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A STUDY OF BENZENESULFINIC AND SELENINIC ACIDS

DETERMINATION AND THEORETICAL INTERPRETATION OF pK*

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Abstract—We have carried out pH measurements for some *para*- and *meta*-substituted benzene–sulfinic and -seleninic acids at 15, 25 and 35° and at constant ionic strength. The pK values of benzene–sulfinic acids extrapolated at $\mu = 0$ are interpreted by a quantum-chemical calculation following the Extended Hückel Theory (EHT) approximations; the results of this procedure, which has been calibrated against benzoic acids, indicate that the conjugation between the benzene ring and the —SOOH group is impeded. A structure, which justifies the experimental results and is in accordance with our calculations, is suggested and discussed.

MANY authors have studied various substituted benzene-sulfinic and benzene-seleninic acids as ligands with transition metals[1–3] and determined the acid dissociation constants.[4–11]

The p*K* values found in the literature are often conflicting and not always reproducible. Frequently the measurements were made against non-buffered ionic strength or using different μ values so that the results of the various authors cannot be compared. For example, in the case of benzene-sulfinic acid Rumpf and Sadet[4] have reported pK = 1·29 at 25°, while for the same acid other authors[5–7] obtained different values (1·80· 1·84, 2·16); similarly, in the case of *p*-toluenesulfinic acid, values can be found ranging between 1·46 and 1·99. The disagreement in the available data exceeds the bounds of acceptable experimental error and casts doubt not only on the validity of the individual measurements but also on the order of magnitude of the results. Burkhard *et al.*[6] has suggested that the instability of sulfinic acids is a possible source of error, while Kice *et al.*[12] studying the mechanism of disproportionation of sulfinic acids proved the formation of sulfonic acid—which is a stronger acid than sulfinic acid (pK = 0·70 at 25$^{\mu}$ for non-substituted[13])—in accordance with the scheme:

$$3\ ArSO_2H \rightarrow ArSO_2SAr + ArSO_3H + H_2O$$

Sulfonic acid may also be produced by oxidation with atmospheric oxygen unless adequate experimental care is taken. The benzene-seleninic acids are more stable than the corresponding sulfinic compounds; nevertheless more detailed information is required.

In this study the p*K* values of *meta*- and *para*-substituted benzene-sulfinic and -seleninic acids (H-, CH_3-, Cl-, Br-, NO_2-, CH_3O-) were measured systematically and the effect of ionic strength and temperature on the p*K* values was determined. In addition, we carried out a simple quantum-chemical study for the interpretation of the dissociation equilibrium. Fig. 1 shows the results obtained at 15, 25 and 35° and at different values of ionic strength in the range $3{\cdot}0 \geqslant \mu \geqslant 2{\cdot}5\ 10^{-3}$.

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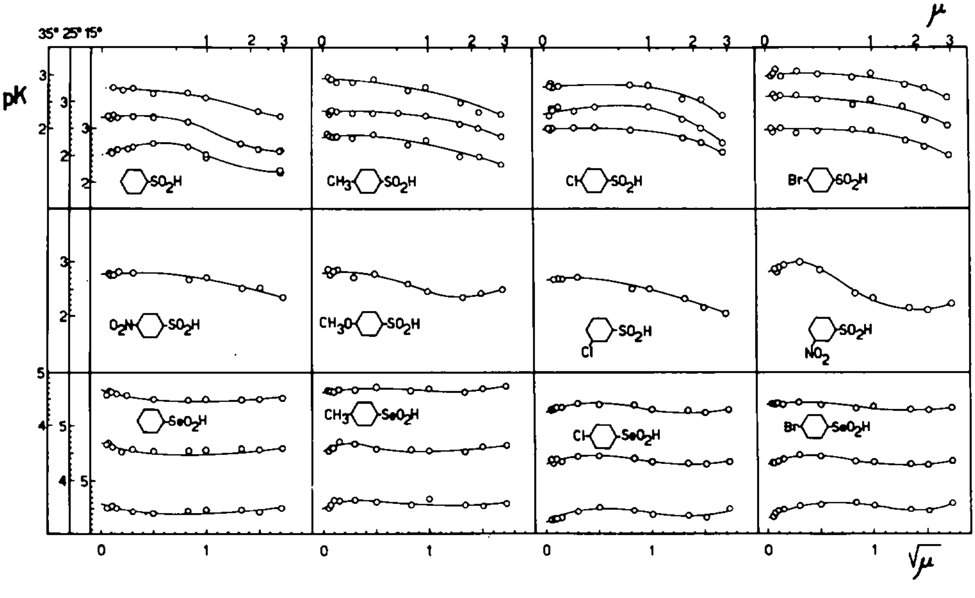

Fig. 1 Plot of pK vs. $\sqrt{\mu}$ at 15, 25 and 35° for benzene-sulfinic and -seleninic acids.

