for the switching-angle sample spinning experiment, we plan to use this method to extend our work.

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Adsorption and Decomposition of Organophosphorus Compounds on Nanoscale Metal Oxide Particles. In Situ GC-MS Studies of Pulsed Microreactions over Magnesium Oxide

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Using an in situ pulse reactor GC-MS system, the thermal decomposition of organophosphorus compounds (as models of nerve agents) has been compared with their destructive adsorption on high surface area magnesium oxide. Dramatically lower temperatures are required when MgO is present. Volatile products evolved were formic acid, water, alcohols, and alkenes. At higher temperatures CO, CH_4, and water predominated. Phosphorus residues remained completely immobilized. Addition of water enhanced the facility of MgO to destroy these compounds, and in fact, water pulses were found to partially regenerate a spent MgO bed. Using ^{18}O labeling, some aspects of the reaction mechanisms were clarified and in particular showed that oxygen scrambling occurred. Surface OH and MgO groups transferred oxygen in the formation of formic acid, and surface mobility and reactivity of adsorbed groups was very high. The substantial capacity of high surface area MgO for destruction and immobilization of such toxic substances makes it attractive for air purification schemes as well as solid reagents for destruction and immobilization of bulk quantities of hazardous phosphorus compounds or organohalides.

Introduction

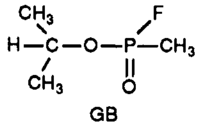
Nanoscale metal oxide particles are proving to be effective new materials for adsorption and decomposition of large amounts of toxic materials.[1,2] The unique properties of these "destructive adsorbents" are due to their ultrahigh surface areas and high surface concentrations of reactive defect sites.

Two applications for these new adsorbents come to mind: (1) for air purification; (2) as reagents for destruction and immobilization of bulk quantities of hazardous chemicals. Both applications interest us, but we wish to draw attention to application 2 especially for organophosphorus compounds (as models of toxic nerve gases) and aromatic chlorocarbons (as models of polychlorobiphenyls). Herein we report more detailed studies of organophosphorus compound decomposition, while work on chlorinated hydrocarbons will be reported later.

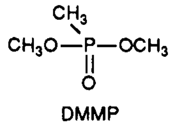
Earlier investigators were mainly concerned with catalytic decomposition of toxic phosphorus compounds. Especially Weller and co-workers efforts with Pt/Al_2O_3 catalysts for air purification should be noted.[3-5] More general surface chemistry appraoches have been discussed by Ekerdt and co-workers,[2] and concern for the dangers of organophosphorus compounds appear in the fields of soil fertility, eutrophication, corrosion control, the detergent industry, and others.[6-8]

In examining the literature dealing with the catalytic or stoichiometric decomposition of organophosphorus compounds, we have noted a wide variety of differing results. A brief review of this literature follows.

Weller's early heterogeneous catalytic decomposition of isopropyl methylphosphonofluoridate, known as GB (nerve agents have similar structures such as GB (Sarin), GD or VX)),[2] and the simulant dimethyl methylphosphonate (DMMP) were studied with Pt/Al_2O_3, pure Al_2O_3, and amberlyst cation exchange resin under oxidizing conditions.[3-5,9] Between 300 and 400 °C, GB yielded CO_2, HF, H_2O, and H_3PO_4 (occurring as a viscous condensate near the sampling valve, although some reacted with the Al_2O_3 to form $AlPO_4$). As catalyst activity declined, the dealkylation product propene became the major product. With DMMP and Pt/Al_2O_3/air the products were CH_3OH and CO_2 while with N_2 flow, CH_3OH.



GB



$CH_3O{-}\overset{CH_3}{\underset{\underset{O}{\|}}{P}}{-}OCH_3$

DMMP

Yates and co-workers have recently announced that a sustained heterogeneous catalytic decomposition of DMMP was achieved under oxidizing conditions on a

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(1) (a) Li, Y. X.; Klabunde, K. J. *Langmuir* **1991**, *7*, 1388. (b) Li, Y. X.; Schlup, J. R.; Klabunde, K. J. *Langmuir* **1991**, *7*, 1394.

(2) Ekerdt, J. G.; Klabunde, K. J.; Shapley, J. R.; White, J. M.; Yates Jr., J. T. *J. Phys. Chem.* **1988**, *92*, 6182.

(3) Tzou, T.-Z.; Weller, S. W. Unpublished paper (private communication in 1991).

(4) Baier, R. W.; Weller, S. W. *Ind. Eng. Chem. Process Des. Dev.* **1967**, *6*, 380.

(5) Graven, W. M.; Weller, S. W.; Peters, D. L. *Ind. Eng. Chem. Process Des. Dev.* **1966**, *5*, 183.

(6) Parfitt, R. L.; Russell, J. D. *J. Soil Sci.* **1977**, *28*, 297.

(7) Lyklema, L. *Environ. Sci. Technol.* **1980**, *14*, 297.

(8) Strumm, W.; Furrer, G.; Kunz, B. *Croat. Chem. Acta* **1983**, 585.

(9) Graven, W. M.; Paton, J. D.; Weller, S. W. *Ind. Eng. Chem. Process Des. Dev.* **1966**, *5*, 34.

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Mo(110) surface in a high-vacuum chamber.[10-12] Surfaces of Pd(111) and Ni(111) were less effective. Their experiments were carried out at 625–780 °C with a 1:2 DMMP/O_2 flux, and the gas-phase products were CO and phosphorus oxide gaseous species. They concluded that the oxidized Mo surface catalyzed DMMP decomposition without phosphorus surface buildup (which did occur in the absence of oxygen).

In related work, Dulcey and co-workers have detected PO radicals desorbed when DMMP or trimethylphosphite [$(CH_3)_3PO$] were allowed to interact with a hot Pt wire.[13] Their laser-induced fluorescence experiments showed the formation of OH radicals when O_2 was also present. However, too much O_2 caused Pt catalyst deactivation, and they ascribed this deactivation to the formation of PO_2 and P_2O_5 on the Pt surface.

