Photoelectron Spectra of Hydroxy- and Mercapto-pyridines and Models of Fixed Structure [1]

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Photoelectron spectra of the title compounds demonstrate that 3- and 4-hydroxy- and 3- and 4-mercapto-pyridine exist in the vapour phase in the hydroxy- and mercapto-forms with less than 5% of the oxo- or thioxo-tautomers. However, although the hydroxy- and mercapto-tautomers are also predominant for the 2-series, significant quantities of 2-pyridone and pyridine-2-thione exist in equilibrium.

THE prototropic equilibria of hydroxypyridines with pyridones have been much studied. In the solid state and in solution in most solvents the pyridone form predominates in the 2- and 4-series, the equilibrium constant depending on the polarity of the solvent and the substituents.[2] For the gaseous state, the first experimental results by Russian authors appeared to favour considerable amounts of the OH form for 2-pyridone,[3] but this was later considered by the same workers[4] as possibly resulting from equilibrium not being established in the gas phase: a similar explanation could have accounted for the results of ionisation potential measurements (as acknowledged by the authors).[5] However, definitive evidence for the predominance of the OH structures for 2- and 4-pyridone in the gas phase *under equilibrium conditions* was provided by Beak *et al.*[6] with $K_{120-140}$ 2.5 ± 1.5 and $K_{250} > 10$ respectively. Independent support for the former value follows from recent gas-phase proton affinity measurements of the methylated model compounds,[7] and mass spectral data are consistent with both values.[8] †

For the 2- and 4-mercaptopyridine–pyridinethione equilibria in aqueous media, the predominance of the NH forms is even greater than for the corresponding hydroxypyridine–pyridone equilibria.[9] Again however the situation is different in the gas phase. Thus ionisation potential measurements,[5] supported by mass spectroscopy,[10] demonstrated the existence of the SH tautomers, and from u.v. spectroscopic data Beak *et al.* recently reported $K_T > 10$ for both isomers.[6b] ‡

In the present work we have studied the prototropic equilibria of hydroxy- and mercapto-pyridines by photoelectron spectroscopy. This technique, which permits the determination of the first ionisation potentials of the compounds in the vapour state, has been used recently for study of the tautomeric equilibrium of acetylacetone.[11] The method adopted involved initial analysis of the photoelectron spectra of methylated models in which the potential tautomerism had been blocked and verification that the first ionisation potentials of each form are sufficiently characteristic to be able to distinguish between them. We then compared the findings with the spectra of the actual tautomeric compounds in order to deduce which form predominated in the vapour state.

Photoelectron Spectra of Fixed Model Compounds.—Oxo-forms. The electronic structure of 1-methyl-4-pyridone can be compared with that of tropone, in which the π orbital localised on the C=C bond has been replaced by the lone pair on the nitrogen atom. The photoelectron spectrum of tropone[12] discloses four low energy bands (Table 1) which are associated with two π molecular orbitals of symmetry B_1 (8.90 and 11.54 eV), one *n* orbital of symmetry B_2 (lone pair of the oxygen atom at 9.27 eV), and one π orbital of symmetry A_2 (10.67 eV). The importance of the through-space interaction between the two semilocalised π orbitals on the double bonds αβ to the carbonyl group is evident. This determines the energy of the π molecular orbital of symmetry A_2 (antisymmetric combination of the two

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Notes added in press. † Personal communications with Professor P. Beak have disclosed and clarified misunderstandings between the Urbana and East Anglia groups, that existed 1968—76. These concerned the effects of phase and solvent on protomeric equilibria, effects which both groups consider to be important in individual equilibria, but which both groups recognised can be at least partially compensated by the comparison of series. This matter is discussed by Professor Beak in *Accounts Chem. Res.*, 1977, in press, and we thank him for making available to us a pre-publication copy of this manuscript.

