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CONFORMATIONAL ANALYSIS OF ALKYL ARYL ETHERS AND ALKYL ARYL SULPHIDES BY PHOTOELECTRON SPECTROSCOPY

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Abstract—Photoelectron spectroscopy shows that in t-butoxybenzenes, but not in methoxy-, ethoxy- or isopropoxybenzenes, there is a loss of p-π orbital overlap. A similar effect is observed in 2,6-dimethylalkoxybenzenes. In alkyl aryl sulphides two conformers predominate, the one with maximum p-π overlap and the other with reduced overlap. The importance of the less conjugated conformer increases monotonously through the series hydrogen, methyl, ethyl, isopropyl and t-butyl in alkyl phenyl sulphides.

Both alkyl aryl ethers[1] and alkyl aryl sulphides[2] are oxidised by manganic acetate. In rate studies it was found that for a series of alkyl aryl ethers the relative rates followed the order Me < Et < i-Pr > t-Bu. In contrast, for a series of alkyl aryl sulphides the order was Me > Et > i-Pr > t-Bu. Recently similar differences in reactivity have been observed in the bromination of ethers and sulphides in acetic acid. In bromination of alkyl aryl ethers[3] rates were Me < Et < i-Pr and of sulphides[4] Me > Et > i-Pr.

To understand the differences of behaviour in our oxidation study we measured $E_{1/2}$ values for the oxidation of ethers and sulphides, and found a good correlation between relative rate and half-wave potential. We now extend this study by reporting the photoelectron spectra (PES) of ethers and sulphides. These results not only clarify the observed rate data for oxidation and bromination, but also explain other differences in physical properties of ethers and sulphides noted earlier, and discussed below. We suggest that the observed rates in the sulphide series are best interpreted by the subsequent analysis, which concludes that in alkyl aryl sulphides two conformers predominate, one having maximum p-π orbital overlap, the other, of increasing importance through the series Me, Et, i-Pr, t-Bu having reduced p-π overlap.

The PES of some aryl alkyl ethers and sulphides had been reported previously.[5,9] In phenol[5,6] and anisole[5,7] overlap interaction between the 'lone pair' and the aromatic π-system is at a maximum but in t-butyl phenyl ether[9] and in 2,6-disubstituted aryl ethers[5] steric interactions between *ortho* substituents and the alkyl moiety destabilized the conformer with maximum p-π orbital overlap. In these hindered ethers the O-alkyl group may be forced out of the plane of the aromatic ring, or the C$\hat{O}$C bond angle may increase. In the case of aryl alkyl sulphides the importance of the different conformers is not clear. Spectra of thioanisole[7] and thiophenol[8] have been recorded and p-π interaction suggested but no hindered sulphides have been examined. Other spectroscopic evidence is not decisive. With t-butyl sulphides a marked reduction in orbital overlap is indicated by the UV spectra[10] and the methyl, ethyl and isopropyl sulphides have spectra suggesting some loss of orbital overlap. However IR spectra[11] suggest steadily decreasing p-π interaction through the series methyl to t-butyl. PES is a satisfactory method of investigating the conformational analysis of the sulphides and we report not only upon this problem but also further data concerning the ethers in view of conflicting conclusions concerning the preferred conformers in anisole,[12] and to better account for our oxidation study.[1]

Vertical ionization potentials (I_v) are listed in Tables 1 and 2 (because of bond overlap adiabatic potentials could normally only be determined for the first band). Spectra are shown in Figs 1 and 2.