White and co-workers have carried out extensive studies of DMMP decompositions on clean Rh(111) and Pt(111) surfaces using high-resolution electron energy loss spectroscopy (HREELS), as well as SSIMS, TPD, AES, XPS, and UPS techniques.[14,15] At low temperature under vacuum they detected H_2, H_2O, CO, CO_2, CH_4, and CH_3OH while P, C, and O residues remained on the surface of the metal. Further studies revealed that PO–CH_3 and P–O-CH_3 bond cleavages occurred at 300–400 K, while 400–500 K was required for P–CH_3 cleavage. Unidentified phosphorus oxides remained on the metal surface. Unlike Mo(110), a catalytically active metal oxide surface was not formed, and so the accumulation of phosphorus residues led to catalyst deactivation. Therefore, White and co-workers have also investigated more readily oxidized metals (i.e., Fe) as well as Fe_2O_3 and SiO_2.[16,17] At low coverage a partially oxidized Fe surface completely decomposed DMMP to CH_3OH, H_2O, CO, H_2, and a phosphorus residue. Addition of water aided this decomposition somewhat. On bulk α-Fe_2O_3 the decomposition of DMMP took place at 170 K, leading to CO_2, CO, CH_3OH, HCOOH, H_2, H_2O, and an adsorbed phosphate residue that migrated into the bulk, allowing further decomposition to take place. On dehydrated SiO_2 little success in DMMP decomposition was encountered.

Alumina (Al_2O_3) surfaces have also been studied, in particular by Templeton and Weinberg.[18,19] A clean Al surface was oxidized and exposed to DMMP. Using inelastic electron tunneling spectroscopy (IETS), these workers found that DMMP was molecularly absorbed at 200 K. Above 295 K, decomposition occurred via cleavage of a phosphorus–oxygen bond. Above 573 K the remaining methylphosphate adsorbed species decomposed to yield a tridentate methylphosphonate adspecies.

Infrared studies by Kuiper and co-workers have demonstrated that Sarin adsorbed strongly on γ-Al_2O_3.[20] Two decomposition products were observed: propane and HF (remained adsorbed). The remaining phosphorus residue was adsorbed through its POO bridge group.

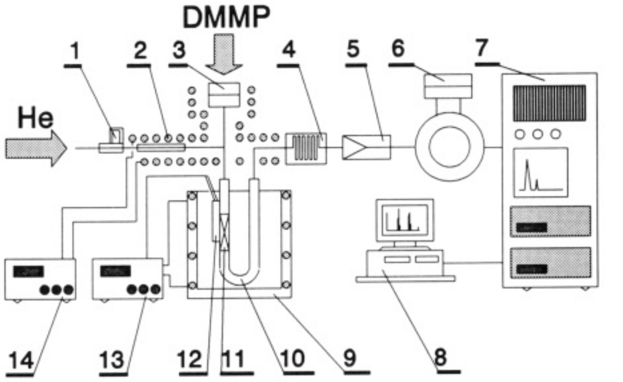

Figure 1. In situ reactor GC-MS device for decomposition of organophosphorus compounds: (1) flow rate controller; (2) heater; (3) injector; (4) GC column; (5) jet-separator; (6) ionizing chamber; (7) spectrometer controller; (8) computer; (9) furnace; (10) reactor; (11) MgO bed; (12) thermocouple; (13) temperature controller; (14) temperature controller.

Finally, we should mention the recent solid-state NMR studies of Lunsford, Maciel, and co-workers.[21-23] Zalewski and Lunsford studied the oxidation of trimethylphosphine [$(CH_3)_3P$] on Y-type zeolites and were able to use this approach to detect acidic sites in the zeolites. Similar solid-state NMR studies have been reported by Maciel and co-workers.

Due to the presence of the phosphorus heteroatom as a catalyst poison and the problems associated with the elution of phosphorus-containing compounds in any form, catalytic approaches have their limitations. *Therefore, the design of more highly efficient adsorbents is desirable, especially those that simultaneously destroy the organophosphorus compounds and immobilize the phosphorus residue.* Thus, we are interested in ultrahigh surface area metal oxides which we study in macroscale reactions under dynamic, atmospheric pressure conditions. In this way products can be produced on relatively large scale. And by variation of contact times, carrier gas, and temperature, a great deal can be learned about the reaction details. To collect data rapidly, we have constructed an in situ reactor GC-MS system that can operate under a wide variety of conditions.

In this report we continue to investigate nanoscale MgO materials. Our choice of MgO is based on its superior performance compared with other oxides, its highly basic character, and simple crystal structure.[24]

Experimental Section

(1) Adsorbents. Two types of MgO were studied. The first possessed a surface area of 130 m^2/g, which is labeled MgO(130). The preparation of this sample was as follows: a high-purity MgO (99.99% pure) from ROC/RIC Chemical Co. was dispersed in 80 °C distilled hot water. The resultant slurry was dried to a solid

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(10) Smentkowski, V. S.; Hagans, P. L.; Yates Jr., J. T. *J. Phys. Chem.* **1988**, *92*, 6352.

(11) Smentkowski, V. S.; Hagans, P. L.; Yates Jr., J. T. U.S. Patent No. 4,871,526.

(12) Guo, X.; Yoshinobu, J.; Yates Jr., J. T. *J. Phys. Chem.* **1990**, *94*, 6839.

(13) Dulcey, C. S.; Lin, M. C.; Hsu, C. C. *Chem. Phys. Lett.* **1985**, *115*, 481.

(14) Hegde, R. I.; Greenlief, C. M.; White, J. M. *J. Phys. Chem.* **1985**, *89*, 2886.

(15) Henderson, M. A.; White, J. M. *J. Phys. Chem.* **1988**, *110*, 6939.

(16) Hegde, R. I.; White, J. M. *Appl. Surf. Sci.* **1987**, *28*, 1.

(17) Henderson, M. A.; Jin, T.; White, J. M. *J. Phys. Chem.* **1986**, *90*, 4607.

(18) Templeton, M. K.; Weinberg, W. H. *J. Am. Chem. Soc.* **1985**, *107*, 97.

(19) Templeton, M. K.; Weinberg, W. H. *J. Am. Chem. Soc.* **1985**, *107*, 774.

(20) Kuiper, A. E. T.; van Bokhoven, J. J. G. M.; Medema, J. *J. Catal.* **1976**, *43*, 154.

(21) Zalewski, D. J.; Chu, P.-j.; Tutunjian, P. N.; Lunsford, J. H. *Langmuir* **1989**, *5*, 1026.

(22) Baltusis, L.; Frye, J. S.; Maciel, G. E. *J. Am. Chem. Soc.* **1987**, *109*, 40.

