

Ionisation Potentials in Structure Analysis of Gaseous Hydroxypyridine 1-Oxides*

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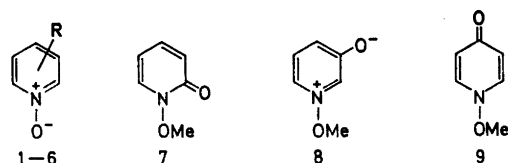
The 3- and 4-isomers of the tautomeric hydroxypyridine 1-oxides exist predominantly in the hydroxy form in the gaseous state in the mass spectrometer. Internal hydrogen bonding in a pseudo-ring structure is suggested for the 2-isomer. The conclusions are based on comparisons of ionisation potential data.

Extensive physical measurements on the tautomerism of hydroxypyridine 1-oxides in solution and solid state have been carried out.² We wish to report studies of hydroxypyridine 1-oxides in the gaseous state by the determination of ionisation potentials (IP). IP determinations have recently been found very useful in structure analysis of gaseous molecules;³⁻⁴ such data for the tautomeric hydroxy and amino pyridines have been interpreted in favour of the hydroxy and amino forms.^{3,4}

Interpretation of the IP data for the hydroxypyridine 1-oxides (1–3) required corresponding data for the phenolic ethers (4–6) and the 1-methoxy analogues (7–9). These derivatives correspond to fixing the hydroxypyridine 1-oxides in either tautomeric form. The IP values were obtained by the semi-log plot method with xenon as reference gas.⁶

The influence of a substituent on the ease of ionisation depends on the nature of other substituents as well as on the ring system and relative position;^{4,7} generally an electron releasing substituent decreases the IP. In the methoxypyridine 1-oxides the IP value (4–6) is increased by 0.2 eV from the 2- to the 3-isomer, but decreased by 0.4 eV from the 3- to

Table 1. Ionisation potentials.



Compound	R	IP (eV)
1	2-OH	8.90
2	3-OH	8.60
3	4-OH	8.18
4	2-OMe	8.21
5	3-OMe	8.40
6	4-OMe	7.98
7		8.32
8		(8.3)
9		8.49

the 4-isomer. The IP decrease of a methyl group relative to that of a hydrogen atom on a phenolic oxygen in simple systems is of the order 0.2–0.3 eV. This corresponds to the observed difference (0.2 eV) between the 3-methoxy isomer (5) and the 3-hydroxy isomer (2). The latter can be assumed to be present in the gas phase as such rather than as its tautomeric 1-hydroxy zwitterion. The charge separation introduced in the zwitterionic form will reduce the volatility compared to that of the non-charged 3-hydroxy form; furthermore, structures with charge separation should be disfavoured in the gas phase because at 10⁻⁶ Torr the charges cannot be dispersed by solvation or other intermolecular interactions. The IP for the 4-methoxy isomer (6) is also about

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Table 2. Characteristic ion intensities in the mass spectra.

Fragment	1	2	3	4 ^b	5	6	7 ^c	9
[M]	75	100	100	29	100	100	84	100
[M-15]			25 ^a	2	5	44	—	21
[M-16]	100	24	79	28	72	81	2	8
[M-17]	—	—	8	62	2	8	2	—
[M-30]				13	3	16	58	9
[M-31]				—	11	5	3	1

^a [M-1]; ^b *m/e* 78 base peak; ^c *m/e* 39 base peak.

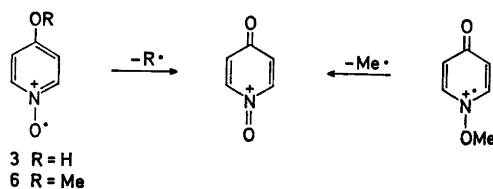
0.2 eV lower than for the 4-hydroxy isomer (3) which supports the hydroxy formulation for the latter. The difference (0.6–0.7 eV) between the 2-isomers (1 and 4), however, is too large to be inherent in the methyl group. Nor can the difference be explained by the molecule being in the form of 1-hydroxypyrid-2-one as IP of the model 1-methoxy derivative (7) is about 0.6 eV below that of (1); the effect of the *O*-methyl group is assumed to be of the same order as discussed above. It is well established, however, that 1 forms strong intramolecular hydrogen bonding.^{3,8} A major part of the observed IP difference in the 2-series is therefore attributed to ground state destabilisation on *O*-alkylation which prevents intramolecular hydrogen bonding. Presumably the 2-hydroxy isomer, therefore, is present in the gas phase as a strongly hydrogen bonded molecule with structure in between those of the two tautomeric forms.

