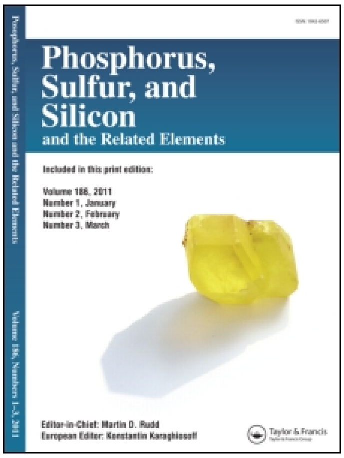

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HYDROLYSIS OF POTASSIUM NITRILOSULFONATE DIHYDRATE

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Potassium nitrilosulfonate dihydrate, $K_3N(SO_3)_3 \cdot 2H_2O$ has been shown to hydrolyse in the solid state to imidosulfonate, $K_2NH(SO_3)_2$, accompanied by formation of pyrosulfate. Pyrosulfate subsequently hydrolyzes to bisulfate. The hydrolysis has been followed by recording infrared spectra over the range 1100–500 cm^{-1}. The intermediate formation of $S_2O_7^{2-}$ in the hydrolysis of $N(SO_3)_3^{3-}$ in aqueous solution has been detected and therefore the commonly accepted pathway for decomposition, which invokes formation of HSO_4^- in the first step, has to be modified.

Although it has been known for some time that potassium nitrilosulfonate dihydrate, $K_3N(SO_3)_3 \cdot 2H_2O$, undergoes gradual hydrolysis on standing in air at ambient temperature,[1] no report concerning the hydrolytic mechanism or the nature of the products of hydrolysis under these conditions has been published. However, a route has been proposed[2,3] for the aqueous solution hydrolysis of nitrilosulfonate. This route, which has been reproduced in the text by Yost and Russell[4] and in other publications[5-8] is described by the following equations.

$$N(SO_3)_3^{3-} + H_2O \rightarrow NH(SO_3)_2^{2-} + HSO_4^- \qquad (1)$$

$$NH(SO_3)_2^{2-} + H_2O \rightarrow NH_2SO_3^- + HSO_4^- \qquad (2)$$

Step (1) is reported to occur readily in neutral solution at ambient temperature but step (2) only in acid solution or in neutral solution at elevated temperatures. It is therefore reasonable to assume that, if the solid-state hydrolysis of $K_3N(SO_3)_3 \cdot 2H_2O$ occurs by the same route, it would not proceed significantly beyond step (1).

During the recording of the infrared spectrum of solid $K_3N(SO_3)_3 \cdot 2H_2O$,† the growth of "new" bands was observed. Although some of these bands could be attributed to potassium imidosulfonate, $K_2NH(SO_3)_2$ and potassium bisulfate, $KHSO_4$, several other bands which were not assignable to the remaining hydrolysis product (potassium sulfamate, KNH_2SO_3) of the reaction sequence (1) and (2) also appeared. This paper shows that the additional features belong to potassium pyrosulfate, $K_2S_2O_7$, and that this is a primary hydrolysis product and the precursor of $KHSO_4$. Also, the intermediate formation of pyrosulfate in the hydrolysis of nitrilosulfonate in aqueous solution has been revealed.

RESULTS AND DISCUSSION

Solid-State Hydrolysis

A quantity of pure $K_3N(SO_3)_3 \cdot 2H_2O$ was exposed to the atmosphere at ambient temperature and its hydrolysis was followed by recording infrared spectra of freshly-mulled samples at intervals over a period of 26 weeks. Figure 1 shows a series of spectra in the region 1100-500 cm^{-1} taken of the pure substance and samples at various intervals during this period.

A band at 906 cm^{-1} (marked n) characteristic of $K_3N(SO_3)_3 \cdot 2H_2O$ disappeared within two weeks and bands at 1089, 1031, 554 and 539 cm^{-1} (i) and at 1068 and 1000 cm^{-1} (b), which are characteristic of potassium imidosulfonate[9] and potassium bisulfate[10] respectively, develop. Other bands, not attributable to any of the above species, which rapidly appear and then diminish in intensity coincide with features known for potassium pyrosulfate.[11,12] These bands (p) appear at 1094, 1045, 791 and 740 cm^{-1}. No potassium sulfamate[13], which would have been detected by its intense, unmasked bands at 3328, 1130 and 810 cm^{-1}, was observed over the duration of the experiment.

