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Hydrolysis of VX on Concrete: Rate of Degradation by Direct Surface Interrogation Using an Ion Trap Secondary Ion Mass Spectrometer

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The nerve agent VX (*O*-ethyl *S*-2-diisopropylaminoethyl methylphosphonothiolate) is lethal at very low levels of exposure, which can occur by dermal contact with contaminated surfaces. Hence, behavior of VX in contact with common urban or industrial surfaces is a subject of acute interest. In the present study, VX was found to undergo complete degradation when in contact with concrete surfaces. The degradation was directly interrogated at submonolayer concentrations by periodically performing secondary ion mass spectrometry (SIMS) analyses after exposure of the concrete to VX. The abundance of the [VX + H]$^+$ ion in the SIMS spectra was observed to decrease in an exponential fashion, consistent with first-order or pseudo-first-order behavior. This phenomenon enabled the rate constant to be determined at 0.005 min^{-1} at 25 °C, which corresponds to a half-life of about 3 h on the concrete surface. The decrease in [VX + H]$^+$ was accompanied by an increase in the abundance of the principal degradation product diisopropylaminoethanethiol (DESH), which arises by cleavage of the P–S bond. Degradation to form DESH is accompanied by the formation of ethyl methylphosphonic acid, which is observable only in the negative ion spectrum. A second degradation product was also implicated, which corresponded to a diisopropylvinylamine isomer (perhaps *N,N*-diisopropyl aziridinium) that arose via cleavage of the S–C bond. No evidence was observed for the formation of the toxic *S*-2-diisopropylaminoethyl methylphosphonothioic acid. The degradation rate constants were measured at four different temperatures (24–50 °C), which resulted in a linear Arrhenius relationship and an activation energy of 52 kJ mol^{-1}. This value agrees with previous values observed for VX hydrolysis in alkaline solutions, which suggests that the degradation of submonolayer VX is dominated by alkaline hydrolysis within the adventitious water film on the concrete surface.

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Introduction

VX is a highly toxic nerve agent that is part of the United States chemical warfare arsenal (*1–3*). At the present time, the U.S. is in the process of destroying VX-containing weapons in compliance with the Chemical Weapons Convention. However, the compound remains of interest because of possible use by rogue nations or terrorist groups. In fact, members of the Japanese terrorist group Aum Shinryko used VX to murder a disaffected cult member who was trying to escape (*4*).

The compound can be persistent in the environment because it is highly adsorptive. On an environmental or industrial surface, VX remains dangerous because dermal contact can result in toxic effects. In addition, the strong adsorptivity can make VX difficult to analyze. For example, in an earlier study, VX disappearance was attributed to strong chemisorption to soil (*5*). Attempts to extract the compound using supercritical CO₂, and to analyze it using thin-layer chromatography, were confounded by its strong adsorptive tendency (*6, 7*). In addition to strong surface adsorption, VX will undergo degradation, which can occur as a result of environmental exposure (*6*) or decontamination efforts (*8–10*). The rate of VX degradation is of particular interest, and is understood as it occurs in alkaline and acid solution. However, degradation pathways and rates occurring on surfaces have been less widely studied. It is known that surface degradation rates can be substantially different from solution degradation rates (*5, 6*). Direct investigation of VX hydrolysis on mineral surfaces has been undertaken by Wagner and co-workers, who have used solid-state NMR to look at reactions on MgO, CaO, and zeolite nanoparticles (*11–14*). But there have been few direct investigations of hydrolysis occurring on naturally occurring or industrial surfaces. Common materials such as soil particles and concrete have highly heterogeneous surfaces which makes characterization difficult.

The occurrence of multiple degradation pathways also complicates investigation of VX behavior. It has been known for some time that the compound can undergo P–S, P–O, and S–C bond cleavages, leading to different hydrolysis products (*6,9,10,15*). Some of these are quite toxic, and others undergo secondary reactions that form yet other toxic compounds. Like VX, most of the resulting compounds are highly surface adsorptive.

