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CATALYZED HYDROLYSIS OF PYROPHOSPHATE BY THORIUM OXIDE

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DATE ISSUED

FEB 16 1960

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ABSTRACT

Thorium oxide in aqueous slurries catalyzes the hydrolysis of $Na_4P_2O_7$ to the orthophosphate. In the initial stages of the hydrolysis, the rate is proportional to the ThO_2 concentration, but this effect rapidly diminishes with time, probably due to the inhibiting effect of orthophosphate adsorbed on the catalyst. The time required for a definite fraction of complete reaction to occur is relatively independent of the initial concentration of $Na_4P_2O_7$, thus indicating that the hydrolysis is of the first order with respect to pyrophosphate. Over the range of temperature of 25 to 100°C, the rate of hydrolysis increases approximately 3-fold for each 10° increase in temperature. An activation energy of 20 kcal per mole was calculated for this reaction.

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INTRODUCTION

In this laboratory it was noted that $Na_4P_2O_7$, when added as a dispersing agent to aqueous slurries of ignited ThO_2, underwent conversion to the orthophosphate. Since the ionic species of the dispersing and stabilizing agent actually present in a slurry of ThO_2 might prove to be of interest in studies of the stability and rheological properties of these slurries, a study was made of some factors which affect the rate of hydrolysis of pyrophosphate in the presence of ThO_2.

The hydrolysis of pyrophosphates to orthophosphates in acidic and basic aqueous media has been studied rather thoroughly.[1,6,7,8,9,10,11] Whereas this conversion is catalyzed by acids, alkaline solutions of pyrophosphates are quite stable at room temperature, and, even at elevated temperatures, long periods of time are required to convert significant amounts of pyrophosphate to orthophosphates, although some kinetic data have also been reported. Morgan and Swoope,[10] in studying the stability of phosphates, found that a 0.2 per cent solution of sodium pyrophosphate (unbuffered at pH 10.3) is slowly hydrolyzed to the orthophosphate at 56°C; 900 hours are required to effect 98 per cent conversion. In 1 N HNO_3 the conversion is complete in five hours at 56°C and in one hour at 85°C. Bell[6] reported, in his study of the hydrolysis of $Na_4P_2O_7$, that at 70°C the rate was negligible but at 100°C the reaction was 40 per cent complete in 50 hours.

In the study of the kinetics of the acid-catalyzed hydrolysis, Friess[8] reported that, for 0.023 M $H_4P_2O_7$ in 0.12 M HCl, the reaction was first order with a k of 1.94×10^{-2} hr^{-1} at 50°C and with an activation energy of 22.8 kcal

per mole. Muus[11] found that the hydrolysis of 8×10^{-4} M $Na_4P_2O_7$ in solutions 0.034 to 0.124 M in HCl and 1 M in KCl, and also without KCl, was first order with respect to pyrophosphate at 20 and 40°C. The ratio $k/[H^+]$ was found to be constant and the kinetic equation was considered to be

$$-d[P_2O_7]/dt = k'[H^+][H_3P_2O_7^-] \quad (1)$$

Since pyrophosphates are present as four individual species at various hydrogen-ion concentrations, Campbell and Kilpatrick[7] investigated the hydrolysis over a wide range of hydrogen-ion concentration and estimated the rate constants and activation energies for the reaction of $H_3P_2O_7^-$ and of $H_2P_2O_7^{-2}$ with water and with hydrogen ions at 50, 60, and 70°C, as well as for the reaction of $HP_2O_7^{-3}$ with water at 70°C.

Comparatively little has been reported on heterogeneous catalysis of the hydrolysis of pyrophosphate to orthophosphate. Bamann et al.[2-5] have noted that a number of hydroxides, including thorium, zirconium, lanthanum, and cerium, catalyze this reaction. They made use of precipitates of hydrous oxides as catalysts and did not study the kinetics of the reactions. In the present investigation, the catalytic effect of an ignited ThO_2 on the hydrolysis of $Na_4P_2O_7$ was determined as a function of the following variables: ratio of ThO_2 to $Na_4P_2O_7$, initial concentration of $Na_4P_2O_7$, and temperature.

