Energetic Metastable Transitions in the Mass Spectrum of *s*-Triazole

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THE existence of energetic metastable decompositions giving rise to "flat-topped" peaks has been documented.[1,2] The uncharged particle in these transitions is normally a small stable molecule or radical, although transitions involving elimination of a nitrogen atom have been reported.[3] A similar unusual reaction is observed in the mass spectrum† of *s*-triazole [(I) or (II)], which reveals two flat-topped metastable peaks at *m/e* 24·4 and 18·7. These metastable peaks correspond to the transitions ($69^+ \rightarrow 41^+ + 28$) and ($42^+ \rightarrow 28^+ + 14$) respectively. The neutral fragment in this latter reaction may be either methylene or a nitrogen atom, both of which are uncommon.

The partial mass spectrum of *s*-triazole is given in the Table. Loss of HCN from the molecule-ion gives the major fragment ion, *m/e* 42. The most likely structure for this ion are (III) and (IV), of which (IV) is the diazirine molecule-ion and should readily eliminate methylene.[4] However, the mass spectrum of [^{2}H-]-1,2,4-triazole (Table) shows that such an elimination does not take place, for the metastable transition now becomes ($43^+ \rightarrow 29^+ + 14$). Thus the neutral fragment is a nitrogen atom. The width of the metastable peak corresponds to a total energy release of 0·45 ± 0·02 ev. The energy release in this reaction is unchanged upon deuteriation of the molecule. The reaction possibilities are illustrated by the sequence (III)$\longleftrightarrow$(V)$\rightarrow$(VI) and (III)$\longleftrightarrow$(VII)$\rightarrow$(VIII).

Partial mass spectrum of 1,2,4-*triazole*

	Relative intensity	
m/e	[$^2H_0$]	[$^2H_1$]
26	3·3	3·7
27	15·8	13·7
28	17·7	16·8
29	6·5	24·2
30	—	9·2
38	5·2	5·8
39	6·5	0·8
40	15·8	12·9
41	11·1	8·3
42	68·3	9·2
43	1·6	73·3
44	—	1·7
69	100·0	—
70	3·3	100·0
71	—	5·0

The total energy released upon elimination of N_2 from the molecule-ion is 1·41 ± 0·02 ev, a

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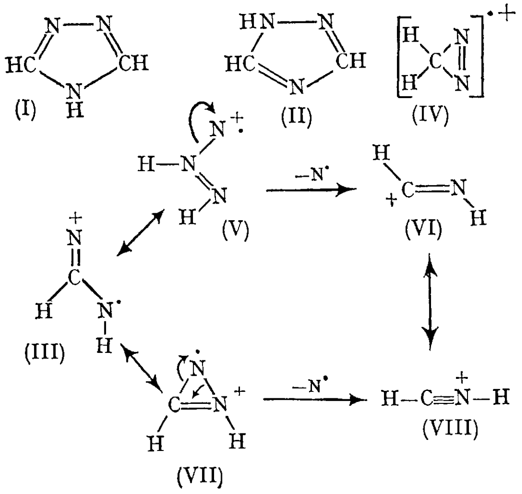
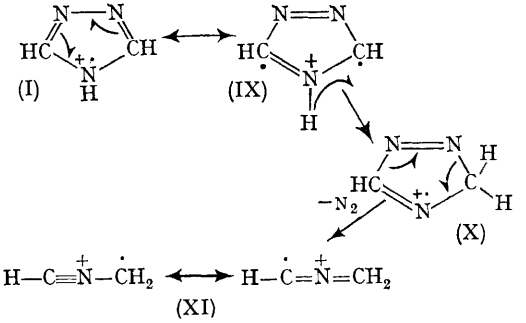
† The mass spectra were recorded with A.E.I. MS-12 mass spectrometer using 75 ev electrons, 100 μA trap current, and 8 kv accelerating potential.

value substantially greater than the 0·48 ev released in the previously reported elimination of N_2 from 3,6-dimethyltetrazine.[3] The top of the metastable peak is concave due to the magnitude of the energy released.[3] Exchange of the active proton with deuterium increases the energy released in the elimination of nitrogen to 1·57 ±0·02 ev. This isotope effect indicates that the transition state for the reaction involves the shift of a hydrogen atom.



There are two likely tautomers of *s*-triazole, (I) and (II). An *X*-ray crystallographic determination[5] favours (II), in the solid state. However, the n.m.r. spectra in acetonitrile,[6] dimethoxyethane, and dimethylformamide show one sharp singlet for the C–H protons and, in the latter two solvents, a broad absorption for the N–H proton, thus favouring structure (I) in solution. The high dipole moment of this compound, 3·17 D,[7] further substantiates this assignment.

A suggested mechanism for the nitrogen elimination from the symmetrical tautomer is given by the sequence (I)→(XI). This mechanism can account for the energy difference observed upon deuteriation, if the hydrogen shift is the rate-controlling step. The nitrogen elimination may be concerted with the hydrogen transfer. The energy difference between H and D transfer is 0·16 ± 0·04 ev or 3·7 ± 0·9 kcal., which is approximately three times as great as the difference in activation energies for H and D abstraction from secondary amines in gas phase radical reactions.[8]



The postulation of a hydrogen transfer to form (X) is further substantiated by the incorporation of two and three deuterium atoms into the *s*-triazole molecule. The reaction of D_2O and *s*-triazole in the inlet system of the mass spectrometer at 150° results in the formation of 20% [$^2H_2$]- and 3% [$^2H_3$]-*s*-triazole, after ½ hr. This observation is best explained by an equilibrium between the neutral structures (I) and (X). The occurrence of such a process under thermal conditions suggests that it will be even more facile as a radical-ion rearrangement due to the substantially greater internal energy of the molecule-ion formed by electron impact.

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[1] J. H. Beynon, R. A. Saunders, and A. E. Williams, *Z. Naturforsch.*, 1965, **20a**, 180.
[2] J. H. Beynon and A. E. Fontaine, *Z. Naturforsch.*, 1967, **22a**, 334.
[3] T. W. Shannon, F. W. McLafferty, and C. R. McKinney, *Chem. Comm.*, 1966, 478.
[4] G. S. Paulett and R. Ettinger, *J. Chem. Phys.*, 1963, **39**, 825.
[5] H. Deuschl, *Ber. Bunsengesellschaft Phys. Chem.*, 1965, **69**, 550.
[6] K. T. Potts and T. H. Crawford, *J. Org. Chem.*, 1962, **27**, 2631.
[7] K. T. Potts, *Chem. Rev.*, 1961, **61**, 87.
[8] P. Gray and A. Jones, *Trans. Faraday Soc.*, 1965, **61**, 2161.