A desire to understand the behavior of VX on concrete (because concrete is widely used in construction of civilian and government installations) motivated the present study. Specifically, we sought to identify reaction pathways and degradation kinetics, so that VX persistence could be estimated after an exposure event. We have attacked this problem by applying static secondary ion mass spectrometry (SIMS) (*16*) to the detection of VX on surfaces: the technique enjoys submonolayer sensitivity, and yields compound-specific information on adsorbed VX and its degradation products. In previous research, identification of VX on soil (*17*) and concrete particles (*18*) was demonstrated using an ion trap (IT-) SIMS instrument. Further experiments showed that VX would degrade to a variety of compounds when in contact with concrete, and that these compounds were detectable. This suggested that degradation pathways and kinetics could be discerned by temporally monitoring ion abundances of batches of concrete exposed to VX. The present study describes these experiments, which resulted in the direct measurement of VX degradation kinetics on concrete, and the calculation of a mean activation energy for the

degradation process which is in reasonable agreement with activation energies for hydrolysis in alkaline solutions.

Experimental Section

Caution. *VX is a highly lethal compound capable of killing or injuring at extremely minute doses. The compound must be handled only in approved chemical warfare surety laboratories by trained agent chemists.*

Sample Generation. All sample preparation and analyses were performed at the chemistry laboratory of the U.S. Army West Desert Test Center (WDTC), Dugway Proving Ground, Dugway, UT; this laboratory is equipped with appropriate engineering and administrative controls for handling chemical warfare agents.

Concrete samples were collected from the Czech republic as part of a companion study to evaluate VX degradation on a variety of concrete samples. The Czech concrete was utilized because it had been previously characterized. The samples had not previously been exposed to VX. Prior to experimentation, the samples were crushed using a hammer, and then ground using a mortar and pestle. The surface areas of the concrete samples were measured using N_2 adsorption (BET method), and found to be 3.5 m^2/g (*19*).

The VX used in the study was the property of the U. S. Army, and was an analytical reference standard. The compound was received and used as either the neat liquid, or as a 1 $\mu g/\mu L$ (2-propanol) standard solution. The primary standard solution was used for serial dilutions. For a given surface coverage, the objective was to dilute the primary standard so that the volume of standard solution (in μL) was roughly equal to the mass of the sample (in milligrams). Crushed and weighed concrete samples (~50 mg) were covered with a volume of the standard solution, which contained a mass of VX equivalent to between 0.3 and 0.5 monolayers, respectively. The mass of VX corresponding to monolayer coverage was estimated by assuming that the molecular area of the compound was equivalent to 95 $Å^2$, which is the area of a circle having a radius equal to half the length of the molecule on the surface (estimated at 5.0 Å). This radius estimate assumed that the molecule laid flat on the surface, and was generated using molecular mechanics calculations (Cerius^2, Molecular Simulations, Inc., San Diego, CA). If the molecule exists on the surface in an upright fashion, or is coiled, then the monolayer coverages will be somewhat less than the values stated in this study.

The samples were also spiked with an organic salt, which was originally intended to serve as an internal standard against which the behavior of VX could be measured. The compound chosen was tetrabutylammonium bromide (TBN, Aldrich, Milwaukee, WI). The TBN was applied in the same fashion as the VX, assuming that the molecular area of the TBN cation was 79 $Å^2$. This quantitation method was superseded by the normalization method described below.

Once the samples were spiked, the solvent was removed under a gentle stream of nitrogen, which generally required 10 to 15 min. As soon as the samples were dry, analysis commenced. Approximately 1 mg of particles were attached to a sample holder (the head of a #18 nail) using double-sided tape. The sample holder was then attached to the probe for analysis.

When the analyses were complete, samples were immersed in bleach solution to neutralize the residual VX. The waste from the decontamination procedure was then treated as hazardous waste and disposed of appropriately.

Additional samples from the same exposure batch were serially analyzed, carefully keeping track of the analysis time relative to the initial exposure. Initial analyses were performed at ambient temperature, which was 24 °C. Subsequent degradation experiments were performed at 30, 35, and 50 °C by placing the vials containing the spiked concrete samples in a constant temperature water bath maintained at these temperatures.

Soil and concrete particles exposed to diisopropylamino-ethanethiol (DESH) were also analyzed, at a concentration of approximately 0.5 monolayer. DESH was applied as a 2-propanol solution starting from the hydrochloride salt (TCI Chemicals, Tokyo). A molecular area of 38 $Å^2$ was used to calculate surface coverage (*18*).

