low pressure and produces a net increase in molar volume. The magnitude of the structural disorder (of the liquid relative to the solid) is expected to decrease with increasing pressure.[18] It is proposed that, above 15 kb., the effect of a coördination number increase is dominant and a net decrease in volume on fusion occurs.

A possible cause of the observed maxima in the melting points of cesium and rubidium has been proposed[14] involving an 'electronic collapse,' into empty inner orbitals, of the liquid under pressure. However, in the case of Bi_2Te_3, this sort of explanation appears less attractive.

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[18] P. W. Bridgman, reference 16, pp. 132–133.

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Hydrolysis of Sodium Pyrosulfate

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Although sodium pyrosulfate is generally thought to hydrolyze almost instantaneously, it has a half-life in water at 25° of 1.7 min. In pure water, hydrolysis occurs according to first-order kinetics, and there is an activation energy of 11.3 kcal. Addition of dioxane reduces the hydrolysis rate much more rapidly than would be expected for uncomplicated second-order kinetics involving the water and pyrosulfate ion.

Introduction

Although the pyrosulfates have been described in the literature for well over a century,[2] it is generally believed that they hydrolyze almost instantaneously in aqueous solution. This instability of the pyrosulfate anion in aqueous solution has been emphasized by Glocker and Meland.[3] As part of a thorough study of inorganic macromolecules, we decided to investigate the rate of hydrolysis of sodium pyrosulfate in water in order to determine whether or not it would be possible, by working rapidly, to detect and prove the existence of the higher pyrosulfates in aqueous solution. We were pleasantly surprised to find that the pyrosulfate ion is moderately stable in water, as shown below.

Experimental

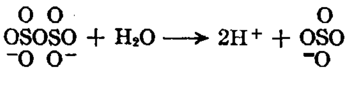
$Na_2S_2O_7$ was prepared by heating $NaHSO_4$ to 150–200° for 3 days. No loss of SO_3 occurred at these temperatures, as evidenced by pH titration of the hydrolyzed pyrosulfate. The X-ray diffraction powder pattern[4] and the infrared spectrum[5] are in accord with the data in the literature. The hydrolysis measurements were carried out with a Danish-made Radiometer Type TTT1 titrator, with Type SBR2/SBU1/TTA2 accessories. In measuring the kinetics, this instrument was used as a pH-stat to control the pH at various set values ranging from 1 to 10. The pH of the solution (made by dropping *ca.* 0.05 g. of the sodium pyrosulfate into 25 ml. of well stirred water in the titrimeter cup) was held constant by rapidly pulsed additions of 1 *N* sodium hydroxide.

Both finely powdered and moderately coarse sodium pyrosulfate were studied and it was found, with the thorough stirring employed, that after about 40 sec. the curves showing the rate of addition of sodium hydroxide merged. A first-order logarithmic plot evidenced only a slight diminution in the initial rate for the coarser particles. It was noted visually that when rate-of-addition curves for the sodium hydroxide merged, all of the particles of sodium pyrosulfate had dissolved. Careful inspection has led us to the conclusion that the rate process described herein is truly the hydrolysis of dissolved sodium pyrosulfate and is not confounded by the rate of dissolution.

The Radiometer titrator also was used to obtain pH titration curves of the sodium pyrosulfate.

Results and Discussion

The hydrolysis investigated in this study is described by eq. 1.



$$\underset{{}^-\mathrm{O}}{\overset{\mathrm{O}}{\mathrm{OS}}}\mathrm{O}\underset{\mathrm{O}^-}{\overset{\mathrm{O}}{\mathrm{S}}}\mathrm{O} + H_2O \longrightarrow 2H^+ + \mathrm{O}\underset{{}^-\mathrm{O}}{\overset{\mathrm{O}}{\mathrm{S}}}\mathrm{O} \qquad (1)$$

As expected for the pH held constant, this process was found to follow first-order kinetics in dilute aqueous solution. The effect of temperature is

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[1] On leave of absence from Göttingen University, Germany, July, 1961–1962.

[2] *E.g.*, P. L. Geiger, *Mag. Pharm.*, **9**, 1251 (1825); H. Rose, *Ann. Physik* (Poggendorff), **38**, 122 (1836); D. A. Rosenstiehl, *Compt. rend.*, **53**, 658 (1861).

