

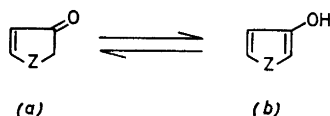
Ionisation Potentials in Tautomeric Analysis of 3-Hydroxy Derivatives of Thiophenes, Selenophenes, and Furans

OLAV THORSTAD,^a KJELL UNDHEIM,^a ROLF LANTZ^b and ANNA-BRITTA HÖRNFELDT^b

^a Department of Chemistry, University of Oslo, Oslo 3, Norway and ^b Chemical Center, University of Lund, Lund, Sweden

Ionisation potentials for tautomeric 3-hydroxy-2,5-dialkyl-thiophenes, -selenophenes and furans have been analysed by comparison with IP data of compounds derived from either tautomeric form. Both the ketone and enol forms are important; the ratios vary from almost pure ketone to considerable amounts of the enol. The isomer ratios depend on the substituents, the nature of the heteroatom and on the relative evaporation rates from rapidly equilibrating samples.

In the preceding paper ionisation potentials (IP) have been applied to the analysis of the tautomeric composition in the gas phase in the mass spectrometer of some 2-hydroxy-thiophenes, -selenophenes and -furans.¹ The gas phase molecules are composed of the two tautomeric lactones with the α,β -lactone as the major species. The ratios, however, depend on the substitution pattern and are similar to what has been found in non-gaseous states. This result stands in contrast to the oxygenated pyridines where the hydroxy structure was the dominating form.² In this report the results from the studies of some tautomeric 3-hydroxy-thiophenes, -selenophenes and -furans are reported.



Scheme 1.

Two tautomeric forms are possible for the 3-isomers (Scheme 1); the ketone (a) and the enol or the hydroxy form (b). Studies in non-gaseous

states¹ have shown that both tautomers are important, but with the ketone (a) as the major isomer.

Most of the compounds available for studies belong to the thiophene series (Table 1) and are therefore first discussed. The data for the selenophenes and the furans are collected in Table 2.

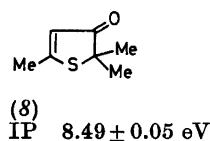
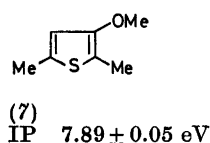
3-Hydroxythiophene and presumably its selenophene and furan analogues are chemically unstable; derivatives stabilised by alkyl groups in both α -positions were therefore employed in these studies. The model compounds necessary for comparative interpretation of the IP data for the tautomeric compounds 1 to 6 were in the usual way available by alkylation of either tautomeric form; the ether 7 and the ketone 8 in Table 1 serve such a purpose.

All compounds gave rise to strong molecular ion signals in the spectra; the molecular ion was often the base peak. The strong molecular ion signal facilitated the determination of IP's.

The influence of a substituent on the ease of ionisation depends on the electron releasing properties, the relative position and on the nature of other substituents as discussed in the preceding paper.¹ Methylation of a phenolic oxygen will reduce the IP of the phenol with ca. 0.2–0.3 eV. Adding this value to the recorded IP value for the ether 7 gives ca. 8.1 eV as the estimated IP for the hydroxy tautomer (b) of the 2,5-dimethyl derivative 1. The substituent effect of the third methyl group in the ketone 3 is assumed to be of the order 0.1–0.15 eV.¹ The estimated IP for the keto form (a) of 1 is thus 8.6–8.7 eV; the experimental value is

Table 1. Ionisation potentials of thiophenes.

	R ¹	R ²	IP ± 0.05 eV
(1)	Me	Me	8.55
(2)	Me	Et	8.34
(3)	Me	i-Pr	8.21
(4)	Me	t-Bu	8.10
(5)	Et	Me	8.22
(6)	t-Bu	Me	8.09



8.55 eV. This value lies between those estimated for the pure tautomers and arise as a mathematical result from the semi-empirical evaluation technique of the ionisation efficiency curves for components with the same mass number.^{4,5} The measured quantities are called IP's rather than appearance potentials (AP) because we are measuring the ease of generating molecular ions. As pointed out in the preceding paper the mathematical IP value for a binary mixture of isomeric compounds does not change in a linear manner with the relative amounts of the components; the decrease from the higher component IP value is more rapid and *vice versa*.⁶