The pK values obtained for benzene-sulfinic acids are higher than those found in the literature. This is not surprising because, in order to avoid spontaneous oxidation and dismutation, we carried out all the experimental operations very quickly, in a deoxygenated nitrogen atmosphere using freshly prepared samples. As pK values of the solutions kept under nitrogen are all reproducible (Fig. 2) these solutions are stable for a much longer period than is necessary for carrying out a single measurement. The benzene-seleninic acids are very stable and are, furthermore, used as oxidants.[14] In this case the results agree with those found in the literature (for non-substituted acid pK is 4·70 against 4·79 found by McCullough *et al.*[9]

As seen from Fig. 1, the influence of temperature on pK values is almost negligible (about 2% in the range 15–35°), but ionic strength has a more significant effect with a maximum of about 0·7–0·8 pK units for *m*-NO_2 and non-substituted benzene-sulfinic acids, in the range investigated ($2{\cdot}5\ 10^{-3} \leqslant \mu \leqslant 3{\cdot}0$).

Table 1 shows the extrapolated values at $\mu = 0$ for sulfinic and seleninic acids together with the values[15] for benzoic acids with the same substituents and at the same temperature.

While the pK values of the benzoic acids are sensitive to the substituent and are contained within one pK unit, the corresponding values for sulfinic acids are all contained within one tenth of a pK unit (between ~2·7 and ~2·8). The behaviour of seleninic acids is intermediate.

In benzoic acids, pK variations are consistent with the usual mesomeric and inductive substituent effects, whereas in benzene-sulfinic acids no qualitative value can be assigned to the small differences; in fact the precision limit of the measurements is $\pm 7{\cdot}10^{-2}$ pK.

We propose to explain this considerable qualitative difference between the pK values of benzoic and benzene-sulfinic acids while we defer for the moment the analysis

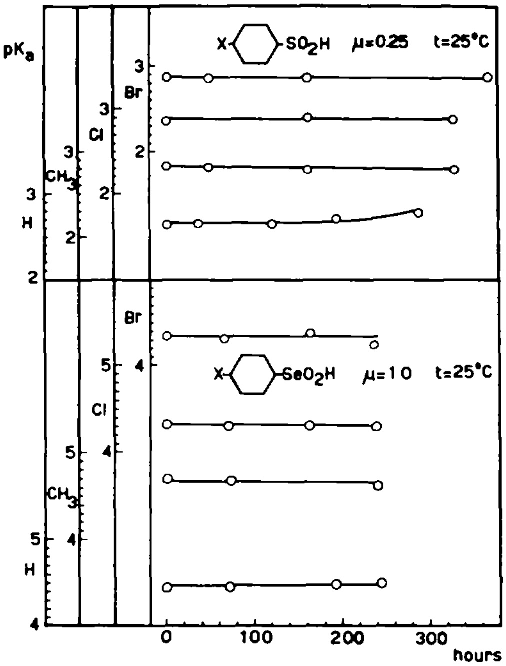

FIG. 2 Reproducibility of pK measurements for benzene-sulfinic and -seleninic acids.

TABLE 1. pK VALUES AT μ = 0 AND 25°

X	X-$C_6H_4SO_2H$	X-$C_6H_4SeO_2H$	X-$C_6H_4CO_2H$[a]
H	2·76	4·70	4·20
p-CH_3	2·80	4·55	4·37
p-Cl	2·76	4·30	3·98
p-Br	3·08	4·28	3·97
p-NO_2	2·77	—	3·42
p-CH_3O	2·72	—	—
m-Cl	2·68	—	3·82
m-NO_2	2·81	—	3·49

[a] pK values for benzoic acids has been obtained from Ref. 15. We have chosen the values corresponding to a minimum of ionic strength.

of the pK of benzene-seleninic acids pending the completion of the measurements on the *meta*-substituted compounds of this series. Preparation and pK determination of benzene-tellurinic acids is also planned.

In dealing with the problem, we accept as valid the proportionality between pK and the energy of ionic dissociation ΔE, evaluation of which is made by a quantum-chemical calculation.

This approximation, on which all previous theoretical pK correlations are based, has been fully discussed.[16] It is certainly valid when dissociation entropy is zero, but in our case ΔS should be practically the same for the whole series of molecules studied, independent of its absolute value. We therefore believe that the approximation $pK \propto \Delta E$ is acceptable, at least for a qualitative comparison of the pK values of the various acids of a series.