Figure 1 shows that the bisulfate component increases relative to imidosulfonate (C, D, E, and F). Since there is no apparent decomposition of imidosulfonate (in particular to sulfamate) it is concluded that the precursor to bisulfate is pyrosulfate. The latter is present before bisulfate appears (B and C)

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† A detailed account of the vibrational spectrum of this compound is in preparation.

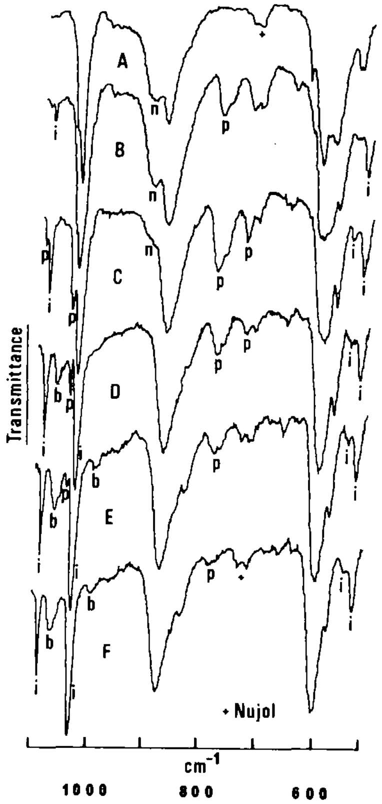


FIGURE 1 Infrared spectra of pure $K_3N(SO_3)_3 \cdot 2H_2O$ (A) and its hydrolysis after 2 days (B), 3 days (C), 2 weeks (D), 6 weeks (E) and 26 weeks (F). Bands labelled n, i, p, b refer to contributions solely from nitrilosulfonate, imidosulfonate, pyrosulfate and bisulfate respectively. Major unlabeled bands following A contain contributions from several hydrolysis products.

and then decreases in intensity as the intensity of bisulfate increases (C, D, E, and F). The first step in the hydrolysis of $K_3N(SO_3)_3 \cdot 2H_2O$ in air at ambient temperature must therefore be the simultaneous formation of $K_2NH(SO_3)_2$ and $K_2S_2O_7$. Conversion of $K_2S_2O_7$ to $KHSO_4$ follows.

A number of synthetic mixtures of the pure compounds $K_2NH(SO_3)_2$, $K_2S_2O_7$ and $KHSO_4$ were prepared and their infrared spectra recorded. By varying the amounts of individual components, excellent reproductions of the spectra shown in Figure 1 were obtained. Also, the $K_2S_2O_7$ bands at 1050 and 1099 cm^{-1} in the spectrum of the pure substance were found to shift to 1045 and 1094 cm^{-1} respectively in the synthetic mixtures (affected by the proximity of intense bands due to $K_2NH(SO_3)_2$) which were the observed values for $K_2S_2O_7$ in the spectra of the hydrolyzed material.

That water was responsible for the changes occurring in Figure 1 was shown by recording infrared spectra of Nujol-mulled samples of $K_3N(SO_3)_3 \cdot 2H_2O$ and separately, the anhydrous material $K_3N(SO_3)_3$. Heating of the mull by the infrared beam accelerated hydrolysis of the dihydrate as observed by repeated scans (1100-500 cm^{-1}) of the one sample over a period of 30 min. Simultaneous formation of $K_2NH(SO_3)_2$ and $K_2S_2O_7$ occurred (commencing after 2-3 min.) followed by conversion of $K_2S_2O_7$ to $KHSO_4$, the latter also being detectable after several minutes. In the case of anhydrous $K_3N(SO_3)_3$ protected as a Nujol mull, no detectable hydrolysis occurred under these conditions. Hence hydrolysis of the dihydrate proceeded via its own water of crystallization. Anhydrous $K_3N(SO_3)_3$ exposed to the atmosphere at ambient temperature was found to hydrolyze in a manner identical to the dihyrate. Also, a freshly prepared sample of $K_2S_2O_7$ slowly converted to $KHSO_4$ when exposed to the atmosphere at ambient temperature over a period of several weeks. The following solid-state hydrolysis sequence and scheme for nitrilosulfonate is therefore proposed.

