was about ±0.0003 in lower temperatures, and about ±0.0004 in higher temperatures.

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RECEIVED for review June 20, 1968. Accepted April 15, 1969.

Kinetics of Reaction between Isopropyl Methylphosphonofluoridate and Hydrogen Chloride

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Rate constants have been determined at 25°, 81.5°, and 100° C. for the reaction of isopropyl methylphosphonofluoridate (Sarin) with anhydrous hydrogen chloride. The reaction rates were measured using proton magnetic resonance spectroscopy. The reaction appears to follow third-order kinetics. An Arrhenius plot for the reaction is linear, with an activation energy of 17.8 kcal. per mole.

ISOPROPYL methylphosphonofluoridate (Sarin) is a highly toxic phosphorus ester. It belongs to a class of compounds that act as inhibitors of cholinesterase, an enzyme in nerve tissue that catalyzes the hydrolysis of acetylcholine. Since this reaction is essential to the proper functioning of the nerves, these compounds are powerful nerve poisons. For intramuscular and oral administration, Askew (*1*) determined the LD_{50} for rats to be 0.17 and 0.6 mg. per kg., respectively, and Grob and Harvey (*2*) estimated the lethal dose in man to be 0.03 and 0.14 mg. per kg., respectively.

Sarin may be prepared by the reaction of 2-propanol with an equimolar mixture of methylphosphonic dichloride and methylphosphonic difluoride (*5*).

$$CH_3P(O)Cl_2 + CH_3P(O)F_2 + 2\ (CH_3)_2CHOH \rightarrow 2\ CH_3P(O)(F)OCH(CH_3)_2 + 2\ HCl \quad (1)$$

Further reaction between the products can occur according to the reaction

$$CH_3P(O)(F)OCH(CH_3)_2 + HCl \rightarrow CH_3P(O)(F)OH + (CH_3)_2CHCl \quad (2)$$

As part of an investigation into the stability of crude Sarin when stored for long periods of time under varying climatic conditions, a knowledge of the kinetics of Reaction 2 seemed desirable. However, very little work has been carried out on this reaction from the standpoint of reaction kinetics. The only available publication is that of Sass *et al.* (*4*), who investigated the reaction for short periods of time over limited concentration and temperature ranges without attempting to determine the rate equation. The purpose of this study was to provide the data necessary to determine a reliable rate equation for Reaction 2.

EXPERIMENTAL

Freshly distilled Sarin was obtained from the Organic Chemistry Section of this laboratory. No impurities were detected in the NMR spectrum of the liquid. Depending on the amount of HCl desired, various amounts of Matheson's tank HCl of 99% purity were passed through an H_2SO_4 drying train into a known weight of Sarin contained in a flask immersed in a dry ice–acetone bath. The amount of HCl added was determined from the increase in weight. Using small funnels with long capillary stems, 1-ml. aliquots of each solution were introduced into each of several 5-mm.-i.d. NMR tubes and flame-sealed. Continued quenching of the reaction was accomplished in all cases by placing each tube in a dry ice–acetone bath immediately after sealing until all tubes were sealed. One of the samples was then warmed to room temperature, and its NMR spectrum obtained to determine the initial concentrations of the reactants. The samples studied at elevated temperatures were transferred together from the cold bath to an oil bath regulated at the desired temperature to ±0.1° C. After various time intervals, the samples were successively withdrawn, and the reaction was quenched by immersion in the cold bath. For the 25° C. measurements, the samples were merely stored in the air-conditioned laboratory maintained at 25° ± 2° C. All spectra, regardless of experimental temperature, were recorded at room temperature using a Varian Associates Model A-60 NMR

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spectrometer. The chemical shift (cps.) of the exchangeable protons in the mixtures was measured to ±0.5 cps. relative to the most upfield peak of Sarin in the absence of an internal standard

