# Effect of a Phenyl Substituent on the Acidity and Rate of Ionisation of Disulphonyl-activated Carbon Acids

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Replacement of one of the acidic hydrogen atoms in bisethylsulphonylmethane by a phenyl group results in a slight increase in the acidity of the other proton (0.38 p*K* units) but reduces the rate of ionisation 15-fold. In a cyclic disulphone in which the bulky sulphonyl groups are 'tied-back', a phenyl substituent has a much larger acid-strengthening effect (1.63 p*K* units) but nevertheless the ionisation rate is only slightly increased. An isoamyl substituent introduced into bisphenylsulphonylmethane also results in a lower rate than predicted from the p*K* value. By comparison with the effects of a phenyl substituent on the p*K* values and rates of ionisation of less sterically crowded monosulphones the unusual effect of the phenyl substituent in the disulphones is explained in terms of steric factors.

IN a previous study [1] of the rates of ionisation of disulphonyl-activated carbon acids an anomalous rate-retarding phenyl substituent effect was observed. The result was noted but not discussed in detail. Whilst this work was in the press, a similar observation based on rates of elimination from certain monosulphones was published.[2] Disulphones offer the advantage of high acidities so that equilibrium studies as well as rate measurements are feasible in aqueous solution. The expected effect of replacing hydrogen by a phenyl group on the carbon which bears the acidic proton is to increase the acidity and rate of ionisation by inductive and conconjugative stabilisation of the carbanion. There are numerous examples in the literature where this occurs. For example the equilibrium acidities and rates of ionisation of phenylmethanes,[3] fluorene,[4] and monosulphones [5] are increased by phenyl substitution. The rates of ionisation of mercaptals and acetals [6] and the equilibrium acidities of ketones [7] and cyanocarbon acids [7] are affected similarly. Hence our observation for disulphones is unusual and consequently we now discuss this result in detail together with some further measurements.

## EXPERIMENTAL

*Materials.*—A sample of 4-methyl-1,1-bisphenylsulphonylpentane was prepared by reaction of isoamyl bromide with bisphenylsulphonylmethane in dimethylformamide in the presence of sodium hydride.[8] Recrystallisation from ethanol gave a *solid*, m.p. 138—139° (Found: C, 59.0; H, 6.3; S, 17.7. $C_{18}H_{22}S_2O_4$ requires C, 59.0; H, 6.1; S, 17.5%); $\delta(CDCl_3)$ 0.78 (d,Me), 1.04 and 2.1 (m, $CH_2CH_2CH$), 4.35 (t, CH), and 7.4—8.0 (m, Ph). 5-Methyl-1,3-benzodithiole 1,1,3,3-tetraoxide was prepared by a method described to us by Professor R. Breslow. 5-Methyl-1,3-benzodithiole was prepared from 1,2-dimercapto-4-methylbenzene and methylene iodide in the presence of sodium hydride and oxidation of the product with hydrogen peroxide in acetic acid, followed by recrystallisation from ethanol gave a *solid*, m.p. 166—167° (Found: C, 41.4; H, 3.6; S, 27.4. $C_8H_9S_2O_4$ requires C, 41.4; H, 3.5; S, 27.6%); $\delta(CD_3COCD_3)$ 2.62 (s, Me), 5.20 (s, $CH_2$), and *ca.* 8.0 (m, ArH). 5-Methyl-2-phenyl-1,3-benzodithiole was prepared

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by condensation of 5-methyl-1,3-benzodithiole with benzaldehyde in ethanol saturated with HCl.[9] The product was oxidised[10] with hydrogen peroxide in an acetic acid–acetic anhydride mixture to give 2-phenyl-5-methyl-1,3-benzodithiole 1,1,3,3-tetraoxide which was recrystallised from ethanol, m.p. 182—183° (Found: C, 54.4; H, 4.0; S, 20.5. $C_{14}H_{12}S_2O_4$ requires C, 54.5; H, 3.9; S, 20.8%); δ($CD_3COCD_3$) 2.63 (s, Me), 6.35 (s, CH), and *ca.* 7.5—8.2 (m, ArH).

*Equilibrium Measurements.*—The dissociation of 4-methyl-1,1-bisphenylsulphonylpentane and 2-phenyl-5-methyl-1,3-benzodithiole 1,1,3,3-tetraoxide in aqueous solution at 25 °C was observed spectrophotometrically at 300 and 320 nm respectively, where the carbanions absorb strongly. For 4-methyl-1,1-bisphenylsulphonylpentane measurements were made in 0.04—1.0M-sodium hydroxide solutions and for 2-phenyl-5-methyl-1,3-benzodithiole 1,1,3,3-tetraoxide 0.0007—0.010M-sodium hydroxide solutions containing sufficient potassium chloride to maintain an ionic strength of 0.10M were used. A p*K* value for 4-methyl-1,1-bisphenylsulphonylpentane referring to infinite dilution was calculated from the measurements by using an $H_-$ acidity function determined for concentrated sodium hydroxide solutions.[11] The value was adjusted to ionic strength 0.10M with the Debye–Hückel approximation and the results for both sulphones are shown in the Table.

*Kinetic Measurements.*—The loss of tritium from the tritiated carbon acids was followed in hydrochloric acid solutions at 25.0 °C and ionic strength 0.10M using a liquid scintillation counter as previously described.[1] The reactions were accurately first order. The observed rate coefficients were reproducible to within ±2% and were identical in 0.10M-HCl and in 0.01M-HCl with 0.09M-NaCl showing that the reaction refers to a slow triton transfer from the carbon acids to water.

