An Investigation by Ion Cyclotron Double Resonance of the Structural Differences of Isomeric Ions using a Direct Insertion Probe

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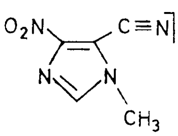
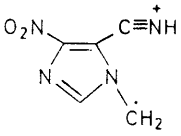
Ions (I) and (II) of *m/e* 152 obtained by electron impact from 1-methyl-4-nitroimidazole-5-carbonitrile and from 1-methyl-4-nitroimidazole-5-carboxamide were separately caused to react with 3,5-dimethylpyridine. Ion (I) reacted only by charge transfer, while ion (II) reacted both by charge transfer and by proton transfer with the base. The different behaviour under identical conditions proved the non-identity of the two ions. As the substances investigated were solids, a direct insertion probe had to be used in the experiments.

In an investigation of the loss of water from 1-methyl-4-nitroimidazole-5-carboxamide under electron impact it was shown that the $[M - H_2O]^{+\cdot}$ ion had structure (II) and was thus different from the isomeric molecular ion (I) of the corresponding nitrile.[1] This conclusion was arrived at by using conventional mass spectrometry on deuterium-labelled compounds and comparing the shapes of metastable peaks due to further loss of NO from (I) and (II). In view of the general importance of the determination of the structures of ions formed in the mass spectrometer, it seemed desirable to confirm this result by other means. The approach chosen and reported on here was to search for a reaction which would discriminate between the two ions, and which could be monitored in a commercially available ion cyclotron resonance (i.c.r.) mass spectrometer. It appears to be the first time that i.c.r. spectrometry has been used to establish the structures of ions obtained from solid compounds. Their low vapour pressures required the use of a direct insertion probe (see Experimental section).



(I)



(II)

RESULTS AND DISCUSSION

The most obvious difference between the ions (I) and (II) is in the position of one of the hydrogen atoms, which in (II) is linked to nitrogen, while in (I) it is linked to carbon, being part of a methyl group. It would be expected that a proton transfer of the imino-hydrogen atom in (II) would occur more readily than a proton transfer of a methyl group hydrogen atom in (I). If a strong base (B) of molecular weight M_B were allowed to react with the ion (II) under suitable conditions, one might expect reaction (1) to occur. Using the technique

$$\begin{array}{ccccc} (\mathrm{II})^{+\cdot} + & \mathrm{B} \longrightarrow & [(\mathrm{II})^{+\cdot} - \mathrm{H}^{+}] & + \ \mathrm{BH}^{+} & (1) \\ m/e = 152 & \text{mass } M_B & \text{mass } 151 & m/e = M_B + 1 & \end{array}$$

of ion cyclotron double resonance,[2] it should be possible to detect this reaction. Thus when observing the ion of $m/e = M_B + 1$, *i.e.* keeping the magnetic field strength and the marginal oscillator frequency (ω_1) constant, and gradually increasing the irradiating second radio-frequency (ω_2), the occurrence of reaction (1) would be proved by a change in the abundance of the BH^+ ion, when ω_2 equals ω_{II}, the angular frequency of the ion (II). A different result obtained when allowing the nitrile ion (I) to react with the same base B, would prove the non-

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[1] G. H. Lord, B. J. Millard, and J. Memel, *J.C.S. Perkin I*, 1973, 572.

[2] A number of review articles have recently been published, *e.g.* (*a*) J. H. Futrell in 'Dynamic Mass Spectrometry,' ed. D. Price, Heyden, London, 1971, vol. 2, pp. 97—133; (*b*) C. J. Drewery, G. C. Goode, and K. R. Jennings in 'M.T.P. International Review of Science (Physical Chemistry),' ed. A. Maccoll, Butterworths, London, 1972, vol. 5, pp. 183—217.

identity of the ion formed by loss of water from the amide and the molecular ion of the nitrile. Such a difference could be either a difference in the sign of the double resonance signal, or the presence of the signal in one case and absence of it in the other. A difference in the size of the signals would only be meaningful if the quantities of the two ions were exactly the same or were known exactly, requirements which would be difficult to realise experimentally.

