[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Potassium Nitrilosulfonate

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A study of the preparation and properties of potassium nitrilosulfonate was undertaken as one phase of an extended investigation of the chemistry of sulfamic acid and its derivatives. The nitrite–bisulfite reaction[1] has been suggested and used for the preparation of sulfamic acid. It is significant, however, that no information concerning the rate of hydrolysis and stability of the primary reaction product, the nitrilosulfonate, or of the intermediate imidodisulfonate, has been recorded. The present paper, therefore, concerns itself with a study of the preparation of potassium nitrilosulfonate and a characterization of its properties, specifically its hydrolysis under carefully controlled conditions. The potassium salts of imidodisulfonic and sulfamic acids were both prepared by hydrolysis of the nitrilosulfonate.

Experimental

Preparation of $N(SO_3K)_3 \cdot 2H_2O$.—The procedure of Claus and Koch[2] was modified as follows: A solution of 25 g. of potassium nitrite (0.294 mole) in 100 ml. of water is added slowly and with constant stirring to a hot solution of potassium bisulfite, prepared by saturating 75 g. (1.34 mole) of potassium hydroxide in 150 ml. of water with sulfur dioxide. Clouding of the solution takes place with formation of a mass of needle-like crystals. After standing for an hour in the mother liquor enough water (about 1500 ml.) is added in order to redissolve the precipitate on heating. The solution is then cooled to effect precipitation of the needle-like crystals which are separated by filtration, washed thoroughly with ice water, alcohol and ether and finally dried in a vacuum desiccator; yield of purified $N(SO_3K)_3 \cdot 2H_2O$, 74 g. (62% based on nitrite employed).

Anal. Calcd. for $N(SO_3K)_3 \cdot 2H_2O$: K, 28.8; S, 23.6. Found: K, 28.8, 28.7; S, 23.4, 23.8.

Care must be taken that the solution remains alkaline during recrystallization. If necessary, a few pellets of potassium hydroxide should be added. If the solution becomes acid the imidodisulfonate, rather than the nitrilosulfonate, will be obtained. It also is necessary that washing be thorough, otherwise some bisulfite may remain behind and bring about rapid decomposition of the nitrilosulfonate. Samples of the potassium salt, prepared as indicated above, have been kept in a vacuum desiccator for several weeks without decomposition.

Theoretically, one would expect a ratio of three moles of bisulfite to one of nitrite to give maximum yields. It is evident, however, from a series of comparable experiments carried out as described above, that excess bisulfite favors the formation of the nitrilosulfonate. With mole ratios of $KHSO_3:KNO_2$ between 6 to 4.5:1 yields of 64–62% were obtained. With smaller relative amounts of bisulfite the yield diminishes, becoming only 15% with a 1.50:1 ratio. Our results may be considered experimental confirmation of Raschig's[3] suggestion that the reaction is best represented by the equation

$$4KHSO_3 + KNO_2 \longrightarrow N(SO_3K)_3 + K_2SO_3 + 2H_2O$$

It is evident, furthermore, that at higher temperatures some nitrilosulfonate is always obtained whenever bisulfite and nitrite are brought together.

Properties of Potassium Nitrilosulfonate.—The compound is only slightly soluble in water and in liquid ammonia. A saturated aqueous solution gives no precipitate on the addition of solutions containing Mn^{++}, Mg^{++}, Ag^{+}, Cd^{++}, Co^{++}, Cu^{++}, and Fe^{++} ions, but, as stated in the literature,[2] gives a white flocculent precipitate with lead acetate. While no precipitate is formed immediately on the addition of Ba^{++}, the solution rapidly clouds on standing due to hydrolytic decomposition. Prior addition of acid to the solution causes immediate precipitation of barium sulfate. Contrary to reports in the literature,[4] a precipitate is obtained on the addition of barium hydroxide. This precipitate is momentarily dissolved by nitric acid, but a cloudiness appears almost immediately thereafter due to formation of sulfate ion by hydrolysis.

Hydrolysis of Potassium Nitrilosulfonate.—The study of the hydrolysis of potassium nitrilosulfonate was restricted to the range of dilute solutions due to the limited solubility of the compound. Duplicate experimental runs were carried out at 25, 40, 67 and 100°. In each case, a 1-g. sample (0.00246 mole) of potassium nitrilosulfonate dihydrate was dissolved in 400 ml. of water preheated to the temperature at which hydrolysis was to be studied. At regular time intervals 25-ml. portions of the solution were removed and titrated with standard sodium hydroxide solution using methylene blue–methyl red indicator. The course of the reaction thus could be followed readily by measuring the increase in the acidity of the solutions, as is evident from the following equations

$$\begin{array}{llr} N(SO_3)_3^{\equiv} + H_2O & \longrightarrow HN(SO_3)_2^{=} + H^+ + SO_4^{=} & (1) \\ HN(SO_3)_2^{=} + H_2O & \longrightarrow H_2NSO_3^{-} + H^+ + SO_4^{=} & (2) \\ \hline N(SO_3)_3^{\equiv} + 2H_2O & \longrightarrow H_2NSO_3^{-} + 2H^+ + 2SO_4^{=} & (3) \end{array}$$

Complete hydrolysis, as represented by Equation 3, results in the formation of two moles of hydrogen ion per mole of nitrilosulfonate employed. The experimental results are represented graphically in Fig. 1 in which moles of hydrogen ion formed are plotted against time.