EXPERIMENTAL

Materials. All reagents, except the thorium oxide, were of analytical reagent grade and distilled water was used in the preparation of the solutions.

The thorium oxide used as the catalyst was prepared by igniting purified thorium oxalate at 650°C. The surface area of this oxide was determined to be 37 m^2/gram by the B.E.T nitrogen absorption method. Thorium oxide, ignited at higher temperatures, was also found to exhibit a catalytic effect; however,

with the higher-fired oxides, qualitative tests indicated the catalytic effect to be lessened.

The Kinetic Experiments. In the study to determine the effect of the amount of ThO_2 added per unit of $Na_4P_2O_7$ on the rate of hydrolysis, different amounts of this oxide (1-, 2-, and 3-gram portions) were suspended in 50 ml of 0.050 M $Na_4P_2O_7$. The suspensions were agitated at 25°C by a mechanical shaker. After various intervals of time, portions of the slurry were withdrawn and the aqueous phases were separated from the solids by centrifugation. The aqueous phases were analyzed for orthophosphate by the colorimetric phosphomolybdate method of Netherton, Wreath and Bernhart,[12] which provides for the determination of orthophosphate in the presence of pyrophosphate.

From previous tests, it was established that thorium oxide adsorbs some PO_4^{-3} from phosphoric acid solutions; the maximum adsorbed was found to be less than 10 mg of orthophosphate per gram of ThO_2. No correction was made for orthophosphate adsorbed by ThO_2 because (1) it is doubtful whether data for adsorption from phosphoric acid solutions can be safely applied to adsorption from solutions of sodium orthophosphate and (2) even if the adsorption is equal to the maximum adsorbed, 10 mg/g of ThO_2, the maximum possible error in the estimation of orthophosphate will be the order of 5%.

In determining the effect of varying the initial concentration of pyrophosphate, solutions that contained 0.025, 0.050, and 0.100 mole of $Na_4P_2O_7$ per liter were used to prepare the ThO_2 slurries. Sufficient ThO_2 was added to portions of the three solutions to make slurries in which the $ThO_2/Na_4P_2O_7$ ratio was maintained constant at 800 grams of ThO_2 per mole of $Na_2P_2O_7$. These suspensions were shaken at 25°C until the hydrolysis was essentially complete; samples of the slurry were removed at various intervals of time. The aqueous phase of the sample was analyzed for orthophosphate.

The effect of temperature on the rate of catalyzed hydrolysis was evaluated at 25, 50, 70, and 100°C. Each of these tests was made with a slurry which contained 40 g of ThO_2 per liter of 0.050 M $Na_4P_2O_7$. These slurries were agitated (shaken or stirred mechanically) and after various intervals of time portions of the slurry were removed and the aqueous phases were analyzed for orthophosphate.

RESULTS AND DISCUSSION

The results of the effect of increasing the ThO_2 concentration, thus the $ThO_2/Na_4P_2O_7$ ratio, are presented in Table I.

Table I

Effect of $ThO_2/Na_4P_2O_7$ Ratio on the Rate at Which Pyrophosphate is Hydrolyzed to Orthophosphate

Solutions were 0.050 M NaP_2O_7 containing ThO_2 catalyst and the temperature was 25°C

	Hydrolysis, Per Cent		
	ThO_2, g/l		
Time, hr	20	40	60
0.1	0.4	0.8	1.2
1	1.9	3.8	4.7
5	7.0	11	14
10	12	18	21
20	20	28	33
32	25	37	43
44	28	42	50
56	34	48	56
68	37	53	59
140	42	66	74
200	53	79	81
300	54	84	88
400	64	90	90
500	69	99	97
600	81		

In the initial stages of the hydrolysis, the rate was proportional to the ThO_2 concentration, but this effect diminished rapidly with time. After 200 hours, with the three concentrations of ThO_2 that were studied, the dependence

of the rate of hydrolysis upon the ThO_2 concentration became small, especially with the two higher concentrations.

