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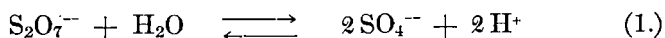
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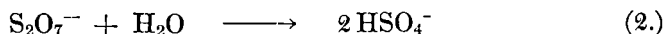
PYRO-SULFATE ION IN SOLUTION

GEO. GLOCKLER AND R. I. MELAND¹

It is well-known that soluble chromates exist in water solution as either chromates or dichromates, depending on the acidity of the solution. A similar question may be asked in connection with pyro-sulfate ion. Is the following equilibrium possible in solution?



It appears² that this equilibrium situation does not exist, because bisulfate ion is formed:

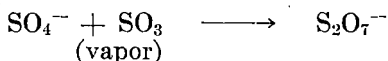


Any change in configuration cannot be followed by noting color changes since the ions involved are colorless. Nevertheless, proof for the transient existence of pyro-sulfate ion upon solution of pyro-sulfate can be given by studying the temperature changes taking place, as a function of time, when the alkali salts are dissolved in water. At first a drop in temperature is noted, indicating that heat is absorbed on solution:

$\text{M}_2\text{S}_2\text{O}_7 + \text{Aqua} \longrightarrow 2[\text{M}(\text{H}_2\text{O})_x]^+ + [\text{S}_2\text{O}_7(\text{H}_2\text{O})_y]^- - \text{heat}$
A rapid rise follows (Fig. 1) which is considered to be due to the heat of hydrolysis of the pyro-sulfate ion. (equation (2)). Berthelot³ made one such observation on potassium pyro-sulfate. These distinctly opposite thermal effects, a notable cooling effect followed by a rapid rise of temperature, indicate clearly the trend of hydrolysis. As indicated by the curves of Fig. 1, the pyro-sulfates of lithium, ammonium, and sodium behave similarly; the lithium salt hydrolyzing the most rapidly, followed in order by the ammonium, sodium, and potassium salts.

Several methods of preparing the pyro-sulfate salts as reviewed in the literature were tested and considered. These included the following:

1. DIRECT SYNTHESIS. The absorption of sulfur trioxide vapor by the dry, powdered sulfates:³⁻⁶



This method was found to be the most satisfactory and was therefore used. Since there is only one product formed, this method

¹ Based on a thesis presented to the faculty of the graduate school of the University of Minnesota by R. I. Meland in partial fulfillment of the requirements for the degree of Master of Science (1934).

² J. N. Friend, Textbook of Inorganic Chemistry, Vol. VII. Part 2, page 147; C. Griffin & Co., Ltd., London (1931).

³ Ber. 16, 381 (1883); Compt. Rend. 96, 208 (1883); Ann. Chim. Phys. (4) 30, 433 (1873).

⁴ A. C. Schultz-Sellack — Ber. 4, 109 (1871); Pogg. Ann., 139, 636 (1885).

⁵ R. Weber — Ber. 17, 2501 (1884).

⁶ H. Rose — Pogg. Ann., 33, 122 (1836).