The problem therefore boils down to carrying out as complete a calculation of ΔE as possible, which can be defined as the energy difference between the dissociated and undissociated species in the ground state and in the reaction environment, which in our case is the aqueous solution.

Daudel[17] makes ΔE correspond to a sum of contributions

$$\Delta E = \Delta E_\sigma + \Delta E_\pi + \Delta E_{\mathrm{St}} + \Delta E_{\mathrm{Sol.}} \qquad (1)$$

This scheme clearly refers to the approximations contained in Hückel's method in so far as it admits a complete σ–π separation and the possibility of calculating *a posteriori* the energy due to non-bonded interactions (E_{St}). Furthermore, to accept (1) is tantamount to admitting that solvation energy does not affect the electronic structure of the molecule (this approximation has been criticised by Klopman[18] who suggested a simple method for including solvation in a semi-empirical quantum-chemical calculation).

Up till now ΔE_π (calculated by more or less sophisticated procedures) has been considered to be the most important index of the strength of a base or of an acid, while some attention has been paid to the rôle of ΔE_{Sol} and ΔE_{St}.[17, 19, 20]

This truncation has been accepted not only for the sake of ease of calculation but also because it could be justified in the limited field of the problems tackled, that is to say in the interpretation of the pK_a values of protonated conjugated bases such as the aza derivatives of benzene, naphthalene and anthracene[17, 21] or pyrrole.[22]

In these cases, the $(\gt\!N{-}H)^+$ group is a part of the π system itself of the "aromatic" ring and the substituent directly affects the electronegativity of nitrogen; this fact is reflected in the wide variation of pK_a (some units) of these protonated bases occurring when the position and nature of the substituent is varied.

In our case, pK values (even those of benzoic acids) show a relatively slight variation with the substituent and preliminary ΔE_π calculations, carried out using a PPP-type method[23] which had been successfully used in the study of chemical and physical π properties of a long series of "aromatic" molecules,[24] proved to be wholly inadequate to explain the difference in acidity between the various terms of the series.

Not even the *a priori* inclusion of solvation following the model proposed by Klopman[18] leads to acceptable results. We then considered the term ΔE_σ. Yonezawa, *et al.*,[25] in an attempt to interpret the pK of the α-amino acids of the proteins, used Hückel's method to calculate the energy of the protonated molecule and of the free base in the following way:

$$E = E_\pi + E_\sigma + \sum_{i>j} \frac{Q_i Q_j}{r_{ij}} e^2 \qquad (2)$$

In (2), E_σ is calculated as the sum of the energies of the σ bonds, which are considered as localized, according to Del Re's method,[26] and the third term accounts, by means of an electrostatic approximation, for the coulomb interaction energy not explicitly contained in Hückel's method.[27] Of course, Q_i derived from the sum of the σ and π net charges on the atom i and r_{ij} is the distance between the atoms i and j.

We have accepted this approximation for the calculation of E but in order to avoid the difficulty connected with the choice of a coherent set of parameters and to be able to account for a certain σ–π interaction in non-planar molecules like benzene-sulfinic acids, we preferred to use the Extended Hückel Theory (EHT).[28] It is a question of solving an LCAO MO problem using all valence-shell atomic orbitals and the complete matrix S of the overlap integrals in the calculation. Thus, in the usual matrix form:

$$\begin{aligned} HC &= SCE \\ C^{+}SC &= 1 \end{aligned} \tag{3}$$

In (3), the diagonal elements of the Hamiltonian matrix H are the ionization potentials of the atomic orbitals[29] and the non-diagonal elements are evaluated with Wolfsberg and Helmholz's approximation[30] as in (4):

$$H_{ij} = \tfrac{1}{2}K(H_{ii} + H_{jj})S_{ij};\ K = 1{\cdot}75 \tag{4}$$

Firstly, we performed a test calculation for benzoic acids using a programme supplied by QCPE[31] for an IBM 7094. In this calculation the structure of benzoic acid is the experimental one[32] while for the substituent groups the bond distances taken from the corresponding benzene derivatives were used. The atomic orbitals are Slater functions 2s, 2p for C, N, O, 3s, 3p for Cl and 1s for H.