(23) Baltusis, L.; Frye, J. S.; Maciel, G. E. *J. Am. Chem. Soc.* **1986**, *108*, 7119.

(24) (a) Lin, S.-T.; Klabunde, K. J. *Langmuir* **1985**, *1*, 600. (b) Klabunde, K. J.; Matsuhashi, H. *J. Am. Chem. Soc.* **1987**, *109*, 1111. (c) Klabunde, K. J.; Hoq, M. F.; Mousa, F.; Matsuhashi, H. *Preparative Chemistry Using Supported Reagents*; Laszlo, P., Ed.; Academic: New York, 1987; p 35. (d) Nieves, I.; Klabunde, K. J. *Mater. Chem. Phys.* **1988**, *18*, 485. (e) Utamapanya, S.; Klabunde, K. J.; Schlup, J. R. *Chem. Mater.* **1991**, *3*, 175. (f) Atteya, M.; Klabunde, K. J. *Chem. Mater.* **1991**, *3*, 182.

and further dried at 120 °C in an oven overnight. Then a 0.1-g sample of the resultant powder was placed under dynamic vacuum (6×10^{-4}–1×10^{-3} Torr) and slowly heated (3 h) to 500 °C and held there for 6 h. Samples prepared in this manner had surface area consistently in the 125–130 m^2/g range and did not change in surface area with time. The density of such samples was 0.64 g/cm^3. The second type of MgO was prepared by a special alco–gel method.[1,24e–g] Briefly, a solution of $Mg(OCH_3)_2$ in methanol/toluene was slowly hydrolyzed with a limited amount of water at room temperature. A gel was formed which was then placed in a high-pressure autoclave under N_2 pressure. The autoclave was heated to 265 °C at a heating rate of 1 °C/min. When this temperature was reached, the autoclave was vented rapidly, removing the solvents. The resultant white powder (light and flocculant) was heat treated under vacuum (6×10^{-4}–1×10^{-3} Torr) by heating to 500 °C over a 3-h period and then held there for 6 h. Samples of MgO prepared in this way had surface areas close to 390 m^2/g and densities of 0.12–0.15 g/cm^3, which we label MgO(390).

(2) Adsorbates. The DMMP was purchased from Strem Chemicals and was freeze–pump–thaw degassed 4–6 times and stored over 5-Å molecular sieves under N_2. Other phosphorus compounds, for instance, trimethyl phosphite $(CH_3O)_3P$, trimethylphosphine $(CH_3)_3P$, triethyl phosphate $(C_2H_5O)_3P{=}O$, and triethyl phosphite $(C_2H_5O)_3P$, were purchased from Aldrich Chemical Co. and were degassed and stored in the same way.

(3) In Situ Reactor GC-MS System. The device we have constructed is diagrammed in Figure 1. A carrier gas such as He passed through a flow-stabilizing valve so that 50 mL/min constant flow was possible. The carrier gas was heated to 200 °C (heater 2) employing temperature controller 14. A measured amount of phosphorus compound, usually 2 μL, was injected (injector 3 heated to 200 °C), and was carried to reactor 10 (6-mm diameter and 200-mm-long U-type stainless steel tube). It passed over the bed of MgO (0.1 g) that was held at a desired reaction temperature controlled by controller 13. The volatile decomposition products then passed into GC column 4 for separation and analysis. In some cases this GC column was an empty stainless steel tube and so the GC spectra simply reflected desorption of products from the MgO bed. The volatile products entered jet separator 5, and part of the sample then entered the MS ionization chamber 6. The GC-MS system is a Finnigan 4021-C controlled by a Finnigan Incos Data System. The energy of the ionizing electrons was set at 20 eV, and the emision current from the filament was 0.25 mA. EM voltage was set at 1700 V, ionizer chamber temperature was 250 °C, and manifold temperature at 110 °C. MS spectra for all compounds of interest in this study were obtained as standards and compared satisfactorily with literature.[25]

Experiments where the effects of water were being studied were carried out in the same way, except that the syringe injections included the desired ratio of water to phosphorus compound.

Results

(1) Effects of Temperature on Decomposition Products of Organophosphorus Compounds in an Empty Reactor (Thermal Decomposition). To compare the effects of MgO as a destructive adsorbent with no adsorbent, we have carried out many pulsed reactor studies with an empty reactor.

Flow rate of carrier gas and the geometrical constraints of the reactor tube allow for a contact time of 7 s in these pulsed experiments (the time for a pulse to move through the entire reactor tube). Under these conditions and atmospheric pressure, pure DMMP, trimethyl phosphate and trimethylphosphine were not thermally decomposed below a reactor temperature of 700 °C. Upon increasing to 750 °C, CH_3 and OCH_3 fragments were lost and a phosphorus-containing fragment CH_3PO_3 was detected by MS at amu 94. At the still higher temperature of 850 °C, further $-CH_3$ and $P-CH_3$ splitting took place and the major products detected were H_2O and ethylene (C_2H_4, amu 28). Interestingly a major MS peak at amu 124 was also detected, and its fragmentation pattern strongly suggests this to be the phosphorus cluster P_4.

For compounds containing ethoxy groups such as $(C_2H_5O)_3P{=}O$ and $(C_2H_5O)_3P$ lower temperatures caused dealkylation reactions. For example at 400–415 °C large amounts of C_2H_4 were released. Also some phosphorus oxides were detected, such as PO_2OH (amu 80) and P_2O_3 (amu 110).

(2) Effect of Water on Decomposition Products of Organophosphorus Compounds in an Empty Reactor (Thermal Decomposition). For the ethoxy-substituted compounds, the presence of water had no effect (see Tables I and II). In other words, thermolysis was more facile than hydrolysis. Similarly, $(CH_3)_3P$ decomposition was not significantly affected. However, for DMMP and $(CH_3O)_3P$ water did have a beneficial effect and decomposition temperature was lowered to about 500 °C, and the main product in their decomposition was CH_3OH. Phosphorus oxides were also detected (amu 80, 110, and 124), although much of the phosphorus oxides deposited on the walls of the reactor and tubing leading to the column and jet separator and never enetered the mass spectrometer.

