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Mass Spectrometry of Onium Compounds. XIX.[1] Ionisation Potentials of Some Pyridines and Pyridinium Betaines. Structure Analysis

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Ionisation potentials for series of *N*-vinylpyrid-2-thiones, 2-vinylthiopyridines and pyridinium betaine analogues have been determined. The values have, together with characteristic fragmentation modes, been used in structure analysis of the volatile components from pyridinium betaines.

Dihydrothiazolo[3,2-*a*]pyridinium derivatives have been studied in the mass spectrometer and structures assigned to the volatile species on the basis of their fragmentation modes.[2,3] Recently it has been found that ionisation potentials (IP) are useful in structure elucidation in the gas phase.[4-6] A very recent article reviews general application of ionisation and appearance potentials (AP) in structure analysis.[7]

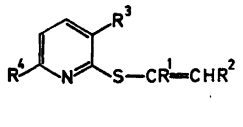
In this work we have determined IP data for certain pyridines as references for our studies [2,3] of the gaseous products formed on evaporation of pyridinium betaines (Table 1).

The first ionisation potential of pyridine corresponds to the removal of an electron from the most energetic occupied aromatic orbital and not from the nitrogen lone pair.[8] Substituent effects on the π-electrons of the nitrogen heterocyclic ring parallel those on the π-electrons of a normal carbo-aromatic ring with decrease in IP for electron releasing substituents and *vice versa*.[9] IP for pyridine is reported as 9.85 eV [9] and for 3-hydroxypyridine as 9.55 eV.[5] The 2-vinylthiogroup in (*1a*) has a large lowering effect on IP (7.95 eV). IP is further decreased (7.52 eV) with a β-carboxy group (*1c*). The allylthio group in (*3*) exerts a similar effect. Table 1 also shows that a 3-hydroxy group in the pyridine reduces the IP with 0.2 – 0.3 eV and a methyl group acts in the same way (0.1 – 0.2 eV). Extension of the conjugative system with a β-phenyl group (*1g*) decreases IP further (7.35 eV). A phenyl group on the α-carbon (*1e*) has less effect (7.8 eV). The latter is formed from the β-carbon acid (*1e*, $R^2 = CO_2H$) which is decarboxylated before evaporation in the instrument. Decarboxylation is also the dominating pyrolytic reaction for the other β-acid analogues which give rise to isomers (*1d*) and (*1f*). The primary site of ionisation is presumably in the pyridine ring since a comparison between (*1h*) and (*1i*) shows that the *para*-nitro group has little effect on the IP.

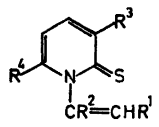
In the *N*-vinyl series (*2*) similar substituent variations in IP are seen (Table 1). The *N*-ethyl-(*4*) and the *N*-vinyl-(*2c*) groups affect to a similar extent the ease of ionisation. Simple *N*-alkylated 2-thiones of pyridine have lower IP's than their isomeric thioethers.[5,10] A comparison of IP's for the vinylthio pyridine (*1a*) and its *N*-vinyl analogue (*2b*) shows that the thioether also in this case has the higher (about 0.4 eV) IP.

Based on the above information IP data for the betaines (Table 2) can be used in structure analysis. Thus the IP's for the *N*-vinyl derivatives (*2b*) and (*2c*) (Table 1) are about 0.3 eV higher than the values for the isomeric betaines (*5a*) and (*5b*) (Table 2). The low IP's for the betaines (*5a* – *5d*) are therefore explained by these molecules being evaporated without structural rearrangement to non-charged molecules. The same conclusion was reached from studies

Table 1. Ionisation potentials of pyridines.



