The Mass Spectra of Some Deuterated Pyrazoles

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During research on the mass spectral behaviour of substituted pyrazoles (1) the pyrazole molecule was deuterated in several positions in order to study the fragmentation of this compound in more detail. A recent article by Jacquier *et al.* (2) however prompts us to report our preliminary results in this note.

Apart from pyrazole (I) the following deuterated analogues have been studied: $1-D_1$- (II), $4-D_1$- (III), $1,4-D_2$- (IV), $3,5-D_2$- (V), and $1,3,5-D_3$-pyrazole (VI).
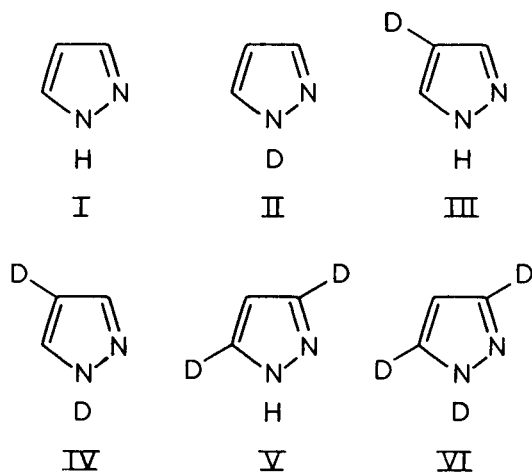
Two of the most important fragmentation reactions, loss of H· and of HCN from the molecular ion, have been investigated. The mass spectra have been corrected for isotopic impurities (see under Experimental). The mass region of the molecular ion is given below:
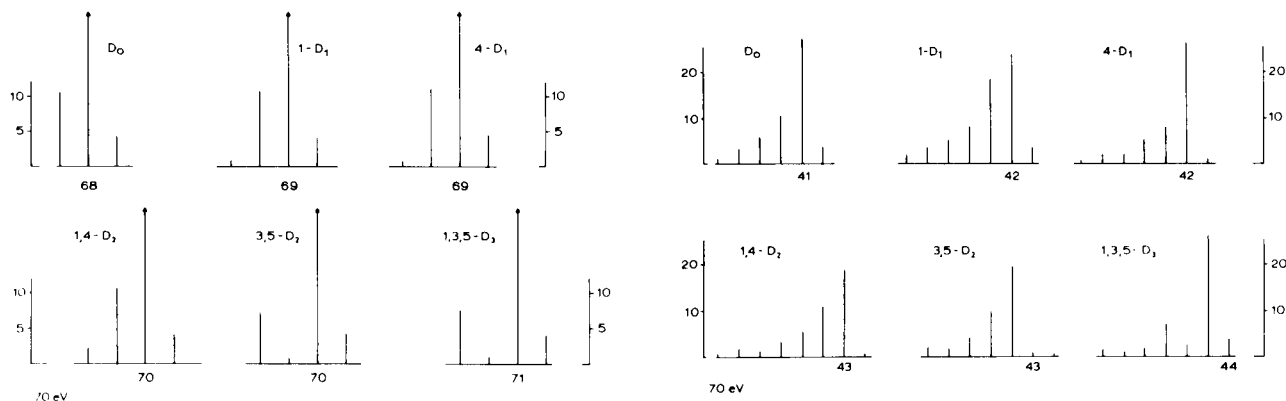
For the D_0 compound the molecular ion, being the base peak (relative abundance 100) appears at m/e 68. In $1-D_1$-, $4-D_1$- and $1,4-D_2$-pyrazole H· is lost in preference to D·, in $3,5-D_2$- and in $1,3,5-D_3$-pyrazole this preference is reversed. H/D randomization appears to be small. This result can be explained in terms of cleavage of a C-H bond in a position α relative to a nitrogen atom. This α-cleavage is a frequently encountered phenomenon in mass spectra of compounds possessing heteroatoms (3).

The loss of HCN from the molecular ion of D_0-pyrazole gives rise to a large peak at m/e 41, accompanied by a number of satellite peaks in the mass region m/e 36-40. The peak at m/e 41 is almost exclusively due to $C_2H_3N^{+·}$ (loss of HCN); the contribution of CHN_2 is 1 per cent (1). The peak at m/e 40 is a singulet ($C_2H_2N^+$) arising from consecutive losses of HCN and H· or of H· and HCN (1).

In a monodeuterated pyrazole primary loss of HCN and of DCN occurs, leading to fragments at m/e 42 and 41, respectively. Since there is also a contribution to m/e 41 from a secondary fragment ($M-H_2CN$), analogous to m/e 40 in D_0-pyrazole, an erroneous conclusion might be drawn from the conventional low resolution mass spectra. A very high resolving power would be needed to determine the individual abundances of such a H_2-D doublet with any degree of accuracy.

The mass region m/e 37-44 is shown below for the compounds studied. The masses indicated for each compound correspond with primary loss of HCN from the particular molecule.

From the mass psectra of $3,5\text{-}D_2$- and of $1,3,5\text{-}D_3$-pyrazole it appears that position $3(5)$ is favoured, but the mass spectra of the other three deuterated compounds do not a priori exclude contributions from the other two positions.