Notes added in proof. ‡ A recent gas phase basicity study (C. B. Theissling, N. M. M. Nibbering, M. J. Cook, S. El-Abbady, and A. R. Katritzky, *Tetrahedron Letters*, 1977, 1777) of 2-mercaptopyridine and related models suggests $K_T = 25$ in favour of the mercapto-form. This form also predominates for the 4-series.

[1] Part 20 of ' Tautomeric Pyridines;' for Part 19, see ref. 7. Part 22 of ' Electronic Structure of Sulphur Compounds;' Part 21, M. F. Guimon, C. Guimon, F. Metras, and G. Pfister-Guillouzo, *J. Amer. Chem. Soc.*, 1976, **98**, 2078.

[2] J. Frank and A. R. Katritzky, *J.C.S. Perkin II*, 1976, 1428.

[3] É. S. Levin and G. N. Rodionova, *Doklady Akad. Nauk S.S.S.R.*, 1965, **164**, 584 (*Doklady Chem.*, 1965, **164**, 910).

[4] É. S. Levin and G. N. Rodionova, *Doklady Akad. Nauk S.S.S.R.*, 1969, **189**, 326 (*Doklady Chem.*, 1969, **189**, 900).

[5] T. Grønneberg and K. Undheim, *Org. Mass. Spectrometry*, 1972, **6**, 823.

[6] (*a*) P. Beak and F. S. Fry, jun., *J. Amer. Chem. Soc.*, 1973, **95**, 1700; (*b*) P. Beak, F. S. Fry, jun., J. Lee, and F. Steele, *J. Amer. Chem. Soc.*, 1976, **98**, 171.

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

[8] A. Maquestiau, Y. Van Haverbeke, C. De Meyer, A. R. Katritzky, M. J. Cook, and A. D. Page, *Canad. J. Chem.*, 1975, **53**, 490.

[9] See A. R. Katritzky and J. M. Lagowski, *Adv. Heterocyclic Chem.*, 1963, **1**, 396.

[10] A. Maquestiau, Y. Van Haverbeke, C. De Meyer, A. R. Katritzky, and J. Frank, *Bull. Soc. chim. belges*, 1975, **84**, 465.

[11] A. Schweig, H. Vermeer, and U. Weidner, *Chem. Phys. Letters*, 1974, **26**, 229.

[12] J. C. Bünzli, D. C. Frost, and L. Weiler, *J. Amer. Chem. Soc.*, 1974, **96**, 1952; C. Müller, A. Schweig, and H. Vermeer, *Angew. Chem. Internat. Edn.*, 1974, **13**, 273; M. Allan, E. Heilbronner, and E. Kloster-Jensen, *J. Electron Spectroscopy*, 1975, **6**, 181.

semilocalised orbitals); the second component (symmetric combination of the two orbitals) of symmetry B_1 interacts with the semilocalised orbitals of the same symmetry $\pi_{C=O}$ and $\pi_{C=C}$ (or π_N for the 1-methylpyridone).

The photoelectron spectrum for 1-methyl-4-pyridone (Table 1) is similar to that for tropone. However there is a destabilisation of the molecular orbital of A_2 symmetry for the pyridone (−10.10 eV) in comparison with that for tropone (−10.67 eV). This difference is well explained by greater through-space interaction between the $\pi_{C=C}$ orbitals in the pyridone due to their greater proximity. In addition, in line with the different energies of the π orbitals localised on methylamino (−9.7 eV[13] in methylamine) and on the C=C bond (−10.51 eV[14] in ethylene) the remaining orbital of symmetry B_1 is also somewhat destabilised (−8.20 eV *cf.* −8.90 eV).