[3] G. Glockler and R. J. Meland, *Proc. Minn. Acad. Sci.*, **6**, 65 (1938).

[4] ASTM Powder Data File Card No. 1-0834.

[5] Y. Garnier and C. Duval, *J. Chromatog.*, **2**, 72 (1959).

shown in Table I, where the standard error is given for those experiments in which three or more replicates were run. A plot of the logarithm of the rate constant *vs.* the reciprocal of the absolute temperature gave a nice straight line, from which an activation energy of 11.3 kcal. was derived.

TABLE I

FIRST-ORDER RATE CONSTANTS FOR PYROSULFATE HYDROLYSIS

Temp.	Constant (min.$^{-1}$)	Std. error of constant[a]
0.0	0.068	0.0017
5.0	.073	...
10.0	.126	...
15.0	.183	.0071
20.0	.226	.0224
25.0	.401	.0298
30.0	.435	.0078

[a] Value not given for duplicate runs.

Within experimental error, the rate constants are independent of pH throughout the wide range from pH 1 to 10. This means that there is no acid or base catalysis.

Figure 1 shows the diminution in the first-order rate constant obtained by adding dioxane to the water. If the dioxane were only acting to diminish the amount of water present and the hydrolysis process were a second-order reaction involving the water and the pyrosulfate anion, the apparent first-order rate constant would decrease according to the dotted line shown in Fig. 1. Correction for the activity coefficient[6] of the water gives an inappreciable change from the dotted line. This means that the large difference between the solid and dotted lines of Fig. 1 is attributable to a rapid initial diminution with added dioxane of the ratio of the activity coefficient of the pyrosulfate anion over the activity coefficient of the activated complex.[7] Since the dielectric constant of dioxane–water mixtures is not much different[8] from that of pure water in the concentration range measured, the pronounced effect of small additions of dioxane on the rate of hydrolysis of the pyrosulfate ion probably is not connected with polarity effects but, instead, is due to preferential solvolysis. An example of this would be dioxane rather than water filling the nearest-neighbor sites around the pyrosulfate ion.

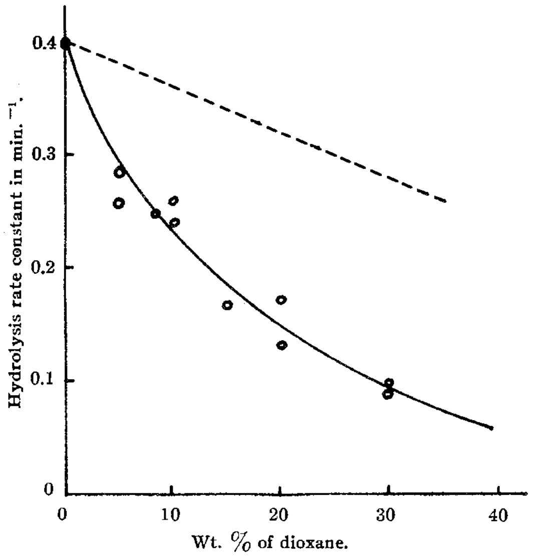

Fig. 1.—Variation of the first-order rate constant for hydrolysis of pyrosulfate at 25° with amount of dioxane added to the water.

It is interesting to compare the hydrolysis of the pyrosulfate anion with that of the pyrophosphate.[9] At high pH values where the activated complex for pyrophosphate hydrolysis probably does not involve the hydrogen ion, the half-life at 25° for the pyrophosphate is about ten million times greater than that of the pyrosulfate, and the activation energy is about three times greater. Moreover, the pyrophosphate ion is strongly acid-catalyzed, with the first-order rate constant changing by a factor of about 10^3 in the range of pH 1–11.

pH titrations of fresh dilute aqueous solutions of pyrosulfate at 0–25° show that both hydrogens are strongly acidic, as is the case with the orthosulfate.

(6) A. L. Vierk, *Z. anorg. Chem.*, **261**, 292 (1950).

(7) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, New York, N. Y., 1953, eq. 25 on p. 121.

(8) P. Farkas, *Z. Elektrochem.*, **38**, 656 (1932); C. A. Kraus and R. M. Fuoss, *J. Am. Chem. Soc.*, **55**, 31 (1933).

(9) J. R. Van Wazer, E. J. Griffith, and J. F. McCullough, *J. Am. Chem. Soc.*, **77**, 287 (1955).