Although one has to take into account a certain degree of H/D randomization, it is possible to obtain more insight into this process by considering the diffuse peaks arising from metastable ion transitions. Thus, for a dideuterated pyrazole loss of HCN from the molecular ion is represented by the reaction $70^+ \rightarrow 43^+ + 27$, which gives a diffuse peak at $m/e = 43^2/70 = 26.41$. Accordingly, loss of DCN from the molecular ion gives a diffuse peak at $m/e = 42^2/70 = 25.20$. This is illustrated below in the cases of $1,4\text{-}D_2$- and $3,5\text{-}D_2$-pyrazole.
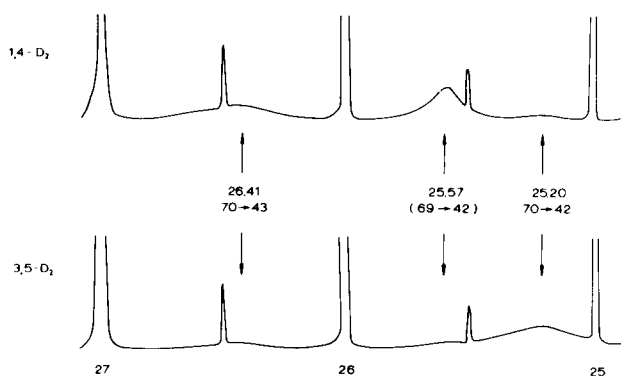
The advantage of comparing diffuse peaks is that there is no direct interference of secondary processes, as these contribute to diffuse peaks at different values of m/e. This is seen above for the loss of HCN from the (M-H)-fragment, which gives a diffuse peak at $m/e = 25.27$. The only interference is by ^{13}C and ^{15}N contributions of the secondary processes, for which a correction can be applied. In the above case this correction amounts to less than 3 per cent of the abundance of the peak of the secondary process. After correction the ratios of the diffuse peaks (M-HCN)/(M-DCN) for $1,4\text{-}D_2$- and $3,5\text{-}D_2$-pyrazole become 7.9 and 0.2, respectively.

These figures indicate that for the metastable ion transitions considered H/D randomization at 70 eV is small. For complete randomization the ratios should become 1. Furthermore they demonstrate that loss of HCN from the molecular ion of pyrazole occurs from the $3(5)$ position with a high specificity.

In a following paper the complete mass spectra of the compounds studied and a more quantitative treatment of the two processes discussed will be presented.

EXPERIMENTAL

The preparations of $4\text{-}D_1$- and of $3,5\text{-}D_2$-pyrazole were carried out by treatment of pyrazole with deuterium oxide under the catalytic conditions described by Chung Wu and Vaughan in a kinetic study (4). During our work Jacquier et al. (2) published a paper describing synthetic details. As these are essentially the same as in this work, they are not given here.

$4\text{-}D_1$-pyrazole was obtained in 22% yield, with an isotopic composition of 3.4% D_0, 95.7% D_1, 0.9% D_2.

For $3,5\text{-}D_2$-pyrazole the yield was 20%, the isotopic composition being 0.1% D_0, 5.3% D_1, 89.8% D_2, 4.8% D_3.

Sites of deuteration were checked by NMR, the D-content by mass spectrometry.

Although N-deuterated pyrazoles can be prepared in high yield by dissolving the pyrazole in deuterium oxide and isolation after 24 hours at room temperature, we found that this procedure also gives C-deuteration. For example, treatment of D_0-pyrazole with deuterium oxide at room temperature for 30 minutes yielded a product containing 26.5% D_0, 70.5% D_1, and 2.9% D_2. NMR demonstrated that D_2 is formed by substitution of D at position 4. Especially in the preparation of $1,3,5\text{-}D_3$- from $3,5\text{-}D_2$-pyrazole such an effect was undesirable, since the exact percentages of the impurities caused by $1,3(5),4\text{-}D_3$- and $3,4,5\text{-}D_3$-pyrazole were not known, and no corrections could be applied.

The same reaction occurred when a slurry of the compound to be N-deuterated in deuterium oxide was introduced into the mass spectrometer by means of the glass inlet system.

Separate introduction of the pyrazole and deuterium oxide into the mass spectrometer through different inlet systems at ion source temperatures below $55°$ resulted, after equilibration times of 20-30 minutes in high conversion rates for N-deuteration and negligible amounts of C-deuteration. Typical isotopic compositions obtained were: for $1\text{-}D_1$-: 7.2% D_0, 92.4% D_1, 0.4% D_2; for $1,4\text{-}D_2$-: 0.2% D_0, 8.5% D_1, 91.3% D_2; for $1,3,5\text{-}D_3$-: 0.7% D_1, 14.5% D_2, 84.0% D_3, 0.8% D_4.

Mass spectra were obtained with an AEI MS-902 mass spectrometer operating at 70 eV: samples were introduced via the glass inlet system at ion source temperatures between $40°$ and $50°$. In the case of N-deuteration deuterium oxide was introduced by means of a separate cold inlet system. The mass spectra of the pure compounds were obtained by subtracting the mass spectra of the isotopic impurities. In the case of $3,5\text{-}D_2$-pyrazole the D_1-contribution was assumed to be $3(5)\text{-}D_1$-pyrazole, the mass spectrum of which was calculated by assuming statistical loss of H(HCN) and D(DCN). The same method was employed for $1,3,5\text{-}D_3$-pyrazole, where a known percentage of $3(5)\text{-}D_1$-, originally present, is converted into $1,3(5)\text{-}D_2$-pyrazole.

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