

Figure 1. MAS NMR spectra obtained for agents added to AP-MgO: (left) GD at (top to bottom) $t = 9.5$ min, 1.0 h, and 23 h; (middle) VX at $t = 8.5$ min, 24 h, and 3 months; (right) HD at $t = 9.5$ min, 3.8 h, and 1 week.

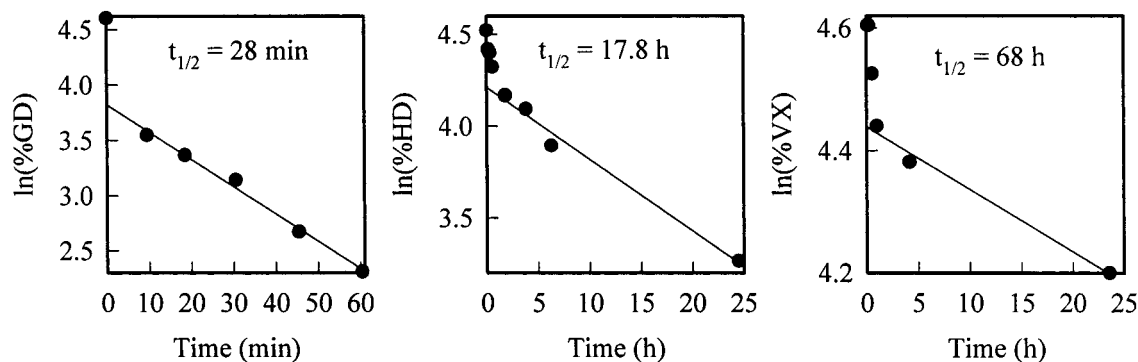
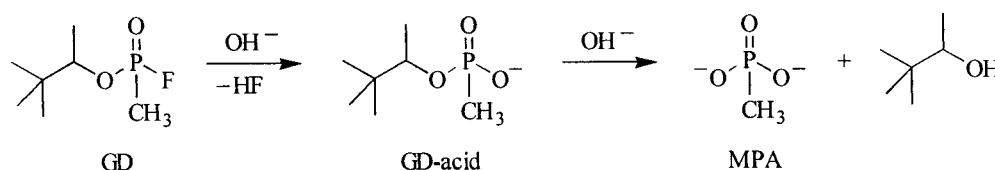


Figure 2. Reaction profiles for GD, HD, and VX liquid on AP-MgO.

SCHEME 1



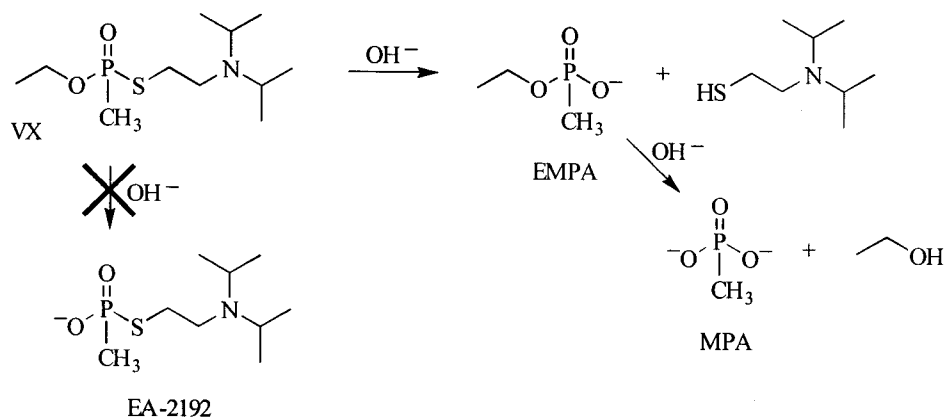
^{31}P NMR peaks is indicative of a strong interaction with the surface (see Discussion). The reaction profile is shown in Figure 2. After a fast initial reaction, a steady state is achieved exhibiting a first-order half-life of 28 min.

VX. Selected ^{31}P MAS NMR spectra obtained for 6 μL of VX added to 104 mg of AP-MgO are shown in the middle column of Figure 1. The intense singlet in the top spectrum at 51.6 ppm is due to VX, and the two smaller peaks are spinning sidebands. VX is slowly hydrolyzed by surface hydroxyls and/or physisorbed water to yield ethyl methylphosphonic acid (EMPA) and MPA, as evidenced by the broad peaks at 25.2 and 19.8 ppm, respectively. No toxic EA-2192 (expected to yield a peak near 40 ppm), which is known to form during hydrolysis in aqueous solution,¹ is observed. The acidic VX products are shown in the ionized form in Scheme 2. Again, the broad lines

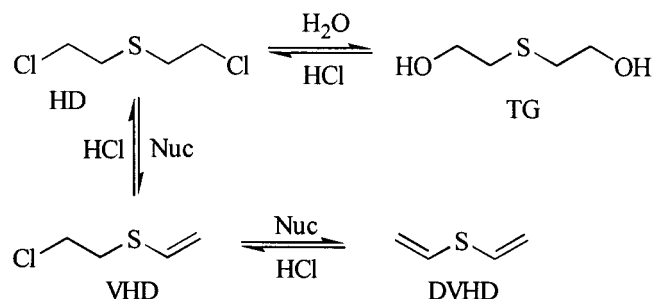
detected for EMPA and MPA reveal a very strong interaction of these species with the surface (see Discussion). The reaction profile is shown in Figure 2. As with GD, the fast initial reaction slows to a steady-state, first-order reaction with $t_{1/2} = 68$ h.