The ionic dissociation energy of each acid is then evaluated in accordance with (2) as follows:

$$\Delta E = \Delta E(\text{EHT}) + \Delta\left(\sum_{i>j} \frac{Q_i Q_j}{r_{ij}} e^2\right) \tag{2}$$

Where ΔE(EHT) is the difference between the ground state energy of the base (B^-) and of the acid (BH) calculated as the sum of the mono-electronic energies (MO). This term does not therefore take into account the electronic interactions and virtually represents the ionic dissociation energy of a (O—H) bond leaving the molecular context out of consideration. For this reason we found a practically constant ΔE(EHT) for all the benzoic acids which is equivalent to 0·105 (a.u.). Thus, in order to explain the different acidities of these compounds one has to rely on the second term of Eq. (5) which represents the Coulomb interaction energy due to the net charges obtained from the "gross atomic populations".[33]

In reality, as suggested by Yonezawa, *et al.* the most significant parameter should be the simple electrostatic interaction between the proton and other atoms of the molecule. This simplification is valid if the relation (6) is valid:

$$\Delta\left(\sum_{i>j} \frac{Q_i Q_j}{r_{ij}} e^2\right) = C - \sum_{i} \frac{Q_H Q_i}{r_{Hi}} e^2 \tag{6}$$

where C is a constant.

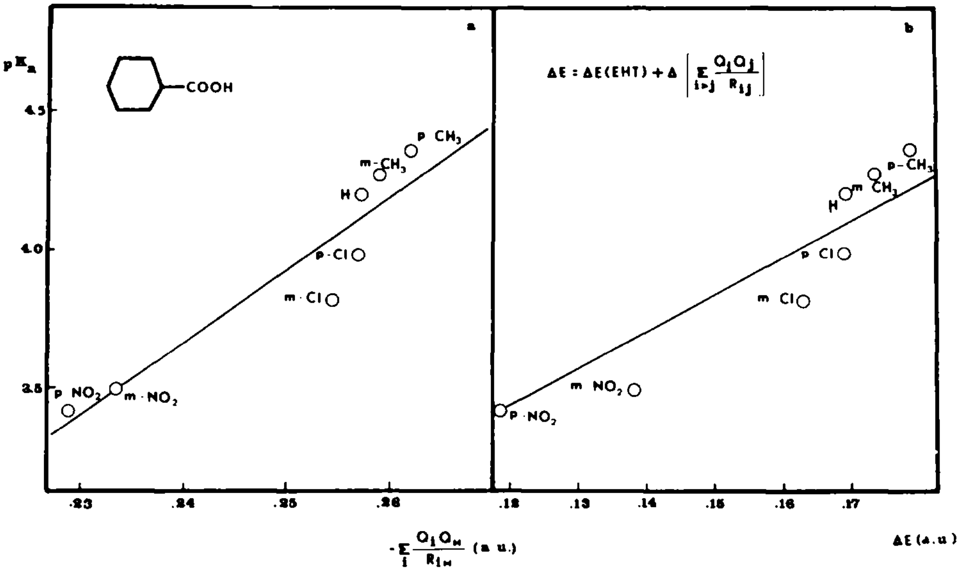

Fig. 3 Correlation between p*K* of benzoic acids and theoretical acidity indexes.

In Fig. 3 we show the p*K* values of benzoic acid and its *meta*- and *para*-derivatives (—CH_3, —Cl, —NO_2) against the parameter

$$-\sum_{i} \frac{Q_i Q_H}{R_{iH}}$$

(Fig. 3a) and ΔE (Fig. 3b) (Eq. 5), both expressed in atomic units. Two facts may be observed:

(i) The proportionality between p*K* and ΔE is satisfactorily verified;

(ii) In our scheme the interaction exerted on the proton by the other atoms of the molecule (Fig. 3a) can be assumed to be the acidity index and it is to this parameter we henceforth refer in the present study.

One might therefore conclude that, given a series of acids of a similar and experimentally determined structure, the procedure adopted by us allows one to predict a scale of p*K* values in qualitative agreement with the experimental. Consequently, the ΔE_{Sol} (Eq. 1) should have a practically constant effect on all the terms of the series.

If this conclusion is correct, the only parameter to fix in order to explain the different behaviour of benzoic and benzene-sulfinic acids, with respect to the substituent effect on the p*K* values, is the structure of the latter.

The structure is certainly not planar (c.f. all the oxygenated compounds of sulphur: sulfones, sulfoxides, etc). We tentatively adopted structure 1 of Fig. 4 obtained by tilting the plane of the O atoms ~54° with respect to the plane of the benzene ring and using $\widehat{OSO}$, $\widehat{OSC}$ bond angles of ~109° (sp^3-type hybridisation of the S atom). The bond distances chosen for the —SOOH group are $r_{SO} = 1{\cdot}44$ (Å), $r_{SO(H)} = 1{\cdot}49$ (Å) and $r_{SC} = 1{\cdot}74$ (Å), while a value was assigned to the other distances equal to the corresponding value in the benzoic acid series. Taking this model as working hypo-