(i) 1-*Methyl*-4-*nitroimidazole*-5-*carbonitrile*.—3,5-Dimethylpyridine was used as the base B to bring about reaction (1). This compound was chosen because of its suitable molecular weight and also because it was expected to be a very strong base in the gas phase, by analogy with the known proton affinity of pyridine of 225 ± 2 kcal mol^{-1}.[3,4] Figure 1 is the i.c.r. spectrum of a mixture of 1-methyl-4-nitroimidazole-5-carbonitrile and 3,5-dimethylpyridine at 153 kHz. Figures 2a and b are the double resonance spectra obtained from this mixture by observing the changes in the abundance of the ions of *m/e* 107 and 108 while sweeping the frequency ω_2 through the mass ranges *m/e* 107—170 (Figure 2a) and *m/e* 130—170 (Figure 2b). The positive signal obtained in Figure 2b at the frequency corresponding to the ion of *m/e* 152 could either be due to a proton transfer from the molecular ions of the nitrile to molecules of the base according to equation (2) or to a charge transfer from the

$$\begin{array}{lclclclc} (I)^{+\cdot} & + & B & \longrightarrow & [(I)^{+\cdot} - H^{+}] & + & BH^{+} & (2) \\ m/e\ 152 & & \text{mass } 107 & & \text{mass } 151 & & m/e\ 108 & \end{array}$$

nitrile ions to molecules of the base having a molecular weight of 108 due to the presence of isotopes, according to equation (3).

$$\begin{array}{lclclclc} (I)^{+\cdot} & + & B_{\text{isotope}} & \longrightarrow & (I) & + & B^{+\cdot}{}_{\text{isotope}} & (3) \\ m/e\ 152 & & \text{mass } 108 & & \text{mass } 152 & & m/e\ 108 & \end{array}$$

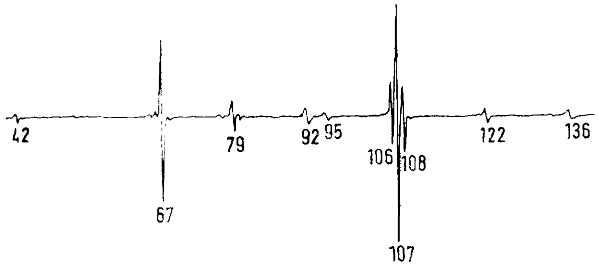

FIGURE 1 I.c.r. spectrum of a mixture of 3,5-dimethylpyridine ($0{\cdot}2 \times 10^{-5}$ Torr) and 1-methyl-4-nitroimidazole-5-carbonitrile ($1{\cdot}0 \times 10^{-5}$ Torr); $\omega_1/2\pi = 153{\cdot}7$ kHz, 20 eV

A comparison with Figure 2a shows that a charge transfer reaction is involved. Figure 2a shows in addition to small signals due to charge transfer reactions from other ions, a large positive signal at the frequency corresponding to the ion of *m/e* 152, indicating that a charge transfer reaction from this ion is involved in the formation of the molecular ion of the base of *m/e* 107. The size of the signal at *m/e* 152 in Figure 2b is *ca.* 9% of the corresponding signal in Figure 2a, obtained under identical conditions. Since this is, within experimental error, in agreement with the ratio (8 : 100) of the abundance of molecules of 3,5-dimethylpyridine of molecular weight of 108 to those of molecular weight of 107 due to the natural abundance of ^{13}C and ^{15}N, it is apparent that the molecular ions of the nitrile (I) react with 3,5-dimethylpyridine by charge transfer and *not* by proton transfer.

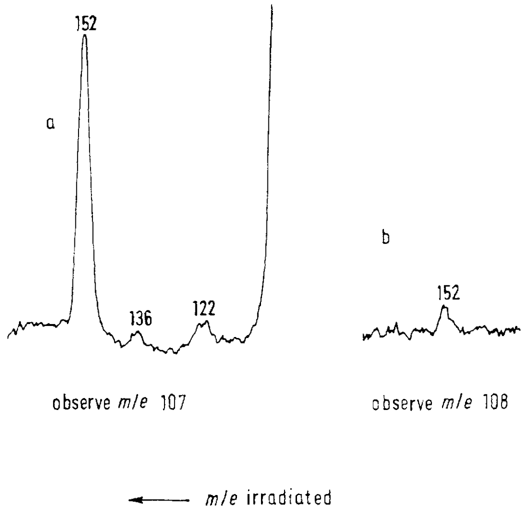

FIGURE 2 The double resonance spectra of a the *m/e* 107 and b the *m/e* 108 ion of 3,5-dimethylpyridine, mixed with 1-methyl-4-nitroimidazole-5-carbonitrile (total pressure $1{\cdot}2 \times 10^{-5}$ Torr). Both ions are observed with $\omega_1/2\pi = 153{\cdot}6$ kHz while frequency ω_2 is swept through the mass ranges *m/e* 107—170 (a) and 130—170 (b). The irradiating voltage is 0·1 V and the electron energy 20 eV. Drop of total ion current at the peaks $<1\%$

