

## Cyclobutadienyl Cations? The Electron-impact Induced Fragmentation of Pyridazine

M. H. BENN\* and T. S. SORENSEN

(Department of Chemistry, The University of Calgary, Calgary, Alberta, Canada)

and A. M. HOGG

(Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada)

WE have studied the electron-impact induced fragmentation of pyridazine (I). The results, which we describe here, reveal that some simple, but structurally tantalizing, ions are formed.

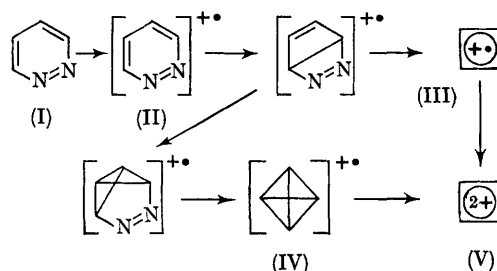
The mass spectrum of pyridazine was determined with an M.S.9 mass spectrometer (heated inlet at 185°) at 70, 15, and 10 ev; the spectra were similar, the figures which we report here are for the 70 ev spectrum.

The base peak (100%),  $m/e$  80, corresponds to the molecular ion, and the only other prominent peaks were at  $m/e$  52 (20%), 51 (20%), 50 (10%), 27 (5%), and 26 (13%). High-resolution measurements revealed that the peak  $m/e$  52 was a doublet  $m/e$  52.0313 (73.5%) (calc. for  $C_4H_4$ : 52.0313) and 52.0187 (26.5%) (calc. for  $C_3H_2N$ : 52.0184). A metastable peak ( $m^*$  34), corresponding to the transition  $m/e$  80  $\rightarrow$   $m/e$  52 confirms that fragmentation of the molecular ion proceeds predominantly by loss of nitrogen to give the species  $C_4H_4^+$ .

Further high-resolution measurements showed that the peaks at  $m/e$  51 and 50 were due to the species  $C_4H_3^+$  and  $C_4H_2^+$  respectively (measured 51.0235 and 50.0156; calc. 51.0235 and 50.0235), and also that the peak at  $m/e$  26 must be due to either the  $C_2H_2^+$  cation radical or the  $C_4H_4^{2+}$  dication (measured 26.0158; calc. 26.0156). That this latter peak is in the main due to the dication was established by examination of a weak peak at  $m/e$  26.5 (ca. 1% of  $m/e$  26), which proved to be due to the species  $^{13}CC_3H_4^{2+}$  (measured 26.5175,

calc. 26.5173). There was also no sign of a metastable peak at  $m^*$  13, required for the transition  $m/e$  52  $\rightarrow$   $m/e$  26 (monocation).

We consider that the  $C_4H_4^{2+}$  species is most probably the cyclobutadienyl dication (V). Amongst the various possible structures for  $C_4H_4^+$  we prefer the cyclobutadienyl cation radical (III), although the tetrahedryl cation radical (IV) is a tempting alternative.



Interestingly, it has recently been concluded that the tetraphenylcyclobutadienyl dication is probably *not* formed in the electron-impact induced fragmentation of tetracyclone,<sup>1</sup> and tetraphenylcyclobutadienylpalladium chloride, contrary to an earlier suggestion,<sup>2</sup> though the monocation radical probably is formed.

(Received, April 24th, 1967; Com. 387.)

<sup>1</sup> J. H. Beynon, R. F. Curtis, and A. E. Williams, *Chem. Comm.*, 1966, 237.

<sup>2</sup> J. H. Beynon, R. C. Cookson, R. R. Hill, D. W. Jones, R. A. Saunders, and A. E. Williams, *J. Chem. Soc.*, 1965, 7052.