Bull. Environ. Contam. Toxicol. (1984) 33:1–5

Environmental Contamination and Toxicology

Stability of Aqueous Solutions of Sarin and Soman: Influence of Concentration and an Equation for Determining Concentration

Ming L. Shih and Robert I. Ellin

U.S. Army Medical Research Institute of Chemical Defense, Aberdeen Proving Ground, MD 21010

Aqueous solutions of sarin (isopropyl methylphosphonofluoridate) and soman (pinacolyl methylphosphonofluoridate) degrade at minimum rates between pH values 4-7 (Epstein 1974). Dilute aqueous solutions containing 10-20 µg per ml (approximately 10^{-4} M) at an initial pH 5 degrade at minimum rates (Ellin et al. 1981). In this paper we report that more concentrated solutions containing 0.2 to 2.0 mg/ml (approximately 10^{-3} and 10^{-2} M) degrade more rapidly than lower concentrations. Since degradation is significant at 25°C in the course of a working day, the concentration of a sample should be addressed throughout an experiment. Procedures used to determine organophosphorus concentrations are by enzyme inhibition analysis (Voss 1968) and/or gas chromatographic procedure provided in this report. For a more convenient method, an equation was derived which permits the investigator to determine the concentration of a degraded aqueous sample of sarin or soman by taking a pH of the solution.

MATERIALS AND METHODS

Sarin and soman were determined to be 99.5 mole % respectively by proton and phosphorus nuclear magnetic resonance analysis. Solutions of each compound were prepared in distilled water at a concentration of 2 mg/ml. Lower concentrations were made by dilution with distilled water. Stability studies were performed at -15°C and 25°C. For the -15°C studies, solutions were placed in individual glass test tubes, stoppered with screw caps and stored in a constant-temperature freezer. At selected time intervals, the contents of the tubes were thawed to room temperature prior to assay. Solutions were kept in an incubated waterbath for studies at 25°C. In assays of sarin, 0.2 ml of 2 mg/ml and 2 ml of 0.2 mg/ml were used; for soman, 0.1 ml of 2 mg/ml and 1 ml of 0.2 mg/ml were used. Samples were assayed in duplicate. Distilled water was added to make a final volume of 10 ml. Final concentrations of sarin and soman were 2.86×10^{-4} M and 1.10×10^{-4} M respectively. Two grams of sodium chloride were then added. To the sarin assay 100 µl of diisopropyl methylphosphonate (DIMP) in water (0.5 mg/ml) were added. For the soman assay 100 µl of diethyl ethylphosphonate (DEEP) in water (0.5 mg/ml) were added.

DIMP and DEEP are internal standards. One hundred µl of $CHCl_3$ was added, the tube was wrist-shaken for one minute, then centrifuged for 3 minutes at 1,200 rpm. One µl of $CHCl_3$ was injected into a Hewlett Packard Model 5880A gas chromatograph fitted with a packed glass column 6 ft x 4mm i.d., containing 10% OV-17 stationary phase on a Chromosorb HP 100/120 support. For the assay of sarin, the temperature conditions were: injection temperature 180°C; detector temperature 250°C; initial oven temperature 140°C for 5 minutes, then programmed 15°C/min to a final hold temperature of 180°C. Isothermal conditions at 170°C were used for soman. The chromatograph was equipped with a flame ionization detector. The flow rate of helium carrier gas was 14 ml/min. Area-concentration plots for sarin and soman were linear from 10-800 µg. Slopes were reproducible with a coefficient of variation of less than ± 2%. The extraction efficiency for sarin was 50% (± 5%) compared to 100% (± 2%) for soman. This may be due to the water solubility of sarin (completely miscible) compared to soman (21 gm/liter).