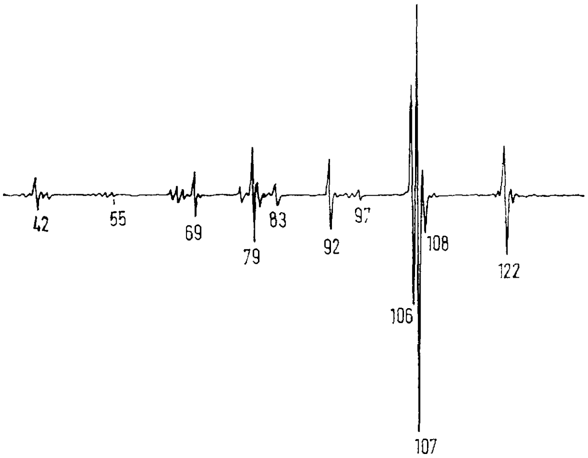

FIGURE 3 I.c.r. spectrum of a mixture of 3,5-dimethylpyridine ($0{\cdot}2 \times 10^{-5}$ Torr) and 1-methyl-4-nitroimidazole-5-carboxamide ($1{\cdot}0 \times 10^{-5}$ Torr): $\omega_1/2\pi = 153{\cdot}5$ kHz, 20 eV

(ii) 1-*Methyl*-4-*nitroimidazole*-5-*carboxamide*.—Figure 3 is the i.c.r. spectrum of a mixture of 3,5-dimethylpyridine

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[3] M. Taagepera, W. G. Henderson, R. T. C. Brownlee, J. L. Beauchamp, D. Holtz, and R. W. Taft, *J. Amer. Chem. Soc.*, 1972, **94**, 1369.

[4] N. M. M. Nibbering, *Tetrahedron*, 1973, **29**, 385.

and 1-methyl-4-nitroimidazole-5-carboxamide at 153 kHz. Figures 4a and b are the double resonance spectra obtained from this mixture by observing the changes in the abundances of the ions of *m/e* 107 and of 108 while sweeping the frequency ω_2 through the mass range *m/e* 107—180.

The large positive signal at the ω_2 frequency corresponding to *m/e* 152 in Figure 4a shows that these ions take part in a charge transfer reaction with the neutral molecules of the base having the molecular weight 107, as expected in view of the earlier argument. When observing the ion of *m/e* 108 under the same conditions (Figure 4b), however, we do not obtain the corresponding positive signal at *m/e* 152 for the charge transfer reaction (4) but find a negative signal instead. This negative signal

$$\underset{m/e\ 152}{(\mathrm{II})^{+\cdot}} + \underset{\text{mass } 108}{\mathrm{B}_{\text{isotope}}} \longrightarrow \underset{\text{mass } 152}{(\mathrm{II})} + \underset{m/e\ 108}{\mathrm{B}^{+\cdot}{}_{\text{isotope}}} \qquad (4)$$

indicates that the ion of *m/e* 152, formed by the loss of water from the amide, is involved in the formation of the ion of *m/e* 108 in a thermoneutral or exothermic reaction.[5] There is no reason to doubt the occurrence of reaction (4) and the appearance of the negative signal under double resonance conditions can only be due to two causes. If the amplitude of the ω_2 irradiating frequency were too large, the ions of *m/e* 152 would be swept out and trapped, before reacting with molecules of the base with molecular weight 108. The observation of the change of intensity of the ions of *m/e* 108 without and with irradiation, would then produce a negative signal. This is, however, not the correct explanation in this case, as Figures 4a and b were obtained under identical conditions, and Figure 4a shows clearly that there was no sweep-out at the irradiating voltage used (0·1 V), *i.e.* a dip at the centre of the signal is not observed. Sweep-out of ions would also lead to a reduction of total ion current, and this was not observed.