RESULTS AND DISCUSSION

The results obtained for the reaction of Sarin with different concentrations of HCl at 25° C. are presented in Table I. In Table II are presented the results for nearly equimolar amounts of the reactants at 81.5° and 100° C. The reported Sarin concentrations are from area calculations, while the HCl concentrations are assumed to follow changes in Sarin concentration according to the stoichiometry of Reaction 2. The precision of the area measurements is ±3.6% and the mole fractions of the components are believed accurate to ±2.0%. Component concentrations can be determined from calibration curves based on the resonance position of the exchangeable protons in the mixtures. The position of this signal depends on the relative concentrations of HCl and methylfluorophosphonic acid, and gradually moves downfield from its original position as the reaction proceeds. However, its position at the beginning and at the end of the reaction must be the same for all mixtures in which the HCl is completely consumed. In such mixtures the initial mole fraction of HCl is less than 0.5. In Table I at zero time, the slight downfield shift of this peak with increasing Sarin concentration may be due to solvent effects, or to small amounts of phosphorus acids present in the Sarin.

As shown in Figure 1, using the data presented in

Table 1. Data for Sarin-HCl Reaction at 25° C.

Time, Hours	Sarin, Mole Fraction	Chemical Shift of Exchangeable Protons, Cps.	Sarin, Moles/Kg. Soln.	HCl, Moles/Kg. Soln.
		Initial Mole Fraction of Sarin = 0.47		
0.0	0.47	337	5.5	6.3
1.6	0.42	386	4.9	5.7
3.6	0.39	420	4.5	5.2
23.8	0.24	532	2.8	3.6
25.0	0.24	536	2.8	3.5
26.9	0.22	543	2.7	3.4
29.3	0.21	550	2.6	3.3
46.5	0.18	576	2.2	2.9
49.0	0.18	582	2.1	2.9
		Initial Mole Fraction of Sarin = 0.57		
0.0	0.57	350	6.0	4.5
2.1	0.52	380	5.6	4.1
4.2	0.50	405	5.3	3.8
21.4	0.41	485	4.4	2.9
23.7	0.42	498	4.2	2.7
27.2	0.38	510	4.1	2.5
69.8	0.34	570	3.4	1.9
74.8	0.32	579	3.3	1.8
141.8	0.26	616	2.8	1.3
167.2	0.26	625	2.7	1.2
180.5	0.26	627	2.7	1.2
189.7	0.25	633	2.6	1.1
		Initial Mole Fraction of Sarin = 0.63		
0.0	0.63	359	6.2	3.6
4.0	0.59	397	5.8	3.2
5.2	0.58	413	5.6	3.1
13.0	0.54	442	5.3	2.8
24.2	0.47	475	5.0	2.5
27.7	0.46	487	4.9	2.3
47.8	0.44	529	4.8	1.9
70.4	0.46	560	4.2	1.6
76.1	0.42	565	4.1	1.6
146.9	0.37	603	3.7	1.2
171.5	0.38	615	3.6	1.1
195.8	0.36	624	3.5	1.0
		Initial Mole Fraction of Sarin = 0.72		
0.0	0.72	374	6.5	2.5
4.2	0.69	397	6.2	2.3
22.6	0.68	435	6.1	2.1
27.0	0.66	445	6.0	2.0
70.7	0.61	502	5.5	1.6
75.6	0.60	509	5.4	1.5
141.8	0.56	553	5.0	1.1
171.6	0.55	569	4.9	1.0
190.6	0.54	577	4.8	0.9
384.2	0.50	622	4.5	0.5

Tables I and II, if the change in mole fraction Sarin as determined from area measurement is plotted against the change in chemical shift of the exchangeable protons, a straight line is obtained which is independent of initial Sarin concentration and of temperature. Points ●, ■, ▲, and ○ represent data from experiments at 25° C. having initial Sarin concentrations of 0.47, 0.57, 0.63, and 0.72 mole fraction, respectively. Points ▼ and ◆ represent data at 81.5° and 100° C., respectively, for experiments having an initial Sarin concentration of 0.47 mole fraction. Based on these data, apparently a linear calibration plot of mole fraction Sarin *vs.* chemical shift of the exchangeable protons could be constructed for any Sarin-HCl mixture of known initial concentration containing less than 0.5 mole fraction HCl, and the concentration of Sarin at any time determined simply by measuring the chemical shift of the exchangeable protons.