(a) *Phenols and aryl alkyl ethers.* Data in Table 1 (Fig 1) are in agreement with published values[5,7,9] with one exception. For 2,6-dimethylanisole (**2b**), Maier and Turner report a band at 9·20 eV and note anomalous features of the spectrum. Our failure to detect the band at 9·20 eV, suggests a probable impurity in the earlier work and we conclude that the spectrum shows no anomalous features. As in a previously reported spectral analysis for compounds **1a** and **1b**, we assign the first and the third ionisations to two of the orbitals that result from strong interactions between a non-bonding oxygen orbital and the two b_1 benzene π-orbitals (the third resultant orbital should give rise to a higher energy ionisation) and we assign the second ionisation to a slightly perturbed a_2 benzene π orbital. For t-butyl

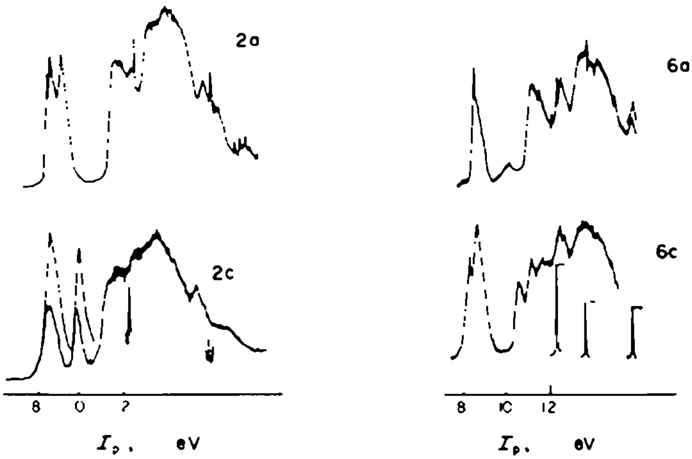

2a
2c
6a
6c
8
10
12
I_p, eV
8
10
12
I_p, eV

Fig 1.

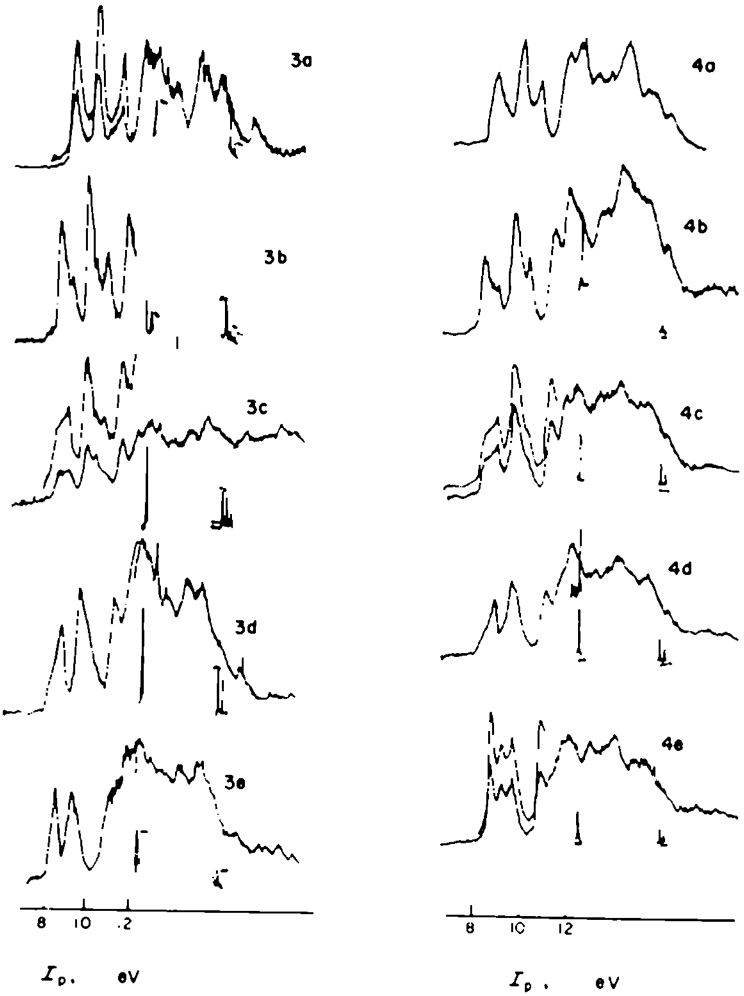

3a
3b
3c
3d
3e
4a
4b
4c
4d
4e
8
10
12
I_p, eV
8
10
12
I_p, eV

Fig 2.