TABLE 1

Vertical ionisation potentials and assignments for model systems

Compound	Ionisation potentials (eV) and orbital assignments [a]				
	First	Second	Third	Fourth	Fifth
Tropone [b]	8.90 πB_1 (1 530 cm^{-1})	9.27 nB_2 (830 cm^{-1})	10.67 πA_2	11.54 πB_1	
1-Methyl-4-pyridone	8.20 πB_1 (1 450 cm^{-1})	8.60 nB_2 (900 cm^{-1})	10.10 πA_2 (1 200 cm^{-1})	11.50 πB_1 (1 400 cm^{-1})	
1-Methyl-2-pyridone	8.41 π (1 100 cm^{-1}	9.54n (1 200 cm^{-1})	10.42 π (800 cm^{-1})	11.63 π (1 100 cm^{-1})	
1-Methylpyridine-4-thione	7.6 πB_1	7.6 nB_2	10.18 πA_2	10.30 πB_1	11.70 πB_1
1-Methylpyridine-2-thione	7.69 π	7.86 n (1 000 cm^{-1})	10.50 π	10.66 π	12.11 π
Pyridine [c]	9.7 nA_1	9.8 πA_2	10.5 πB_1	12.6 πB_1	
4-Ethoxypyridine	9.25 πB_1	9.4 πA_2	9.6 nA_1	11.63 πB_1 or n_O	
3-Hydroxypyridine	9.15 π (800 cm^{-1})	9.71 n_N	10.37 π	12.56 π or n_O	
2-Methoxypyridine	8.82 π (800 cm^{-1})	9.82 n_N	10.20 π	11.45 π or n_O	
4-Methylthiopyridine	8.73 πB_1	9.76 $n_N A_1$	9.76 πA_2	11.08 πB_1	11.7 n_S
3-Mercaptopyridine [d]	8.89 π	9.78 n_N	10.25 π	11.32 π	
2-Methylthiopyridine	8.24 π	9.56 n_N	10.25 π	10.62 π	11.47 n_S

[a] Figures in parentheses are the principal vibrational frequencies of the corresponding ions. [b] Ref. 12. [c] Ref. 15. [d] The values for 3-methylthiopyridine are respectively 8.41, 9.60, 9.99, and 10.80 (same assignments as for 3-mercaptopyridine). We have not given its spectrum because it shows two parasitic bands associated with impurities.

For 1-methyl-2-pyridone the interactions between the semilocalised $\pi_{C=C}$, $\pi_{C=O}$, and π_N orbitals are qualitatively similar to those of 1-methyl-4-pyridone and, although the symmetries of the two compounds are different (C_s and C_{2v}), the first four bands in the spectrum (Figure 1) are assigned to n and π orbitals (Table 1) by analogy with the previous assignment. For the three peaks corresponding to the ionisation of the π electrons, the vibrational spacing observed is less than that found for 4-pyridone (1 100, 800, and 1 100 cm^{-1}, *cf.* 1 450, 1 200, and 1 400 cm^{-1}). This possibly corresponds to more delocalisation of the π electrons in 2-pyridone because of loss of symmetry.

The vibrational spacing for the band at 9.54 eV, which is associated with the ionisation of electrons from the lone electron pair n of oxygen, occurs at 1 200 cm^{-1}. This higher frequency relative to the 4-isomer appears to be linked with a diminution of the coupling of this orbital with the π system, a view confirmed by the strong stabilisation of the n orbital in comparison with that of 4-pyridone. The stabilisation does not appear to originate solely in the inductive effect of the neighbouring nitrogen atom.

Methoxy-compounds. Heilbronner and his coworkers'[15] interpretation of the first ionisation potentials of pyridine is given in Table 1. The effect of an alkoxy-group should depend on its position of substitution: thus substitution in the 4-position should cause destabilisation of the molecular orbitals of symmetry B_1, whereas substitution in the 2- or 3-position should influence more the molecular orbital of symmetry A_2. In contrast, the orbital of symmetry A_1 localised mainly on the lone pair of the nitrogen atom should be sensitive

