Spectral Behaviour of 2-(Arylsulphinyl)acetophenones & A Study of Their Substituent Effects & Ionization Constants

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UV spectra of 2-(phenylsulphinyl)acetophenones(I-V) have been recorded in various organic solvents. A band around 240-288 nm has been assigned to l_{L_b} transition and charge - transfer. Ionization constants, pK_a, have been determined spectrophotometrically in 60% (v/v)ethanol. Excellent linear correlations are obtained when pK_a values are plotted against the substituent constants σ_x and the polar substituent constants $\sigma_x^* C_6H_4$ for substituted phenyl group. The linear relations are represented by equations, $pK_a = 10.67 - 2.03\ \sigma_x$ and $pK_a = 11.71 - 1.85\ \sigma_x^*\ C_6H_4$ respectively. The pK_a values have also been correlated with the extended Hammett equation. The correlation follows the equation; $pK_a = 10.743 - 1.826\ \sigma_{I\ x} - 1.956\ \sigma_{R\ x}$. The characteristic IR bands have been assigned and correlated with the substituent constants σ_x.

ALTHOUGH sulphoxides are an interesting group of compounds, they have not been investigated as extensively as the sulphides or the sulphones[1-5]. Chelating ability, NMR and IR spectra and acid properties of some β–keto sulphoxides have been previously investigated[6-9]. However, little attention has been paid to the spectral behaviour of such compounds in organic solvents and to the relationship between the substituent and acid dissociation constant, pK_a. β-Keto sulphoxides behave as mono acids. In aqueous alkaline solution they dissociate and form the corresponding carbanions :

$$Ph-SO-CH_2-CO-Ar + B \overset{K}{\rightleftharpoons} Ph-SO-\bar{C}H-CO-Ar + HB^+$$
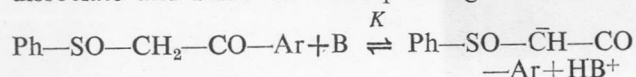
The present investigation is devoted to the preparation and study of a series of β-ketosulphoxides (I—V) on the basis of UV and IR spectral methods.

$$C_6H_5 - SO - CH_2 - CO - C_6H_4\ X$$
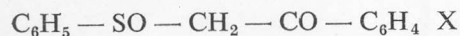
X = H(I), 4-CH$_3$O(II), 4-CH$_3$(III), 4-Br(IV) and 4-NO$_2$(V). Correlation of their ionization constants has been attempted using the simple and extended Hammett Eqs 1 and 2 respectively.

$$Q_x = \sigma_x + h \qquad ..(1)$$
$$Q_x = \alpha\ \sigma_{I,x} + \beta\ \sigma_{R,x} + h \qquad ..(2)$$

Materials and Methods

Infrared spectra of the solid compounds were recorded in KBr using a Pye-Unicam SP 1000 spectrophotometer. Electronic absorption spectra were recorded on Beckman DK 2 and Pye-Unicam SP 1000 spectrophotometers. Microanalysis were performed at the Microanalytical Unit, Faculty of Science, University of Cairo. 2-(Phenylsulphinyl)aceto-

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phenone derivatives (I-V) were prepared following the recommended procedures[10-13]. Their melting points agreed well with the literature data. The UV and the IR spectra of the compounds prepared are summarized in Tables 1, 3 and 6. A radiometer pH meter type 63 fitted with a combined glass electrode type GK 2301 C was employed for the determination of pH. The instrument was accurate to $\pm$ 0.01 pH unit. Measurements of pH* values of partially aqueous solvents were carried out according to Bate et al.[14]; $pH^* = pH_{(R)} - \delta$. The values of δ for partially aqueous mixtures were obtained from the data given by Douheret[15], Ong[16] and Van Veen[17]. The experimental values were corrected in each case and the ionic strength was adjusted to 0.10 at 30 $\pm$ 0.10°. The acid dissociation constants of (I-V) were evaluated spectrophotometrically and the values of pK_a were calculated using the modified limiting absorbance method[18] and Colleter's method[19]. Each compound was subjected to, at least, ten pK_a determinations, and the average values (Table 3) are accurate to $\pm$ 0.01-0.03 pk_a units.