Table 1. PES of aryl alkyl ethers (eV)

Compound	Planar conformer $\pi(b_1)$*	$\pi(a_2)$	n_O^*	Distorted conformer $\pi(b_1) + \pi(a_2)$	n_O
1a	8·67	9·35	†	—	—
b	8·46	9·32	11·03	—	—
c	8·41	9·26	10·96	—	—
d	8·32	9·25	10·88	—	—
e	—	—	—	8·66 + 9·23	9·69
2a	8·34	8·82	*	—	—
b	—	—	—	8·53	9·98
c	—	—	—	8·49	9·85
d	—	—	—	8·49	9·81
e	—	—	—	8·47	9·50

*There is considerable mixing of the n_o and $\pi(b_1)$ orbitals.

†Band position obscured.

Table 2. PES of aryl alkyl sulphides (eV)

Compound	Planar conformer n_S^*	$\pi(a_2)$	$\pi(b_1)$*	Non-planar conformer n_S	$\pi(b_1) + s\pi(a_2)$
3a	8·47	9·40	10·62	—	—
b	8·07	9·30	10·15	8·60	†
c	8·0	†	10·12	8·53	9·29
d	†	†	†	8·46	9·24
e	—	—	—	8·40	9·14 + S
4a	8·33	9·42	10·33	—	—
b	7·87	9·24	9·89	8·50	†
c	7·9	†	9·8	8·45	9·20
d	S	†	†	8·38	9·12
e	—	—	—	8·31	8·84 + 9·27
5a	8·44	9·20	10·45	—	—
b	8·00	9·02	9·98	8·50	†
c	7·92	†	9·88	8·42	8·96 + S
d	S	†	S	8·38	8·96
e	—	—	—	8·35	8·90
6a	†	†	10·03	—	—
b	—	—	—		8·25–8·55
c	—	—	—		8·18–8·50
d	—	—	—		8·17–8·50
e	—	—	—		8·15–8·40
7a	8·31	9·05	10·42	—	—

*There is considerable mixing of the n_S and $\pi(b_1)$ orbitals.

S Shoulder.

†Band position obscured.

phenyl ether we make a similar assignment of the bands and, hence accept that orbital interactions are markedly smaller than in the other ethers. The reduction in orbital overlap indicates a significant difference in conformation between the t-butyl ether and any of the other ethers. The recent suggestion of Allinger *et al.*[12] that there is a close balance between a planar and a non-planar conformer in anisole is not supported by our results.

If there was no conformational change on introducing Me groups into ring positions of phenyl ethers then the effects on the stabilities of the benzene π-orbitals in an ether should be appxoximately as listed in Table 3. The values listed were determined by analysing PE spectra of methyl benzenes.[11]

Table 3. Predicted ring methyl group shifts (eV)

Site(s) of methyl group(s)	$b_1(e_{1g})$	$a_2(e_{1g})$	$b_1(a_{2u})$
2 or 3	0·16	0·29	0·23
4	0·35	0·10	0·23
2,6	0·32	0·57	0·44
2,4,6	0·67	0·67	0·67

On introducing Me groups into the 2 and 6 positions of phenol we obtain shifts of 0·33 eV and 0·53 eV respectively in the first two ionisations. Clearly the Me groups in 2,6-dimethylphenol have no significant conformational effects. However comparison of the alkyl phenyl ethers (**1b** to **1d**) with the 2,6-dimethyl analogues (**2b** to **2d**) shows that the nuclear Me groups markedly reduce orbital overlap between the O atom and benzene ring. By contrast there appears to be no further reduction in orbital overlap on going from t-butyl phenyl ether (**1e**) to the 2,6-dimethyl analogue (**2e**). We conclude that in compounds **1a**–**1d** and **2a** the predominant conformer has maximum p-Π overlap but in **1e** and in **2b**–**2e** the preferred conformer has greatly reduced overlap.