HD. Selected ^{13}C MAS NMR spectra obtained for 5 μL of HD* added to 111 mg of AP-MgO are shown in the right column of Figure 1. The two intense peaks in the top spectra are due to HD* (43.2 ppm, CH_2Cl ; 34.0 ppm, SCH_2). The small peak at 63.3 ppm is due to an impurity in the HD* ($\text{CH}_3\text{C}(\text{O})\text{O}^*\text{CH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{Cl}$). Three products are observed during the course of the reaction: thiodiglycol (TG, broad peaks at 60.5 and 33.4 ppm), vinyl HD (VHD, 132.8, 111.0, 44.7, and 35.4 ppm), and divinyl HD (DVHD, 131.2 and 113.1 ppm). Thus, HD undergoes both hydrolysis and elimination of HCl. These reversible reactions are shown in Scheme 3. The precise

SCHEME 2



SCHEME 3



nature of the nucleophile performing the elimination is not clear since this reaction is not afforded by hydroxide in solution (see Discussion). The VHD eventually undergoes a second elimination of HCl to quantitatively yield DVHD. The final product ratio is about 50% TG and 50% DVHD. The broadened ^{13}C NMR lines detected for TG indicate a strong interaction of this compound with the surface (see Discussion). Conversely, the sharp lines for DVHD reveal a distinct lack of surface interaction. The reaction profile is shown in Figure 2. As with the other agents, the fast initial reaction is replaced by a pseudo-first-order reaction with $t_{1/2} = 17.8$ h.

Discussion

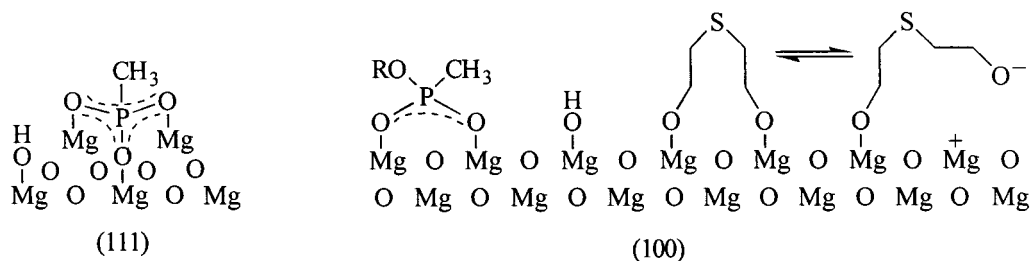
Surface Reactions. The hydrolysis reactions observed for GD, VX, and HD are as expected due to the basic MgO surface and are strictly analogous to the known solution chemistry of the agents.^{1a,b} But the final state of the products is quite different from that in solution. For VX and GD, the broad ^{31}P NMR lines observed for their products are consistent with the formation of surface-bound magnesium phosphonates, which are only soluble in water at low pH.⁶ Thus G and V agent products are not extracted from inorganic oxides using water⁷ or organic solvents but may be “dissolved” and extracted by acidic media.^{3c} Proposed structures for the surface-bound metal phosphonates^{1c,8} are shown in Scheme 4. Owing to exposure to air, the MgO

surface surely contains surface hydroxyl groups, as shown. The precise role of such surface hydroxyls and/or physisorbed water on the observed agent reactions is not yet known. The geometry of the predominant (100) plane of conventional MgO is suitable for the bidentate species GD-acid and EMPA, as shown, but the tridentate MPA may require the trigonal symmetry of sites found on the (111) face (thought to be favored in AP-MgO⁴) or at an edge or corner site.^{4a} Indeed, such sites may actually encourage MPA formation since they possess the proper geometry to hydrolyze the bound bidentate species.⁹ For HD, the strong surface interaction evidenced by the broadened ^{13}C NMR lines for TG may be due to either hydrogen-bonding with the surface or the formation of a reactive magnesium alkoxide, as shown in Scheme 4. Additional evidence for the latter surface species is provided by the VHD and DVHD products. Alkoxides are known to effect rapid elimination of HCl from HD in homogeneous solution.^{1a,b} But the ability of various sites on the AP-MgO surface to perform the observed HCl elimination cannot be ruled out.