Ion-Trap Secondary Ion Mass Spectrometry (IT-SIMS). An IT-SIMS instrument located at the WDTC was used in the current study. The instrument has been described previously; briefly, it is based on a Teledyne Discovery 2 IT mass spectrometer (Mountain View, CA) that was modified for SIMS (*20−22*). The vacuum housing containing the IT was located in a chemical warfare agent surety hood, where all agent operations were performed. The vacuum housing was connected to the power supplies and computer by elongated cables. Two mechanical pumps which back-pumped the turbomolecular pump and the insertion lock were also located outside the hood, but were vented back into the hood with Tygon tubing.

The Teledyne IT was modified for SIMS by the addition of an ReO_4^- primary ion gun, an offset dynode/multichannel plate detector system, and an insertion lock for introducing the sample using the direct insertion probe. The ReO_4^- beam is directed through the ion trap along the main axis of the device, passing through a hole in one end cap, and striking the sample holder (containing the concrete particles), which is located behind a 1-mm diameter hole in the opposite end cap. The ReO_4^- ion gun was operated at 4.5 keV, at a primary ion current of 30 pA (measured using a Faraday cup probe). The ReO_4^- beam is gated to impact the sample only during the initial period of the IT-SIMS analysis sequence. Secondary ions sputtered from the sample surface are focused into the ion trap by a small, cylindrical, electrostatic lens. The electrostatic potential of the sample holder is not controlled; instead, the potential of the sample holder floats at the ambient (and variable) potential of this region of the ion trap (*23*). Upon entering the trap, the secondary ions undergo collisions with the He bath gas (3×10^{-5} Torr), and lose sufficient kinetic energy such that they are trapped by the oscillating RF field. Once trapped, the ions can be mass selectively ejected from the ion trap to the detector (MS^1), which is located off-axis on the same side of the ion trap as the ReO_4^- primary ion gun.

In a typical MS^1 experiment, the ion trap was operated at base RF amplitude corresponding to a low mass cutoff of 40 amu. Ionization time was typically 250 ms, after which the mass spectrum was recorded. A single "scan" consisted of 10 summed spectra. A normal analysis would consist of about 30 scans, or 300 summed spectra.

The primary ion dose for a typical analysis was calculated at about 1.5×10^{12} ions/cm^2, using the ionization time and scan acquisition information above, the area irradiated (8×10^{-3} cm^2), and the primary ion current (30 pA). At this dose, the surface of the sample is not considered to have been seriously perturbed (*24−26*); observed secondary ion yields remained relatively constant over the duration of analysis.

Results and Discussion

The objective of the present study was to identify VX degradation pathways and rate of disappearance of sub-monolayer concentrations of VX on concrete samples. This was accomplished using SIMS, and for this reason, the origin of the peaks observed in the SIMS spectra must be understood. In the SIMS spectrum of 0.5 monolayer of VX collected 21 min after spiking at 24 °C, the intact molecule was observed in the protonated form $[VX + H]^+$ at m/z 268 (Figure 1). More abundant ions derived from VX were observed at m/z 128 and 86. M/z 128 has multiple origins (Scheme 1): ionic
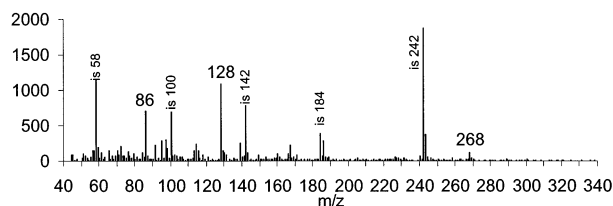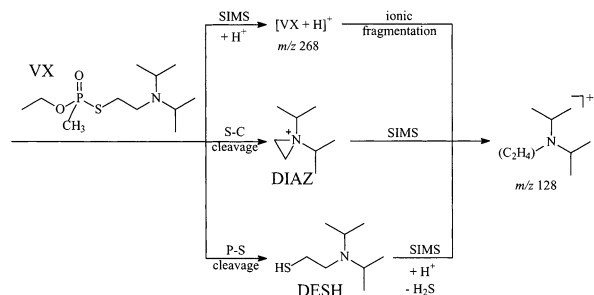
FIGURE 1. Cation IT-SIMS spectrum of 0.5 monolayers of VX on concrete, acquired 21 min after spiking. Ions derived from the internal standard are denoted by 'is'.

SCHEME 1. Formation Routes Resulting in Observation of *m/z* 128.

fragmentation of sputtered, gaseous $[VX + H]^+$, S—C cleavage of surface-bound VX followed by sputtering to the gas phase, and P—S cleavage of surface-bound VX followed by sputtering and ionic fragmentation.