(3) Decomposition Products from Organophosphorus Compounds Passed over MgO(130). Using MgO(130), decomposition products of several phosphorus compounds are listed in Table III. Since the length of the MgO bed in the reactor was about one-tenth of the total reactor length, the contact time of the organophosphorus compound with the MgO would be about 0.7 s (or one-tenth of the 7 s needed to traverse the entire reactor). Temperatures of decomposition *were dramatically lowered* compared with simple thermal decomposition. All the organophosphorus compounds except $(CH_3)_3P$ began to decompose as low as 170 °C over MgO. For DMMP and $(CH_3O)_3P$ the major product was formic acid (amu 46). For the ethoxy-substituted compounds $(C_2H_5O)_3P{=}O$ and $(C_2H_5O)_3P$, ethanol was a major product initially. When the temperature of the MgO bed was 200 °C, *complete decomposition of these four compounds was found.* Product compositions did not change at higher temperatures, until 500 °C for DMMP and $(CH_3O)_3P$ and 300 °C for the ethoxy compounds. At the higher temperatures (e.g., 600 °C) DMMP and $(CH_3O)_3P$ yielded CH_4 (amu 16), H_2O (amu 18), CO (amu 28), CO_2 (amu 44), and some HCOOH. At 700 °C the same products without HCOOH were observed, and control experiments showed that formic acid decomposed at these temperatures to CO + H_2O. The $(C_2H_5O)_3P{=}O$ and $(C_2H_5O)_3P$ over MgO at 300 °C yielded only ethene (C_2H_4, amu 28), and here it is likely that the initial product ethanol decomposed to C_2H_4 and H_2O. Finally, at 600 °C or higher, $(CH_3)_3P$ decomposed yielding mainly CH_4 (amu 16).

For all of these experiments, no compounds containing phosphorus were observed—all the phosphorus residues remained immobilized on the MgO.

(4) Effect of Water on Decomposition of Organophosphorus Compounds over MgO(130). Significant beneficial effects of added water were observed (see Table IV and Figure 2). For DMMP and $(CH_3O)_3P$, HCOOH was no longer a product; instead CH_3OH became the principle product in the temperature range 170–500 °C. Over 500 °C MgO, secondary products CH_4, H_2O, CO, and CO_2 were observed. Even for $(CH_3)_3P$, water had a beneficial effect, and at 500 °C CH_3OH and a small amount of HCOOH were found.

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[25] Stehnagen, E., Abrahamsson, S., McLafferty, F. W., Eds. *Atlas of Mass Spectral Data*; Interscience Publishers: New York, 1969; Vols. 1, 2.

Table I. Effect of Temperature on Decomposition Products in Empty Reactor (Thermal Decomposition)

	DMMP		$P(OCH_3)_3$		$P(CH_3)_3$		$(C_2H_5O)_3P{=}O$		$P(OC_2H_5)_3$	
temp, °C	*m/e*	assgnt[a]	*m/e*	assgnt[a]	*m/e*	assgnt[a]	*m/e*	assgnt[a]	*m/e*	assgnt[a]
200							182	und[b]	166	und
300							182	und	166	und
400							M 182[c]	M und	M 166	M und
							S 28	S C_2H_4	S 28	S C_2H_4
500	124	und	124	und	76	und	S 182	S und	166	und
							M 28	M C_2H_4	28	C_2H_4
600	124	und	124	und	76	und	28	C_2H_4	28	C_2H_4
							80	PO_3H	80	PO_3H
							110	P_2O_3	110	P_2O_3
700	124	und	124	und	76	und	28	C_2H_4	28	C_2H_4
							80	PO_3H	80	PO_3H
							110	P_2O_3	110	P_2O_3
									124	P_4
750	94	$(CH_3)PO_3$	S 79	S PO_3	76	und				
	30	C_2H_6	S 30	S C_2H_6						
	124	und	124	und						
800	94	$(CH_3)PO_3$	28	C_2H_4, CO	76	und				
	30	C_2H_6	124	P_4						
	124	und								
850	16	CH_4	16	CH_4	16	CH_4				
	28	C_2H_4, CO	28	C_2H_4, CO	28	C_2H_4				
	79	PO_3	79	PO_3		CO				
	94	$(CH_3)PO_3$	124	P_4	124	P_4				
	124	P_4								
900	16	CH_4	16	CH_4	16	CH_4				
	28	C_2H_4, CO	28	C_2H_4, CO	28	C_2H_4				
	124	P_4	124	P_4	124	P_4				

[a] Here only parent ion *m/e* is listed and assignment also based on fragmentation pattern. [b] Und means undecomposed phosphorus compound. [c] S means small amount, M means major product.

Table II. Effect of Water on Decomposition Products on Empty Reactor (Thermal Decomposition) (Phosphorus Compound:Water = 1:1)[a]

		temp, °C		
organophosphorus compd		500	600	700
DMMP	*m/e*	S 32, 18, M 124	18, 32, 63, 124	18, 32, 80, 110, S 124
	assgnt	S CH_3OH, H_2O, M und	H_2O, CH_3OH, PO_2, und	H_2O, CH_3OH, PO_3H, P_2O_3, und
$P(OCH_3)_3$	*m/e*	18, 32, 110, 124	18, 32, 110 S 124	18, 32, 80, 110 S 124
	assgnt	H_2O, CH_3OH, P_2O_3, und	H_2O, CH_3OH, P_2O_3, S und	H_2O, CH_3OH, PO_3H, P_2O_3, S und
$P(CH_3)$	*m/e*	76	76	76
	assgnt	und	und	und
$(C_2H_5O)_3P{=}O$	*m/e*	S 182 M 28	28, S 80, 110	28, S 80, 110
	assgnt	S und M C_2H_4	C_2H_4 S PO_3H, P_2O_3	C_2H_4 S PO_3H, P_2O_3
$P(OC_2H_5)_3$	*m/e*	166, 28	28 S 80, 110	28 S 80, 110, 124
	assgnt	und, C_2H_4	C_2H_4 S PO_3H, P_2O_3	C_2H_4 S PO_3H, P_2O_3, P_4

[a] All footnotes are the same as those in Table I.

For the ethoxy phosphorus compounds, water did not have any significant effect on decomposition temperature or products.

To learn more about this water effect, a series of experiments were carried out with varying amounts of water at 500 °C. In Figure 2 the ratios of products CH_3OH to HCOOH vs water to DMMP are plotted. When no water was added to the DMMP, only HCOOH was the product. As more water was added, CH_3OH eventually became the main product.