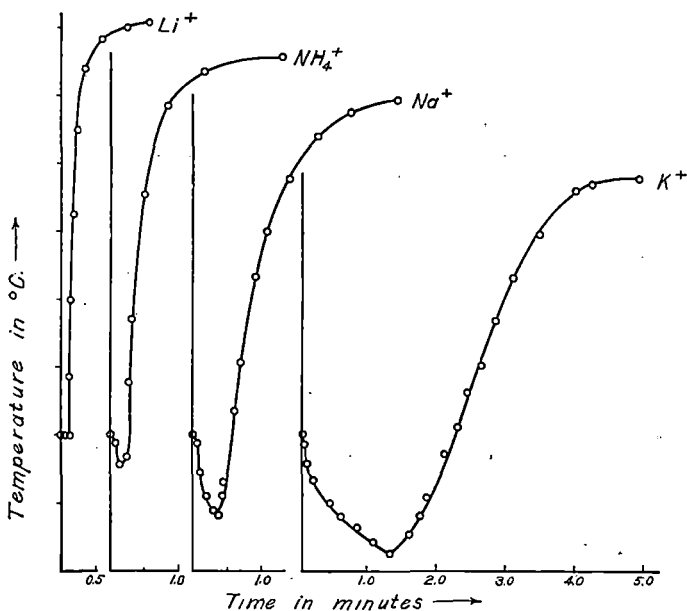


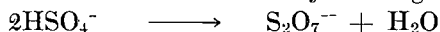
FIGURE 1

Temperature changes when alkali salts are dissolved in water.

had the additional advantage of giving a product free from impurities.

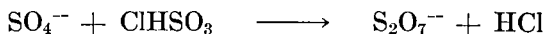
2. DIRECT SYNTHESIS. The treatment of the dry sulfates with liquid sulfur trioxide:⁷

3. DECOMPOSITION of the bisulfate by heating:⁸



This is a much disputed method and proved unsatisfactory. Since the ammonium salt decomposes at a relatively low temperature the method was not applicable in its preparation. J. Baum states that the reaction does not proceed to completion and the product is therefore mixed with sulfates.

4. REACTION of chlorosulfonic acid on the sulfate salts:^{7, 9}



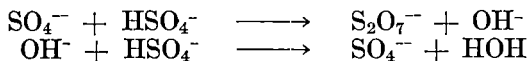
The reaction proceeds nicely to completion because of the formation of volatile hydrogen chloride. The excess chlorosulfonic acid is driven off by heating. The product is never quite pure, however, since it is impossible to free it completely of chlorine.

⁷ H. Schulze — Ber. 17, 2705 (1884).

⁸ J. Baum — Ber. 20, 752 (1887).

⁹ H. Schiff — Liebig's Ann. 126, 168 (1863).

5. TREATMENT of the sulfate salts with concentrated sulfuric acid:^{4, 10, 11}

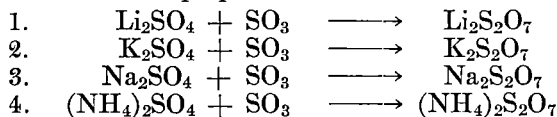


The product probably contains small amounts of sulfate as impurity.

The direct synthesis method, number 1 above, proved to be the most suitable, and since it also yielded the purest product, it was adopted. Fuming sulfuric acid was used as the source of sulfur trioxide, the SO_3 being carried over from a specially constructed generator into the reaction chamber by dried compressed air. The reaction chamber consisted of a specially designed furnace made from a 3-inch pyrex glass tube, wound with wire as a heating unit, and coated with an insulating layer of plaster of paris. One end of the tube was sealed off and fitted with a thermometer well and a three-way stopcock. The other end of the tube was beveled and ground to fit a glass stopper containing an outlet tube.

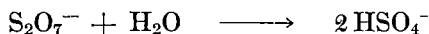
The temperature was controlled by use of a variable external resistance. During synthesis a temperature of 150° Centigrade was maintained except in the case of the ammonium salt, which was prepared at 120° - 125° C. The reaction time varied from 20 to 40 hours.

The following equations represent the synthesis of the four salts which were prepared:



Since these substances are extremely hygroscopic they were handled in a dry-box fitted with rubber gloves for outside manipulation. The salts were analyzed by appropriate volumetric and gravimetric methods.

Summary: Experiments show that pyro-sulfates hydrolyse rapidly in solution



and that no equilibrium of the chromate-dichromate type exists. The pyro-sulfate ion ($\text{S}_2\text{O}_7^{--}$) has only transient existence in water solution.

¹⁰ P. L. Geiger — Mag. Pharm. 9, 251 (1825).

¹¹ V. A. Jacquelin — Ann. Chim. Phys. (2) 70, 311 (1839).