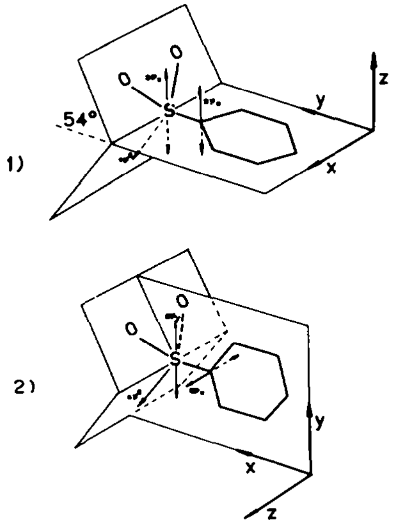

FIG. 4 Structures used in the calculations for benzene-sulfinic acid. Hydrogen atoms are not drawn in this figure for the sake of simplicity; the proton is situated in the plane of SOO group and it is bonded with an oxygen atom in accordance with an IR study by Detoni and Hadzi (43).

hypothesis, we used the QCPE 64 programme to perform calculations for all the benzene-sulfinic acids studied, with the usual basis of pure atomic orbitals (3s, 3p for S). In this way we excluded any effect due to a possible valence-shell expansion of sulphur. This limitation is justified in our case; in fact the chemical properties should mainly be related to the availability of a lone-pair. The results of this calculation are shown in Table 2 labelled with the letter A as are the corresponding results for benzoic

TABLE 2. COMPARISON BETWEEN THE VALUES OF OUR INDEX OF ACID STRENGTH AND EXPERIMENTAL pK ($\mu = 0$) FOR BENZOIC AND BENZENESULFINIC ACIDS.

Benzoic acids	$-\sum_i \frac{Q_iQ_H}{R_{iH}}$ (a.u.)		pK	benzensulfinic acids	$-\sum_i \frac{Q_iQ_H}{R_{iH}}$ (a.u.)			pK
	A	*B*			A	*B*(1)	*B*(2)	
C_6H_5–COOH	$0{\cdot}257_1$	$0{\cdot}259_3$	4·20	C_6H_5–SOOH	$0{\cdot}263_1$	$0{\cdot}288_2$	$0{\cdot}265_7$	2·76
p-CH_3	$0{\cdot}262_2$	$0{\cdot}259_5$	4·37	p-CH_3	$0{\cdot}265_8$	$0{\cdot}288_3$	$0{\cdot}265_8$	2·80
p-Cl	$0{\cdot}257_0$	$0{\cdot}257_4$	3·98	*p*-Cl	$0{\cdot}261_7$	$0{\cdot}299_0$	$0{\cdot}261_4$	2·76
p-NO_2	$0{\cdot}229_1$	$0{\cdot}230_9$	3·42	*p*-NO_2	$0{\cdot}186_0$	$0{\cdot}240_8$	$0{\cdot}240_0$	2·77
				p-CH_3O	$0{\cdot}263_6$	$0{\cdot}301_5$	$0{\cdot}265_1$	2·72
m-CH_3	$0{\cdot}259_1$	$0{\cdot}259_5$	4·27	*m*-CH_3	$0{\cdot}265_0$	$0{\cdot}288_3$	$0{\cdot}265_8$	—
m-Cl	$0{\cdot}254_6$	$0{\cdot}254_6$	3·82	*m*-Cl	$0{\cdot}260_6$	$0{\cdot}293_0$	$0{\cdot}261_2$	2·68
m-NO_2	$0{\cdot}233_6$	$0{\cdot}235_6$	3·49	*m*-NO_2	$0{\cdot}232_0$	$0{\cdot}270_8$	$0{\cdot}242_5$	2·81

A—EHT calculation (programme QCPE 64). For benzensulfinic acids we have used structure 1 of Fig. 4.
B—EHT calculation following the approximation: $\psi_{tot} = \phi_\sigma \cdot \phi_\pi$ where ψ_σ is a product of bond orbitals based on a set of canonical hybrid atomic functions; (1) and (2) figures refer to use of the structures 1 and 2 (Fig. 4) respectively for benzensulfinic acids.

acids. The behaviour of the theoretical acidity index for sulfinic acids is in sharp contrast with experiment, in so far as it shows differences of acidity between the various terms of the series which are qualitatively similar to those of benzoic acids and quantitatively much more marked. A reason for this failure may be due to the fact that, despite the tilting of the plane of the O atoms, and because of the use of pure atomic orbitals, the overlap integrals between the $3p_z$ orbital of sulphur and the $2p\pi$ orbitals of the C atoms of benzene are unchanged with respect to a planar structure and thus conjugation has considerable influence. A different result, even if qualitatively similar, would be obtained by tilting the benzene plane in relation to the plane of the —SOOH group. This, as is pointed out by Pople, *et al.*,[34] depends on the fact that the EHT calculation is not invariant under a rotation of local axes.