Results and Discussion

The UV absorption spectra of the compounds I-V were scanned in ethanol, chloroform, CCl$_4$ and cyclohexane. The spectra exhibit one broad band near 260 nm. However in some cases two bands (A and B) are observed, the former band (A) lies near 220 nm while the second one (B) is a broad band in the region 240-288 nm (Table 1). The first notable observation is that even saturated sulphoxides have an absorption band near 220 nm in ethanol, with a relatively low absorptivity of about 1500. The same band occurs in methyl, 2-methylallyl and diallyl sulphoxides although with somewhat increased intensity[20]. In these compounds this band is strongly solvent-dependent and was assigned to n-π* transition[20]. In dibenzyl sulphoxide[21] the characteristic l_{L_b} band of the phenyl chromophore
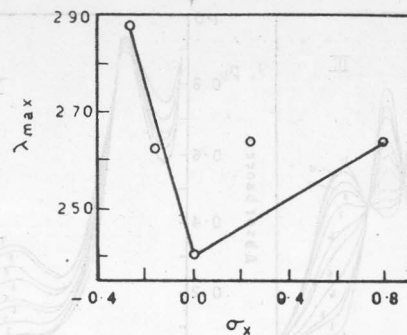
TABLE 1 — ABSORPTION SPECTRA OF 2-PHENYLSULPHINYL ACETOPHENONES IN DIFFERENT ORGANIC SOLVENTS

Compound	Solvent	Band A		Band B	
		$\lambda_{max.}$	$\epsilon_{max} \times 10^{-3}$	λ_{max}	$\epsilon_{max} \times 10^{-3}$
I	Ethanol	220	18.33	240	20.36
	Cyclohexane	218	15.70	243	18.01
II	Ethanol	222	25.90	288	30.50
	Chloroform			290	26.97
	Carbon tetrachloride			285	28.66
	Cyclohexane	223	24.50	284	28.01
III	Ethanol	221	23.00	261	26.67
	Chloroform			265	
	Cyclohexane	220	25.20	258	27.90
IV	Ethanol	215	20.50	264	24.00
	Chloroform			269	24.50
	Carbontetra chloride			268	24.00
	Cyclohexane	218	17.12	266	21.60
V	Ethanol	211	16.75	264	20.00
	Chloroform			266	22.01
	Carbon tetra chloride			264	23.37
	Cyclohexane	215	17.83	262	21.80

Fig. 1 — Correlation of λ_{max}. of band B with Hammett substituent constants, σ_x.

transitions found in the molecule are mainly due to the phenyl rings and the benzoyl system. Also, the band suffers a shift in its position due to changing the polarity of the solvent. Thus, the band B corresponds to l_{Lb} state of the phenyl rings as well as to π–π^* transition of the carbonyl group influenced by charge-transfer originating from the substituted phenyl ring to the carbonyl group as acceptor. The support for the charge-transfer character of this band can be gathered by computing the energy of charge-transfer using Eq. 3 (ref. 22–24).

$$E_{C.T.} = (I_p - E_A) + C \qquad ..(3)$$

The experimental values of the energy of charge-transfer in ethanol and cyclohexane coincide fairly well with those calculated (Table 2). The charge-transfer interaction can be represented as follows :
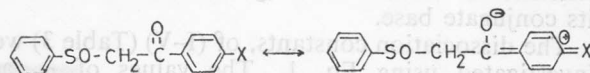
The UV spectra of I-V in solutions, containing 60% (v/v) ethanol, of varying pH values are represented in Fig. 2. The spectra in acidic solutions of pH < 3 are characterised by a strong band at 250, 245, 263 and 262 nm in I-IV respectively. This band is due to absorption of the non-ionized molecules liable to exist in such solutions. The absorption of this band decreases gradually while a new band appears around 300 nm with increasing pH attaining a limiting value at pH 11–12. The spectrum of V displays a strong band at 234 nm in solutions of pH < 3. The band is slightly influenced as the pH value of the solution increases while a new band starts to appear

