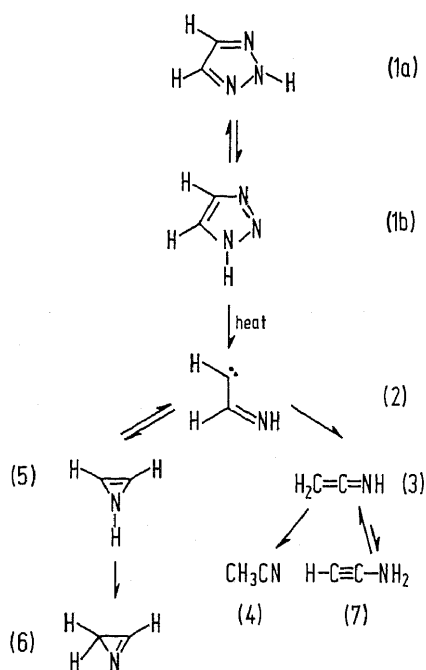


Gas Phase Pyrolysis of 1,2,3-Triazole†

MANFRED WINNEWISSER,*^a JÜRGEN VOGT,^a and HUBERTUS AHLBRECHT^b^aPhysikalisch-Chemisches Institut, Justus Liebig-Universität Giessen, D-6300 Giessen^bInstitut für Organische Chemie, Justus Liebig-Universität Giessen, D-6300 Giessen

An example of recent research concerning unstable intermediates is the investigation by Gilchrist and Rees of the pyrolysis of substituted 1,2,3-triazoles.^{1,2} They came to the conclusion that there is strong evidence for the existence of the potentially antiaromatic 1*H*-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 1*H*-azirine directly.



Scheme Decomposition of the 1,2,3-triazole

In the Scheme Gilchrist and Rees's decomposition mechanism has been transferred to the unsubstituted 1,2,3-triazole and slightly extended. The possibility of the existence of the ethynylamine tautomer (7) should not be excluded, although it should be rather unstable in comparison with both the acetonitrile (4) and the vinylideneamine (3) tautomers. To date, 1*H*-azirine (5), ethynylamine (7), and vinylideneamine (3) are unknown, whereas 2*H*-azirine (6) has recently been detected by Ford.³

*To receive any correspondence.

†This is a Short Paper as defined in the Instructions for Authors [*J. Chem. Research (S)*, 1977, p. iv of Issue no. 2]; there is therefore no corresponding material in *J. Chem. Research (M)*.

As is well known,⁴ 1,2,3-triazole exists in two tautomeric forms, of which only the 1*H*-tautomer (1b) should lose nitrogen easily. In the liquid phase the tautomeric equilibrium lies towards the side of the 2*H*-tautomer (1a) and is shifted towards the 1*H*-form with increasing temperature.⁴ However, the gas phase spectra^{5,6} have been assigned to the 1*H*-form, and the interpretation of the microwave spectrum of 1,2,3-triazole deuteriated on the nitrogen atom supported this result.⁷

The vapour of 1,2,3-triazole, prepared by the slightly modified method of Wiley, Hussung, and Moffat,⁸ 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.⁹ 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.¹² 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,¹³⁻¹⁵ supported our chemically derived assumption that the tautomeric equilibrium must lie unfavourably on the side of the 2*H*-tautomer (1a) in the gas phase. The microwave spectrum of 1,2,3-triazole, which was previously assigned only to the 1*H*-tautomer (1b), was unexpectedly weak despite the large dipole moment which could be determined from the spectrum. Nielsen, Nygaard, and Sørensen¹³⁻¹⁵ could not explain this fact. In order to circumvent the line broadening due to the nuclear hyperfine structure of ¹⁴N they made a special search for the 2*H*-tautomer in the vapour of [¹⁵N₃]-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 1*H*-form is 4.38 ± 0.04 D, whereas the total dipole moment of the 2*H*-form is 0.21 ± 0.01 D, values which are in good agreement with the dipole moments of the *N*-methylated derivatives.⁴ The important 2*H*:1*H* 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 1*H*-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 1*H*-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 1*H*-azirine in detectable quantities. The corresponding potentially antiaromatic heterocycles thiiren and seleniren have recently been identified in the photolysis products of 1,2,3-thiadiazole and 1,2,3-selenadiazole in solid low temperature matrices.¹⁶

We thank Dr. C. J. Nielsen and Dipl. Chem. W. Raab for stimulating discussions. We also thank Dipl. Chem. W. Raab for the preparation of the 1,2,3-triazole and Dr. B. P. Winnewisser for her comments on the manuscript. This work was supported, in part, by funds from the Deutsche Forschungsgemeinschaft and the Max Planck-Gesellschaft.

Paper: E/059/78 Received: 24th April 1978

References:

- ¹ T. L. Gilchrist, G. E. Gymer, and C. W. Rees, *JCS Perkin I*, 1975, 1.
- ² T. L. Gilchrist, C. W. Rees, and C. Thomas, *JCS Perkin I*, 1975, 8.
- ³ R. G. Ford, *J. Amer. Chem. Soc.*, 1977, 99, 2389.
- ⁴ P. Mauret, J. P. Fayet, M. Fabre, J. Elguero, and M. del Pardo, *J. Chim. phys.*, 1973, 70, 1483.
- ⁵ E. Borello, A. Zecchina, and E. Guglielminotti, *J. Chem. Soc. (B)*, 1969, 307.
- ⁶ O. L. Stiefvater, H. Jones, and J. Sheridan, *Spectrochim. Acta*, 1970, 26A, 825.
- ⁷ G. O. Sørensen, L. Nygaard, and M. Begtrup, *JCS Chem. Comm.*, 1974, 605.
- ⁸ R. H. Wiley, K. F. Hussung, and J. Moffat, *J. Org. Chem.*, 1956, 21, 190.
- ⁹ M. S. Cord, M. S. Lojko, and J. D. Petersen, *Microwave Spectral Tables*, National Bureau of Standards Monograph 70, vol. V, Washington, 1968.
- ¹⁰ D. R. Johnson and F. J. Lovas, *Chem. Phys. Letters*, 1972, 15, 65.
- ¹¹ R. Pearson and F. J. Lovas, *J. Chem. Phys.*, 1977, 66, 4149.
- ¹² H. Bock, B. Solouki, G. Bert, and P. Rosmus, *J. Amer. Chem. Soc.*, 1977, 99, 1663.
- ¹³ C. J. Nielsen, L. Nygaard, and G. O. Sørensen, Fourth European Microwave Spectroscopy Conference, Tübingen, 1977, Paper D7.
- ¹⁴ C. J. Nielsen, personal communication.
- ¹⁵ L. Nygaard, personal communication.
- ¹⁶ A. Krantz and J. Laurenzi, *J. Amer. Chem. Soc.*, 1977, 99, 4842.