(5) Decomposition of DMMP on MgO(390). A direct comparison of high surface area MgO(390) and lower surface area MgO(130) was made. Product distributions from DMMP decomposition are shown in Table V. No changes in product distributions were found. However, the much greater capacity of MgO(390) for decomposing DMMP was reconfirmed,[1a] and decomposition of the most stable compound $(CH_3)_3P$ was enhanced.

(6) Water Regeneration of Exhausted MgO. After MgO(130) or MgO(390) beds had been completely exhausted by repeated DMMP injections until no more DMMP decomposed, we began to inject 2-μL pulses of pure water (or D_2O). It was found that *about 30% of the MgO capacity for DMMP decomposition could be regenerated at 500 °C.*

The surface-adsorbed species that were released *did not contain any phosphorus*. The only major product was CH_3OH along with small amounts of HCOOH from either MgO(130) or MgO(390). When D_2O was used as the regenerating agent, CH_3OD was the major product.

Table III. Decomposition of Several Organophosphorus Compounds on MgO(130) at Different Temperatures[a]

temp, °C		DMMP	$P(OCH_3)_3$	$P(CH_3)_3$	$(C_2H_5O)_3P{=}O$	$P(OC_2H_5)_3$
150	*m/e*	124	124	76	182	166
	assgnt	und	und	und	und	und
170	*m/e*	S 46	S 46	76	S 31, 182	S 31, 166
	assgnt	S HCOOH	S HCOOH	und	S C_2H_5OH, und	S C_2H_5OH
200	*m/e*	46	46	76	31, 182	31, 166
	assgnt	HCOOH	HCOOH	und	C_2H_5OH, und	C_2H_5OH, und
300	*m/e*	46	46	76	31, 28, S 182, 18	31, 28, S 166, 18
	assgnt	HCOOH	HCOOH	und	C_2H_5OH, C_2H_4 S und, H_2O	C_2H_5OH, C_2H_4 S und, H_2O
400	*m/e*	46	46	76	28	28
	assgnt	HCOOH	HCOOH	und	C_2H_4	C_2H_4
500	*m/e*	46	46	76	28	28
	assgnt	HCOOH	HCOOH	und	C_2H_4	C_2H_4
600	*m/e*	16, 18, 28, 44, 46	16, 18, 28, 44, 46	76 S 16	28	28
	assgnt	CH_4, H_2O, CO, CO_2, HCOOH	CH_4, H_2O, CO, CO_2, HCOOH	und S CH_4	C_2H_4	C_2H_4
700	*m/e*	16, 18, 28, 44	16, 18, 28, 44	76 S 16	28	28
	assgnt	CH_4, H_2O, CO, CO_2	CH_4, H_2O, CO, CO_2	und S CH_4	C_2H_4	C_2H_4

[a] All footnotes are the same as those in Table I. The MS spectrum for C_2H_5OH showed the peak with *m/e* 31 as the most intense.

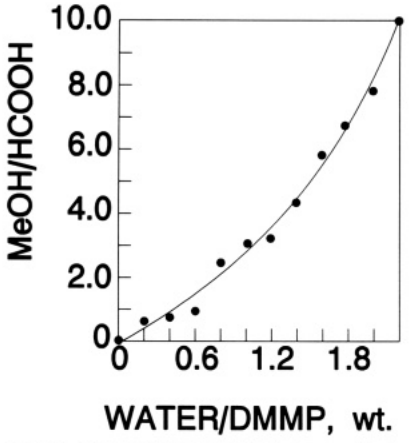

Figure 2. Ratio of MeOH/HCOOH in product vs ratio of H_2O/DMMP in feedstock.

The MgO samples before and after water regeneration were analyzed for C, H, and P residues (Table VI). The results add support to our earlier conclusions about the chemical nature of the residue.[1] The species $(CH_3O)(CH_3)POO(MgO)$ was proposed earlier. Reaction of water with this material caused the removal of most of the CH_3O groups (but not all) and this correlated with the CH_3OH product observed and approximately with the C/H and P/C ratio changes.

Discussion

(A) Cleavage of Bonds in Organophosphorus Compounds. (1) Thermal Cleavage in Empty Reactor. Under the conditions we employed, 1 atm of He flow, 7-s residence time in the reactor, we found that the ethoxy compounds $(C_2H_5O)_3P{=}O$ and $(C_2H_5O)_3P$ thermally decomposed about 400 °C by splitting out C_2H_4 (a C_2H_5–O bond cleavage). Water addition or increased temperature had little further effect. Thus, dealkylation by C_2H_4 loss was most facile, and extensive dealkylation also caused the elution of phosphorus-containing compounds PO_3H, P_2O_3, and at higher temperatures P_4.

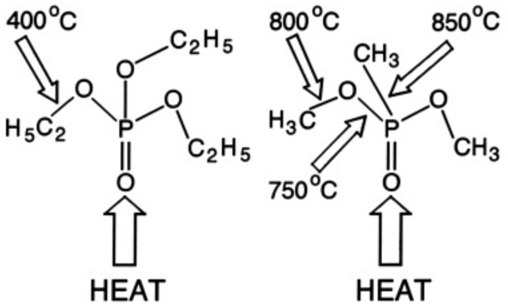

Figure 3. Cleavages of bonds in $(C_2H_5O)_3P(O)$ and DMMP under thermal decomposition condition.

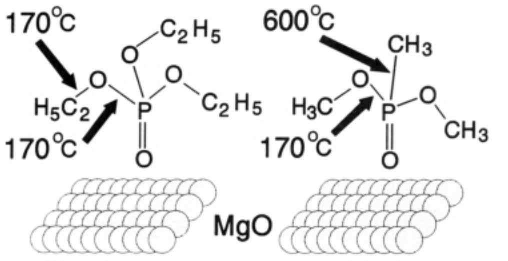

Figure 4. Cleavages of bonds of $(C_2H_5O)_3P(O)$ and DMMP on MgO.

These reactor conditions did not cause decomposition of the methoxy substituted DMMP and $(CH_3O)_3P{=}O$ until quite high temperatures were employed. Only at 750 or 800 °C did substantial decomposition take place, and CH_3O–P bonds were cleaved and phosphorus species $(CH_3)PO_3$, PO_3 and P_4 eluted.[26]

Figure 3 illustrates the conclusions based on these studies. We should again emphasize that our experimental conditions are very different from those employed earlier by White, Weinberg, Graven, and co-workers.[5,15–19] Decomposition temperatures reported varied widely in these reports. In our studies of thermal decomposition under dynamic He flow, it is not easy to decompose these compounds, in particular DMMP and $(CH_3O)_3P$.