The ionic fragmentation of $[VX + H]^+$ has been established in previous studies using MS^2 (*17, 18*). S—C cleavage of VX has been previously observed as an anchimerically assisted process in alkaline solutions by Yang and co-workers (*27*). Formation of *m/z* 128 from P—S cleavage occurs by sputtering the P—S cleavage product DESH into the gas phase as $[DESH + H]^+$ followed by ionic fragmentation. The spectra acquired also contained lower abundance background ions, and ions derived from the internal standard tetrabutylammonium (TBN).

TBN was added as an internal standard to attempt to improve the precision of the abundance measurements. Precision for analyses of environmental samples from the same batch is typically on the order of 30% relative standard deviation, and sample-to-sample variability is potentially great for concrete particles. Tetraalkylammonium salts are known to be easily and sensitively detected on surfaces using SIMS (*28, 29*), and TBN (*30*) was selected as a nonreactive compound to serve as an internal standard. The ions attributable to TBN are *m/z* 242, 186, 184, 142, 100, and 58. Our attempts to improve the precision by normalizing $[VX + H]^+$ abundance to $[TBN]^+$ were unsuccessful, perhaps because the surface concentration of TBN, like that of VX, was variable. However, the precision of the VX-derived ions was better when TBN was present. We believe that this is due to TBN playing a significant role in maintaining surface charge balance by providing a mechanism for positive ion emission (*23*). The relative and absolute abundances of the TBN-derived ions did not significantly change as a function of time over the course of a VX degradation run. Normalization by internal standard was superseded by normalizing the VX-related ion abundances relative to the total abundance, as described below.

The relative abundances of the VX-derived ions were observed to change with increasing time. Over the course of a day's analysis, the abundance of $[VX + H]^+$ (*m/z* 268) decreased, as did *m/z* 128, while significant ions at *m/z* 160, 118, and 114 appeared and became more abundant (Figure 2). *M/z* 160, 118, and 114 are derived from the P—S cleavage product diisopropylaminoethanethiol (DESH). The com-
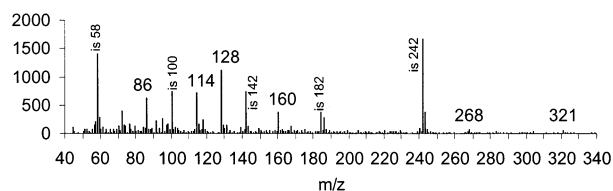

FIGURE 2. Cation SIMS spectrum of VX on concrete after 163 min, showing the decrease in the abundance of $[VX + H]^+$ and increase in the abundance of ions derived from DESH.
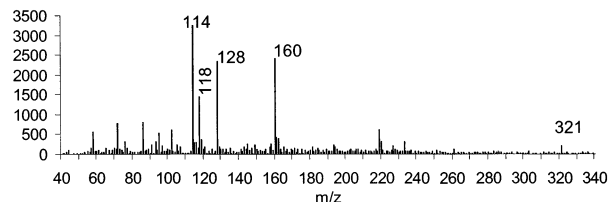

FIGURE 3. IT-SIMS spectrum of DESH on concrete particles.

pound displays unusual behavior when analyzed using SIMS, in that it readily forms a stable $[DESH - H]^+$ ion at *m/z* 160 (Figure 3). $[DESH - H]^+$ undergoes elimination of C_3H_6 and $CH_2=S$ to form *m/z* 118 and 114, respectively (previously demonstrated by MS^2). DESH also undergoes protonation, to form a low abundance $[DESH + H]^+$ at *m/z* 162, which produces fragment ions at *m/z* 102 and then 60 by sequential losses of C_2H_4S and C_3H_6.

The abundance of *m/z* 128 in the spectra of concrete exposed to VX for long time periods was consistent with the existence of a second degradation process that operated by cleavage of the S—C bond, forming a diisopropylaziridinium (DIAZ) product (as in alkaline solution (*10*), Scheme 1). No standards for DIAZ were available, and thus acquisition of a standard spectrum (as in the case of DESH) was not possible. This precluded any attempt to measure relative compound detection sensitivities and subsequent degradation product distributions. Nevertheless, by assuming that the DIAZ and DESH detection sensitivities were similar, we estimated the degradation product distribution was 30% DIAZ and 70% DESH.