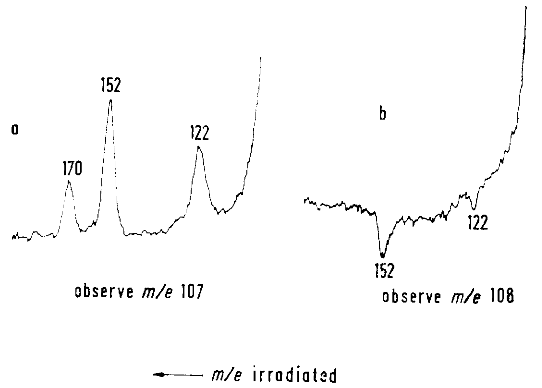

FIGURE 4 The double resonance spectra of a the *m/e* 107 and b the *m/e* 108 ion of 3,5-dimethylpyridine, mixed with 1-methyl-4-nitroimidazole-5-carboxamide (total pressure $1{\cdot}2 \times 10^{-5}$ Torr). Both ions are observed with $\omega_1/2\pi = 153{\cdot}4$ kHz while frequency ω_2 is swept through the mass range *m/e* 107—180. Other conditions as Figure 2

The negative signal is, therefore, not due to sweep-out of the ion of *m/e* 152, but must be due to the occurrence of a second reaction involving this ion in addition to reaction (4). This second reaction linking the ion of *m/e* 152 with the formation of the ion of *m/e* 108 can only be the transfer of a proton to the base according to reaction (5). While the ion of *m/e* 152 obtained from the

$$\underset{m/e\ 152}{(\mathrm{II})^{+\cdot}} + \underset{\text{mass } 107}{\mathrm{B}} \longrightarrow \underset{\text{mass } 151}{[(\mathrm{II})^{+\cdot} - \mathrm{H}^{+}]} + \underset{m/e\ 108}{\mathrm{BH}^{+}} \qquad (5)$$

nitrile thus reacts with the base *only* by charge transfer, the ion of *m/e* 152, obtained from the amide by loss of water, reacts with the base *both* by charge transfer *and* by proton transfer. However, irrespective of the details of the reactions involved, the fact that the two ions react differently with the same reagent under identical conditions is proof by itself that they are not identical.

EXPERIMENTAL

The spectra were obtained with a Varian V-5903 i.c.r. spectrometer (serial number 126), fitted with the standard flat three-section cell and a dual inlet system.

3,5-Dimethylpyridine was admitted from a glass sample bottle *via* one of the sample leak valves to the i.c.r. cell without any heating being employed.

For the (solid) imidazole derivatives a direct insertion probe, manufactured by Varian, was used. This probe allows the introduction of the sample *via* a vacuum lock into the ionisation chamber close to the filament. Once in position the probe can be heated to volatilise the sample. Condensation is prevented by heating the i.c.r. cell.

Very careful control of temperature was necessary to obtain a reasonable working pressure and to hold the vapour pressure constant, while at the same time preventing too fast evaporation and loss of sample. The most critical temperature was that of the probe, which was held at 100° for the nitrile (Figures 1 and 2) and at 125° for the amide (Figures 3 and 4). The other temperatures were T_{cell} *ca.* 80°, T_{oven} *ca.* 90°, and $T_{\text{vacuum lock}}$ *ca.* 100° (Figures 1—4). The electron energy was set using a digital voltmeter, and pressures were determined from the ion pump current meter. The emission current was 0·06—0·10 μA, giving total ion currents within the range $1\text{—}5 \times 10^{-11}$ A. The electron collector voltage was zero. The radiofrequency level of the marginal oscillator was set at such a value, that it did not produce a change in the total ion current at resonance. Single resonance spectra were obtained in the field modulation mode (amplitude 20 G) with a sweep rate of 10 min, response 0·3 s. In the ion cyclotron double resonance experiments square wave modulation was employed and the spectra were recorded with a sweep rate of 10 min, response 3 s. The irradiating oscillator was applied to the source region and during the scans the total ion current was also monitored as recommended by Jennings *et al.*[6]

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[3/1354 *Received, 27th June,* 1973]

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[5] J. L. Beauchamp and S. E. Butrill, *J. Chem. Phys.*, 1968, **48**, 1783.

[6] G. C. Goode, A. J. Ferrer-Correia, and K. R. Jennings, *Internat. J. Mass Spectrom. Ion Phys.*, 1970, **5**, 229.