RESULTS AND DISCUSSION

The degradation of aqueous 2.0 and 0.2 mg/ml concentrations of sarin and soman at -15°C and 25°C are shown in Tables 1 and 2. The major degradation products, the corresponding phosphonic acid and HF, are responsible for the drop in pH. The pH of sarin solutions falls below pH 4 faster than soman solutions. After 24 h at 25°C, the 2.0 and 0.2 mg/ml sarin solutions degraded 98 and 19% respectively. Sarin concentrations showed considerable degradation even after one day at -15°C. At this temperature soman solutions, quantitated by the gas chromatographic procedure given above, retained potency during the five day test period. At 25°C, 2 mg/ml soman solutions degraded 1% per hour during the first 4 hours, then more rapidly, such that 62% was hydrolyzed after 24 h. A 0.2 mg/ml soman solution was stable for 8 h; only 8% degraded after 24 h.

An equation was derived for estimating the degradation of sarin or soman in aqueous solutions. This was established by using a proton balance equation where the sum of the concentration for species that form by proton consumption is equal to the sum of the concentration terms for species that are formed by the release of a proton (Martin et al. 1961). The species of major concern are HF for both sarin and soman and isopropyl methylphosphonic acid (IPA) and pinacolyl methylphosphonic acid (PPA) respectively for sarin and soman.

The stability of aqueous unbuffered solutions of sarin and soman are pH dependent. Between pH 4 to 6 hydrolysis is both minimal and constant; below pH 4 their rates of hydrolysis increase exponentially. The concentration of sarin and soman solutions affect rates of hydrolysis because of subsequent pH changes caused by hydrogen fluoride and the corresponding phosphonic acid. Equivalent concentrations of sarin are less stable than those of soman since the phosphonic acid formed from sarin is more acidic

Table 1. Stability of aqueous solutions of sarin and soman at 25°C.

Time h	% Remaining			
	2 mg/ml sarin	0.2 mg/ml sarin	2 mg/ml soman	0.2 mg/ml soman
0	100	100	100	100
2	91	100	99	100
4	85	98	95	100
8	54	92	87	100
15	16	87	70	94
24	2	81	38	92

Table 2. Stability of aqueous solutions of sarin and soman at -15°C.

Time days	% Remaining			
	2 mg/ml sarin	0.2 mg/ml sarin	2 mg/ml soman	0.2 mg/ml soman
0	100	100	100	100
1	80	84	98	100
2	64	71	97	100
3	54	57	97	98
4	40	48	100	102
5	24	30	99	100

The proton balance equation for sarin or soman is:

$$(H_3O^+) = (OH^-) + (A_1^-) + (A_2^-) \quad (1)$$

where (A_2^-) is fluoride concentration and (A_1^-) is the corresponding phosphonate concentration. The equations for concentrations of A_1^- and A_2^- as functions of (H_3O^+) are:

$$(A_1^-) = \frac{K_1 C_{HA_1}}{(H_3O^+) + K_1} \quad (2) \qquad (A_2^-) = \frac{K_2 C_{HA_2}}{(H_3O^+) + K_2} \quad (3)$$

where K is the dissociation constant of the phosphonic acid and C_{HA} is the concentration of dissociated and undissociated acid. pK_a values for HF, IPA and PPA are 3.19, 1.96 (Epstein 1974) and 2.54 (Harris et al. 1964) respectively. On substitution into equation (1), the proton balance equation becomes:

$$(H_3O^+) = \frac{K_w}{(H_3O^+)} + \frac{K_1 C_{HA_1}}{(H_3)^+) + K_1} + \frac{K_2 C_{HA_2}}{(H_3O^+) + K_2} \quad (4)$$

Equation (4) can be rearranged to:

$$(H_3O^+)^4 + (H_3O^+)(K_1 + K_2) + (H_3O^+)^2 (K_1K_2 - K_w - K_1C_{HA_1} - K_2C_{HA_2}) - (H_3O^+)(K_w(K_1+K_2) + K_1K_2C_{HA_1} + K_1K_2C_{HA_2}) - K_1K_2K_w = 0 \quad (5)$$