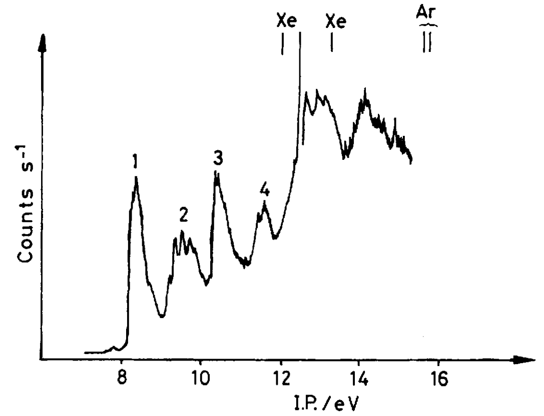

FIGURE 1 Photoelectron spectrum of 1-methyl-2-pyridone

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[13] A. B. Cornford, D. C. Frost, F. G. Herring, and C. A. McDowell, *Canad. J. Chem.*, 1971, **49**, 1135.

[14] D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, ' Molecular Photoelectron Spectroscopy,' Wiley, London, 1970.

[15] E. Heilbronner, J. P. Maier, and E. Haselbach, in ' Physical Methods in Heterocyclic Chemistry,' ed. A. R. Katritzky, Vol. VI, Academic Press, New York, 1974, p. 22; R. Gleiter, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, 1972, **55**, 255.

only to the relatively weak inductive effects of the alkoxy-group.

The assignments for 4-ethoxypyridine, 2-methoxypyridine (Figure 2), and 3-hydroxypyridine given in Table 1 are based on, and in good agreement with, these expectations (3-hydroxypyridine must exist only in the hydroxy-form in the vapour phase because of the high polarity of the alternative betaine tautomer).

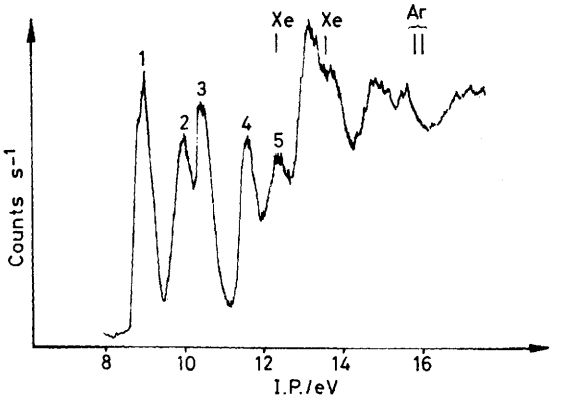

FIGURE 2 Photoelectron spectrum of 2-methoxypyridine

Thioxo-forms. The π and n orbital energies of the carbonyl and thiocarbonyl groups are rather different: thus in thiofenchone n_S is -8.1 eV and $\pi_{C=S}$ -9.6 eV,[16] whereas in acetone n_O is -9.73 eV and $\pi_{C=O}$ -12.65 eV.[17] It follows that thiocarbonyl derivatives show in the region of low potential (7—8.5 eV) two bands associated with the ionisation of a π electron and an n electron of the thiocarbonyl group.[16–18] The relative order of these two ionisation potentials depends on the extent of conjugation in the molecule. Thus for the majority of cyclic unsaturated thiocarbonyl compounds the π ionisation is generally at lower energy or at least equal to that for the lone pair on the sulphur atom.[17,18] This is the case for 1-methylpyridine-4-thione, where the spectrum shows a first intense band (7.6 eV) resulting from the superposition of these two bands. However for 1-methylpyridine-2-thione (Figure 3) the proximity of the nitrogen and sulphur atoms stabilises the non-bonding n_S orbital (*cf.* 1-methyl-2-pyridone, above), and thus raises the accidental degeneracy of these two orbitals, which are now associated with peaks at 7.69 and 7.86 eV (Table 1).

