^+$ (m/z = 61). As seen with the other product ions, the minimum energy geometry for this ion is 2-CEES$^+$ with the C_2H_4Cl chain removed, followed by a H migration to the terminal S atom as shown in Figure 6a. The $C_2H_5S^+$ structure (Figure S6b) obtained by simply cleaving the S−C_2H_4Cl bond is a transition state lying 276 kJ mol^{-1} (2.9 eV) higher in energy. The fragment ion (6a) is structurally similar to the 75 amu structure in Figure 5a with an additional loss of −CH_2 and to the 89 amu structure in Figure 3a with a loss of C_2H_4. This product ion has been observed with the reactions of O_2^+, CH_3^+, and $CH_3OH_2^+$, where neutral fragments CH_3Cl and/or HCl must be formed for this reaction pathway to be exothermic for the latter two reactant ions. This product ion may be formed by breaking two bonds, which is obviously a much more complicated, but still viable, reaction mechanism.

7. CH_2SH^+ (m/z = 47). The global minimum energy geometry for this cation in Figure S7 has a CH_2SH^+ mercapto methyl arrangement. The thiomethoxy CH_3S^+ ion is 130 kJ mol^{-1} higher in energy, in decent agreement with the 138 kJ mol^{-1} difference found by Radom and co-workers using G2 theory.[13,15] This product channel has only been observed with O_2^+ and NO^+ as reactants. For the O_2^+ reaction, the mechanistically simplest exothermic pathway involves loss of CH_3 from the −C_2H_5 chain and C_2H_3Cl from the −C_2H_4Cl chain. However, the exothermic route for the NO^+ reaction utilizing the least number of bond fission and creation processes would involve creation of CH_2ClNO with loss of C_2H_4 from the ethyl chain.

Experiments with $C_3H_7S^+$ ions show that the $CH_3CHSCH_2^+$ ion dissociates via either C_2H_4 or H_2S elimination.[23−25] Thus, it is possible that the minor 47 amu product ions originate from the 75 amu $CH_3CH_2SCH_2^+$ ion originally produced from 2-CEES$^+$, which can isomerize to an ion−neutral complex that dissociates to CH_2SH^+ and C_2H_4 as calculated by Chalk et al. using G2 theory.[14] However, they have found a 204 kJ mol^{-1} (2.1 eV) barrier to this isomerization step on the potential energy surface. While the exothermicity of the reactions producing $C_3H_7S^+$ here would be sufficient to overcome the barrier, this hindrance would limit the amount of 47 amu product ions formed, consistent with CH_2SH^+ being a minor product ion.

Discussion

By surveying different types of ions, we have gained insight into the reaction mechanisms of 2-chloroethyl ethyl sulfide (2-CEES). Combining the experimental results with the calculations of the various affinities and energetics of both 2-CEES and mustard allows for sound transfer of the present results to mustard detection schemes that may be used in both CIMS and ion mobility instruments. As shown in Table 4, the calculated ionization potential (IP) and proton affinity (PA) differences between 2-CEES and mustard are only 0.15 and 0.28 eV, respectively. These small differences strongly indicate that the charge and proton transfer kinetics should be similar for mustard and 2-CEES. The best CIMS schemes involve fast reactions that make unique ions, and a number of such reactions have been found here. A small difference in the kinetics of the two neutrals will stem from the fact that the mustard collision rate constants will be about 30% smaller than those involving 2-CEES because the former is more symmetric and consequently has a smaller dipole moment than the latter.