(2) Decomposition on MgO. The presence of MgO dramatically lowers the required temperatures for decomposition, when comparing identical experimental conditions (compare Figures 3 and 4). *It is clear that the MgO surface serves as an extremely reactive environment and encourages dealkylation reactions, proton abstractions,*[27]

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[26] We should point out that DMMP and P_4 have the same nominal mass (amu 124). However, they were easily distinguished by fragmentation pattern.

[27] Hoq, M. F.; Nieves, I.; Klabunde, K. J. *J. Catal.* **1990**, *123*, 349.

Table IV. Effect of Water on Decomposition of Organophosphorus Compounds on MgO(130) at Different Temperatures (Phosphorus:Water = 1:1)[a]

temp, °C		DMMP	$P(OCH_3)_3$	$P(CH_3)_3$	$(C_2H_5O)_3P{=}O$	$P(OC_2H_5)_3$
150	*m/e*	124	124	76	182	166
	assgnt	und	und	und	und	und
170	*m/e*	S 46 32, 124	S 46 32, 124	76	S 31, 182	S 31, 166
	assgnt	S HCOOH CH_3OH, und	S HCOOH CH_3OH, und	und	S C_2H_5OH und	S C_2H_5OH und
200	*m/e*	32, S 46	32, S 46	76	31, 182	31, 166
	assgnt	CH_3OH, S HCOOH	CH_3OH S HCOOH	und	C_2H_5OH, und	C_2H_5OH, und
300	*m/e*	32 S 46	32 S 46	76	31, 28 S 182,	31, 28 S 166
	assgnt	CH_3OH S HCOOH	CH_3OH S HCOOH	und	C_2H_5OH, C_2H_4 S und	C_2H_5OH, C_2H_4 S und
400	*m/e*	32 S 46	32 S 46	76	28	28
	assgnt	CH_3OH S HCOOH	CH_3OH S HCOOH	und	C_2H_4	C_2H_4
500	*m/e*	32 S 46	32 S 46	S 32, 46 76	28	28
	assgnt	CH_3OH S HCOOH	CH_3OH S HCOOH	S CH_3OH, HCOOH und	C_2H_4	C_2H_4
600	*m/e*	16, 18, 28, 44	16, 18, 28, 44,	16, 28, 44, 76	28	28
	assgnt	CH_4, H_2O, CO, CO_2	CH_4, H_2O, CO, CO_2	CH_4, CO, CO_2, und	C_2H_4	C_2H_4
700	*m/e*	16, 18, 28, 44	16, 18, 28, 44	16, 28, 44 S 76	28	28
	assgnt	CH_4, H_2O, CO, CO_2	CH_4, H_2O, CO, CO_2	CH_4, CO, CO_2 S und	C_2H_4	C_2H_4

[a] All footnotes are the same as those in Table I.

Table V. Decomposition of Several Organophosphorus Compounds on MgO(390) at Different Temperatures[a]

temp, °C		DMMP	$P(OCH_3)_3$	$P(CH_3)_3$	$(C_2H_5O)_3P{=}O$	$P(OC_2H_5)_3$
170	*m/e*	46, 124	46, 124	76	S 31, 182	S 31, 166
	assgnt	HCOOH, und	HCOOH, und	und	S C_2H_5OH, und	S C_2H_5OH, und
300	*m/e*	46	46	76	28	28
	assgnt	HCOOH	HCOOH	und	C_2H_4	C_2H_4
500	*m/e*	46	46	S 32, 76	28	28
	assgnt	HCOOH	HCOOH	S CH_3OH, und	C_2H_4	C_2H_4
700	*m/e*	16, 18 S 46	16, 18 S 46	16, 76	28	28
	assgnt	CH_4, H_2O S HCOOH	CH_4, H_2O S HCOOH	CH_4, und	C_2H_4	C_2H_4

[a] All footnotes are the same as those in Table I. The MS spectrum for C_2H_5OH showed the peak with *m/e* 31 as the most intense.

Table VI. Residue on Exhausted MgO before and after Water Regeneration

	wt %			atomic ratio	
	C	H	P	C/H	P/C
MgO before water regeneration	2.04	0.50	2.82	1/2.94	1/1.89
MgO after water regeneration	1.70	0.58	3.65	1/4.14	1/1.17

and nucleophilic displacements. The capacity for these reactions is directly dependent on surface area. However, in the case of $(CH_3)_3P$, the high surface area MgO(390) possesses an intrinsically higher activity for $(CH_3)_3P$ decomposition. Since defect sites are probably the reactive sites for these reactions[24d,28] and since higher surface area material (nanoscale particles of 40-Å crystallite sizes) should possess a wider variety of such defect sites, it seems likely that specific sites are necessary to aid decomposition of $(CH_3)_3P$.

The products of these decomposition reactions are interesting. We have mentioned that HCOOH, CH_3OH, C_2H_5OH, CO, H_2O, and C_2H_4 are primary products. Note that HCOOH, C_2H_5OH, and a possible product CH_3OCH_3 all have the same molecular weight (amu 46). However, GC retention times coupled with variation in fragmenta-

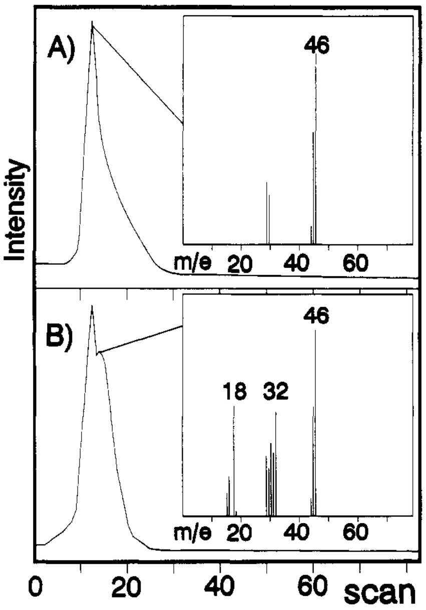

Figure 5. GC-MS spectra of decomposition products of DMMP on MgO: (A) product at the beginning of the decomposition; (B) products after five injections.