On the basis of the above discussion the tabulated data for the tautomeric molecules 1 to 6 clearly show that the keto tautomer (a) is the major gaseous component in all cases. Solution studies have shown that equilibrations between the two forms are rapid and neither form was isolated in a pure tautomeric state. For the 2,5-dimethyl compound 1 the ketone-enol isomer ratio varies from about 2 in the neat liquid to almost 10 in chloroform.³ In the 5-

homologue series 1 to 4 the preference for the keto form is slightly reduced with increase in the size of the substituent. The change has been explained by decreasing hyperconjugative stabilization of the double bond in the ketone.³

The IP for 1 indicates that only about 10 % of the gaseous species have the hydroxy form (b) implying tautomerisation of the liquid sample. The indirect insertion system of the instrument was used, and the samples were evaporated at 30–35 °C into the reservoir which was kept at 130 °C. Intramolecular prototropic shifts in the gas phase are assumed to be slow.⁷ Isomerisation of the gaseous molecules on contact with the heated walls is probably not significant as the experimental time is of the order 10 min.¹ This locates the isomerisation to the liquid sample. It is natural to expect the ketone (a) and the hydroxy isomer (b) to have different volatilities, the ketone being the more volatile. It will be recalled that equilibration in the 3-hydroxy derivatives is rapid.³ This allows the more volatile component to become enriched in the gas phase.

Inspection of the IP's in the 5-homologue series 1 to 4 reveals that the IP is decreased stepwise. The decrease in each step is slightly larger than expected to be inherent in the additional methyl group substitution on the α -carbon of the side chain. This is interpreted in

Table 2. Ionisation potentials of furans and selenophenes.

	(a)	(b)
(9)	Z = O	IP 9.23 ± 0.05 eV
(10)	Z = Se;	IP 8.24 ± 0.05 eV
(11)	Z = O;	IP 9.04 ± 0.05 eV
(12)	Z = Se;	IP 8.21 ± 0.05 eV
(13)	Z = O;	IP 7.86 ± 0.05 eV
(14)	Z = Se;	IP 7.69 ± 0.05 eV

terms of a slight relative increase in the hydroxy isomer (*b*).

The IP difference (0.33 eV) between the 2-ethyl-(5) and the 2-methyl-(1) isomer indicates that the ketone-enol isomer ratio has been decreased with the increase in the size of the 2-substituent. The *t*-butyl derivative 6, however, appears to have almost the same isomer ratio as 5. This observation is not in accord with solution studies in carbon disulfide which show that the ketone-enol ratio depends on the 2-substituent.³ The gas phase ratios are therefore best understood in terms of relative rates of evaporation of the tautomers combined with rapid equilibrations in the liquid samples evaporated.

In the furan series the IP's for the model compounds 11 and 13 suggest IP *ca.* 9.2 eV for the keto form (*a*) of 9 and *ca.* 8.0 eV for the hydroxy form (*b*). The experimental value is 9.23 eV which shows that the furan in the gas phase is present as the ketone (*a*). The selenophene 10, however, has IP 8.24 eV which lies between the values which can be estimated for the pure tautomer from the IP's of compounds 12 and 14. Comparisons of the data indicate 10–20 % of the hydroxy isomer. A similar result is arrived at for the thiophenes by comparisons of the corresponding figures. From recent accumulations of data on the physical and chemical properties of selenophenes it is evident that the selenophene system resembles closely the thiophene system.⁸ A similar tautomeric behaviour is therefore not unexpected. The aromatic stabilisation of the furan system is less which is probably a major reason why 9 exists preferentially in its keto form (*a*).

Thiophene and furan have IP's 8.80 and 8.85 eV, respectively;⁴ the values for the methoxy analogues 7 and 13 are also the same within the experimental error, 7.89 and 7.86 eV, respectively. IP for the selenophene 14 is slightly less (7.69 eV). These observations strongly indicate that the primary ionisation occurs from the aromatic π -electron cloud rather than from the heteroatom. In the keto forms, however, the IP's for the hetero-analogues 8, 11, and 12 differ in a manner according to the electron releasing properties of the heteroatom; the same observation has been made in the 2-hydroxy series.¹

EXPERIMENTAL

The ionisation efficiency curves were recorded with an AEI MS-902 mass spectrometer and the IP's obtained by the semilog-plot method as previously described;^{1,6} xenon was the reference gas. The samples were introduced by the indirect method at 30–35 °C. The reservoir and the connecting tubes were kept at 130 °C and the ion source at 230 °C. The IP's are the average of three determinations, the deviation being ± 0.05 eV.

The compounds used in this investigation were available from other work or were prepared according to literature: 1–6;^{3,9} 7, 8, 12–14;¹⁰ 9;^{10,11} 11.^{10,12}

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