It will therefore be necessary to choose hybrid orbitals as basis functions so as to fix a precise direction of the lone-pair of the S atom and thus avoid absurd results. Taking into account the degree of approximation of the calculation we used a simple basis of canonical hybrids (sp^2 for C, N, O, Cl; sp^3 for S and C of the CH_3 group). We believe that the use of more specific hybrids for the molecules in question, for example, those defined with the criterion of the maximum localization,[35] may at most bring about a slight quantitative improvement and yet not occasion any inversion in the results. First of all a test calculation with hybrid orbitals was performed for benzoic acids. It was assumed, as usual, that the localization is complete and therefore the overlap matrix is factorized in as many 2×2 blocks as there are σ bonds plus a block corresponding to the fully delocalized π system. The results, obtained using a computer programme written by us, are shown in Table 2 (column B). It may be seen, as expected, that for benzoic acids the transformation of the basis of AO's does not bring about any qualitative change in the results (with the complete localisation of the σ bonds only the effect of the Me groups is lost). For benzene-sulfinic acids, a problem arises as regards "π" overlaps. If the structure **1** (Fig. 4) is maintained, in passing from a basis of pure atomic orbitals (calc. A) to one of hybrid orbitals the overlap between the non-linked sp^3 orbital of the S atom and the $2p\pi$ orbital of the adjacent C atom decreases very little (from $\sim 0{\cdot}17$ to $\sim 0{\cdot}14$), while the corresponding overlap between the S atom and O atoms increases appreciably (from $\sim 0{\cdot}08$ to $\sim 0{\cdot}12$). In this case the criterion of the complete localization is not justified and the conclusion may be reached that the lone-pair of S atom makes possible a "π conjugation" between the benzene ring and O atoms. The results of a calculation using structure **1** (Fig. 4) and the complete π overlap matrix are shown in Table 2 (column B(1)). The effect of the conjugation is reflected in the wide differences in acidity predicted by calculation B(1) between variously substituted benzene-sulfinic acids, in contrast with experiment. One should therefore conclude that the results of calculation A are due not only to a failure of the method but also to the structure assigned to benzene-sulfinic acids (Fig. 4.1). With the basis of atomic orbitals used by us the only structure that justifies *a priori* the experimental data is that suggested in Fig. 4.2, where the plane of SOOH group is rotated through 90° with respect to the plane of the benzene ring. In this way, of course, overlaps between the sp^3 orbital of S atom and $2p\pi$ orbitals of the benzene ring are equal to zero and conjugation is completely impeded.

The results of the calculation based on structure **2** of Fig. 4 are shown in Table 2 and labelled with the symbol B(2). It may be seen that this calculation provides a satisfactory explanation of the insensitivity of the p*K* of benzene-sulfinic acids to the position of the substituent, while a residual difference of acidity is still foreseen between the benzene-sulfinic acid and its nitro and chlorine derivatives.

This result may be due to the overstimation of charge polarizations (characteristic of the EHT method) which a strong electron donor or acceptor substituent brings about in the benzene ring and which causes long-range interactions which are too high. However, to conclude, we believe that the pK of benzene-sulfinic acids may be explained by admitting that the "lone pair" of the S atom is not available for a conjugation between π electrons of the benzene ring and those of the O atoms of the (—SOOH) group. Such an interpretation is also in agreement with information obtained from a comparison of the UV spectrum (in EtOH and in H_2O) of benzene-sulfinic acid with that of benzoic acid.[36] Indeed, the red shift of the characteristic benzene bands α and p(^1L_b, ^1L_a), which is considerable in benzoic acid, appears negligible in benzene-sulfinic acid.

Whether the structure we had to use for the calculation (Fig. 4,2) in order to justify the experimental data is realistic or not is uncertain, according to the following arguments. If one admits that the C—S bond is practically a simple bond then the most probable structure will be that for which the interaction energy between non-bonded atoms is minimum. In our scheme this energy is accounted for by the term $\sum_{i>j} \frac{Q_iQ_j}{r_{ij}}.e^2$ of Eq. 2. In Fig. 5 is shown the variation of this term as the rotation angle between the plane of SOOH group and that of the benzene ring goes from zero to 180°; it may be seen that, according to this calculation, the most probable structure