(b) *Thiophenols and aryl alkyl sulphides.* The PES of thiophenol[8] (**3a**) and thioanisole[7] (**3b**) have been previously interpreted as reflecting extensive orbital interaction between the S atom and the benzene ring. However Fig 2 shows that no regular progression is immediately apparent for further members of the series **3c**–**3e**. The spectra cannot be explained by analogy with the ethers. Instead we suggest that a conformational equilibrium exists in each case, with two predominant conformers—one essentially planar with maximum p-π interaction and the other with the p orbital orthogonal to the π-system. In the latter conformation steric interaction between the thioalkyl group and the *ortho* H atoms of the benzene ring is at its minimum. It has already been noted[11] that an energy minimum could arise for this conformation because of overlap of the occupied benzene π-orbitals with the vacant sulphur d_{xy} orbital. The assumption of the conformational equilibria leads to the assignments in Table 2. The further assumption of similar ionisation cross-sections for the conformers enables the percentage of the non-planar conformer to be roughly estimated. For thiophenol no non-planar conformer is detected but the percentage increases through the series (**3b** ~ 10%), (**3c** ~ 60%), (**3d** ~ 85%), and (**3e** ~ 95%). Our assignments of the PES of corresponding phenyl sulphides and phenyl ethers in their planar conformations differ from one another only in the degree of mixing of the non-bonding orbital of the substituent and the b_1 π-orbitals of the benzene ring. The non-bonding orbital is more than 1 eV less stable in aliphatic sulphides[14] than in corresponding aliphatic ethers[15] and the sum of I_1 and I_3 is smaller in planar phenyl sulphides than in planar phenyl ethers by a similar amount. The quantitative effects of ring methyl groups on the spectra of our planar conformers are very close to the values predicted by applying the shifts listed in Table 3.

On going from a planar to a non-planar conformer in a phenyl sulphide we would expect the energy of the ionisation from the perturbed a_2 orbital to change by very little, and the sum of the energies of the ionisations from the non-bonding sulphur orbital and the less stable of the b_1 benzene bonding orbitals to be almost unchanged. The main difference between the two conformers should be a reduction in the value of the parameter B_0 which is a measure of the interaction between the non-bonding sulphur orbital and the less stable b_1 benzene bonding orbital. The difference in the values of B between the planar and the orthogonal conformers can be calculated using the formula[5]

$$\Delta E = [(A_S - A_{b_1})^2 + 4B_0^2]^{1/2}$$
$$= [(I_1, \text{non-planar} - I_1, \text{non-planar})^2 + 4B_0^2]^{1/2}$$

and assuming B_{90} is zero. For each alkyl phenyl sulphide we considered, the change in the value of B lay in the range of 0·88 eV to 0·92 eV. The narrowness of the range suggests to us that the non-planar conformation is in each case the one in which the alkylthio group is orthogonal to the benzene ring. The changes in the value of B are sensible for 90° twists of the alkylthio groups since the values[16] in anilines are about 1·2 eV.

Because of band overlap it is not possible to accurately measure the effect of substitution of Me groups in the aromatic ring upon the spectra of the non-planar conformers. Spectra of series **4a**–**4e** and **5a**–**5e** are very similar to those of series **3a**–**3e**. In the spectrum of **4e** all three bands are clearly visible (Fig 2). The spectra of **6a**–**6e** are featureless and not easy to interpret clearly. However the position of the first band indicates that in **6a** there is considerable p-π orbital overlap but in **6b**–**6e** this is markedly reduced. We attribute this change to the destabilisation of the planar conformers by the 2- and 6-Me substituents.

These results clarify the known reactivity of aryl ethers[1] and aryl sulphides[2] in oxidation processes. The reactivity towards oxidation by manganic acetate closely parallels the $E_{1/2}$ values (Table 4). The latter are influenced by I_1 for the planar conformer and by the relative importance of that conformer. Although the ionisation potentials are the only parameters determined in the gas phase we have no reason to believe that the conformer ratio is greatly different in the gas phase from in solution. With the ethers $E_{1/2}$ is determined by I_1 for the planar conformer but with t-butyl ethers this conformer is unimportant and hence $E_{1/2}$ in this case is determined by I_1 for the non-planar conformer. The intensity of the UV band at 280 nm shows the loss of p-Π interaction in the t-butyl ethers.