is observed with typical vibrational structure at 260 nm in ethanol. The l_{La} band occurs at 222 nm and the n–π^* transition of the dialkyl sulphoxides apparently is hidden below the l_{La} band, or may be responsible for a shoulder at 215 nm. In cyclohexane the l_{La} band is almost unaffected, and the l_{Lb} transition only appears as a shoulder at 265 nm. This broadness of the l_{La} band may be due to the n–π^* bands, occurring at longer wavelength in the less polar solvent (somewhere in the region 230–240 nm), which are poorly resolved[21]. The spectra of the aryl alkyl sulphoxides and diaryl sulphoxides are a good deal more complicated, particularly since considerable solvent effects come into play. Diphenyl sulphoxide has been reported to have two absorption bands at 226 and 267 nm in cyclohexane, and at 233 and 265 nm in ethanol[21]. It is suggested that they are due to strongly perturbed l_{La} and l_{Lb} transitions respectively. Close examination of the spectra in cyclohexane and in ethanol, suggests that the n–π^* transition occurs between the l_{La} and l_{Lb} bands, at about 250 nm in cyclohexane and is shifted below the l_{La} band in ethanol.

The band (A) located near 220 nm in the spectra of compounds (I-V) in ethanol and cyclohexane may be possibly interpreted as arising from the l_{La} band of benzene with, however, very considerable perturbation due to two-fold resonance interaction with the sulphoxide group. The band is characterised by ϵ_{max} values of 20,000 litre mole^{-1} cm^{-1}. It suffers a slight red shift on going from ethanol to cyclohexane. The second broad band (B) observed at 240–288 nm in ethanol shows a bathochromic shift whether the substituent is an electron donor or acceptor. This fact can be supported by the plot of λ_{max} versus Hammett substituent constants σ_x (Fig. 1). The band has high absorptivity value indicating its π–π^* nature. The assignment of this band can be made on the basis that the SO and CH$_2$ groups act as insulaters for the two phenyl rings. Thus, the possible

TABLE 2 — ENERGY OF THE CHARGE-TRANSFER BAND FOR 2-(PHENYLSULPHINYL) ACETOPHENONES

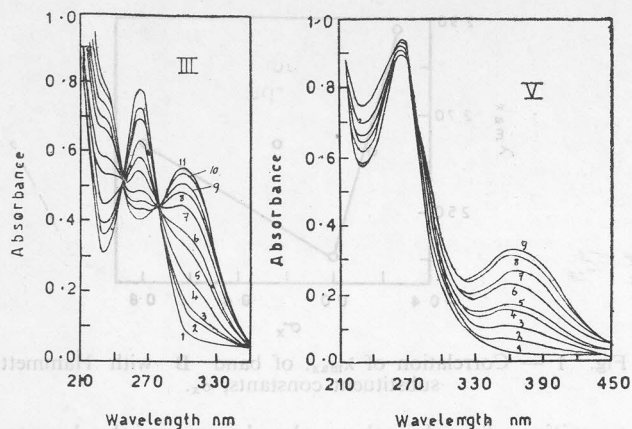| Compound	Energy (eV)		
	Calc.	Exp.	
		Ethanol	Cyclohexane
I	5.04	5.17	5.11
II	4.02	4.31	4.37
III	4.78	4.81	4.81
IV	4.72	4.70	4.67
V	4.62	4.70	4.74

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Fig. 2 — Absorption spectra of compounds III ($5 \times 10^{-5}M$) and V ($5.56 \times 10^{-5}M$) at 30°C and different pH values in 60% (v/v) ethanol [Compound III : curve (1), pH = 3.0; curve(2), pH = 9.90; curve (3), pH = 10.05; curve (4), pH = 10.35; curve(5), pH = 10.65; curve (6), pH = 10.80; curve (7), pH = 11.05, curve (8), pH = 11.25; curve(9), pH = 11.45; curve (10), pH = 11.75, curve (II), pH = 12.0. Compound V : curve(I), pH = 2.80; curve (2), pH = 8.25 curve (3), pH = 8.80; curve(4), pH = 9.00; curve (5), pH = 9.15; curve(6), pH = 9.25, curve (7), pH = 9.65; curve (8), pH = 10.20 curve (9), pH = 11.80].