Surface Kinetics. The kinetic behavior of the reactions is actually consistent with the immediate, destructive adsorption of all three agents on the AP-MgO surface, which is highly reactive. However, the agents react in a stoichiometric fashion; i.e., the surface sites do not “turn over” (in the catalytic sense) to react with additional agent. The peculiar nature of the reaction, i.e., a fast initial reaction followed by a slow, pseudo-first-order reaction, is merely reflective of the ability of the agent molecules to reach fresh, unreacted surface from the bulk liquid. This process is controlled by various physical properties of the agents. The salient properties are shown in Table 1.

The fast reaction results from the spreading of the liquid agent through the pore structure of the AP-MgO^{4b} to form a “wet spot”. As a minor fraction of the bulk, liquid agent rapidly reacts along the wave front, the surface becomes poisoned or passivated against further reaction by the strongly-bound products discussed above. The spreading stops at the point where the liquid achieves its volume in the pores (the “wet spot”),

SCHEME 4



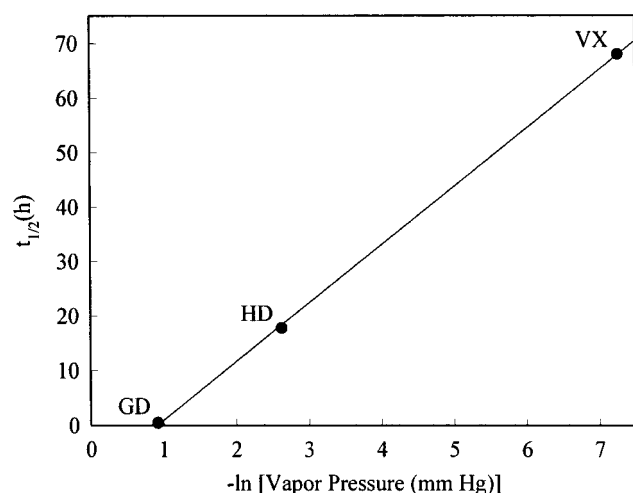


Figure 3. Dependence of steady-state half-life on vapor pressure.

TABLE 1: Physical Properties of GD, HD, and VX at 25 °C

	surface tension (dynes/cm)	viscosity (cs)	vapor diffusion coeff (cm ² /s)	vapor pressure (mm Hg)
GD	24.5	3.098	0.047	0.4
HD	42.5	3.1147	0.060	0.072
VX	31.3	9.958	0.034	0.0007

and the fast reaction ceases. The spreading process is presumably mediated by the surface tension and viscosity of the agent. Thus GD, possessing the lowest surface tension and viscosity, spreads the fastest. In the reaction profile shown in Figure 2, it is evident that this process for GD takes less than 10 min, the time at which the steady-state reaction begins. For HD and VX, the steady-state reaction begins at about 2 and 1 h, respectively. The viscosity of VX is much greater than that of HD, but it has a smaller surface tension. Therefore, it appears that surface tension (the ability of the liquid to expand its surface area) is more important with regard to spreading through AP-MgO than viscosity (the resistance to flow).

Once the liquid spreading ceases and the "wet spot" is established, the only mechanism by which agent molecules (present as bulk liquid within the pores) can reach fresh surface is by evaporation and diffusion in the gas phase. Diffusion-limited reactions exhibit first-order behavior, but gas phase diffusion is most likely not limiting the reactions as all three agents have vapor diffusion coefficients of the same order of magnitude. Rather, it is the disparate vapor pressures, a measure of the rate of evaporation, that is responsible for the slow, steady-state reaction of the agents with AP-MgO. GD has a significantly higher vapor pressure than either HD or VX. Therefore, GD has the fastest steady-state reaction ($t_{1/2} = 28$ min). HD has an intermediate vapor pressure and reaction rate ($t_{1/2} = 17.8$ h), and VX has the lowest vapor pressure and

slowest reaction rate ($t_{1/2} = 68$ h). Definitive evidence that the steady-state reaction is mediated by evaporation of the ensconced liquid agent in the "wet spot" is given by the dependence of the pseudo-first-order steady-state half-lives on the vapor pressure, as shown in Figure 3. This empirical relationship may provide the ability to predict the persistence of various agents on AP-MgO based solely on their vapor pressure.

Conclusions

The surface of AP-MgO is highly reactive toward GD, VX, and HD. The reaction is only limited by the physical processes of liquid spreading and evaporation, mediated primarily by the liquid surface tension and vapor pressure, respectively. These physical processes are responsible for the fast, initial reaction (liquid spreading) and the ensuing slow, steady-state pseudo-first-order reaction evaporation observed for all three agents. A simple empirical relationship exists between the steady-state half-life and the liquid vapor pressure of the agent, which allows the prediction of the persistence of other agents on AP-MgO.

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References and Notes

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