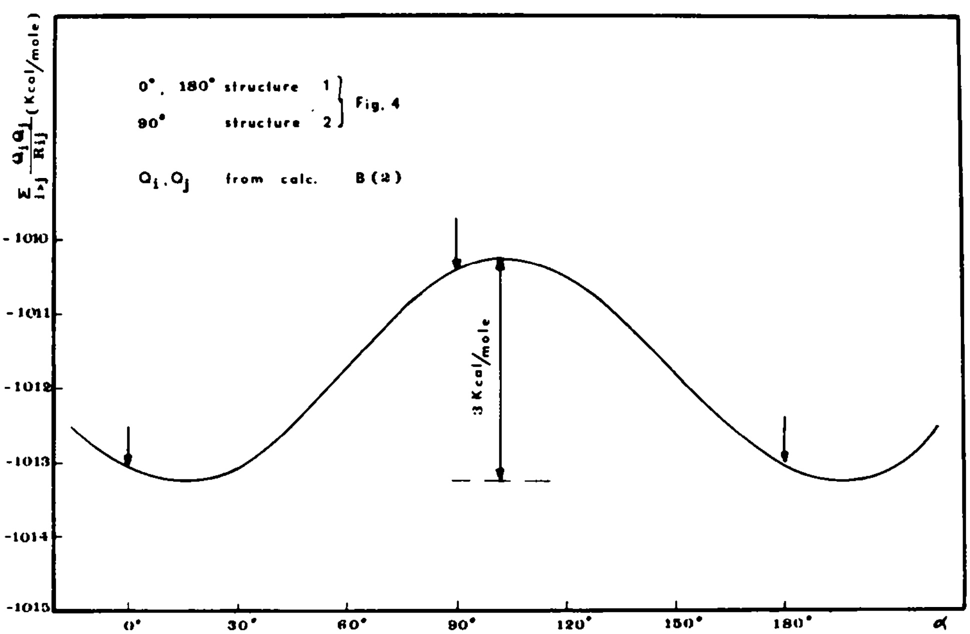

FIG. 5 Plot of coulomb interaction energy of benzene-sulfinic acid against the rotation angle between the plane of SOOH group and that of benzene ring.

should be one which is very close to structure **1** (Fig. 4), even if the difference in energy between structures **1** and **2** is not very large (~3 K cal/mole). If this conclusion is accepted the non-availability of the lone-pair of sulphur for π "conjugation" is not accounted for by the calculation; it could be due to other causes that arise in solution or to the fact that the lone-pair of sulphur must be considered almost completely localized. As far as any participation by the d orbitals of sulphur is concerned it must be said that the two structures are equivalent as in both cases the S atom has a d_{yz} orbital of π symmetry.[37]

Finally, we must point out that our acidity index for the isolated molecule predicts a dissociation energy for benzoic acids which is slightly lower than that of benzene-sulfinic acids. This is only in apparent contrast with the experiment. For if, following Daudel's suggestion,[17] we calculate the variation of solvation energy during dissociation according to the formula (7):

$$\Delta E_{\mathrm{Sol}} = -\Delta\left\{\sum_i \frac{Q_i^2}{2r_i}\left(1 - \frac{1}{D}\right)\right\} \tag{7}$$

(where r_i is the effective ray of the atom i and D is the dielectric constant of the solution) we find that, independently of the type of calculation (A, B), the ΔE_{Sol} of sulfinic acids is greater than that of benzoic acids (~1 (eV)). This implies that solvation favours the dissociation of benzene-sulfinic acids more than that of benzoic acids and this can explain the greater acidity of the former. As was foreseen, no significant variations were found between the ΔE_{Sol} values of the various components in each series.

EXPERIMENTAL

Benzene-sulfinic and benzene-seleninic acids are crystalline solids, white or pale-yellow, fairly soluble in water and very soluble in methanol or ethyl ether.

Preparation

(A) Benzene-sulfinic acid was obtained by heating benzene and SO_2 in the presence of $AlCl_3$.[38] The crude product was precipitated with cold H_2SO_4 (HCl is not advisable as it promotes decomposition).

(B) *para* Substituted sulfinic acids *p*-CH_3-, *p*-Cl-, *p*-Br-, *p*-CH_3O-, *m*-NO_2- and *p*-NO_2 were obtained from the corresponding sulfonyl chlorides by reduction with Zn powder or by means of a soln of Na_2SO_3.[39, 40] The crude product was precipitated with cold H_2SO_4.

(C) The *m*-Cl and *m*-NO_2 compounds were prepared by saturating a soln of the corresponding diazonium sulfate with SO_2 at 0° and reaction in the presence of Cu powder, and separation of the sulfinic acid.[41] The resulting products, were very impure and the yield was poor. *meta*-Substituted acids are better prepared by reaction at 45° between diazonium salt and potassium ethylxanthate, the product being hydrolysed by alkali. Acidification of the thiophenate thus obtained yielded the corresponding thiophenol which was oxidized with Cl_2 and the sulphinic acid separated by subsequent alkaline hydrolysis.