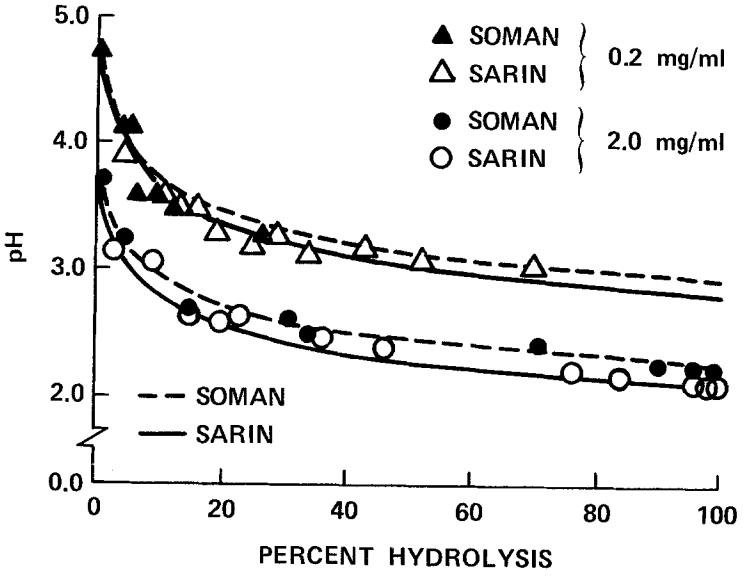

Fig. 1 The change in pH of aqueous solutions of sarin and soman with hydrolysis at 25°C. The solid and spaced lines are calculated from Eq. (7). The symbols are experimental values.

All terms containing K_w (dissociation constant of water) may be ignored. During hydrolysis of sarin and soman, equal molar concentrations of phosphonic acid and HF are produced. Since $C_{HA_1} = C_{HA_2}$, equation (5) simplifies to:

$$(H_3O^+)^3+(H_3O^+)^2(K_1+K_2)+(H_3O^+)\,[K_1+K_2-C_{HA_1}(K_1+K_2)\,]\,-$$
$$2C_{HA_1}K_1K_2 = 0 \qquad (6)$$

The concentration of the phosphonic acid equates to:

$$C_{HA_1} = \frac{(H_3O^+)\,[\,(H_3O^+)+K_1\,]\,[\,(H_3O^+)+K_2\,]}{(H_3O^+)(K_1+K_2)+2K_1K_2} \qquad (7)$$

pH values were experimentally determined at the time solutions of sarin and soman degraded. A plot of pH values calculated from Eq. 7 versus determined pH values for 2 mg/ml and 0.2 mg/ml sarin and soman resulted in curved lines (Figure 1). Experimental pH values were in excellent agreement with calculated values.

than that of soman. The use of buffers to maintain stability is not recommended as anions of buffers can act as nucleophiles which catalyze hydrolysis (Ellin et al. 1981).

An equation is presented which permits an investigator to determine the concentration of the corresponding phosphonic acid and consequently the concentration of sarin or soman by taking a pH of degraded aqueous samples.

ACKNOWLEDGMENTS

The assistance of H. Klapper and L. L. Szafraniec for performing the nuclear magnetic resonance analyses of sarin and soman is gratefully acknowledged.

The opinions or assertions contained herein are the private views of the authors and are not to be construed as official or as reflecting the views of the Army or the Department of Defense.

REFERENCES

Ellin RI, Groff WA, Kaminskis A (1981) The stability of sarin and soman in dilute aqueous solutions and the catalytic effect of acetate ion. J Environ Sci Health 16:713-717

Epstein J (1974) Properties of GB in water. J Am Water Works Assoc 66:31-37

Harris LW, Braswell LM, Fleisher JP, Cliff WJ (1964) Metabolites of pinacolyl methylphosphonofluoridate (soman) after enzymatic hydrolysis in vitro. Biochem Pharmacol 27:757-761

Martin AN, Swarbrick J, Cummarata A (1969) Physical pharmacy. Lea and Febinger, Philadelphia

Voss H (1968) The fundamental kinetics of cholinesterase reaction with substrates and inhibitors in an automated continuous flow system. Residue Rev 23:71-93

Received October 24, 1983; accepted December 2, 1983