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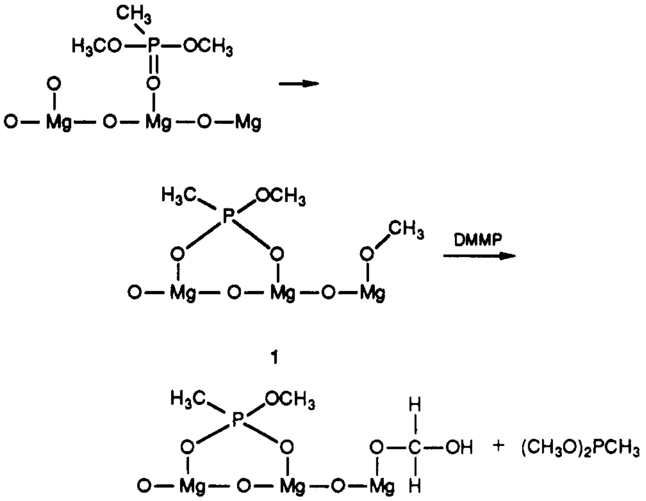
(28) Morris, R. M.; Klabunde, K. J. *Inorg. Chem.* **1983**, *22*, 682.

tion patterns for these compounds allowed these compounds to be readily differentiated.

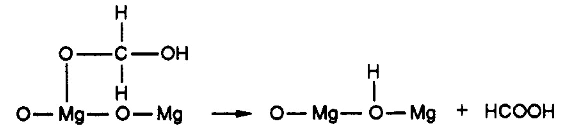
How are these products formed and how and why does water affect the product distribution? Basically we need to discuss possible mechanisms, and this discussion will be based on earlier FT-IR work[1b] coupled with data herein, including isotope labeling. We will separate the discussion into consideration of products that are related or interdependent.

(a) HCOOH, CH_3OH, and H_2O. Formic acid is a ubiquitous product from methoxy-substituted organophosphorus compounds. To form HCOOH, an adsorbed methoxy group must be oxidized. In an earlier report we proposed that this oxidation occurs by a second molecule, for example, DMMP.[1a]

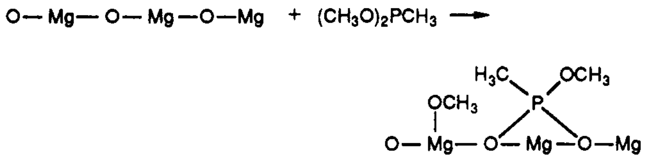


1

During this process a CH_3O group is adsorbed and oxidized, and then released as HCOOH, generating an adsorbed H(a) group.



Also a deoxygenated DMMP is released and probably adsorbs to the surface through surface oxygen species.



2

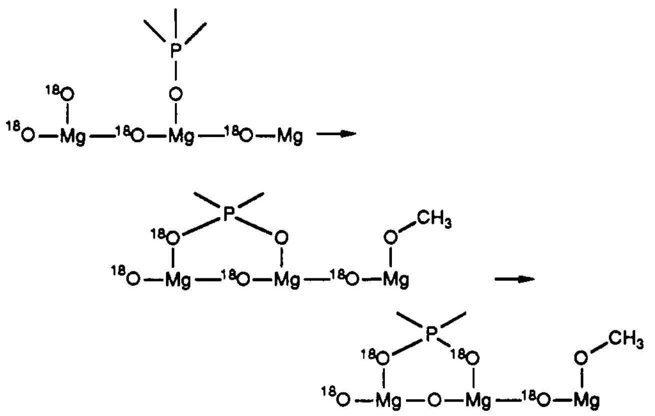
In this way another adsorbed CH_3O group is formed along with residue 2 that is very similar to residue 1. However, note that in residue 1 one bridging oxygen originated with the MgO, but for residue 2, both bridging oxygens originate with the MgO.

The overall reaction stoichiometry could be represented as follows:

$$3[CH_3(CH_3O)_2P{=}O] \xrightarrow{MgO} \underbrace{[CH_3(CH_3O)PO](a)}_{\text{residue 1}} + 2\underbrace{[CH_3(CH_3O)P](a)}_{\text{residue 2}} + 2HCOOH + CH_3O(a) + 2H(a)$$

If this sequence is correct, it would be expected that as the reaction proceeds to exhaustion of the MgO surface capacity, more and more $[H]_a$ would be formed, and this would encourage the release of more CH_3OH before it can be oxidized to HCOOH. This is indeed what is found and is illustrated by Figure 5. With the first pulse of DMMP, the only volatile product is HCOOH. However, with continued pulsing, CH_3OH and H_2O begin to elute as well. Furthermore, it would be expected that *addition* of water would cause the formation of abundant $[OH]_a$ and $[H]_a$ species, and CH_3OH would quickly become the favored product. Our water addition experiments strongly support this concept (Figure 2). In addition, when D_2O was added instead of H_2O, the product was CH_3OD, showing that the $[CH_3O]_a$ species is indeed released by reaction with $[D]_a$, and does not undergo H-D exchange on the carbon atom.

An important question remains, however. Is it true that the oxygen for oxidation of $[CH_3O]_a$ comes from a second DMMP molecule or from the MgO? An ^{18}O labeling experiment would be helpful here. To do this we prepared pure $Mg^{18}O$.[29] We then pulsed DMMP over this sample and found that one ^{18}O was incorporated in the HCOOH. This indicates that rapid oxygen exchange occurs on the surface. At what stage it occurs is unclear at this time, but it seems likely that the oxygen bridged phosphorus residue would be mobile, and this could serve to scramble the unlabeled oxygen onto the surface and partially with the lattice, perhaps as shown here:



If the residues 1 and 2 are mobile on the surface the normal ^{16}O oxygen would quickly become overwhelmed by ^{18}O, and the oxidizing power of the second molecule of DMMP would serve as a surface-bound oxidizing agent for $[OCH_3]_a$.

Is there other evidence that the P=O moiety serves to oxidize $[OCH_3]_a$? If this were true, it would be expected that $(CH_3O)_3P$, an isomer of DMMP, would not yield HCOOH as a product. However, we do observe some formic acid production suggesting that $(CH_3O)_3P$ can also provide some oxidizing power, perhaps through an isomerization process to DMMP. However, we observed that the capacity for MgO decomposition of $(CH_3O)_3P$ is considerably less than for DMMP.[1a] Although more definitive information is needed, we suggest that initially $(CH_3O)_3P$ can be isomerized to DMMP and then the chemistry described for DMMP holds. However, as the surface of the MgO slowly becomes more saturated with phosphorus residue and $[H]_a$, the ability to isomerize $(CH_3O)_3P$ lessens, and a different decomposition pathway ensues and less capacity for $(CH_3O)_3P$ decomposition is realized by this pathway.