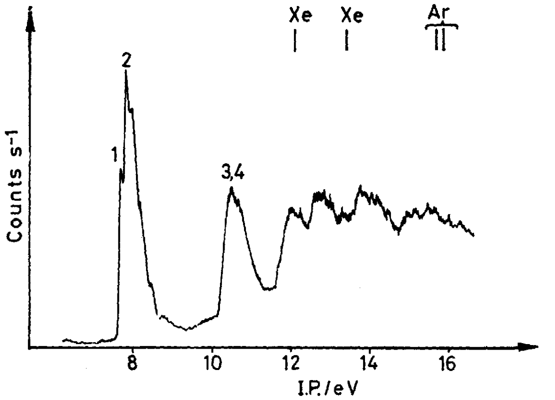

FIGURE 3 Photoelectron spectrum of 1-methylpyridine-2-thione

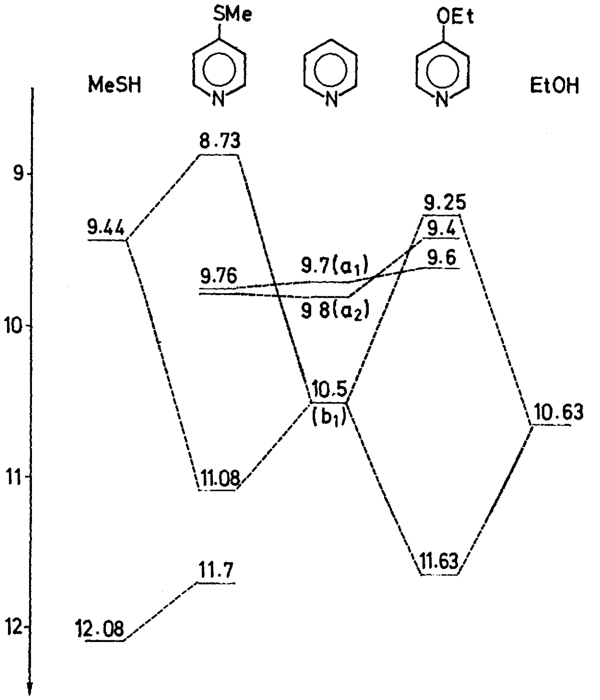

FIGURE 4 Correlations between the highest occupied molecular orbitals of methanethiol,[19] 4-methylthiopyridine, pyridine,[15] 4-ethoxypyridine, and ethanol [20]

For both these compounds the two high ionisation potentials have rather similar values and are to be attributed to the π electrons of the ring.

Alkylthiopyridines. The photoelectron spectra of alkylthiopyridines are different from those of the alkoxypyridines because of the difference in energy between the lone electron pair on sulphur and that on oxygen, *cf.* the ionisation energy for methanethiol (-9.44 eV) relative to methanol (-10.95 eV)[19] and ethanol (-10.63 eV).[20] Bock and his co-workers[21] compared the photoelectron spectra of benzene, anisole, and thioanisole, and we have done the same for pyridine, 4-ethoxypyridine, and 4-methylthiopyridine, as shown

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[16] C. Guimon, D. Gonbeau, G. Pfister-Guillouzo, L. Asbrink, and J. Sandström, *J. Electron Spectroscopy*, 1974, **4**, 49.

[17] C. Guimon, Doctorat ès-Sciences Thesis, Pau, 1976.

[18] (*a*) C. Guimon, G. Pfister-Guillouzo, M. Arbelot, and M. Chanon, *Tetrahedron*, 1974, **30**, 3831; (*b*) C. Guimon, M. Arbelot, and G. Pfister-Guillouzo, *Spectrochim. Acta*, 1975, **31A**, 985; (*c*) D. Gonbeau, C. Guimon, J. Deschamps, and G. Pfister-Guillouzo, *J. Electron Spectroscopy*, 1975, **6**, 99; (*d*) C. Guimon and G. Pfister-Guillouzo, *ibid.*, **7**, p. 191; (*e*) C. Guimon, G. Pfister-Guillouzo, and M. Arbelot, *Tetrahedron*, 1975, **31**, 2769; (*f*) C. Guimon, G. Pfister-Guillouzo, and M. Arbelot, *J. Mol. Structure*, 1976, **30**, 339.

[19] H. Ogata, H. Onizuka, Y. Nihei, and H. Kamada, *Bull. Chem. Soc. Japan*, 1973, **46**, 3036.