The IP of 2-CEES at 8.59 eV is lower than any of the charge transfer cations we have studied, in particular, the IPs of O_2 (12.07 eV) and NO (9.26 eV).[39] The IP of mustard is also lower than that of NO. The reactions of these ions with 2-CEES are rapid, showing that they are good candidates for mustard detection. However, O_2^+ produces mainly dissociative charge transfer with 2-CEES and will not be as selective as NO^+ that produces $C_4H_9SCl^+$ in 76% of the reactions. At higher reaction pressures, it is possible that dissociation will be suppressed.[40−42] Nevertheless, similar results are expected for reactions with mustard. Therefore, the commercial SYFT and SIFT-MS instruments,[11] which use NO^+ as a chemical ionization agent, may be useful for mustard detection. One caveat is that the reactions of the $C_4H_9SCl^+$ product ion with major air components such as H_2O, O_3, and CO_2 have not been studied. Cordell et al. have reacted H_3O^+ with 2-CEES in humid air from 0 to 80% humidity and have found no change in detection sensitivity (i.e., the $C_4H_9SCl^+$ peak height) in the CIR-TOF-MS.[32] However, a fast reaction with any of these species will degrade the scheme. A future study in our laboratory will address this issue.

Other studies of these reactant ions with comparable neutral molecules have shown similar results. Španěl and Smith have observed dissociative charge transfer in O_2^+ reactions with other dialkyl sulfides in a SIFT at 298 K, namely, diallyl sulfide, $(CH_2{=}CH{-}CH_2)_2S$, and dimethyl sulfide, $(CH_3)_2S$,[43] including loss of alkanes and alkenes as seen with 2-CEES. Španěl and Smith have also observed the formation of hydrocarbon cation products in the reaction of diallyl sulfide with O_2^+.[43] Elimination of H_2S from $CH_3CH_2SCH_2^+$ would produce $C_3H_5^+$ at m/z = 41 amu, which has not been observed in the reactions of 2-CEES with any of the positive ions in the SIFT. Chalk et al. have shown that this pathway for loss of H_2S requires several isomerization steps with barriers to each step,[14] possibly explaining why this ion is not seen in the current SIFT experiments. While we cannot observe the associated neutral fragments, the reaction energetics indicates that some of the minor product channels must incorporate the corresponding neutral of the reactant ion into the neutral fragment to be energetically allowed at room temperature. Similar reactivity has been seen in previous SIFT experiments in the reactions of NO^+ with hydrocarbons[44] and ethers.[45]

The present results show that other promising reaction schemes could be based on reactions of a protonated molecule with 2-CEES or mustard through either proton transfer or clustering. Both mechanisms produce ions incorporating 2-CEES. The PA of 2-CEES has been calculated using G3(MP2) theory to be 823 kJ mol^{-1}, which is bracketed by the PA of acetone (812 kJ mol^{-1}) and ammonia (854 kJ mol^{-1}). This value is consistent with the product ion distributions observed for these two protonated reactant ions in Table 1. Protonated acetone only reacts via nondissociative proton transfer indicating the similarity of the proton affinities of 2-CEES and acetone. The fact that the reaction occurs at the collisional value within the uncertainty indicates that the sign of the calculated energetics is correct. NH_4^+ gives both proton transfer and association product ions; yet, proton transfer is calculated to be 34 kJ mol^{-1} endothermic. However, the amount of rovibrational energy stored in 2-CEES and NH_4^+ is substantial and can easily drive this reaction. By using the vibrational frequencies calculated here, it is estimated that, on average, 27 kJ mol^{-1} is available to drive the reaction. In considering that the proton transfer channel is only 16% efficient, there is sufficient energy to drive a slightly endothermic process. Calculations for the mustard agent, $C_4H_8Cl_2S$, give a PA of 796 kJ mol^{-1} at the G3(MP2) level of theory. The PA difference may mean that protonated acetone will not transfer its proton efficiently to mustard, although the level of uncertainty and the amount of available energy are sufficient to preclude a definitive conclusion.