At longer times, a low abundance ion at *m/z* 321 became measurable that corresponded to protonated bis[2-diisopropylaminoethyl]disulfide (DES_2). The formation of DES_2 resulted from the dimerization of DESH (*6*). The changing abundances of these ions indicated that the rate of VX degradation could be measured by monitoring ion abundances as a function of time.

Conspicuously absent was any evidence for *S*-2-diisopropylaminoethyl methyl phosphonothioic acid (*8*) which has the U.S. Army designation EA-2192. A sample on glass was analyzed using the IT-SIMS, and was readily observable as the intact, protonated molecule at *m/z* 240, with a dominant fragment ion at *m/z* 128 again. The compound is formed in alkaline solution as a minor product (yields up to 22%) and is significant because, like VX, it is a potent acetylcholinesterase inhibitor. Although EA-2192 can be detected by SIMS on inert surfaces, it was difficult to detect on concrete, perhaps because of anion exchange and incorporation of the phosphonate into the ionic mineral matrix of the concrete. Future efforts may be made to monitor EA-2192 by reconfiguring the IT for anionic secondary ion analysis.

The rate of VX disappearance on concrete was calculated by plotting "fractional" $[VX + H]^+$ abundance versus time. Fractional $[VX + H]^+$ abundance at time t (denoted $F_{268}(t)$) was calculated by normalizing the absolute $[VX + H]^+$ abundance ($I_{268}(t)$) by the sum of the VX-derived ion
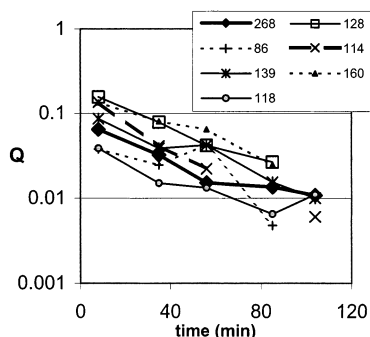
FIGURE 4. Attenuation of VX at m/z 139 and 268 in the IT-SIMS spectrum of exposed concrete, recorded at 50 °C. The appearance of DESH at m/z 114, 118, and 160 and the mixed behavior of m/z 86 and 128 are also plotted.

abundances

$$F_{268}(t) = I_{268}(t)/\sum_n I_n(t)$$

where n represents the ensemble of VX-derived ions. This ensemble of ions n consisted of m/z 321, 268, 220, 167, 160, 128, 118, 114, and 86. The fractional ion abundance was calculated in a similar fashion for all of the ions in the ensemble.

To examine the rate of growth of product ions together with the rate of decay of VX ions, the fractional intensities were then subtracted from their final values (as time $\rightarrow \infty$), and the absolute value was taken

$$Q_n(t) = |F_n(t) - F_n(\infty)|$$

Thus $Q_n(t)$ is a quantity that decays toward zero for all ions n as time increases.

Plots of ln Q against time were linear for all ions monitored, indicating a first-order or pseudo-first-order reaction at the surface, with the exception of m/z 86, which displayed nonlinear behavior in several of the experiments. Note that at any single time value, replicate analyses were not possible, because the time from VX exposure constantly increased, and only one sample at a time could be analyzed. Figure 4 depicts a typical semilogarithmic plot of Q over time for all monitored ions. The slope of each plot is equal to $-k$, the rate constant for the first-order kinetic equation:

$$dQ_n(t)/dt = -k\,Q_n(t)$$

The rate constants (k values) for the seven ions monitored were not significantly different, within the error on the slope, for each degradation condition. Therefore, pooled estimates for k were obtained by taking the weighted mean of all seven k values (each weighted by the variance on its slope).

The rates calculated from the data collected at 24 °C resulted in a value of $k = 0.005$ min^{-1}. The experiments were repeated at 30, 35, and 50 °C to establish the temperature dependence of the reaction (Table 1). An Arrhenius plot of ln k versus $1/RT$ resulted in a linear relationship with an activation energy of 52 kJ mol^{-1} (Figure 5). The activation energy agrees with values calculated by Yang and co-workers for hydrolysis of VX in alkaline solutions, where P—S cleavage producing DESH was calculated at 53–61 kJ mol^{-1}, with an overall (composite) activation energy of 60–63 kJ mol^{-1} (31). The alkaline nature of the concrete was verified by immersing 35 g of the powdered concrete in approximately 20 mL of deionized H$_2$O and measuring the pH, which resulted in a value of 12. This indicates a material having a substantial population of basic surface sites.