[20] M. I. Al-Joboury and D. W. Turner, *J. Chem. Soc.*, **1964**, 4434.

[21] H. Bock, G. Wagner, and J. Kroner, *Tetrahedron Letters*, 1971, 3713.

schematically in Figure 4. The bands in the spectrum of 4-methylthiopyridine are thus to be associated with a π orbital mainly localised on the sulphur atom (—8.73 eV), with an *n* orbital of the σ lone pair of the nitrogen atom of almost the same energy as the antisymmetric π orbital (—9.76 eV), with a π orbital localised mainly on the nitrogen (—11.08 eV), and finally with an *n* orbital localised on the σ lone pair of the sulphur atom (—11.7 eV).

In contrast, as for the corresponding oxygen compound, the π orbital localised on the *S*-methyl or SH of 2-methylthiopyridine and 3-mercaptopyridine (Figure 5, Table 1) interacts mainly with a π orbital of symmetry A_2 of pyridine (maximum overlap) at —9.8 eV, giving two molecular orbitals, one at —8.24 eV (—8.73 eV) (localised mainly on the sulphur) the other at —10.25 eV (—10.25 eV) (localised on the ring). The $n(A_1)$ and $\pi(B_1)$ orbitals of pyridine are less displaced (Table 1).

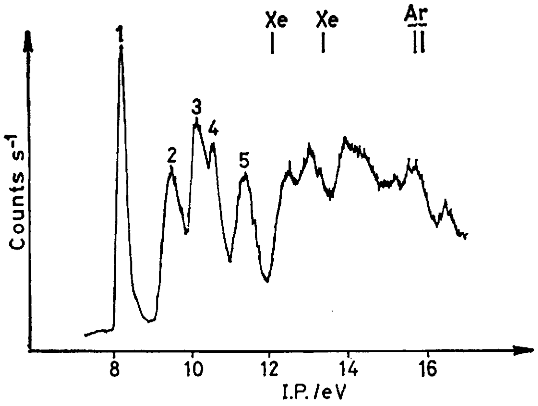

FIGURE 5 Photoelectron spectrum of 2-methylthiopyridine

Photoelectron Spectra of the Tautomeric Compounds.— 4-*Substituted derivatives.* Comparison of the spectra of 4-hydroxy- and 4-mercapto-pyridine with those of the fixed derivatives demonstrates conclusively the great predominance in the vapour state of the hydroxy- or mercapto-form. As expected, the ionisation potentials (Table 2) for the symmetrical π orbitals (B_1) show a much greater sensitivity towards methylation than those for the antisymmetrical π orbitals (A_2) or the non-bonding orbitals associated with the σ lone pair on the nitrogen atom (A_1). Detailed consideration of the spectra indicates that the proportion of 4-oxo- and 4-thioxo-forms is less than 5% (assuming that the photoionisation cross-sections of the alkylated compounds and the corresponding prototropic forms are comparable)..

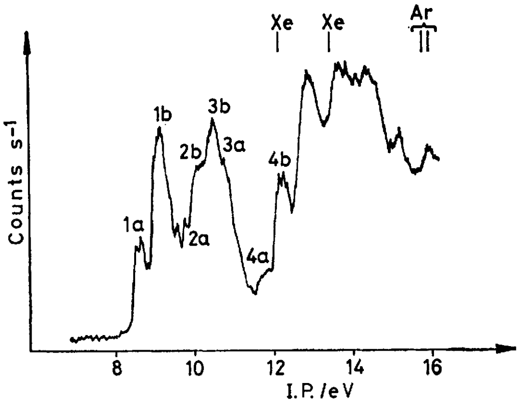

FIGURE 6 Photoelectron spectrum of the tautomeric mixture at equilibrium of (a) 2-pyridone and (b) 2-hydroxypyridine