1



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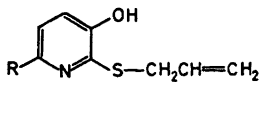

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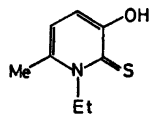


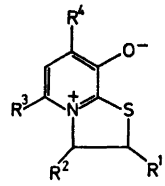
4

Comp.	R^1	R^2	R^3	R^4	IP ± 0.05 eV
1a	H	H	OH	H	7.95
1b	H	CO_2H	H	H	7.80
1c	H	CO_2H	OH	H	7.52
1d	Ph	H	H	H	(8.0)[a]
1e	Ph	H	OH	H	(7.8)[a]
1f	Ph	H	OH	Me	(7.5)[a]
1g	H	Ph	OH	H	7.35
1h	H	Ph	OH	Me	7.25
1i	H	*p*-NO_2-Ph	OH	He	7.28
2a	H	H	H	H	7.75
2b	H	H	OH	H	7.57
2c	H	H	OH	Me	7.35
2d	Me	H	H	H	7.49
2e	Me	H	OH	H	7.31
2f	Me	H	OH	Me	7.07
2g	H	Ph	OH	H	7.60
2h	H	Ph	OH	Me	7.38
3a	R = H				7.72
3b	R = Me				7.50
4					7.37

[a] Formed by pyrolysis in the instrument from the respective β-carboxylic acids ($R^2 = CO_2H$).

of the fragmentation patterns.[2] The substituent effect of the 7-bromine in (*5c*) is as expected of little importance since pyridine and 4-bromopyridine have almost the same IP's.[9] The weak effect of the 7-*p*-nitrophenyl group in (*5d*) indicates primary ionisation in the hetero-aromatic ring. Similarly the 3-phenyl derivatives (*5h*) (7.02 eV) and (*5i*) (6.73 eV) have IP's 0.6 eV below those of the respective isomeric *N*-vinyl analogues (*2g*) and (*2h*). Direct evaporation without structural change is therefore again implied. The conclusion is further supported by differences in the fragmentation patterns of the

Table 2. Ionisation potential of pyridinium betaines.



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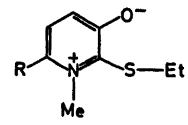
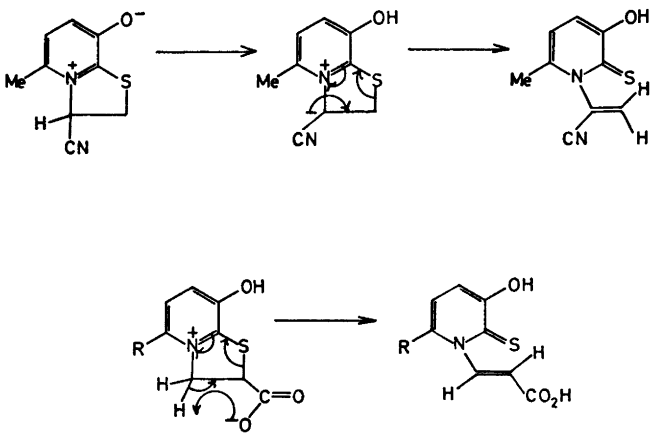


6

Comp.	R^1	R^2	R^3	R^4	IP ± 0.05 eV
5a	H	H	H	H	7.32
5b	H	H	Me	H	7.02
5c	H	H	Me	Br	7.05
5d	H	H	Me	*p*-NO_2-Ph	7.15
5e	H	$CONH_2$	Me	H	(7.4)[a]
5f	H	CN	Me	H	(7.51)[b]
5g	Ph	H	Me	H	7.04
5h	H	Ph	H	H	7.02
5i	H	Ph	Me	H	6.73
5j	CO_2H	H	H	H	(7.64)[b]
5k	CO_2H	H	Me	H	(7.43)[b]
6a	R = H				7.16
6b	R = Me				6.92

[a] Mixture of the *N*-vinyl isomer and the betaine in the gas phase. [b] The IP values refer to the *N*-vinyl isomers in the gas phase.

vinyl derivatives and the betaines. The *N*-vinylpyrid-2-thiones and their vinylthio analogues have very similar spectra. The principal primary fragmentation is rationalised by expulsion of a substituent on the β-carbon of the side-chain to a common thiazolo[3,2-*a*]pyridinium ion with low tendency for further fragmentation.[3] Accordingly the simple vinylthio derivative (*1a*) expels a hydrogen radical and the vinylthio acids (*1b*) and (*1c*) expel a formyloxy radical; the same ions are formed by hydrogen radical expulsion from the *N*-vinyl derivatives (*2a*) and (*2b*). The *N*-vinyl derivatives with terminal methyl group (*2d* – *2f*) have [M – 15] as base peak, the relative intensities for the molecular ion and the [M – 1] peaks being of the order 30 and 10 %, respectively. Similarly the fragmentation of the α-phenyl derivatives (*1d* – *1f*) and (*2g*, *2h*) are characterised by [M – 1] being the base peak. For the vinylthio-β-phenyl derivatives (*1g* – *1i*) other fragmentations are also important. Typical percentages for relative intensities being [M] 10, [M – H] 10, [M – Ph] 50



