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# DECOMPOSITION OF PHOSPHONOFLUORIDATES ON GLASS

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## SUMMARY

Neat droplets of O,O-diisopropylphosphorofluoridate (DFP) and O-1,2,2-trimethylpropyl methylphosphonofluoridate (Soman) decompose on glass. In thirty hours at room temperature over 40% of the Soman has been decomposed while nearly 15% of the DFP has been degraded. NMR spectroscopic analysis of the Soman showed that Soman decomposed exclusively by scission of the P-F bond to form O-1,2,2-trimethylpropyl methylphosphonic acid. The rate of decomposition of the two organophosphorus fluorine substrates is proportional to the rate of hydrolysis. The results are consistent with earlier studies which showed that silica or magnesia promoted the decomposition of sarin (O-2-propylisopropyl methylphosphonofluoridate). The rate of decomposition on glass is accelerated in the presence of high humidity.

## INTRODUCTION

Organophosphorus esters containing a P-F bond are potent neurotoxins. Compounds such as Soman, (O-1,2,2 trimethylpropyl methylphosphonofluoridate), inactivate acetylcholinesterase by phosphorylation of a serine group in the active site of the enzyme with concomitant release of fluoride ion [1].

Our laboratory has been trying to identify both homogeneous and heterogeneous catalysts to detoxify these agents. During the course of one study, we exposed Soman to vials containing a flat piece of a thin film impregnated with a compound intended to detoxify the Soman. At recorded times, 0.5 μL of neat Soman was

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added to each vial using a 1-μL Hamilton syringe. Each vial was quickly recapped after the agent was added. The vials were stored at room temperature (24°C ± 2°C) for 0, 1, 3, 5, 8, 12, or 24 hr. The appropriate vials from each of the six sets (blanks plus five with film) were quenched by the addition of 3 mL of tetrachloroethylene. The tetrachloroethylene solutions were transferred to the GC sample injector vials for analysis of residual Soman by GC.

The results are summarized in Table 1. The zero time analyses show that Soman is recovered with a sample standard deviation of 4-5%. There is no evidence of evaporation or loss of Soman within 12 hr, yet there is clearly a significant loss of Soman in the vials stored for twenty-four hours which may be due to a reaction between the Soman and glass. Since there was only one sample run as a control, we elected to repeat the control experiments with replicates and to also add DFP (O,O-diisopropyl phosphorofluoridate) as well as Soman as substrates exposed to the glass.

TABLE 1

Recovery of 0.5 L of Soman exposed to candidate reactive substrates

| Time,hr | Glass Control | Test Substrate |
|---|---|---|
| 0 | 15.9[a] | 16.2 ± 0.6 (5)[b] |
| 1 | 16.2 | 15.9 ± 0.3 (5) |
| 3 | 14.5 | 15.7 ± 0.9 (4) |
| 5 | 16.2 | 16.7 ± 0.5 (5) |
| 8 | 14.4 | 16.2 ± 1.1 (3) |
| 12 | 15.2 | 15.3 ± 0.7 (5) |
| 24 | 10.2 | 10.3 ± 0.7 (5) |

[a] Numbers represent kilocounts from GC.

[b] Number of replications are in parentheses; error is sample standard deviation.

## EXPERIMENTAL

One microliter of substrate was added to a series of vials (3.7 mL vial equipped with a tightly fitting screw-top and Teflon$^{R}$-faced septum). After the appropriate reaction time, the substrates were quenched with addition of one mL of isopropanol and transferred to the GC for analysis.

Soman was taken from a stock available at our Center and was 95% pure by NMR. DFP was obtained from Sigma and was 94% pure by NMR. Both materials displayed only one peak under the GC conditions described below. Solvents were reagent grade.

Analyses of residual Soman and DFP were done by GC under identical conditions. We used a Shimadzu GC-9A with an FPD in the phosphorus mode and a 50-sample autoinjector. Injection volume (nominal) was 1 μL. The column was a Supelco SBR-5 wide-bore capillary, 0.75 mm x 30 ft. No sample splitter was used. The carrier was helium at 5 mL/min with appropriate make-up at the detector. The chromatograms were acquired by a Shimadzu 3-R recording integrator. Prior to the analysis of the unknowns, a set of five standards were run. The plots of peak area *vs*. concentration were either linear or showed slight curvature at higher concentrations. In the cases where curvature was observed, the data were fitted to a second-order polynomial without constant. All the data provided excellent agreement (3%) between calculated and experimental values.

## RESULTS AND DISCUSSION

Table 2 summarizes the results of these experiments. It is clear that both agents decompose in the presence of the glass in accord with the earlier single run with a glass control sample.

To further characterize that a reaction was taking place, we used $^{31}$P NMR to analyze one of the quenched Soman samples that had spent 17 hours in contact with the glass.