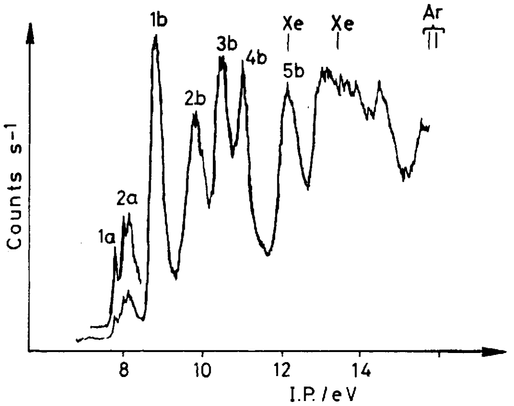

FIGURE 7 Photoelectron spectrum of the mixture at equilibrium of (a) pyridine-2-thione and (b) 2-mercaptopyridine

TABLE 2

Vertical ionisation potentials and assignments for tautomeric compounds

Compound	Ionisation potentials (eV) and orbital assignments *				
	First	Second	Third	Fourth	Fifth
4-Hydroxypyridine	9.8 B_1	9.8 A_1	9.8 A_2	12.4 B_1	
4-Mercaptopyridine	9.25 B_1	9.8 A_1	9.95 A_2	11.55 B_1	
2-Hydroxypyridine	9.11 π	10.08 n_N	10.48 π	12.22 π or n_O (800 cm^{-1})	
2-Pyridone	8.62 π (1 000 cm^{-1})	9.77 n_O	10.78 π	11.72 π	
2-Mercaptopyridine	8.79 π	9.86 n_N	10.47 π	11.02 π	12.15 n_S
Pyridine-2-thione	7.80 π	8.01 *n* (1 200 cm^{-1})			

* Figures in parentheses are the principal vibrational frequencies of the corresponding ions.

2-*Substituted derivatives.* In contrast to the preceding compounds, the photoelectron spectra of 2-hydroxy- and 2-mercapto-pyridine (Figures 6 and 7) show the existence of a prototropic equilibrium in the vapour state between the oxo- and hydroxy- and the mercapto- and thioxo-forms. By comparison with the ionisation potentials of the corresponding fixed derivatives (Tables 1 and 2) and taking account of the expected influence of methylation we have assigned the bands to the two species, as shown in Table 2.

In both cases the hydroxy- or mercapto-form is clearly preponderant because these correspond to the most intense peaks. According to the observed relative intensities it appears that under the same conditions of temperature and pressure the percentage of oxo-form is rather larger than that of the thioxo-form. If the assumption again is made that the photoionisation cross-sections of the fixed models and their corresponding prototropic tautomers are comparable, then integration of band areas indicates *ca.* 25% of oxo-form in the hydroxy–oxo equilibrium and *ca.* 10% of the thioxo-form in the mercapto–thioxo equilibrium.

Conclusion.—Although it is evident that substantial amounts of the oxo- and thioxo-forms in the 2-series do coexist in the vapour phase, the quantitative significance of the integration results is not clear. However the quantities quoted for both the 2- and 4-series are in good accord with the results of the gas-phase equilibration studies of Beak's group.[6] The apparent absence of 2-pyridone in the mass spectrometer[8] might imply that the sample vaporises as the hydroxy-form and does not equilibrate under the experimental conditions.

EXPERIMENTAL

Photoelectron spectra were recorded on a Perkin-Elmer PS 18 spectrometer with He^I source (584 Å or 21.21 eV). They were calibrated by using the $^2P_{1/2}$ and $^2P_{3/2}$ doublets of argon (15.755 and 15.93 eV) and of xenon (12.13 and 13.43 eV). The ionisation potentials recorded are accurate to within 30 meV with the exception of superimposed peaks. The pressure in the ionisation chamber was *ca.* 3×10^{-2} mmHg. At this pressure, the pressure of the vapour of liquids at room temperature is sufficient. Solid specimens were heated to between 40 and 150 °C. Spectra of the tautomeric compounds were recorded at 75 °C for 2-hydroxypyridine, 2-mercaptopyridine, and 4-mercaptopyridine and at 90 °C for 4-hydroxypyridine (at 3×10^{-2} mmHg).

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