When nearly equimolar amounts of Sarin and HCl are present the rate equation is

$$\frac{dx}{dt} = k\,(a - x)^n \qquad (3)$$

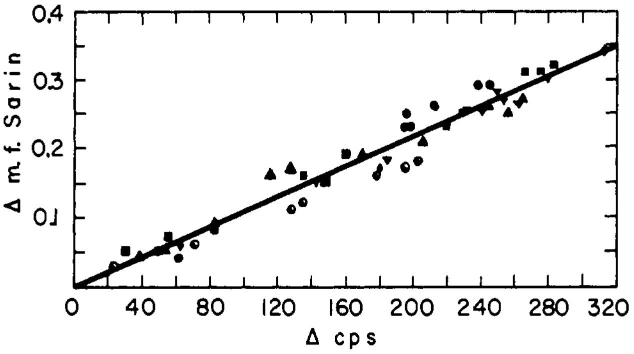

Figure 1. Relation between change in exchangeable proton shift and change in Sarin concentration

Thus the order of the reaction may be determined from a plot of log $\frac{dx}{dt}$ *vs.* log $(a - x)$, the slope being equal to n. A slope of 3.0 is obtained from such a plot in Figure 2, using the data for Sarin from Table I at an initial concentration of 0.47 mole fraction Sarin. The order may also be determined by integrating Equation 3 and plotting log t *vs.* log $(a - x)$, the slope being $1 - n$. Such a plot of the data where Sarin and HCl are present in nearly equimolar amounts gave n equal to 3.5, which is a reasonable result considering that the initial concentrations of the reactants are not exactly equal.

For a third-order reaction with two reactants, the following equation applies for nonfractional exponents (*3*).

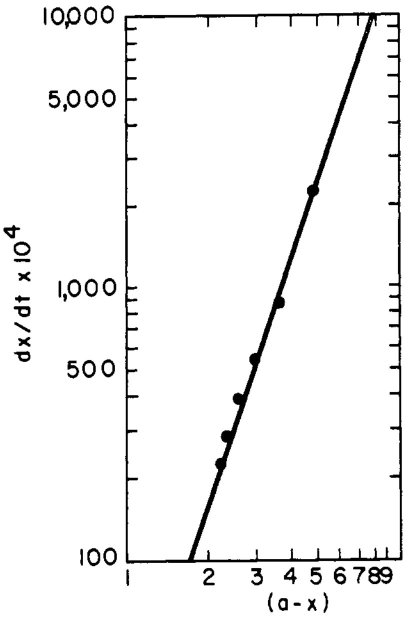

Figure 2. Log-log plot of *dx/dt vs.* (*a* — *x*) at 25° C.

Table II. Data for Sarin-HCl Reaction
Initial Mole Fraction of Sarin = 0.47

Time, Min.	Sarin, Mole Fraction	Chemical Shift of Exchangeable Protons, Cps.	Sarin, Moles/Kg. Soln.	HCl, Moles/Kg. Soln.
		Temperature = 81.5° C.		
0.0[a]	0.42	367	5.0	5.7
5.0	0.27	510	3.2	4.0
10.0	0.24	552	2.7	3.5
20.0	0.17	599	2.1	2.9
30.0	0.17	608	2.0	2.8
41.0	0.16	630	1.7	2.5
50.0	0.14	616	1.6	2.4
		Temperature = 100.0° C.		
0.0	0.47	337	5.5	6.3
1.0	0.41	400	4.8	5.5
3.0	0.30	518	3.2	4.0
6.0	0.20	590	2.3	3.1
10.0	0.17	617	2.0	2.7
20.0	0.13	650	1.5	2.3

[a] Delay of about 2 hours before heating began, during which time some reaction occurred. New zero time taken just before tubes were heated.

