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Alkaline Hydrolysis Products of Ammonium Nitridotris(sulfate)

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The products of the alkaline hydrolysis reaction of ammonium nitridotris(sulfate) were first identified as imidobis(sulfate) and sulfate by ion-exchange separation and infrared spectroscopy.

It has been known since 1896, that the hydrolysis reaction of nitridotris(sulfate) ($\underset{\sim}{1}$) proceeds only in acidic or neutral solution.[1-4] In the course of our chromatographic studies of aquo-ammono-sulfuric acids, however, we found that the hydrolysis reaction of ($\underset{\sim}{1}$) occurs also in alkaline solution. Recently, it has been recognized that ($\underset{\sim}{1}$) is one of the main species produced in alkaline flue gas wet desulfurization and denitrification process.[5] Therefore, understanding of the products and kinetics of the alkaline hydrolysis of ($\underset{\sim}{1}$) are significant for developing wet scrubber system to remove NO_X and SO_X from flue gas. Here we describe the first direct observation of species in this hydrolysis reaction.

Hydrolysis reaction was carried out at 49.5 °C. A 616 mg (0.2 m mol) sample of ammonium nitridotris(sulfate) was dissolved in 250 ml of 0.5 M NaOH. One ml aliquots were withdrawn from a reaction mixture at time intervals, neutralized with acid under cooling condition, and charged onto a cooled ion-exchange column immediately. All of the chromatographic runs were performed on a automatic liquid chromatograph equipped with a thermal detector. In addition to this automatic detection, a manual turbidimetric detection[6] was performed using an effluent from the autoanalyser. The ion-exchange resin used was BIO-RAD AG 1X8 (Minus 400 mesh) in chloride form. The column bed was 58 cm long and 0.8 cm in diameter. Aqueous 0.45 M KCl was used as an eluent.

A typical clean cut elution pattern for the hydrolysis reaction products is shown in Fig.1. The upper diagram indicates a chromatogram by thermal detection and the lower one, that by turbidimetric detection. To identify the peak in chromatogram, the infrared spectroscopy was used. The fractions of each region of A, B, and C were collected and then evaporated to dryness under vacuum. The dried sample containing the eluting agent was run as KCl salt disc. Observed frequencies for A, B, and C were (1110,618), (1386, 1265,1031,875,600), and (1400,1291,1265,1039, 891,598,538) cm^{-1}, respectively. By comparing the data with those of authentic samples, these were confirmed as SO_4^{2-}, $HN(SO_3)_2^{2-}$, and $N(SO_3)_3^{3-}$. On the other hand, quantitative analysis of A and B by turbidimetry[6] shows that the molar ratio of A to B was equal to unity at time intervals. (Fig.2).

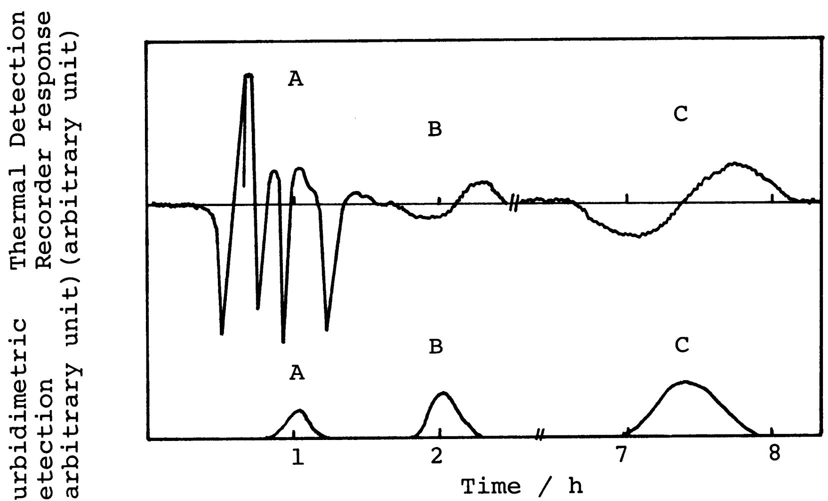

Fig.1. The elution pattern for the hydrolysis reaction products.
(A) SO_4^{2-} (B) $HN(SO_3)_2^{2-}$ (C) $N(SO_3)_3^{3-}$

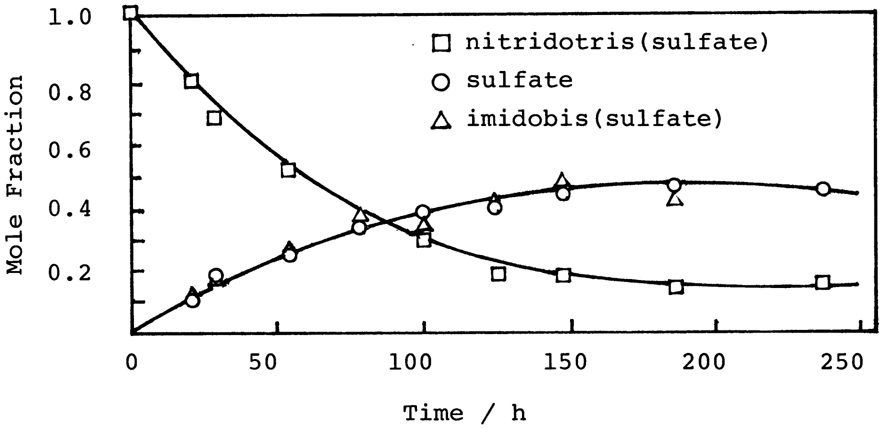

Fig.2. Time dependence of alkaline hydrolysis reaction of $N(SO_3NH_4)_3$ in 0.5 M NaOH at 49.5 °C.

These results suggest that the alkaline hydrolysis reaction proceeds to form imidobis(sulfate) and sulfate as follows

$$N(SO_3)_3^{3-} \xrightarrow{OH^-} HN(SO_3)_2^{2-} + SO_4^{2-}$$

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