



Survey of ion energetics properties of chemical weapon agent (CWA) breakdown products using G3(MP2) theory

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ABSTRACT

The ion energetics properties of the major breakdown products of chemical weapons agents (CWAs) have been calculated using G3(MP2) theory to gain insight into which reactant ions in chemical ionization mass spectrometry (CIMS) would be optimal for detecting the CWAs. These results would also offer insight into which ions are formed in ion mobility spectrometry (IMS) detectors for CWA that use atmospheric pressure ionization sources. The ionization energies (IEs), proton affinities (PAs), electron affinities (EAs), and fluoride affinities (FAs) have been calculated for the major degradation products of sulfur mustard, the G-series nerve agents, and VX based on optimized structures using G3(MP2) theory. Electron attachment is found to yield an unstable parent anion or leads to an ionic structure with negative EA. The sulfur and nitrogen containing degradation products all have IEs < 9 eV, implying that charge exchange with NO⁺ should be a favorable detection route. The strictly alkylphosphorus compounds all have IEs around 10 eV, implying that they would likely form a unique association product with NO⁺. All of the compounds with a P=O moiety most favorably add an H⁺ on the O atom with PAs of ~900 kJ mol⁻¹. 2-(Diisopropylamino) ethane thiol (DESH) and ethyl-N,N-dimethyl phosphoramidate (EDPA) both have amine nitrogens that can readily accept a proton, with PAs > 900 kJ mol⁻¹. The least favorable protonation site is the oxygen that connects the phosphorus center to the different alkyl groups. The PAs indicate that non-dissociative proton transfer with protonated acetone or ammonia should provide good selectivity, likely with a large rate constant as seen in previous kinetics studies with CWA simulants. All of the breakdown products except 1,4-dithiane can attach a F⁻ ion in at least one stable location. However, the corresponding FAs are too low to favor this process with the normal CIMS fluoride transfer anions.

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1. Introduction

Being able to rapidly detect chemical threats with high sensitivity is a major focus for defense and security efforts domestically and internationally [1–3]. Favored methods, such as mass spectrometry (MS) [4–7] and ion mobility spectrometry (IMS) [1,8,9] require ionizing the sample for detection, preferably by ion–molecule reactions that generate a single distinct ionic species for accurate identification. Detecting chemical weapons agents (CWA) that can cause harm at extremely low exposure levels is a very important application for protecting security personnel, first responders and the general public under scenarios where they may be exposed to these compounds [1,2,10]. Schematic structures for the common CWA are shown in Fig. 1 adapted from the literature [11,12].

A recent review highlights the current and future applications of IMS [10], which has been widely deployed in field detectors for CWA. In addition, a National Academy of Sciences report [13] from 2005 indicates that chemical ionization mass spectrometry (CIMS) [14–19] demonstrates the most promise for rapid development into a real-time air monitor. Consequently, this report has prompted a recent series of experiments into the ionization chemistry of CWA simulants [20–22].

Surveys of the kinetics of reactions with structurally analogous simulants for sulfur mustard, sarin, soman and VX have identified several ion–molecule reactions that have large rate constants and generate signature product ions, both of which are important for accurate, sensitive detection with either CIMS or IMS [4–6,20–24]. The experimental data have been further validated by theoretical calculations of the ion energetics properties and reaction mechanisms. In turn, calculations of the ion energetics properties of the actual CWA molecules have afforded extrapolation from the measurements and energetics of the simulants to isolate potential reactant ions for live agent detection [20–22,25].

It is likely that any detection application for CWA will be sampling agents that have decomposed, particularly in the disposal

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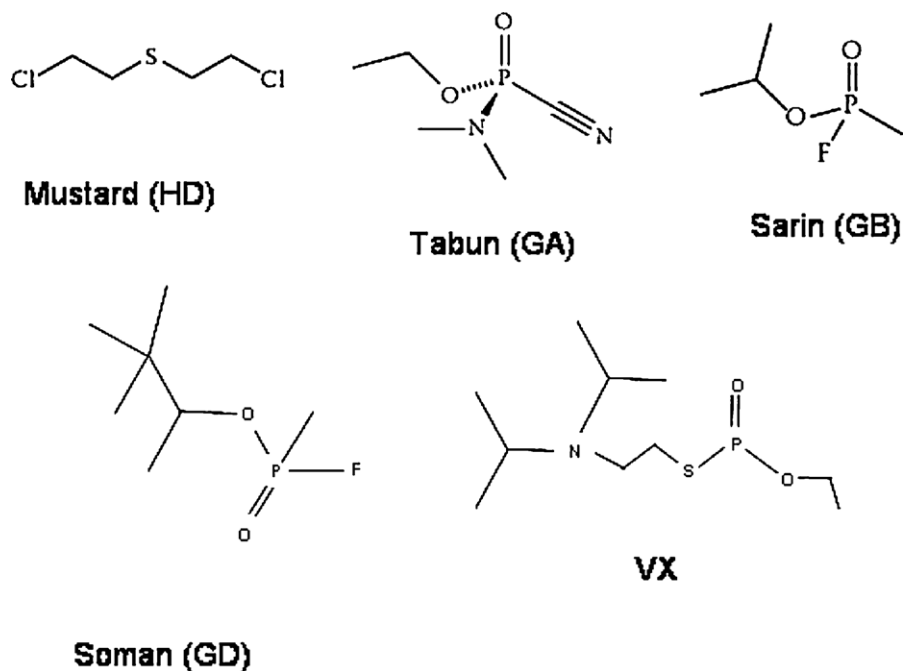


