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THE IONISATION POTENTIAL OF SOME SUBSTITUTED PYRIDINES*

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Abstract—The ionisation potentials of pyridines substituted with electron-donating and electron-withdrawing substituents in positions 2, 3 and 4 have been determined.

IN CONNECTION with an investigation of the influence of polar substituents on the mass spectrometric fragmentation of benzoyl pyridines and related compounds,[2] we were interested in the effects of these substituents on the ionisation potential (IP) of pyridine. The substituent effects on the IP of benzene have been investigated both by experimental and theoretical methods, but the IP's of substituted pyridines have been determined in only a few cases. Basila and Clancy[3] reported upon the IP's of some 2- and 4-substituted pyridines, and Grønneberg and Undheim[4] measured the IP's of pyridine derivatives with OR and SR substituents ($R = H, CH_3$), respectively, in the three different positions at the aromatic nucleus. From these results, one can conclude that the effect of the substituents on the IP's of pyridine and benzene is similar, as expected, but that the IP of a substituted pyridine depends not only on the nature of the substituent, but also on its position. The intensities of certain fragment ions in the mass spectra of the positional isomers of some substituted pyridines[5] are different, and therefore the dependence of the IP's of these compounds on the nature *and* position of the substituent may be of importance for the direction of the fragmentation of the molecular ions.

The values of an IP, determined by electron-impact and by the method of a semilog plot,[6] sometimes depend on instrumental parameters. To obtain a set of IP's of substituted pyridines, which have been measured under identical experimental conditions, we determined the IP's of a series of pyridines, including substituents with strongly electron-withdrawing properties, that have not been investigated before. The results are given in Table 1, together with the relevant data from the literature. The compounds investigated are either commercially available or have been prepared by standard literature methods. The ionisation efficiency curves were obtained by a Varian MAT CH-7 mass spectrometer (electron trap current 30 μA; ion source temperature 200 °C). The nitropyridines and hydroxypyridines were admitted to the ion source by a direct insertion system, and the remaining compounds and benzene or toluene, which were used as reference substances, respectively, by a heated inlet system (150 °C). The IP's were determined graphically from a semilog plot of the ionisation efficiency curves; in each case these curves were parallel for the sample and the reference compound in the region from a value of some % to 1‰ of the ion

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TABLE 1. IONISATION POTENTIAL (IN eV) OF SUBSTITUTED PYRIDINES X – C_5H_4N

	IP(*o*-X)			IP(*m*-X)			IP(*p*-X)			$IP(XC_6H_5)$	
X	This work	Lit.	Ref.	This work	Lit.	Ref.	This work	Lit.	Ref.	Lit.	Ref.
H	9·85	9·85	9	—	—	—	—	—	—	9·5	9
Cl	9·9	9·91	3	9·75	—	—	10·0	10·15	3	9·6	9
Br	9·7	9·65	3	9·75	—	—	9·95	9·54	3	9·5	9
CH_3	9·4	9·56	3	9·4	—	—	9·5	9·67	3	9·2	9
OH	9·0	9·28	4	9·5	9·55	4	9·6	9·70 9·89	3 4	9·16	9
OCH_3	8·9	8·96	4	—	9·34	4	—	9·58	4	8·95	9
NH_2	8·5	—	—	8·7	—	—	8·8	8·97	3	8·32	9
$N(CH_3)_2$	7·8	—	—	—	—	—	8·3	—	—	—	—
COOR	—	—	—	9·85[a]	—	—	9·75[b]	—	—	—	—
CN	10·5	—	—	10·4	—	—	10·4	—	—	9·95	9
NO_2	10·1	—	—	10·3	—	—	10·2	—	—	10·18	9

[a] R = CH_3.
[b] R = C_2H_5.

current at 30 eV. The results are the average of two or three determinations, run on different days, the maximum deviation being ±0·1 eV.

Our values for the IP's of substituted pyridines refer to an IP (benzene) of 9·5 eV, which has previously been determined on the same instrument, and which has also been found by others[7,8] to correspond to the vertical IP of benzene and to an IP (toluene) of 9·2 eV. As can be seen from Table 1, the agreement between our values and those of Basila and Clancy[3] is good. There is a slight tendency in our values to be lower than those previously reported, and especially those of Grønneberg and Undheim.[4] This may be due to the different reference gases used. However, as the structure of the molecules of 2- and 4-hydroxypyridine in the gas phase is not definitely known because of the tautomeric equilibrium between hydroxy and lactam forms, the lower values of the IP's of these compounds in our experiments may also be due to a larger concentration of the lactams. The IP's of these lactams have been estimated to 8·2 eV and 8·1 eV, respectively.[4]

As has been noted before, the influence of a substituent on the IP of pyridine is clearly related to its electron-donating or electron-withdrawing property. The IP's of the nitropyridines and those of the cyanopyridines are approximately 0·4 eV and 0·6 eV, respectively above the IP of pyridine. The IP's of the aminopyridines are about 1·1 eV lower than that of the parent compound, and a further decrease in the IP is observed for the dimethylamino derivatives, as expected. However, the correlation between the variation of the IP's and the substituent constant σ^+ is not very good, for the 2-, 3- or the 4-substituted derivatives. A somewhat better correlation is observed for the IP's of the substituted pyridines and the corresponding benzene derivatives,[7] especially in the cases of *m*- and *p*-substituted pyridines.

$$IP(o\text{-}XC_5H_4N) = 1{\cdot}09\ IP(XC_6H_5) - 0{\cdot}68 \quad \text{s.e. } 0{\cdot}24$$

$$IP(m\text{-}XC_5H_4N) = 0{\cdot}93\ IP(XC_6H_5) + 0{\cdot}96 \quad \text{s.e. } 0{\cdot}12$$

$$IP(p\text{-}XC_5H_4N) = 0{\cdot}85\ IP(XC_6H_5) + 1{\cdot}79 \quad \text{s.e. } 0{\cdot}13$$

The IP of a substituted pyridine is also influenced by the position of the substituent relative to the nitrogen atom. In the series of pyridines substituted by electron-donating groups, the IP's rise in going from the *ortho* to the *para* isomers. As has been discussed before,[3,4] this effect can be explained by the electrostatic polarisation model. This model also explains why this effect is absent or probably reversed in the case of nitro- or cyanopyridines. However, the positional effect of a substituent on the IP of pyridine is rather small, and as long as one assumes that a variation in the charge distribution of the molecular ions of substituted pyridines is reflected in a change of the corresponding IP, this effect does not explain the much larger positional effects on certain fragmentation pathways of the molecular ions.

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