It is quite evident from Fig. 1 that hydrolysis with

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[1] Divers and Haga, *J. Chem. Soc.*, **69**, 1634 (1896).

[2] Claus and Koch, *Ann.*, **152**, 336 (1869).

[3] Raschig, "Schwefel- und Stickstoffstudien," Verlag Chemie, Berlin, 1924, p. 8.

[4] Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Company, New York, N. Y., 1928, Vol. VIII, p. 668.

formation of one mole of hydrogen ion is quite rapid, even at 25°. This corresponds to the intermediate formation of the imidodisulfonate, as represented by Equation 1. The formation of the second mole of hydrogen ion is considerably slower, leading to the conclusion that the rate determining reaction in the complete hydrolysis of the nitrilosulfonate is that represented by Equation 2.

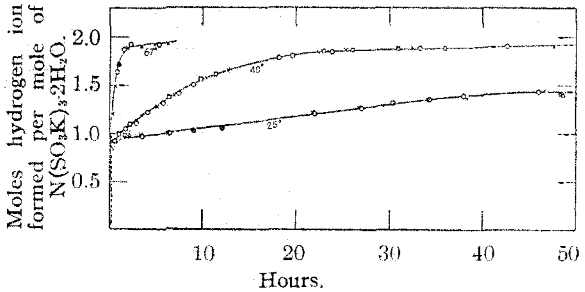

Fig. 1.—Hydrolysis of potassium nitrosulfonate.

In checking this assumption experimentally, it was found that neutral solutions of the intermediate product, potassium imidodisulfonate, did not become acid, that is, undergo hydrolysis, even over a period of eighteen hours at 67°. However, addition of an equimolar quantity of potassium acid sulfate, thus approximating the composition and concentration of the solution after the nitrilosulfonate had hydrolyzed in accordance with Equation 1, was found to bring about hydrolysis. In following the increase of acidity with time, results were obtained which checked satisfactorily with those plotted in Fig. 1.

It is significant that alkaline solutions of potassium nitrilosulfonate are resistant to hydrolysis, whereas neutral solutions undergo rapid decomposition. Solutions of the imidodisulfonate[5] seem to be quite stable, but in the presence of hydrogen ion undergo hydrolysis, thus leading to the conclusion that the reaction is acid catalyzed. Since the acid concentration approaches a constant value of two moles per mole of nitrilosulfonate hydrolyzed, it is apparent that the end-product, potassium sulfamate, H_2NSO_3K, is quite stable, even in presence of acid.

As is evident from Fig. 1 rise in temperature quite naturally increases rate of hydrolysis. Experiments carried out at 100°, using solutions of the same concentration, demonstrated that hydrolysis to the sulfamate is complete within one-half hour.

Potassium Imidodisulfonate.—In preparing this intermediate product the following procedure was adopted: 38 g. of $N(KSO_3)_3 \cdot 2H_2O$ was moistened with 16 ml. of 2% sulfuric acid and allowed to stand for twenty-four hours. The pasty mass was then filtered and the solid residue washed with 60 ml. of ice water. This product was recrystallized from a solution containing 10 ml. of concentrated aqueous ammonia in 60 ml. of water. The crystals obtained on cooling were washed with ice water, alcohol and ether and dried in a vacuum desiccator over sulfuric acid; yield, 12 g. (51%).

Anal. Calcd. for $HN(SO_3K)_2$: N, 5.53; K, 30.9. Found: N, 5.75; K, 30.4

Potassium imidodisulfonate is much more soluble in water than the nitrilosulfonate. The addition of $BaCl_2$–HCl solution gives no immediate precipitate. Upon warming, or after standing for a short time, barium sulfate begins to form. This shows qualitatively that the imidodisulfonate is much more stable to hydrolysis than the nitrilosulfonate.

Preparation of Potassium Sulfamate by Hydrolysis of Potassium Nitrilosulfonate.—Sixty grams of potassium nitrilosulfonate (0.147 mole) was suspended in 300 ml. of water and boiled for seventy-five minutes. The solution was then neutralized with 20 g. of potassium carbonate (0.145 mole) and evaporated to dryness. The residue was placed in a Soxhlet apparatus and extracted with 80% ethanol for forty-six hours. Potassium sulfamate crystallized from the alcoholic extract on cooling; yield, 13.5 g. (67%).

Summary

1. Maximum yields of potassium nitrilosulfonate are obtained when the ratio of $KHSO_3$: KNO_2 is 4:1, or greater, and when the reaction is carried out at higher temperatures.

2. The hydrolysis of potassium nitrilosulfonate has been studied at 25, 40, 67 and 100°. The nitrilosulfonate is rapidly converted into the imidodisulfonate, which in turn hydrolyzes more slowly to give the sulfamate as the final product.

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[5] It is of interest to point out the relationship between imidodisulfonic, pyrosulfuric, trithionic and hydroxylaminodisulfonic acids. In each of these compounds the SO_3H radicals are linked together by one of the following isosteric atoms or groups: O, S, NH, NOH. If these isosteres are represented by R the hydrolysis of any one of these four acids may be represented by the general equation:

$$R\begin{cases} SO_3H \\ SO_3H \end{cases} + H_2O \longrightarrow HRSO_3H + HOSO_3H$$