Fig. 1. Schematic chemical representations of the major chemical weapon agents (CWA) adapted from the literature [11,12]. In the order shown, they are: sulfur mustard (HD); tabun (GA); sarin (GB); soman (GD); and VX.

of stockpiles of CWA that have been stored for many years. The major decomposition products of CWA are well known and have been thoroughly reviewed [26,27]. Hydrolysis is the major degradation pathway especially for mustard-based munitions that have been uncovered in marine environments and for the more persistent agents such as VX. Therefore, an additional consideration when choosing reactant ions for introduction into analyzers such as CIMS and IMS will be the ion peaks produced by the breakdown products that will undoubtedly be present [26,27].

While it would be ideal to conduct similar ion-molecule chemistry surveys for the major breakdown products using selected ion flow tube-mass spectrometry (SIFT-MS) as done for the CWA surrogates [20–22], the large number of product compounds makes this task impractical, as does the inability to obtain or use some of them in a standard laboratory facility. However, the previous combination of experiment and theory has shown that the theoretical calculations agree very well with the experimental data [20–22,25]. Thus, the calculations have proven to be an accurate guide to predicting what ion-molecule reactions to target for practical detection schemes.

Consequently, a series of calculations have been performed at the G3(MP2) level of theory for reactions involving the main positive and negative ion CIMS candidates used in the earlier SIFT-MS work [20–22] to find ion energetics properties of the major degradation products of sulfur mustard, the G-series nerve agents, and VX [26,27]. A schematic illustration of the breakdown products studied is shown in Fig. 2 again adapted from the literature [11,12]. The trends observed in the previous surrogate chemistry studies have shown that positive ion reactions are most promising, particularly proton transfer or charge exchange [20–22]. Consequently, the ionization energies (IE) and proton affinities (PA) of nine predominant decomposition products have been determined. As CIMS field instruments have often used negative ion reactions, both F^- transfer and electron attachment reactions with surrogates were also investigated despite finding limited utility for anion chemistry in the earlier studies, even when reaction was energetically allowed [20–22].

2. Material and methods

The 0 K energies and 298 K enthalpies were calculated for structures optimized using the compound G3(MP2) theory [28] in *Gaussian 09* [29], in which structures were determined at the MP2 (Full)/6-31G(d) level. This level of theory was adopted in the previous combined SIFT-MS experimental and theoretical studies for understanding the observed product distributions based upon the ion energetics properties [20–22], largely because the computational cost was lower [28], while maintaining a level of accuracy similar to the more costly G3 method [30].

For each of the breakdown products, the structural optimization was carried out for the neutral molecule, singly charged cation, and the singly charged anion in order to obtain the IE and EA, respectively. The stable protonation and fluorination sites found are shown in Fig. 3 and cross referenced in Table 2 for the energetics calculated. Bera et al. published an exhaustive theoretical study of the products of protonation and fluorination for VX [25]. In that work, they calculated minimum energy structures for bonding to each of the 16 heavy atom sites of VX with approach from a total of 80 paths for H^+ and 76 paths for F^- . Just under 70% of the paths led to stable structures with the proton on the oxygen of the P=O moiety, the amine N, the oxygen linking the phosphorus and alkyl groups (P–O–C), or the sulfur [25]. Previous calculations for the mustard and nerve agents also showed that the proton was more favorably added to the sulfur or oxygen constituencies. Therefore, structure calculations for the protonated degradation products were primarily focused on attaching the proton to functional groups that were present in the various breakdown product molecules. However, attempts were also made to put the H^+ on select alkyl carbons as done by Bera et al. [25]

Ionization energies (IEs) and electron affinities (EAs) were determined as the difference in the 0 K energies of the neutral molecule and the molecular cation and anion, respectively, with both species in their ground electronic, vibrational, and rotational states. As done previously, fluoride affinities (FA) were determined as the difference between the G3(MP2) 298 K enthalpy for the

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