and [M − PhC≡CH] 50 with the base peak of *m/e* 39. The 3-phenyl betaine isomers (5h, 5i) have the base peak at [M − PhC≡CH]. Other characteristic peak intensities are due to [M] 60 − 90, [M − H] 40, [M − SH] 10, [M − Ph] 35 − 50 %. This mode of fragmentation is significantly different from that of vinyl analogues. The same conclusion is reached for the 2-phenyl derivative (*5g*) which is characterised by [M − PhC≡CH] being the base peak.

IP for the 3-nitrile (*5f*) is found to be 0.5 eV higher than for the parent compound (*5b*). The relatively large difference cannot be ascribed to the nitrile substituent alone. In fact the observed IP is comparable to the values for the *N*-vinyl analogue (*2c*) (7.35 eV) and the vinylthio acid (*1c*) (7.52 eV). It is therefore concluded that the betaine has suffered ring-opening before evaporation. This conclusion is supported by its spectrum which is characterised by the [M − H] species. Ring-opening to its *N*-vinyl isomer is explained by strong activation of the methine carbon by the quaternary nitrogen atom and the cyano group. The phenolate ion in a neighbour molecule is the base.

3-Carboxy derivatives of the betaine (*5*) are decarboxylated before evaporation in the mass spectrometer. The 2-carboxy derivatives, however, give a molecular ion corresponding to the mass number for the betaine.[2] The fragmentation patterns suggest *N*-vinyl formation.[2] The same conclusion is arrived at from the IP data (Table 2) for (*5j*; 7.64 eV) and (*5k* 7.43 eV). The values are about 0.4 eV higher than for the betaines (*5a*, *5b*) and comparable to those of the parent *N*-vinyl compounds (*2b*, *2c*) in Table 1. *N*-Vinyl rather than *S*-vinyl formation is also supported by the fragmentation patterns which is characterised by formyloxy radical expulsion.

The proton on the methine carbon in the 3-carboxamide (*5e*) is less acidic than in the nitrile (*5f*). The compound is sensitive to recording conditions which indicates a mixture of the amide and its ring-opened analogue in the gas phase.[2] The intermediate IP value (7.4 eV) is in accordance with this conclusion.

The IP's for the monocyclic pyridinium betaines (*6*) are of the same order as found for the bicyclic analogues (*5a*, *5b*). It is therefore concluded that these are also evaporated directly without any structural rearrangement.

EXPERIMENTAL

The mass spectra were recorded on an AEI MS-902 mass spectrometer attached to an AEI DS-30 data system. The compounds were introduced by direct insertion with source temperature 200 − 225 °C. Low resolution spectra were recorded at 70 eV electron energy and 100 μA trap current. During recording of the ionisation efficiency curves, the repeller was a cage potential and the ionising current was 20 μA. Xenon (12.127 eV) and iodobenzene (8.91 eV) were the reference compounds. The IE-curves were interpreted by the semilog plot method.[11] The recorded values, with the exception for (*1d* − *1f*) and (*5e*), are the average of three determinations, the deviation being ± 0.05 eV.

The IP values for (*2c*) and (*4*) (7.35 eV) differ from that originally published (7.75 eV).[5] This is due to a systemic error of some 0.3 − 0.4 eV for the low IP substances in the originally published report. The relative differences in IP's

in the series of compounds investigated, however, is the same and confirms previous conclusions.

The compounds used in these investigations were available from other work: (*1b*, *1c*),[3] (*2a*),[3] (*5a*–*5g*),[2] (*5j*, *5k*),[2] (*6*),[2] (*1a*),[12] (*1d*–*1f*),[12] (*2b*–*2h*),[12] (*3*),[12] and (*5h*, *5i*).[12]

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