(D) The benzene-seleninic acids were prepared by reacting 0·95 moles of finely ground, dry selenium with 1 mole of the corresponding PhMgBr in the dark in a stream of deoxygenated N_2 and under vigorous stirring. The mixture was decanted by nitrogen pressure onto excess ice and treated with 2 moles cold conc HCl. The selenophenol thus obtained was not separated but oxidized in a stream of O_2, ether being eliminated and diselenide being precipitated. After recrystallization from ether, it was slowly oxidized in dioxan soln with 6 moles of 33% H_2O_2 at 0° and under vigorous stirring.

Purification

(A) *para*- and *meta*-Substituted sulfinic acids were purified by extracting the crude product with ether and crystallizing repeatedly from this solvent. *meta*-Substituted acids were also purified by dissolving in conc Na_2CO_3aq, and reprecipitation with cold conc H_2SO_4, extraction with ether and recrystallization.

The acids being unstable were stored as sodium salts, obtained by neutralization of MeOH solns with NaOMe and subsequent crystallization.

(B) Crude benzene-selenic acid was dissolved at 80° in the minimum quantity of water, filtered hot, decolourized several times with Norite and slowly crystallized by ice-cooling. The treatment was repeated three times.

(C) *para*-Substituted selenic acids, which are not sufficiently soluble in water to purify as outlined, were dissolved in 10% excess of NH_3 (15M) filtered, decolourized, slowly precipitated with HCl (6N) washed with water at 0° and, finally, dissolved in MeOH and reprecipitated with excess hot water. The treatment was repeated several times.

All the acids were dried in vacuum on drierite.

The purity of the sulfinic acids was determined by means of potentiometric titration with 0·1N NaOH or by means of oxidimetric reactions using the method reported by Lindberg.[42] The equivalent weights obtained did not differ from the theoretical weight by more than 1%.

The equivalent weights of the seleninic acids were determined by potentiometric titration with 0·1N NaOH or by reaction with KI in acid and titration of the iodine by the dead-stop method; seleninic acid oxidizes the iodide quantitatively according to the reaction:[14]

$$2\,X\text{-}C_6H_4SeO_2H + 6\,KI + 3\,H_2SO_4 \longrightarrow (X\text{-}C_6H_4Se\text{-})_2 + 4\,H_2O + 3\,I_2 + 3\,K_2SO_4$$

Determination of pK

Freshly prepared samples of each acid (from 5 to 80 mg) were dissolved in 50 ml of 11 solutions of $NaClO_4$ having an ionic strength in the range 3·0–2·5 10^{-3} and then titrated with carbonate-free 0·1N NaOH at most 1 hr from the moment of their preparation. From 1 to 2 ml NaOH were used in the titration, the quantity being measured with a microburette with 1/100 ml markings. In the case of substituted benzeneseleninic acids, which are not very soluble in water, 2 ml MeOH was added (for the calculation of p*K* a constant correction was evaluated which was lower than the average deviation of the results).

All solns were prepared with twice distilled water in a stream of N_2, conserved in polythene containers and drawn off under pressure of the same gas. Titration was also carried out in a N_2 stream so as to exclude any contact with the atmosphere.

The temp of the cell was maintained constant by use of a constant-temp bath (±0·05°). Titration was followed with a glass electrode (ref. Ag/AgCl) and a Polymetron 42B or G.P. Dat 2002 pH-meter, with precision of ±0·01 pH unit. Every titration was repeated at least twice obtaining more than 2000 experimental values for each acid.

Processing the data

The results of the experimental measurements were processed using a special programme for an IBM 1620 designed to extract an average p*K* value from all values not differing from one another by more than 5% (generally the discarded experimental values represented only a very small fraction). At the same time the programme calculated the value of the ionic strength corresponding to each point of the titration, taking into account the different concentration of sulfinite or seleninite formed and considering the remaining acid fraction to be non-dissociated. The ionic strength was practically constant throughout titration.

The p*K* values obtained can be reproduced with an average deviation of about ±0·07 p*K* units.

Stability of the solutions

Solns of benzene-sulfinic and benzene-seleninic acids with an ionic strength of 0·25 and 1·0 respectively were maintained at 25° under N_2 for more than 400 hr. Samples of the solns were taken at different intervals and titrated by the methods previously described, the corresponding p*K* values being calculated. The results obtained are shown in Fig. 2. The solutions were stable for much longer than is necessary for the execution of each measurement.

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