These observations are of importance in considering the mechanism of the catalytic reaction. It may be postulated that the following steps are involved: (1) diffusion of pyrophosphate to the surface of the catalyst, (2) adsorption of pyrophosphate onto the catalyst, (3) hydrolysis of pyrophosphate, and (4) desorption of orthophosphate. If one of these steps is much slower than the others, it will control the reaction rate. Infrared spectra have shown that the adsorption of pyrophosphate results in the presence of orthophosphate on the surface of the ThO_2.[13] If the desorption of orthophosphate is relatively slow, the area of active surface of the catalyst will be decreased as the orthophosphate concentration increases. As a result, the rate at which pyrophosphate is hydrolyzed might well be progressively decreased.

The time required for a definite fraction of complete reaction to occur, e.g., one half of the reaction, is independent of the initial concentration for a process of first order. In the tests where the initial concentration of $Na_4P_2O_7$ was increased 4-fold (0.025 to 0.050 and to 0.100 M) the half-life increased from 55 to 63 and to 82 hours, respectively. This small increase in half-life is in agreement with the established fact that the reaction for the acid catalyzed hydrolysis of pyrophosphate is first order with respect to pyrophosphate. The slight increase in half-life further indicates that keeping the $ThO_2/Na_4P_2O_7$ ratio constant was not sufficient to overcome the inhibiting effect of adsorbed orthophosphate.

Increases in temperature greatly accelerated the rate of the catalyzed hydrolysis. Between 25 and 100°C, the rate was found to increase approximately 3-fold for each 10° increase in temperature. The half-life periods as a function of temperature are presented graphically in Figure 1. For a

slurry composed of 40 g of ThO_2 per liter of 0.050 M $Na_4P_2O_7$, the half-life at 25, 50, 70, and 100°C was, respectively, 62, 7.4, 1.0, and 0.1 hours. While 500 hours were required for essentially complete hydrolysis at 25°C, only 2 hours were required at 100°C. When the hydrolysis data obtained at the various temperatures are studied by plotting the natural log of the per cent of unhydrolyzed $Na_4P_2O_7$ versus time, the points fall closely on a straight line over the range of approximately 10 to 50 per cent hydrolysis (Fig. 2). This linearity made possible the calculation of first order rate constants from the slopes of these lines. These first order rate constants, i.e., the specific rate constants are shown in Table II.

Table II

Specific Rate Constants for the Catalyzed Hydrolysis of Pyrophosphate at Various Temperatures

Solutions: 0.050 M $Na_4P_2O_7$ containing 40 g ThO_2/liter.

Hydrolysis Range: 10 - 50 per cent.

Temperature, °C	Specific Rate Constant, hr^{-1}
25	0.0126
50	0.084
70	0.67
100	0.14[a]

[a] min^{-1}

From the rate constants determined for the hydrolysis in the 10 to 50 per cent range at the various temperatures, the activation energy, E, of the reaction was calculated by means of the Arrhenius equation. In Figure 3, the natural log of the rate constants are plotted versus the reciprocal of the

absolute temperature. From the slope of the straight line which best fits these points, the activation energy was calculated to be 20 kcal per mole.

From the data accumulated in this study, the hydrolysis reaction,

$$P_2O_7^{-4} + H_2O \longrightarrow 2\ PO_4^{-3} + 2\ H^+ \qquad (2)$$

was found to be catalyzed by ignited ThO_2 and may be considered first order with respect to $P_2O_7^{-4}$ concentration during the first stages of the reaction. As the concentration of orthophosphate builds up, the catalysis is probably inhibited by adsorbed orthophosphate on the ThO_2.

