

The Catalytic Effect of CrO_4^{2-} , MoO_4^{2-} and WO_4^{2-} on the Hydrolysis of *iso*Propoxy-methyl-phosphoryl Fluoride (Sarin)

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The catalytic effect of eighteen anions on the hydrolysis of Sarin has been examined. Based on these results a detailed study of the effect of chromate, molybdate and tungstate ions has been performed. The catalytic constants of these ions, as well as their energies and entropies of activation, have been given. The catalytic effect of the ions has been ascribed mainly to complex formation of the ions with the Sarin molecule.

In the study of the pH-dependence of the hydrolysis of *iso*propoxy-methyl-phosphoryl fluoride (Sarin) in different buffer solutions it was evident that, in addition to the catalytic effect of the hydroxyl ions, the ions included in the buffer solutions also influenced the rate of hydrolysis. For that reason the hydroxyl ion catalyzed hydrolysis of Sarin was studied by means of an automatic titrator which maintained the pH constant at a preselected value in the absence of disturbing ions¹. The influence of some ions on the hydrolysis of di*iso*propoxy-phosphoryl fluoride (DFP) has earlier been reported by Kilpatrick². Wagner-Jauregg *et al.* have shown that the hydrolysis of DFP is accelerated by some metal salts and complexes, in particular copper(II) chelates of dipyridyl and histidine³. It was also shown that sodium molybdate markedly catalyzed the hydrolysis.

It was thus of interest to study the catalytic effect of a lot of common anions on the rate of hydrolysis of Sarin. The effect of chromate, molybdate and tungstate ions was of special interest and was the object of a more detailed study.

A similar study of the effect of different anions on spontaneous and enzymatically catalyzed hydrolysis of dimethylamido-ethoxy-phosphoryl cyanide (Tabun) has been performed by Augustinsson⁴.

EXPERIMENTAL

Materials. Sarin was synthesized in this institute and a stock solution of Sarin in dioxane (E. Merck c.p. purified from peroxides and redistilled over sodium) was prepared¹.

The salts used were of anal. reagent grade except sodium persulphate which was chemically pure, and sodium hypochlorite which was supplied as a solution, the exact concentration of which was determined iodometrically.

Kinetic measurements. Procedure I. Introductory experiments were performed by a Warburg manometric method, and the technique closely adheres to that described by Augustinsson⁵. The reaction took place at 25°C in a sodium bicarbonate buffer at pH 7.6. The amount of CO₂ evolved during the reaction was read at intervals during 60 min and from these data the rate of the reaction was determined. The initial concentration of Sarin was 5.0 mM, and that of the catalyst was 1.0 mM.

Procedure II. The detailed study of the catalytic effect of chromate, molybdate and tungstate ions was performed by means of an automatic recording titrator⁶ at 15°C, 25°C and 35°C at pH 8.50, and at 25°C also at pH 9.00. A solution containing 38.00 ml of 0.10 M potassium chloride and 1.00 ml of appropriately diluted solution of the catalyst was adjusted by the titrator to the desired pH-value, after which 1.00 ml of the stock solution of Sarin was added. In other respects the procedure adheres to that described in an earlier paper¹. The initial concentrations of Sarin and the catalysts in the different runs appear in Table 1.

RESULTS

Introductory experiments

From the introductory experiments performed by the manometric Warburg method the following results were obtained:

1) Potassium sulphate, ammonium chloride and sodium chlorate, perchlorate, sulphite, azide, hypophosphite, formate and salicylate showed no, or slight, catalytic effect.

2) Potassium persulphate and sodium nitrite and phosphate showed a small catalytic effect.

3) Sodium molybdate (Na₂MoO₄) and ammonium molybdate ([NH₄]₆Mo₇O₂₄) showed a marked, catalytic effect.

4) A considerable acceleration of the hydrolysis was obtained with sodium hypochlorite and perborate (the effect of the latter can probably be attributed to the formation of perhydroxyl ions).

The hydrolysis of Sarin catalyzed by hypochlorite ions has been described by Epstein *et al.*⁷, and the reaction of perhydroxyl ions with Sarin has recently been published^{8,9}.

Catalytic effect of chromate, molybdate and tungstate ions

When the recorded curves from the automatic titrator were treated according to Guggenheim, straight lines were obtained indicating that the catalyzed hydrolyses proceed as first-order reactions. This fact shows that the chromate, molybdate and tungstate ions are not consumed in the reactions but function as true catalysts. From the slopes of the straight lines the observed rate constants, k_{obs} , were determined, and the catalytic constants, k_c , were calculated from the expression:

$$k_c = \frac{k_{\text{obs}} - k_s}{c_c}$$

Table 1. Rate constants for the hydrolysis of Sarin catalyzed by chromate, molybdate and tungstate ions at various concentrations, pH-values and temperatures.