## RESULTS AND DISCUSSION

The rate coefficients for detritiation of 4-methyl-1,1-bisphenylsulphonylpentane, 5-methyl-1,3-benzodithiole 1,1,3,3-tetraoxide, and its 2-phenyl derivative were used to calculate forward and reverse rate coefficients for the water catalysed ionisation of the carbon acids [equation (1)].

$$RCH + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} RC^- + H_3O^+ \qquad (1)$$

A value for the equilibrium constant is required and an isotope effect ($k^H/k^T$ 3.1) previously obtained[1] for a sulphone of similar acidity was assumed. The results together with some from the earlier study are given in the Table. In comparing the different compounds, it should be noted that for an acid with two identical protons, the p*K* value will be 0.3 unit lower than for an acid with one proton and that the rate of ionisation will be a statistical factor of two higher. Hence for compounds (1) and (2), the phenyl substituent increases the acidity of one ionisable proton by 0.38 p*K* units and decreases the rate of ionisation per proton by a factor of 15.

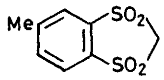
Values of p*K* and $k_1$ and $k_{-1}$ [equation (1)] for compounds (1)—(6) *

| Compound | p*K* | $10^5k_1$/ l mol$^{-1}$ s$^{-1}$ | $10^{-10}k_{-1}$/ l mol$^{-1}$ s$^{-1}$ |
|---|---|---|---|
| (1) | 11.95[12] | 30.7[1] | 1.6 |
| (2) | 11.87[12] | 1.06[1] | 0.045 |
| (3) | 12.38[13] | 48.0 | 6.4 |
| (4) | 11.05 | 66.0 | 0.41 |
| (5) | 10.96[13] | 408.0[1] | 2.1 |
| (6) | 12.89 | 0.95 | 0.41 |

* Results refer to 25.0 °C and ionic strength 0.1M.

$(EtSO_2)_2CH_2$

(1)



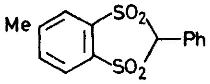
(3)

$(PhSO_2)_2CH_2$

(5)

$(EtSO_2)_2CHPh$

(2)



(4)

$(PhSO_2)_2CHCH_2CH_2CHMe_2$

(6)

It was found previously[1] that the rate coefficients for proton transfer to water from five disulphones [including (1) and (5)] varied directly with the acid dissociation constant of the disulphone and consequently the reverse rate coefficients for protonation of the carbanions were constant. The values ($1.8 \pm 0.5 \times 10^{10}$ l mol$^{-1}$ s$^{-1}$) were close to the diffusion limit. It was therefore concluded that in the transition state for ionisation of these carbon acids proton transfer is virtually complete. Compounds (2), (4), and (6) do not fit in with this pattern and the reverse rate coefficients are below the diffusion limit. These compounds show further unusual features. Comparison of the results for (1) and (2) shows that a phenyl substituent decreases the rate coefficient for proton transfer 15-fold despite an increase in the acidity of the carbon acid (0.38 p*K* unit). In compounds (3) and (4) a phenyl substituent decreases the p*K* substantially (1.63 p*K* units) but the rate of ionisation is only increased *ca.* three-fold. The lower reverse rate coefficient calculated for (6) compared with (5) means that an isoamyl substituent introduced into (5) decreases the rate of ionisation by a factor of five more than expected from the decrease in acidity, based on our previous correlation obtained for five disulphones.[1]

The results for (2), (4), and (6) are best explained by steric effects. The difference in acidity[5c] between $PhCH_2SO_2CH_2Ph$ (p*K* 23.9) and $CH_3SO_2CH_3$ (p*K* 31.1) demonstrates that the carbanion stabilising effect of a phenyl substituent is quite large in a monosulphone. A large enhancement in the ionisation rate of monosulphones by a phenyl substituent is also observed. For example the rates of isotope exchange[5a,b] for $C_6H_{13}CH(Me)SO_2Ph$ and $PhCH(Me)SO_2Ph$ differ by a factor of *ca.* $10^4$. However Stirling[2] has found by an analysis of rates of elimination from monosulphones having bulky leaving groups that a phenyl substituent decreases the rate of ionisation in these cases. We can therefore conclude that the unusual phenyl substituent effects can be accounted for by steric factors which arise

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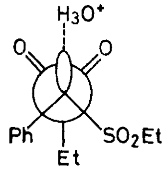
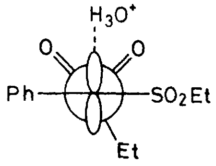
when a phenyl group is attached to carbon possessing bulky sulphonyl substituents. The effects do not appear to be observed for carbon acids with activating groups other than sulphonyl.

Models show that a planar or pyramidal carbanion derived from (2) is quite strained. In particular the conformation in which the lone pair orbital is perpendicular to the plane of the phenyl ring is severely strained and it is therefore unlikely that the phenyl group can exert the maximum conjugative effect. This would account for the smallness of the p*K* difference between (1) and (2). In compound (4) where the sulphone groups are 'tied-back,' the conjugation between the phenyl group and lone pair may be less hindered and a sizeable increase in acidity of (4) over (3) is observed. It has been found [14] that in the transition state for ionisation of a sulphone the proton enters and leaves in a direction which is *syn* to the sulphone oxygen atoms; this is illustrated for pyramidal and planar transition states in (7) and (8) respectively. This additional conformational requirement for the transition state may mean that the latter is more strained than the carbanion and may lead to a primary steric effect in the ionisation of (2). A similar effect may operate for (4) in which the phenyl group has a much smaller activating effect on the ionisation rate than on the acidity of the carbon acid.



(7)



(8)

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