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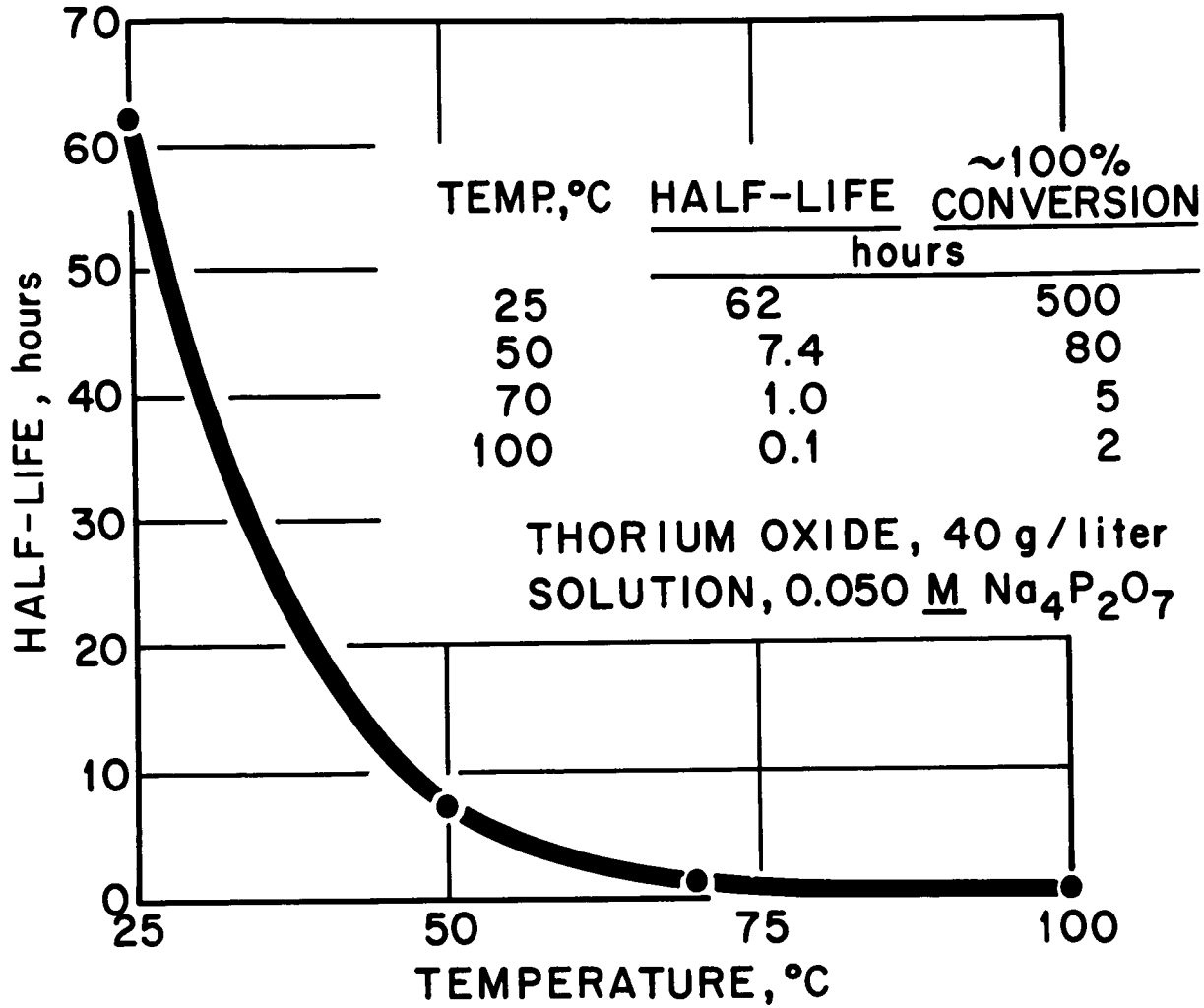