Table III. Change of Specific Rate Constant, k, with Temperature

Sarin, Initial Mole Fraction	k, Kg.^{2}/Mole^2/Min.	Temp., ° C.
0.72	$(1.4 \pm 0.1) \times 10^{-5}$	25.0
0.63	$(1.7 \pm 0.1) \times 10^{-5}$	25.0
0.57	$(1.7 \pm 0.1) \times 10^{-5}$	25.0
0.47	$(1.7 \pm 0.1) \times 10^{-5}$	25.0
. . .	8.7×10^{-5} [a]	40.0
. . .	19×10^{-5} [a]	50.0
0.47	$(1.9 \pm 0.4) \times 10^{-3}$	81.5
0.47	$(6.6 \pm 0.7) \times 10^{-3}$	100.0

[a] Calculated from data of Sass *et al.* (*4*).

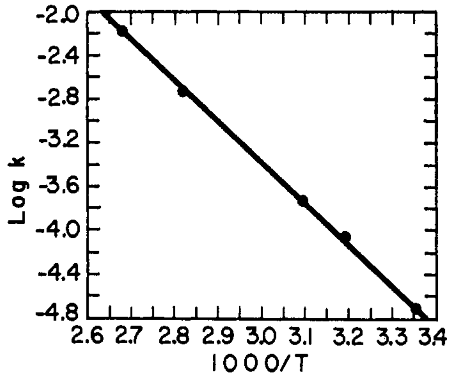

Figure 3. Arrhenius plot for third-order rate constant

$$\frac{dx}{dt} = k\,(a - x)^2\,(b - x) \tag{4}$$

When integrated, Equation 4 becomes

$$k = \frac{1}{t\,(a - b)}\left[\frac{2.303}{(a-b)}\log\frac{b\,(a - x)}{a\,(b - x)} - \frac{x}{a\,(a - x)}\right] \tag{5}$$

The best indication of a third order for the reaction is the constant value of the rate constant, k, both within a given run and between runs having different initial concentrations of reactants when the experimental data are tested with Equation 5. By using a least squares procedure, the rate constant from each experiment was determined (Table III). Values for k at 40° and 50° C. have been calculated, using data from the earlier work of Sass *et al.* (*4*), and are also included. From an Arrhenius plot of these rate constants in Figure 3, the activation energy is 17.8 kcal. per mole. The linearity of the Arrhenius plot and the magnitude of the activation energy indicate that the reaction is homogeneous.

NOMENCLATURE

LD_{50} = lethal dose 50, dose in mg. per kg. of body weight which will kill 50% of a group of animals
x = moles of Sarin or HCl per kg. of solution reacting in time t
t = time
k = specific rate constant, kg.^{2}/mole^2/min.
n = order of reaction
a = initial moles of HCl per kg. of solution
b = initial moles of Sarin per kg. of solution
Δ m.f. Sarin = difference in mole fraction of Sarin when measured at time zero and time t
Δ cps. = difference in position of resonance signal for exchangeable protons at time zero and time t, measured in cycles per second at 60 megacycles per second frequency relative to most upfield line of Sarin spectrum
T = temperature, ° K.

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RECEIVED for review October 28, 1968. Accepted August 15, 1969.

Sodium Carbonate–Bicarbonate Equilibrium with Monoethanolamine Additive

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CARBON DIOXIDE is absorbed from a gas in many industrial processes. A satisfactory absorbing medium will preferentially absorb the gas and be economical to regenerate. Aqueous solutions of sodium carbonate and sodium bicarbonate are often used as the absorption medium. Additives such as amines are sometimes used industrially to increase the equilibrium constant, to effect separation more easily. The effect of monoethanolamine has not been reported and would have some economic advantages as an additive.

Design of an absorption system requires a knowledge of the equilibrium characteristics of the system. The equilibrium constant of the sodium carbonate–sodium bicarbonate system is a measure of the equilibrium carbon dioxide partial pressure of carbon dioxide above the solution. A higher equilibrium constant corresponds