Scheme 1, which suggests that *one* water oxygen atom interacts with *two* sulfur atoms (one from each of two adjacent $N(SO_3)_3^{3-}$ ions) simultaneously, and thereby becomes the bridging atom in pyrosulfate, is supported by the X-ray structure[14] of $K_3N(SO_3)_3 \cdot 2H_2O$. Each water oxygen atom in solid $K_3N(SO_3)_3 \cdot 2H_2O$ is situated such that it is approximately equidistant from *four* sulfur atoms, *two* from the one $N(SO_3)_3^{3-}$ ion and *one* from each of two other adjacent $N(SO_3)_3^{3-}$ ions. Interaction between a water oxygen atom and two sulfur atoms of the same ion to form pyrosulfate apparently does not occur since the simultaneous formation of sulfamate which would result is not observed.

Hydrolysis in Aqueous Solution

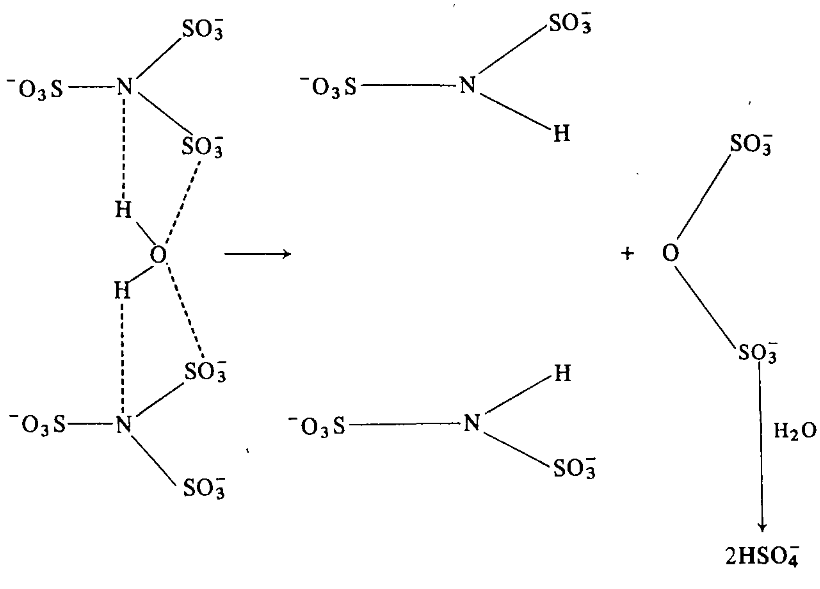
Hydrolysis of nitrilosulfonate in aqueous solution is considered to proceed via steps (1) and (2). Rutenberg *et al.*[15] showed that acid hydrolysis in ^{18}O-water produced sulfate containing *one* oxygen atom per SO_4^{2-} derived from the solvent. Since the proposal for solid-state hydrolysis (steps (3) and (4)) is consistent with this result, it seemed a reasonable proposition that pyrosulfate be also involved in hydrolysis in aqueous solution. Hofmeister and Van Wazer[16] have shown pyrosulfate to have a half-life of 1.7 min. in water at 298 K, and that it hydrolyzes to bisulfate. Dissolution of $K_3N(SO_3)_3 \cdot 2H_2O$ in water followed by rapid crystallization of hydrolysis products may

$$2N(SO_3)_3^{3-} + H_2O \rightarrow 2NH(SO_3)_2^{2-} + S_2O_7^{2-} \quad (3)$$

$$S_2O_7^{2-} + H_2O \rightarrow 2HSO_4^- \quad (4)$$

(overall)

$$2N(SO_3)_3^{3-} + 2H_2O \rightarrow 2NH(SO_3)_2^{2-} + 2HSO_4^- \quad (5)$$



Scheme 1

therefore yield spectroscopically detectable $K_2S_2O_7$, if pyrosulfate occurs as an intermediate in aqueous solution.