HALF-LIFE OF HYDROLYSIS AS A FUNCTION OF TEMPERATURE

FIGURE 1

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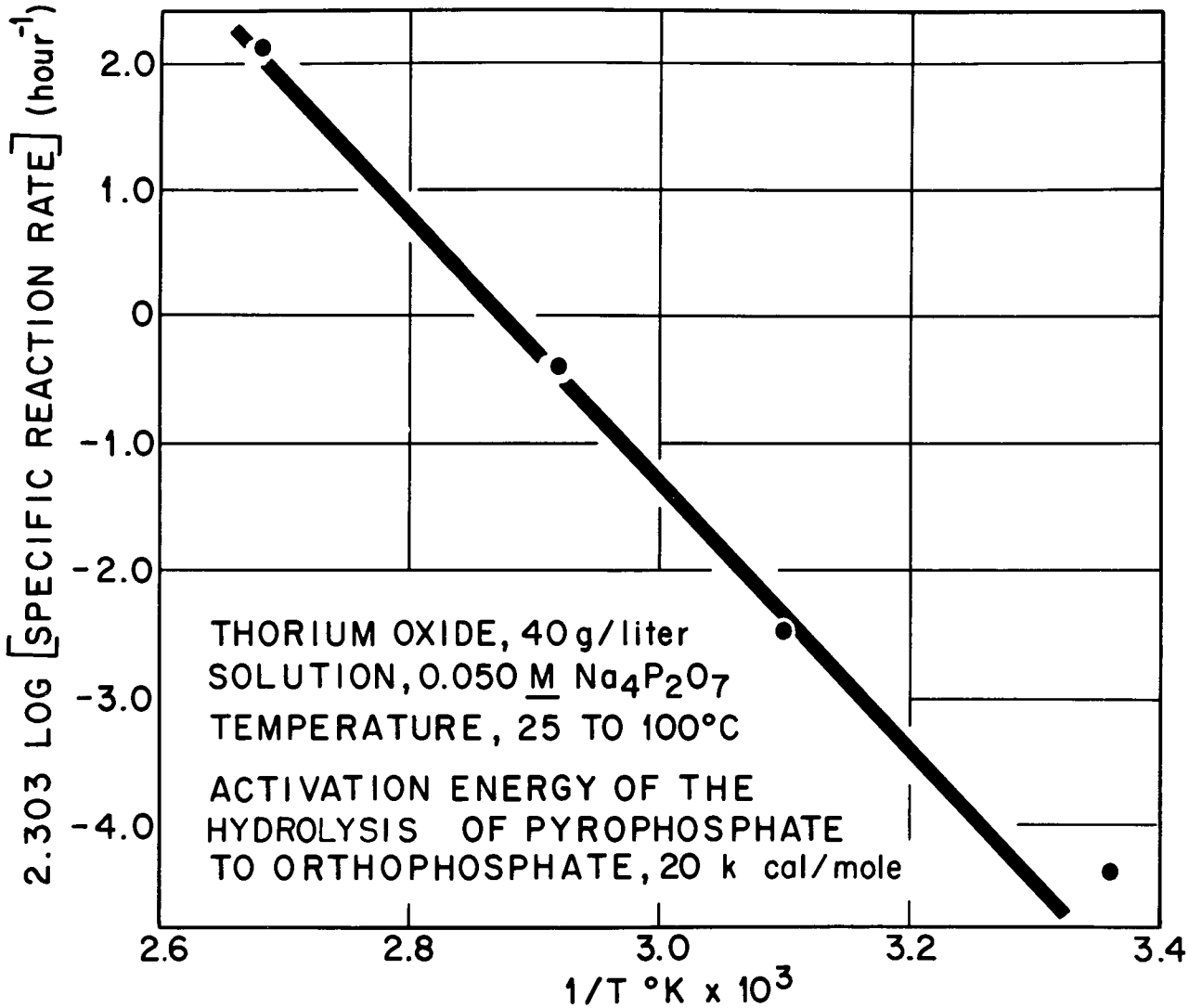
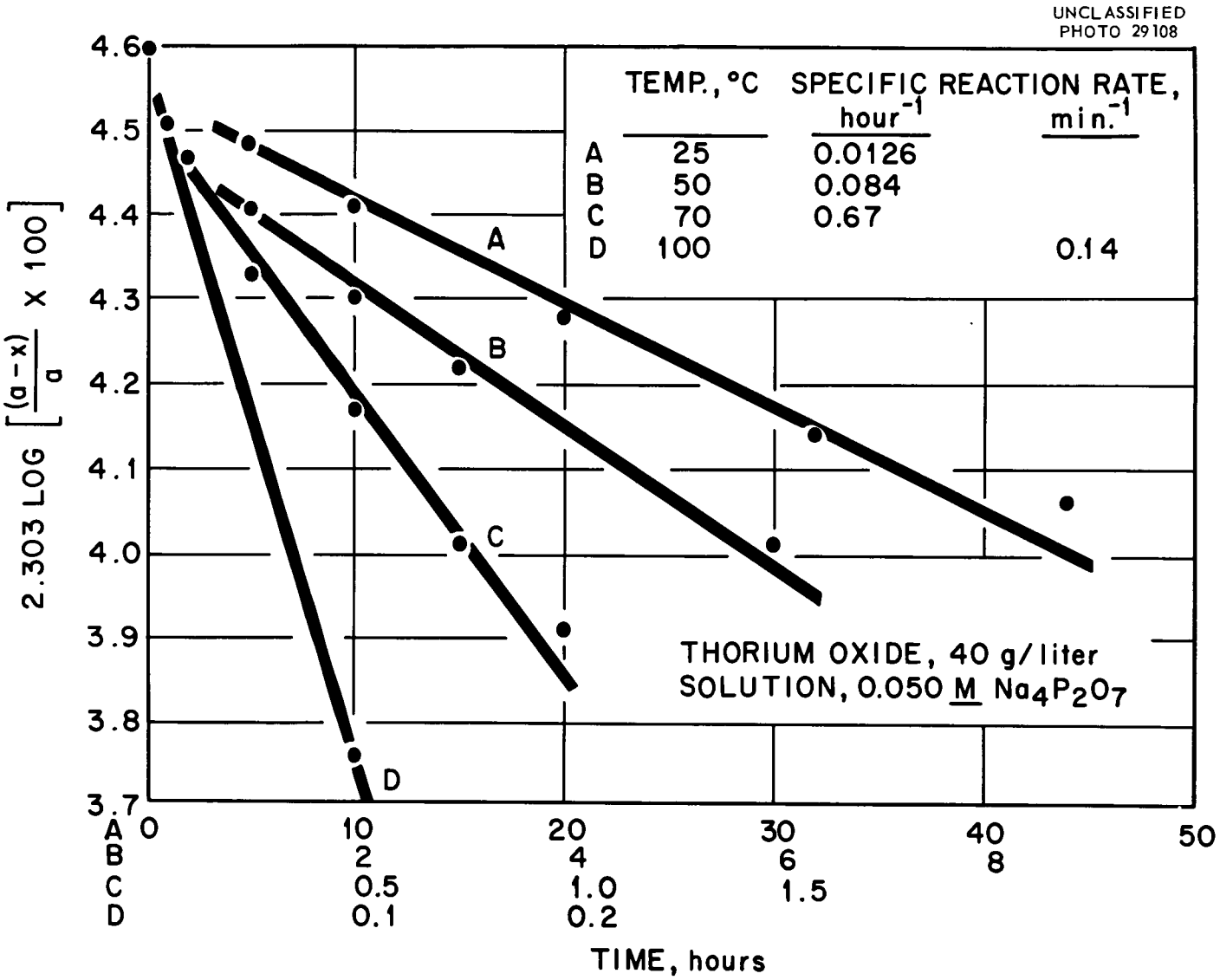


VARIATION OF SPECIFIC REACTION RATE WITH TEMPERATURE

FIGURE 3



HYDROLYSIS OF PYROPHOSPHATE TO ORTHOPHOSPHATE AS A FIRST ORDER REACTION

FIGURE 2

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