

A Novel Mass-spectroscopic Technique for the Investigation of Vapour-phase Tautomeric Equilibria

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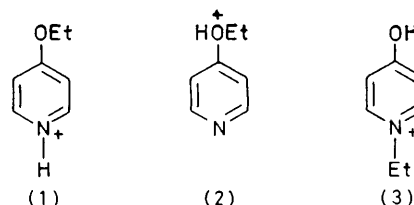
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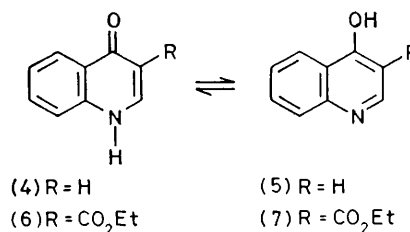
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Summary Comparison of collision-induced dissociation-mass analysed ion kinetic energy (CID-MIKE) spectra of cations found by chemical ionisation ethylation with those of chemical ionisation protonation of fixed ethyl derivatives, allows identification of predominant tautomers in vapour phase equilibria.

ETHYLATIONS and protonations of molecules have frequently been observed in CI (chemical ionisation) mass spectra.¹ We have now shown that (kinetically controlled) protonation of 4-ethoxypyridine gives a mixture of cations (1) and (2), identified by their CID (collision induced dissociation) mass spectra analysed by the MIKE technique (mass-analysed ion kinetic energy). Similarly, we find that 1-ethyl-4-pyridone on protonation yields solely (3). Comparison of the cation formed by ethylation of gaseous 4-pyridone-4-hydroxypyridine with the preceding spectra



Similar study of the *O*- and *N*-ethyl and tautomeric compounds of the 4-hydroxyquinoline series shows clearly that here the 4-quinolone structure (4) predominates over (5). However, for the corresponding 3-ethoxycarbonyl derivative it is the hydroxy tautomer (7) which is preferred to (6). Furthermore, it can be deduced that 2-quinolone predominates over 2-hydroxyquinoline. These equilibria have not previously been investigated in the gas phase.



The above work demonstrates that the CID-MIKE technique possesses considerable potential for the structural study of cations generated by chemical ionisation techniques. We believe that significant conclusions could already be drawn with the present technique for a wide variety of tautomeric problems, and with better resolution and deeper understanding of fragmentation mechanisms, the method will become even more powerful. It forms a most useful adjunct to the previous mass spectroscopic,³ ion cyclotron resonance,⁴ and photoelectronic spectroscopy techniques,⁵ which have been used to investigate vapour phase tautomeric equilibria.

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¹ F. H. Field in 'Ion-Molecule Reactions,' ed. J. L. Franklin, Plenum, New York, 1972, Vol. 1, p. 261.

² P. Beak, *Accounts Chem. Res.*, 1977, **10**, 186, and references therein.

³ Ionisation potentials: T. Grønneberg and K. Undheim, *Org. Mass Spectrom.*, 1972, **6**, 823; isotopic effects: A. Maquestiau, Y. van Haverbeke, C. de Meyer, A. R. Katritzky, M. J. Cook, and A. D. Page, *Canad. J. Chem.*, 1975, **53**, 490; *in situ* formation of individual tautomers: A. Maquestiau, Y. van Haverbeke, R. Flammang, and H. Mispreuve, *Org. Mass Spectrom.*, 1977, **12**, 205.

⁴ M. J. Cook, A. R. Katritzky, M. G. Taagepera, T. D. Singh, and R. W. Taft, *J. Amer. Chem. Soc.*, 1976, **98**, 6048.

⁵ M. J. Cook, S. El-Abbady, A. R. Katritzky, C. Guimon, and G. Pfister-Guillouzo, *J.C.S. Perkin II*, 1977, 1652.

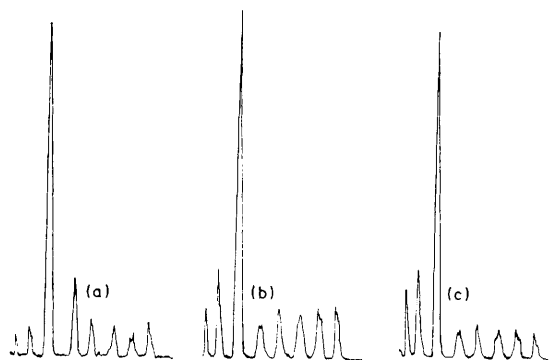


FIGURE. CI-CID-MIKE spectra: (a) protonation of 4-ethoxypyridine; (b) protonation of 1-ethyl-4-pyridone; (c) ethylation of 4-pyridone-4-hydroxypyridine.

(Figure) shows clearly its structure as (3), and consequently demonstrates the preponderance of 4-hydroxypyridine in the vapour phase equilibrium, in agreement with other work.²