TABLE 1. Rate Constants Calculated for the Degradation of VX on Concrete Surfaces, for Czech Concrete.

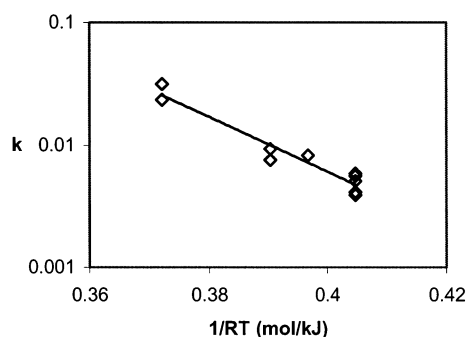| temp (°C)	1/RT (mol/kJ)	k
24	0.40476	0.0039
24	0.40476	0.0056
24	0.40476	0.0059
24	0.40476	0.0041
24	0.40476	0.0051
30	0.39674	0.0082
35	0.39031	0.0093
35	0.39031	0.0076
50	0.37219	0.0314
50	0.37219	0.0235

FIGURE 5. Arrhenius plot of ln k versus $1/RT$ for the degradation of VX on Czech concrete samples.

The efficacy of the basic concrete substrate in the degradation of VX was substantiated by a comparison with degradation occurring on a neutral soil. Sandy soil samples were spiked with VX solution, allowed to dry, and then analyzed over the course of 2 days. In these experiments, the abundance of the [VX + H]$^+$ signal was practically constant over the period of time examined for the concrete degradation studies, and there was no mass spectral evidence for the formation of DESH or DIAZ. Thus, on the sandy soil particles, VX was either not degrading, or degrading at a rate that was orders of magnitude slower than that observed on concrete. Further evidence for the inert nature of the sandy soil relative to VX is the fact that intact VX could be detected in abundance on sandy soil samples stored at 4 °C more than one year after they had been exposed (17).

The degradation results also agree closely with observations by Wagner et al. of the degradation of VX on crushed concrete by ^{31}P MAS NMR spectroscopy, where they observed the apparent first-order degradation of VX with a half-life of 2.2 h ($k = 0.0053$ min^{-1}) at room temperature, up to a reactive capacity of about one monolayer (14). At higher VX exposures, a second, and slower, VX attenuation was observed that proceeded with a half-life of 28 days to 3 months ($k = 1.7 \times 10^{-5} – 5.3 \times 10^{-6}$ min^{-1}). The degradation of VX on concrete can also be compared to behavior of the compound on MgO, CaO, and zeolite. Wagner and co-workers spiked neat VX onto high surface area MgO and CaO (12, 13) and measured a bimodal disappearance behavior using solid-state NMR spectroscopy. They interpreted their results in terms of very rapid P—S cleavage on the metal oxide surface which was complete within 2 h, followed by a much slower disappearance process. The latter process was also reported to be due to surface P—S cleavage, but was limited by the rate of VX evaporation from passivated sites to active basic sites. In contrast, a bimodal disappearance plot was not observed in the present concrete experiments, presumably because here the VX was deposited homogeneously as a dilute solution over the solid surface, whereas Wagner et al. applied neat VX to a very high surface area solid, which certainly resulted

initially in inhomogeneous VX distribution. P−S cleavage was also observed on the surface of a silver substituted Y zeolite, however in this report the cleavage appeared to be catalyzed by Ag (*11*). Interestingly, no S−C cleavage was reported in the metal oxide nor zeolite degradation studies.

The results of this surface kinetics study show that submonolayer VX rapidly degrades on the surface of concrete in the absence of any visible solvent. The reaction products, the reaction rates, and the temperature dependence bear a strong similarity to degradation reactions occurring in alkaline solution. At an ambient temperature of 24 °C, VX could be expected to degrade to 1% of its initial concentration within 15 h, and to 1 part in 10^6 within 50 h. At higher temperatures, the rate constants are substantially greater. It should be emphasized in this research that the samples used were crushed concrete, which may be substantially more alkaline than intact weathered concrete as encountered in the environment. An assessment of the reactivity of weathered concrete surfaces represents an important direction for additional studies.

The research also shows that IT-SIMS is very well suited to the characterization of a compound prone to undergo surface degradation, provided the molecule and its degradation products are observable in the SIMS spectrum. In the case of VX and its degradation products, this is readily accomplished because the basicity of the compound leads to sensitive detection using a SIMS method.

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