In related studies, Smith and Španěl have seen that H_3O^+ reacts with both diallyl sulfide and dimethyl sulfide only by nondissociative proton transfer at the collision rate constant.[43] Adams and co-workers have also found that H_3O^+ undergoes nondissociative proton transfer with methyl ethyl sulfide, $CH_3SC_2H_5$.[46] These observations are consistent with the proton affinities of dimethyl sulfide of 833 kJ mol^{-1} and methyl ethyl sulfide of 845 kJ mol^{-1}. Diethyl sulfide has a literature PA of 858 kJ mol^{-1},[39] further supporting the calculated PAs. The trends are again consistent with the current experimental results and calculated PAs. However, the additional channel for loss of Cl with 2-CEES arises with the protonated reactants because formation of HCl is highly exothermic. Cordell et al. have seen many similarities in the product ions observed in the mass spectra for 2-CEES and mustard,[32] which follows given the similarity in both the structures and the energetics calculated for the surrogate and the chemical agent.

The most common positive CIMS agent, H_3O^+, and its hydrates may work as effective ionization agents. The bare and hydrated forms of H_3O^+ all protonate 2-CEES, although the bare ion generates $C_4H_{10}SCl^+$ in only about 50% of the collisions. This fraction is still substantial, and the ease of use of this scheme may prove important. Furthermore, clustering of the species with high proton binding energy may also provide a potential detection scheme. These reactions are fast; that is, the rate constant is slightly less than collisional, but the effective two-body rate constants may increase at higher pressure. Selectivity should occur because the neutral stays intact. Whether or not protonated 2-CEES reacts with common air molecules also needs to be investigated.

The negative ion reactions show two basic trends. First, the ions that react to give unique association product ions have bimolecular rate constants that are far below the collision rate constant. Second, the ions that react fastest all give the same product ion, Cl^-, which would not make them very useful as detection agents. These trends are consistent with the G3(MP2) calculations of the FA of 2-CEES and mustard that show only a weak binding for F^- and no stable structures for adding either an electron or an O^-ion. The association reactions with ions such as NO_3^- and NO_2^- generate unique product ions. As the present chemistry has been measured at low pressure (0.4 Torr He buffer gas) and it involves three-body processes, a reasonable bimolecular rate constant may be found in a higher pressure CIMS apparatus. Thus, these reactions might still be possible candidates for selective and sensitive detection schemes, but their success obviously remains uncertain.

Conclusions

A survey of the reactions of numerous positive and negative ions with mustard surrogate 2-chloro ethyl ethyl sulfide (2-CEES) has been conducted in a selected ion flow tube (SIFT) at 298 K. The rate constants and product ion branching ratios have been measured to search for ion−molecule reactions that have large rate constants and produce unique product ions. The experimental measurements are supplemented by G3(MP2) calculations for the 2-CEES product cations and the closely related mustard (HD) molecule so that the 2-CEES data can be transferred to finding suitable reagent ions for use in a CIMS instrument for real time detection of the mustard. The negative ions typically used in CIMS instruments are essentially unreactive with 2-CEES. A few negative ions do undergo three-body association to give a unique product ion, but the rate constants are small in the SIFT. The three-body nature of the reactions raises the possibility that the rate constants could increase to values that could be reasonable for mustard detection in higher pressure CIMS instruments, but their utility remains dubious.

Positive ions, on the other hand, typically react at the collisional limit, primarily by charge and proton transfer, some of which is dissociative. For ions with high proton binding energies, association has also been observed. Many of these reactions produce ions with the 2-CEES intact, including the parent cation, the protonated cation, and clusters. Given the structural similarities of 2-CEES and mustard from the theoretical calculations, the various affinities determined for 2-CEES and mustard indicate that the present results for 2-CEES should allow an appropriate reactant ion to be selected for testing with mustard. Any of a number of reagent ions appears likely to have both the sensitivity and the selectively for mustard detection. These include ions in use in common commercial instruments.[11] Consequently, the combination of experimental studies of 2-CEES chemistry and theoretical calculations on ionic properties of 2-CEES and mustard appears to show great potential in determining the optimal ion chemistry that can be extrapolated to mustard detection via CIMS. Future studies will examine reactions of the ionized forms of 2-CEES with common air molecules that might be encountered in a field CIMS instrument.

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Supporting Information Available: Energetics results and figures containing parameters for optimized geometries. This material is available free of charge via the Internet at .

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