Alkyl Cyanates

XIII. Thermal Degradation of Isotopically Labelled 5-Isobutoxy-1,2,3,4-thiatriazole

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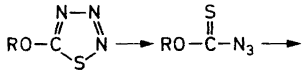
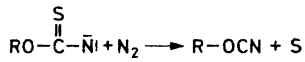
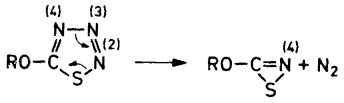
In a recent paper Jensen, Burmester and Bak reported an investigation into the kinetics of decomposition of 5-alkoxy-1,2,3,4-thiatriazoles into alkyl cyanates, nitrogen, and sulfur.[1] The reaction was found to be first in order in alkoxythiatriazole with an activation energy of 24.8 kcal·mol^{-1} and an activation entropy of 4.1 cal·mol^{-1}·°K^{-1} (measured for 5-ethoxythiatriazole). This was assumed to be consistent with the following mechanism:

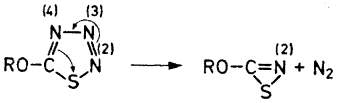




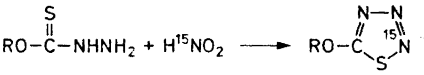
However, the possible intermediate nitrene has not been observed either in spectroscopic or chemical investigations.[2] Several other pathways are possible, *e.g. via* the hitherto unknown 3-membered thiazirin:



This could be formed directly from the alkoxythiatriazole or from the above mentioned nitrene in an almost simultaneous reaction, in both cases with loss of nitrogen from position N(2) and N(3) in the thiatriazole. However, if the decomposition of the alkoxythiatriazole to alkyl cyanate takes place without formation of intermediates, *i.e.* a concerted reaction, nitrogen may also be lost from position N(2) and N(3). Loss of nitrogen from position N(3) and N(4), on the other hand, would strongly suggest the presence of a three-membered intermediate.



Because a three-membered ring has not been observed, its possible formation must rapidly be followed by decomposition into sulfur and alkyl cyanate. Accordingly, we have prepared 5-isobutoxy-1,2,3,4-thiatriazole, labelled with ^{15}N at the N(2) position. The procedure normally used for the preparation of alkoxythiatriazoles was followed[3] using $Na^{15}NO_2$ (97.4 % ^{15}N).



The thiatriazole formed was then allowed to decompose in a small amount of paraffin oil, in an evacuated ampule. The contents of the ampule were heated to 40°C at which temperature the reaction takes place rapidly. After about 1 h the ampule was attached to a mass spectrometer and the nitrogen formed was introduced into the mass spectrometer. During this the alkyl cyanate formed was trapped by cooling in liquid nitrogen. After the gases had been removed the alkyl cyanate was analysed by heating the ampule to room temperature, which was sufficiently high to allow introduction of the cyanate into the mass spectrometer.

The analysis clearly showed that the nitrogen lost in the decomposition is from position N(2) and N(3) since the nitrogen formed contained 96.4 % of $^{15}N^{14}N$ (corrected for background) which corresponds to 98.9 % loss of nitrogen from these positions. The analysis of the isobutyl cyanate substantiated this as no ^{15}N was found to be present in the cyanate. In order to distinguish between $^{29}N_2$ and other fragments of nominal mass 29 a double focusing mass spectrometer, type AEI—MS 902 was used. This instrument has a resolution of 10 000.

1. Jensen, K. A., Burmester, S. and Bak, T. A. *Acta Chem. Scand.* **21** (1967) 2792.
2. Holm, A. *To be published.*
3. Jensen, K. A., Due, M. and Holm, A. *Acta Chem. Scand.* **19** (1965) 438.

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