$t^{\circ}\text{C}$	pH	c_s mM	c_c mM	$k_{\text{obs}} \times 10^4 \text{ sec}^{-1}$			$k_s \times 10^4 \text{ sec}^{-1}$	$k_c \times 10^3 \text{ l mole}^{-1} \text{ sec}^{-1}$			
				CrO_4^{2-}	MoO_4^{2-}	WO_4^{2-}		CrO_4^{2-}	MoO_4^{2-}	WO_4^{2-}	
15.0	8.85	0.300	2.50	1.59	2.35	2.62	0.62	3.86	6.90	7.96	
		0.300	2.50	1.62	2.28	2.47		4.00	6.63	7.40	
25.0	8.50	0.420	1.00	2.01	2.35	2.54	1.06	9.39	12.8	14.7	
		0.420	1.00	2.03	2.47	2.59		9.65	14.0	15.2	
		0.420	2.50	3.45	4.31	4.61		9.55	13.0	14.2	
		0.300	2.50	3.34	4.36	4.66		9.50	13.2	14.4	
	9.00	0.300	1.00	4.32	4.63	4.83	3.37	9.49	12.6	14.6	
		0.300	1.00	4.20	4.63	4.77		8.29	12.6	14.0	
	35.0	8.18	0.300	2.50	6.42	8.50	8.92	1.76	18.6	27.0	28.6
			0.300	2.50	6.73	8.59	8.66		19.9	27.3	27.6

where k_s is the rate constant of the spontaneous hydrolysis¹ and c_c is the concentration of the catalyst.

The constants are given in Table 1, where it is shown that the catalytic constants are independent of pH above 8.50. The catalytic ions are probably present in the monomeric form, *i.e.* CrO_4^{2-} , MoO_4^{2-} and WO_4^{2-} . In the preliminary experiments at pH 7.6 $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$ was found to be 6—7 times more effective a catalyst than Na_2MoO_4 , which supports this hypothesis. The mean values of the catalytic constants given in Table 2 are calculated from the values obtained only at pH 8.50, because the difference between k_{obs} and k_s at pH 9.00 is so small that it markedly influences upon the accuracy of k_c .

By plotting $1/T$ against k_c straight lines were obtained. From the slopes of the lines, calculated by the method of least squares, the energies of activation were obtained. The entropies of activation were calculated from the equation of absolute reaction rates. The values of the entropies and energies of activation are given in Table 2.

Table 2. Catalytic constants, and energies and entropies of activation for the hydrolysis of Sarin catalyzed by chromate, molybdate and tungstate ions.

Catalyst	$k_c \times 10^2 \text{ l mole}^{-1} \text{ sec}^{-1}$			E_a kcal.mole ⁻¹	ΔS^\ddagger E.U.
	15.0°C	25.0°C	35.0°C		
CrO_4^{2-}	3.93 ± 0.07	9.52 ± 0.13	19.3 ± 0.7	14.0 ± 0.4	-18 ± 1
MoO_4^{2-}	6.77 ± 0.14	13.3 ± 0.7	27.2 ± 0.2	12.3 ± 0.4	-23 ± 1
WO_4^{2-}	7.68 ± 0.28	14.6 ± 0.6	28.2 ± 0.5	11.5 ± 0.3	-26 ± 1

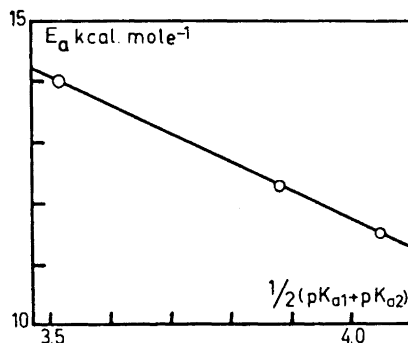


Fig. 1. Relationship between $\frac{1}{2}(pK_{a1} + pK_{a2})$ and E_a in the hydrolysis of Sarin catalyzed by chromate, molybdate and tungstate ions.

DISCUSSION

For reactions involving nucleophilic displacements in general Edwards¹⁰ has pointed out that the character of a nucleophilic reagent is related to its electrode potential as well as to its basicity. It has, however, been reported that the thiosulphate ion which has a high electrode potential but low basicity, has no effect upon the hydrolysis of either Tabun⁴ or Sarin⁷. On the other hand it has been shown from a study of the reaction of Sarin with catechols that the rate of the reactions is related to the basicity of the catechols¹¹. This favours the theory that the basicity of the reagent is the decisive factor in nucleophilic attacks on the phosphorus atom.

As appears from Fig. 1, the activation energies of the hydrolysis of Sarin catalyzed by chromate, molybdate and tungstate ions are found to be inversely proportional to the negative logarithms of the mean dissociation constants of the acids given by Schwarzenbach¹², indicating the relationship between the catalytic effect and the basicity of the catalysts. The slight catalytic effects obtained in the preliminary experiments with other ions of about the same basicity as chromate, molybdate and tungstate ions indicate, however, that the catalytic effects of the latter ions cannot be attributed only to the basicity of the ions. Moreover, a lower energy of activation of the alkaline hydrolysis of Sarin¹ would be expected if such a relationship were valid. In the main the catalytic effect of the ions can probably be ascribed to complex formation of the ions with the Sarin molecule which facilitates the cleavage of the P—F bond. The decreasing entropy of activation, when going from chromate to tungstate ions, is consistent with an increasing stability of the activated complex. The tendency of chromate, molybdate and tungstate ions to form complex with phosphorus compounds is also wellknown from their insoluble complex with phosphate ions.

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