In this regard, some further consideration of water effects are appropriate. From the data in Tables II and IV it is apparent that the presence of water does not affect the temperature of decomposition, although it does affect product distributions. Such changes were particularly

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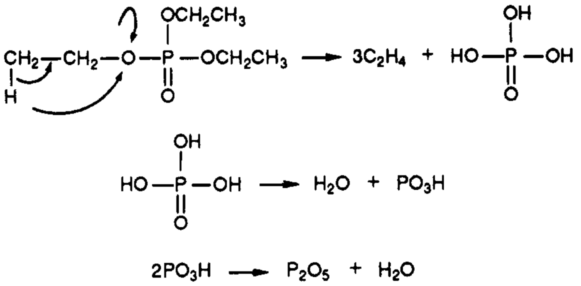
[29] Li, Y.-X., unpublished work from this laboratory.

evident for DMMP and $(CH_3O)_3P$ (Table IV). It would appear that on MgO these compounds very readily lose a CH_3O species, which is adsorbed, and if sufficient $[H]_a$ is available, protonation to form CH_3OH occurs. And if $[H]_a$ groups are not abundant, oxygen is scavenged to yield HCOOH.

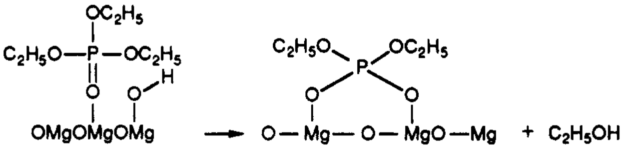
In contrast, however, $(CH_3)_3P$ decomposition temperature was affected by the presence of water and at 500 °C CH_3OH and HCOOH are products in small amounts. These results indicate that if the termperature is high enough, even $H_3C–P$ bonds can be attacked. Upon pushing the temperature higher, then CH_4 became predominant. Note though that CO and CO_2 were also formed, and this obviously requires some oxygen to be supplied by the MgO, probably with concomitant formation of magnesium phosphides. We intend to do further $Mg^{18}O$ studies in the future to clarify this point.

It should be reemphasized that at the higher temperatures the primary product HCOOH decomposed to CO and H_2O (usually at about 600 °C).

(b) C_2H_4 and C_2H_5OH. For the ethoxy-substituted compounds ethylene was the major gaseous product upon thermolysis. Additional eluted products were H_2O, PO_3H, and P_2O_5. It seems clear that thermolysis simply involves β-hydrogen elimination:



When MgO was present, a completely different reaction path was followed, and C_2H_5OH was the primary volatile product. This reaction depends on the presence of $[H]_a$:



This concept is supported by the fact that initially C_2H_5OH is the primary product, and when $[H]_a$ is exhausted, C_2H_4 starts to form. The presence of added H_2O aids the formation of C_2H_5OH, as expected.

An experiment where $Mg^{18}O$ was employed showed that the C_2H_5OH initially formed did not contain ^{18}O. Therefore, the oxygen in the C_2H_5OH comes from the organophosphorus molecule, and not the MgO surface.

In the absence of added H_2O as a reagent, with continued injections of the $(C_2H_5O)_3P{=}O$, ethylene and water are also formed. The H_2O as a product could serve to extend the hydrolysis effectiveness of the MgO. Overall the reaction products are given by

$$(C_2H_5O)_3P{=}O \xrightarrow{MgO} [PO_2]_a + 2C_2H_5OH + C_2H_4$$

In the case of $(C_2H_5O)_3P$, the stoichiometry is slightly altered:

$$(C_2H_5O)_3P \xrightarrow{MgO} [PO_2]_a + C_2H_5OH + 2C_2H_4 + [H]_a$$

(At higher temperatures, of course, C_2H_5OH decomposes quickly to C_2H_4 plus H_2O.)

It should be reemphasized that the capacity of MgO for destructive adsorption of these ethoxy compounds is very high, even higher than with DMMP.[1a] This indicates that nearly all the surface MgO moieties are effective in this hydrolysis/decomposition process, and we suspect that the phosphorus residue is more completely dealkylated than with DMMP. This is why we prefer to indicate the residues as $[PO_2]_a$ rather than still partially alkylated.

Conclusions

Thermal decomposition under dynamic flow conditions without MgO causes the cleavage of $PO–C_2H_5$ at 400 °C, $P–OCH_3$ at 750 °C, $PO–CH_3$ at 800 °C, and $P–CH_3$ at 850 °C.

Decomposition on MgO under dynamic flow conditions causes the cleavage of $PO–C_2H_5$ at 170 °C, $P–OCH_3$ at 170 °C, and $P–CH_3$ at 600 °C.

Addition of water to the organophosphorus compound dramatically enhances the facility of MgO to destroy the phosphorus compounds.

Water pulses can be used to partially regenerate a spent MgO bed.

Dealkylation is a facile reaction for ethoxy-substituted systems, and the primary product is C_2H_5OH when water is present. If water is not present, C_2H_4 predominates. At the higher temperatures C_2H_5OH decomposes to C_2H_4 and H_2O.

For methoxy-substituted systems, an important product is formic acid, and it is formed by oxidation of adsorbed methoxy groups. Oxidation power may initially be provided by surface defect sites but mainly is provided by the $P{=}O$ group, and the oxygen is transferred to the MgO surface (scrambled on the surface) before being transferred to the $[CH_3O]_a$, as shown by ^{18}O-labeling experiments.

In the presence of water the formic acid product gives way to CH_3OH. At higher temperature in the absence of H_2O, HCOOH decomposes to CO and H_2O.

If the methoxy phosphorus compound does not contain a $P{=}O$ bonds, it is still decomposed over MgO, but the capacity of the MgO is not as high. This is probably due to the fact that $[CH_3O]_a$ cannot be as readily oxidized and removed from the surface, since $P{=}O$ is not present to provide oxidizing power.

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Registry No. DMMP, 756-79-6; $P(OCH_3)_3$, 121-45-9; $P(CH_3)_3$, 594-09-2; $(C_2H_5O)_3PO$, 512-56-1; $P(C_2H_5O)_3$, 122-52-1; MgO, 1309-48-4; water, 7732-18-5.