From a consideration of the solubility of $K_3N(SO_3)_3 \cdot 2H_2O$ (20 g l^{-1} at 296 K)[4]† and calculated half-lives of $S_2O_7^{2-}$ at various temperatures, it was decided to check the above possibility by conducting an hydrolysis experiment at 338 K at which the half-life of $S_2O_7^{2-}$ is calculated to be 15 sec. $K_3N(SO_3)_3 \cdot 2H_2O$ (~1 g), held in a sintered glass filter funnel was washed with 50 cm^3 of water (preheated to 338 K) and dissolved at the same time as the solution was drawn through the sinter by reduced pressure into an ice-cooled Buchner flask. The flask contained a 1:1 ethanol-ether mixture (500 cm^3) which caused crystallization of products approximately 2 sec. after dissolution of the solid.

The infrared spectrum of the precipitated material showed some unhydrolyzed nitrilosulfonate together with bands ascribable to $K_2NH(SO_3)_2$, $KHSO_4$ and $K_2S_2O_7$. Indeed, the spectrum was in good agreement with that of Figure 1, spectrum C.‡

When $K_3N(SO_3)_3 \cdot 2H_2O$ (~1 g) was thoroughly mixed for 5 sec. with 500 cm^3 of a cold 1:1 ethanol-ether mixture to which 50 cm^3 of water (preheated to 338 K) had just been added, no hydrolysis was spectroscopically apparent. Hydrolysis of $N(SO_3)_3^{3-}$ in the former experiment therefore took place in solution and not after precipitation from the mixed solvent medium.

When an aqueous solution of $K_3N(SO_3)_3 \cdot 2H_2O$ (~2 g) was heated for ~5 min. at 338 K and poured into into an ice-cold 1:1 ethanol-ether mixture, the precipitated material was found to contain $K_2NH(SO_3)_2$, $KHSO_4$ and K_2SO_4, the latter being identified by its characteristic infrared bands at 1115 and 610 cm^{-1}. Pyrosulfate was absent, its hydrolysis to bisulfate being complete.

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† This solubility is probably greater than the actual value because of hydrolysis to the more soluble products on dissolution in non-alkaline medium.

‡ An X-ray diffraction powder photograph of a synthetic mixture of these four components showed the same number of lines and spacings as a photograph of the precipitated material.

EXPERIMENTAL SECTION

Infrared spectra were run as Nujol mulls on a Perkin-Elmer Model 225 spectrophotometer and calibrated using polystyrene film. The spectra in Figure 1 were obtained using a low source current in order to reduce the heating effect of the beam on the sample and its consequent hydrolysis.

Potassium Nitrilosulfonate Dihydrate, $K_3N(SO_3)_3 \cdot 2H_2O$

The compound was prepared by the method of Sisler and Audrieth.[17] The initial precipitate was recrystallized from hot 1 M KOH solution. The anhydrous material was obtained by subjecting the dihydrate to reduced pressure (10^{-3} mm Hg) at ambient temperature.

Anal. Calc. for $K_3NS_3O_{11}H_4$: S, 23.6; N, 3.4; K, 28.8; H_2O, 8.8. Found: S, 23.5; N, 3.5; K, 28.8; H_2O, 8.8.

Potassium Imidosulfonate, $K_2NH(SO_3)_2$

The compound was prepared by the method of Sisler and Audrieth.[6]

Anal. Calc. for $K_2NHS_2O_6$: S, 25.3; N, 5.5; K, 30.9; Found: S, 25.0; N, 5.5; K, 30.5.

Potassium Pyrosulfate, $K_2S_2O_7$

Potassium bisulfate was heated to 690 K under reduced pressure (10^{-3} mm Hg) and maintained at this temperature for 15 min. Water evolved during the conversion was pumped off continuously. On cooling, $K_2S_2O_7$ solidified as a hard, white mass. The infrared spectrum showed no bands due to $KHSO_4$.

Anal. Calc.. for $K_2S_2O_7$: K, 30.8. Found: K, 30.7.

Potassium Bisulfate, $KHSO_4$

Analytical Reagent grade potassium bisulfate was dried at 453 K under reduced pressure (~3 mm Hg) for 1 hour.

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