The NMR procedure went as follows: 1 mL of sample was placed into a 5-mm o.d. Pyrex NMR tube, and the $^{31}$P NMR spectrum was recorded using a Varian XL-200 Superconducting FT-NMR system operating at 81 MHz in an unlocked mode. The spectrum was obtained at a probe temperature of *ca*. 21°C, and phosphoric acid

TABLE 2

Recovery of Soman and DFP from capped glass vials[a]

| Time,hr | Soman, L | DFP, L |
|---|---|---|
| 0 | 0.986 ± .006 | 0.997 ± .013 |
| 2 | .957 ± .010 | .992 ± .045 |
| 6 | .855 ± .013 | .997 ± .030 |
| 17 | .435 ± .010 | .926 ± .018 |
| 24 | .554 ± .007 | .924 ± .020 |
| 30 | .574 ± .021 | .869 ± .060 |

[a] Mean recovery from five replicates at each time. The error is the sample standard deviation.

(85%) was used as the external reference. The chemical shift values reported are good to ±0.2 ppm; a positive chemical shift value indicates that the resonance is downfield with respect to the reference. Approximately 13,000 transients were accumulated using a pulse width of 3 sec (33°), a sweep width of 20 kHz, an acquisition time of 1.6 sec, and a pulse delay of 2.5 sec. Gated decoupling was used to eliminate any nuclear Overhauser effects, and quantitative data were obtained by digital integration of the peak areas.

The NMR analysis showed that O-1,2,2-trimethylpropyl methylphosphonic acid (PMPA) ( $^{31}$P: 25.0 ppm) was the only phosphorus species other than Soman ( $^{31}$P: 29.2, 30.1 ppm $J_{P-F}$ = 1040Hz)and that the two phosphorus compounds accounted for all the original Soman added to the vial. NMR analysis yielded 39 mole % Soman while GC analysis of the same sample showed that 41 mole % of the original Soman was left in the vial. The Soman decomposition of DFP relative to Soman is consistent with a heterogeneous reaction releasing fluoride ion, since Soman hydrolyzes twice as rapidly as DFP [2,3].

These results are also consistent, with earlier studies by Dutch workers [4,5] who demonstrated that Sarin (O-isopropyl methylphosphonofluoridate) was decomposed on alumina or magnesia.

Posner [6] also showed that DFP was decomposed in an ether-alumina slurry, although only loss of DFP was monitored. The present studies are unique in that neat droplets of agent react with glass and that NMR analysis provides conclusive evidence that the only reaction is scission of the P-F bond to form phosphonic acid.

The minimum Soman recovered at 17 hours is interesting, since it raises the possibility that HF may be reacting with PMPA to reform Soman. One needs to follow such reactions either to completion or show that some equilibrium is formed among Soman, PMPA, and HF.

One final set of runs was done to see the effect of humidity on the reaction. A capillary tube sealed at one end was placed in each vial. The tube was open at one end and short enough so that the capillary could stand upright in each vial. The capillary was approximately half-filled with water. Table 3 lists the amount of Soman or DFP left in each vial in the presence of the water-filled capillary. It is clear that the presence of water accelerates the heterogenous decomposition of the phosphorus-fluorine substrates. Again, the relative rate of reaction is indicative of the relative ease of hydrolysis of two agents.

TABLE 3

Recovery of Soman and DFP from capped glass vials in the presence of water vapor[a,b]

| Time,hr | Soman, µL | DFP, µL |
|---|---|---|
| 0 | 0.994 ± .017 | 0.987 ± .010 |
| 2 | 0.619 ± .74 | 0.949 ± .005 |
| 6 | 0.135 ± .035 | 0.833 ± .028 |
| 17 | ---- | 0.599 ± .006 |
| 25 | ---- | 0.433 ± .025 |
| 30 | ---- | 0.334 ± .033 |

[a] Mean recovery from five replicates at each time.
[b] The error is the sample standard deviation.

## REFERENCES

1 B.C. Saunders, Phosphorus and Fluorine. The Chemistry and Toxic Action of Their Organic Compounds, Cambridge University Press, London, 1957.

2 R.L. Gustafson, S. Chabarek, and A.E. Martell, J. Am. Chem. Soc., 85 (1963) 598.

3 J.R. Ward, Y. Yang, R.B. Wilson, W.D. Burrows, and L.L. Ackerman, Bioorg. Chem., 16 (1988) 12.

4 A.E.T. Kuiper, J.J.G.M. van Bokhoven, and J. Medema, J. Catal., 43 (1976) 154.

5 J.J.G.M. vanBokhoven, A.E.T. Kuiper, and J. Medema, J. Catal., 43 (1976) 168.

6 G.H. Posner, J.W. Ellis, and J. Ponton, J. Fluorine Chem., 19 (1981) 191.