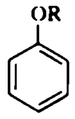
With the sulphides the importance of non-planar conformers influences the reactivity of not only the t-butyl sulphides but also the isopropyl sulphides. The reactivity of the methyl and ethyl sulphides is determined by I_1 for the planar conformer. The UV spectra support this analysis.

The difference in timescale for the process of electron transfer at an electrode, or in reaction with a chemical oxidant and the electron transfer associated with the measured vertical ionisation potential could well lead to little correlation between $E_{1/2}$ and I_1. Although a fairly good linear correlation

Table 4

Compound	Relative rate of oxidation by Mn^{3+}	$E_{1/2}$(v)	I_1(eV) planar conformer	non-planar conformer	λ_{max} (nm)	ϵ_{max}
8b	1.00	1·18	8·16	—	280	2590
8c	1·30	1·12	8·13	—	280	1750
8d	1·89	1·09	8·09	—	281·5	1860
8e	0·64	1·17	—	8·23	277	810
4b	38	0·93	7·87	8·50	255	12,100
4c	40	0·98	7·85	8·45	257	9330
4d	6·0	1·05	7·8	8·38	257	6310
4e	0·9	1.14	—	8·31	263	1820
5b	12	1·02	8·00	8·50	255	9330
5c	11	1·03	7·92	8·42	259	7945
5d	5·2	1·08	7·8	8·38	257	6030
5e	1·1	1·19	—	8·35	267	1700

has been found between $E_{1/2}$ and vertical ionisation potential[17] a recent analysis of tetraalkylhydrazines[18] which can adopt different conformations with substantially different I_1 values, shows that for these compounds there is little correlation between $E_{1/2}$ and I_1. Our results confirm the importance of considering conformational effects in oxidations and show the value of PES in studying such effects.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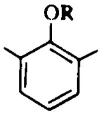
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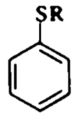
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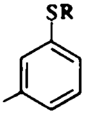
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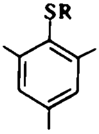
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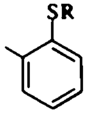
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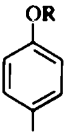
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a: R = H
b: R = Me
c: R = Et
d: R = i-Pr
e: R = t-Bu

EXPERIMENTAL

Materials. All ethers and sulphides were prepared by reaction of the corresponding phenol or thiophenol with MeI for methyl ethers and sulphides, ethyl iodide for ethyl ethers and sulphides, 2-bromopropane for i-propyl ethers and sulphides and isobutene for t-butyl ethers and sulphides. Ethers and sulphides were purified by fractional distillation.

UV spectra. Spectra were recorded using a Perkin-Elmer 450 Spectrometer.

Half-wave potentials. Half-wave potentials were measured using a Chemical Electronics Valve Potentiostat and a Chemical Electronics Pulse Generator RBI. A 3-compartment cell was used, the working and secondary electrodes separated by a glass sinter and the reference electrode separated from the working electrode by a tap and luggin capillary. The working electrode was platinum wire and the secondary electrode was platinum foil. The reference electrode consisted of a silver wire in a 10^{-2} M soln of silver perchlorate, a 0·2 M soln of sodium perchlorate made up in purified methyl cyanide. The current/potential curves were run in 0·5 M sodium perchlorate with a 10^{-2} M concentration of the electro active species in methyl cyanide at a sweep rate of 0·1 v/sec.

Photoelectron spectra. Vacuum UV photoelectron were recorded using a Perkin-Elmer PS 18 spectrometer. Calibration was made using the 15·76 eV argon line and the 12·13 eV xenon line.

Vertical ionisation potentials were recorded.

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