A further comparison of the IP data for the 4-isomers (6 and 9) supports the hydroxy formulation for 3. Assuming similar effect from the methyl groups (0.2 eV) the estimated IP's for 4-hydroxypyridine 1-oxide and 1-hydroxypyrid-4-one are 8.2 and 8.7 eV, respectively; the former is in agreement with the observed value (8.18 eV).

The reproducibility of IP for the betaine (8) was poor; the value also appears higher than expected for a pyridinium betaine, and [M-O]⁺ is a major fragment in its spectrum. The data are consistent with a large degree of transmethylation to the 3-methoxy derivative (5) before evaporation.

To verify that the gaseous molecules studied have not undergone structural rearrangements their characteristic primary fragmentations are

summarised in Table 2. The mass spectra of heteroaromatic *N*-oxides are characterised by the [M-O]⁺ and [M-OH]⁺ fragments; the latter is the more important if a hydrogen can readily be abstracted from an α -substituent.^{9,10} In the present series the molecular ion is the base peak except for the 2-isomers. The near absence of [M-OH]⁺ in the spectrum of 2, which has [M-O]⁺ as base peak, shows that hydrogen abstraction is unfavourable when the hydrogen is situated on an electronegative atom such as oxygen. The [M-OH]⁺ fragment is important, however, for the 2-methoxy derivative (4), presumably because of hydrogen abstraction from the *O*-methyl group. The isomeric 1-methoxypyrid-2-one (7) is characterised by the [M-CH₂O]⁺ fragment. An interesting feature for the 4-isomers is loss of the substituent on the oxygen atom (Scheme 1). The driving force may be preferable charge stabilisation on the nitrogen atom with formation of a quinonoid structure.



Scheme 1.

EXPERIMENTAL

The mass spectra were recorded on an AEI MS-902 mass spectrometer attached to an AEI DS30 data system. The electron energy was 70 eV and the ionising current 100 μ A. During recording of the ionisation efficiency curves the repeller was at cage potential and the ionising

current 20 μ A. Xenon was the reference compound. The IE-curves were interpreted by the semi-log plot method. The recorded IP values are the average of three determinations, the deviation being ± 0.05 eV except for compound 8 as discussed above. The compounds 1, 7 and 4, 5, 9 were introduced by the indirect insertion system at 100 and 150 °C, respectively, and the remaining compounds by the direct insertion probe. The source temperature was 220 °C.

The compounds used were prepared according to the literature;^{8,11,12} the reactive betaine (8) was isolated from its MeHSO₄-salt by freeze-drying of the eluate from an Amberlite IRA-400 (OH⁻) column.

REFERENCES

1. Undheim, K., El-Gendy, M. A. F. and Hurum, T. *Acta Chem. Scand. B* 28 (1974) 743. Part XXVI.
2. Katritzky, A. R. and Lagowski, J. M. *Chemistry of the Heterocyclic N-oxides*, Academic, New York 1971, p. 407.
3. Grønneberg, T. and Undheim, K. *Org. Mass Spectrom.* 6 (1972) 823.
4. Grønneberg, T. and Undheim, K. *Tetrahedron Lett.* (1972) 3193.
5. Jalonen, J. and Pihlaja, K. *Org. Mass Spectrom.* 7 (1973) 1203.
6. Hvistendahl, G. and Undheim, K. *Org. Mass Spectrom.* 6 (1972) 217.
7. Crable, G. F. and Kearns, G. L. *J. Phys. Chem.* 66 (1962) 436.
8. Gardner, J. N. and Katritzky, A. R. *J. Chem. Soc.* (1957) 4375.
9. Grigg, R. and Odell, B. G. *J. Chem. Soc. B* (1966) 218.
10. Bild, N. and Hesse, M. *Helv. Chim. Acta* 50 (1967) 1885.
11. Undheim, K., Nordal, V. and Borka, L. *Acta Chem. Scand.* 23 (1969) 2075.
12. Ochiai, E. *J. Org. Chem.* 18 (1953) 534.

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