Gas Phase Pyrolysis of 1,2,3-Triazoles

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An example of recent research concerning unstable intermediates is the investigation by Gilchrist and Rees of the pyrolysis of substituted 1,2,3-triazoles. They came to the conclusion that there is strong evidence for the existence of the potentially antaromatic 1H-azirines. In the present work we undertook the pyrolysis of the unsubstituted 1,2,3-triazole in order to try to detect the so far unobserved 1H-azirine directly.

As is well known, 1,2,3-triazole exists in two tautomeric forms, of which only the 1H-tautomer (1b) should lose nitrogen easily. In the liquid phase the tautomeric equilibrium lies towards the side of the 2H-tautomer (1a) and is shifted towards the 1H-form with increasing temperature. However, the gas phase spectra have been assigned to the 1H-form, and the interpretation of the microwave spectrum of 1,2,3-triazole deuterated on the nitrogen atom supported this result.

The vapour of 1,2,3-triazole, prepared by the slightly modified method of Wiley, Hussung, and Moffat, was pyrolysed in a 25 cm long quartz tube 10 mm in diameter. The products were immediately pumped through the absorption cell of a Hewlett-Packard microwave spectrometer. The pyrolyses were performed in a temperature range up to 1000 °C at various sample pressures, both with and without quartz wool in the pyrolysis tube, and with and without argon as buffer gas.

All recorded absorption lines could be assigned to four known products by using the NBS spectral tables. Acetonitrile was the main product, and hydrogen cyanide and ammonia occurred as by-products. Propionitrile was identified under some conditions in traces. There was no absorption that might be due to an unknown substance. Since only substances with permanent dipole moments can be detected by absorption in the microwave region and no supplementary detection methods were used, the number of pyrolysis products is not necessarily complete. H2, N2, and perhaps C2N2 would pass through the spectrometer undetected. However, all the products expected according to the Scheme should exhibit a microwave spectrum.

In order to test the assumption that the gold plating of the absorption cell might catalyse the decomposition of the expected unstable intermediates after pyrolysis, the pyrolysis products were pumped through a glass free-space cell and investigated in the millimetre wavelength region. Unfortunately, no new lines were detected. The pyrolysis apparatus was also checked to see whether it was able to produce unstable intermediates from other chemical systems. A positive result was obtained in the pyrolysis of methylamine:10,11 methyleneamine was produced and detected.

The most surprising observation was that 1,2,3-triazole was decomposed quantitatively at about 850 °C, an unexpectedly high pyrolysis temperature as compared with 600 °C for 1,2,3-thiadiazole. In our opinion this fact is due to the tautomeric equilibrium lying more towards the side of the structure (1a) of the starting material in the gas phase, which, however, cannot occur in the case of 1,2,3-thiadiazole. Recent results of a microwave
spectroscopic investigation of 1,2,3-triazole, presented in part at the Fourth European Microwave Conference last year, supported our chemically derived assumption that the tautomeric equilibrium must lie unfavourably on the side of the 2H-tautomer (1a) in the gas phase. The microwave spectrum of 1,2,3-triazole, which was previously assigned only to the 1H-tautomer (1b), was unexpectedly weak despite the large dipole moment which could be determined from the spectrum. Nielsen, Nygaard, and Sørensen could not explain this fact. In order to circumvent the line broadening due to the nuclear hyperfine structure of $^{14}$N they made a special search for the 2H-tautomer in the vapour of [15N$_3$]-1,2,3-triazole. Indeed they found this tautomer and determined the dipole moment by means of the Stark effect. The total dipole moment of the 1H-form is 4.38 ± 0.04 D, whereas the total dipole moment of the 2H-form is 0.21 ± 0.01 D, values which are in good agreement with the dipole moments of the N-methylated derivatives. The important 2H : 1H ratio was determined to be approximately 100 : 1, consistent with our pyrolysis results. Since no unstable intermediates were detected in the pyrolysis products of 1,2,3-triazole, we conclude that the rather high pyrolysis temperature due to the unfavourable tautomeric equilibrium was too high to allow the formation of any unstable intermediates.

The critical step in the formation of the 1H-azirine is the ring closure of the iminocarbene (2); however Wolff rearrangement to the vinylideneamine (3) is probably more favourable. Therefore, thermal formation of the 1H-azirine must start preferentially from precursors which already contain the three-membered heterocycle and only the C=C double bond must be created. By this criterion the pyrolysis of 1,2,3-triazole offers little chance of producing the unsubstituted 1H-azirine in detectable quantities. The corresponding potentially antiaromatic heterocycles thireno and selenireno have recently been identified in the photolysis products of 1,2,3-thiadiazole and 1,2,3-selenadiazole in solid low temperature matrices.

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References:
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