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Notes

Search for Hydrogen Bonding in Thiophenols through Heats of Vapourisation Measurements

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The heats of vapourisation of a number of phenols, thiophenols and their methyl ethers have been determined. While the heats of vapourisation of the intermolecularly H-bonded phenols are higher than those of their methyl ethers, the reverse is true for the intramolecularly H-bonded phenols. In the case of thiophenols no such difference is observed. The heats of vapourisation of all thiophenols are lower than those of their methyl ethers, indicating absence of H-bonding or presence of weak H-bonding in thiophenols.

The vapour pressure of a compound like *o*-nitrophenol with intramolecular H-bonding is higher at any given temperature as compared to those of intermolecularly H-bonded isomers, *m*-nitro- and *p*-nitro-phenols. Thus for *o*-, *m*- and *p*-nitro-phenols the vapour pressures at 100°C are 2.92, 0.196 and 0.083 mm, respectively[1]. In the liquid state the three isomers have almost the same energies, while in the vapour phase they have different energies. The *m*- and *p*-isomers, which are extensively associated in the liquid state, undergo dissociation during vapourisation as these two isomers exist mostly in the monomeric form in the vapour state. These isomers, therefore, require greater energy for vapourisation than the *o*-isomer which exists in the chelated monomeric form in both the states.

While the ability of the $-OH$ group in phenols to enter into inter- or intra-molecular H-bonding is well known, the ability of the $-SH$ group to enter into such bonding has not been so well studied. A good number of investigators[2-23] found that the $-SH$ group is capable of forming H-bonds, though the bonds are reported to be weak in many cases. Some workers[24-28] have, however, reported negative evidence for H-bond formation involving $-SH$. With a view to studying this problem further, the heats of vapourisation of a number of phenols, thiophenols and their methyl ethers have now been determined.

The purities of the compounds were checked by GLC. The heat of vapourisation was determined by measuring the vapour pressure at different temperatures (usually about 15 values were taken) and plotting log p versus 1/T. The slope of the linear plot, which was in excellent agreement with that calculated by the method of least squares, was used to obtain the heat of vapourisation, employing the Clausius-Clayperon equation. The values are given in Table 1.

The heats of vapourisation clearly indicate that the phenols, listed in Table 1, fall into two categories: (i) those that associate due to intermolecular H-bonding; and (ii) those that do not associate due to intramolecular H-bonding. The phenols of category (i) have higher heats of vapourisation than those of the corresponding methyl ethers, while the reverse is true for the phenols of category (ii). The differences appear

Table 1—Heats of Vapourisation (in kJ mol^{-1}) of Phenols, Thiophenols and Their Methyl Ethers

No.	Substituent	$R.C_6H_4.OH$ (a)	$R.C_6H_4.OCH_3$ (b)	Difference (b)-(a)	$R.C_6H_4.SH$ (c)	$R.C_6H_4.SCH_3$ (d)	Difference (d)-(c)
1.	H	51.05	41.00	−10.05	43.51	47.70	4.19
2.	*p*-CH_3	53.97	46.02	−7.95	46.44	50.21	3.77
3.	*p*-Cl	53.97	47.70	−6.27	48.53	53.14	4.61
4.	*p*-Br	58.58	50.63	−7.95	52.30	55.65	3.35
5.	*p*-OCH_3	58.58	51.46	−7.12	51.05	53.56	2.51
6.	*m*-Cl	52.30	48.12	−4.18	48.53	51.88	3.35
7.	*m*-Br	55.23	50.21	−5.02	51.05	54.40	3.35
8.	*o*-CH_3	50.21	45.19	−5.02	46.02	50.21	4.19
9.	*o*-CHO	47.70	55.23	7.53	—	—	—
10.	*o*-$COCH_3$	50.21	56.48	6.27	—	—	—
11.	*o*-Cl	45.19	49.37	4.18	47.70	53.55	5.85
12.	*o*-Br	50.21	52.30	2.09	50.63	56.48	5.85

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quite revealing. In the case of chelated phenols (Nos. 9-12 in Table 1) the stronger the intramolecular H-bonding, the greater is the difference, thus the abilities of the groups to chelate with the *ortho* $-OH$ decrease in the order: $-CHO > -COCH_3 > -Cl > -Br$. In the case of associated phenols (Nos. 1-8; Table 1) no generalisation seems possible regarding the influence of substituents on association. This is understandable since these differences are dependent on the intermolecular attractions in the ethers also, which are governed by several factors like polar and steric effects, H-bonding etc.

In the case of thiophenols and their methyl ethers, it is observed that all the methyl thioethers have higher heats of vapourisation than those of the corresponding thiophenols. From the observed values it is difficult to say that there is no association in thiophenols (corresponding to Nos. 1-8). If phenols have higher heats of vapourisation than their methyl ethers, their association becomes clearly revealed. The lower heats of vapourisation of thiophenols do not make their behaviour very clear; this can be either due to absence of association or due to presence of weak association. If the thiophenols are weakly associated and if the intermolecular H-bonding that causes association gets cleaved during heating—requiring for the cleavage of H-bonds an amount of heat which is less than the difference between the heats of vapourisation of unassociated ArSH and $ArSCH_3$—then also the thiophenols will have lower heats of vapourisation than their methyl ethers. Hence it can be concluded that the thiophenols other than *o*-chloro and *o*-bromothiophenols are weakly associated, if association at all exists.

The concept of weak association gets some support from the fact that the heats of vapourisation of *o*-chloro- and *o*-bromo-thioanisoles are higher than those of the corresponding thiophenols by 5.85 $kJmol^{-1}$. This value is significantly higher than the differences observed for other $ArSH - ArSCH_3$ pairs. The higher difference observed for the *o*-halogeno compounds may be due to either absence of chelation or the presence of very weak chelation of the halogeno substituent with the *ortho* $-SH$ group. If the thiophenol is chelated, it can have a lower heat of vapourisation than its *m*- and *p*-isomers, provided the intramolecular H-bonding of the former is relatively weaker than the intermolecular H-bonding of the latter. One mol of *p*-chloro- or *p*-bromothiophenol thus requires more heat for vapourisation than one mol of the *o*-isomer.

The higher difference (5.85 $kJ\,mol^{-1}$) observed for the *o*-halogeno compounds can also be explained on the basis of strong chelation of the $-SH$ with the *o*-halogeno substituent and the molecules going into the vapour state with the chelation intact. But this possibility seems to be unlikely considering the results of a UV spectral study[29].

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