Fig. 3 — Dependence of absorbance of 2-(Phenylsulphinyl) acetophenones (I-V) on pH

at longer wavelengths exhibiting a maximum at 360 nm. The spectra are characterised by two isobestic points around 250 and 280 nm. The absorbance-pH curves (Fig. 3) obtained at various wavelengths are characterised by one inflection similar to the dissociation or association curves according to whether the chosen wavelength is of the acid form or its conjugate base.

The dissociation constants, of (I–V) (Table 3) were investigated using Eq. 1. The values of σ_x and $\sigma^*_{x\,C6H4}$ were taken from the work of Ritchie and Sager[25] and Nagai et al.[26]. As shown in Fig. 4, excellent linear relations were obtained in both cases when the data of compounds I-V were utilized. The regression lines expressing such correlations follow Eqs. 4 and 5 respectively.

$$pK_a = 10.67 - 2.03 \, \sigma_x \quad (r = 0.997; \; s = \pm 0.08) \quad ..(4)$$

$$pK_a = 11.71 - 1.85 \, \sigma^*_{xC6H4} \quad (r = 0.990; \; s = \pm 0.05) \quad ..(5)$$

The slopes and intercepts were computed by the method of least squares[27]. The values of s and r

Fig. 4 — Correlations of acid dissociation constants, pK_a, of 2-(phenylsulphinyl)acetophenones with the substituent constants, σ_x (A) and $\sigma^*_{xC_6H_4}$ (B)

in both cases indicate that the pK_a values correlate well with the substituent constants σ_x and $\sigma^*_{xC_6H4}$. Also, the ionization constants of I-V were correlated with the extended Hammett Eq. 2 by multiple regression analysis[28]. The data used in the correlation are given in Table 4. For the para substituents, the $\sigma_{I,x}$ were taken from the collection of Taft and coworkers[29]; the $\sigma_{R,x}$ constants were obtained from the following relation (Eq. 6).

$$\sigma_{R,x} = \sigma_{p,x} - \sigma_{I,x} \quad ..(6)$$

The results of the correlation with Eq. 2 are presented in Table 5. The values of the multiple correlation of 0.999 indicates an excellent correlation.

The pK_a values of β-keto sulphoxides are higher than those of the corresponding β-keto sulphones[20]. Thus, the greater acidities of latter can be explained in terms of the greater electron withdrawal character of the sulphone than the sulphoxide group.

The IR spectra of compounds I-V were recorded in KBr. The CH$_2$ group and the alkyl substituents

TABLE 3 — SPECTRAL DATA IN 60% (v/v) ETHANOL SOLUTIONS OF VARYING pH VALUES AND IONISATION CONSTANTS, pK_a, OF 2-(PHENYLSULPHINYL)ACETOPHENONES

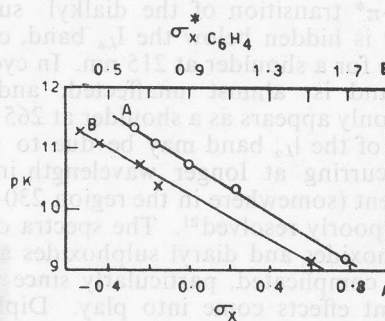| Compound	Neutral form (pH, 2 -3)		Anion (pH,11-12)		pK_a*	$\triangle G^*$ (kcal/mol)
	λ_{max}	$\epsilon_{max} \times 10^{-3}$	λ_{max}	$\epsilon_{max} \times 10^{-3}$		
I	250	14.75	306	9.62	10.69	14.90
II	240	14.30	285	16.50	11.35	15.82
III	264	15.70	305	11.00	11.10	15.47
IV	262	22.00	310	9.66	10.39	14 48
V	263	16.45	360	5.75	9.17	12.78

*Standard deviation = ± 0.01 - 0.03.

TABLE 4 — SUBSTITUENT CONSTANTS USED IN THE CORRE-
LATIONS WITH IONISATION CONSTANTS, pK_a, OF SUBSTITUTED
2-(PHENYLSULPHINYL) ACETOPHENONES.

Compound	σ_x	σ_{Ix}	σ_{Rx}	$\sigma^*_{xC_6H_4}$
I	0.00	0.00	0.00	0.58
II	—0.27	0.27	—0.54	0.36
III	—0.17	—0.04	—0.13	0.46
IV	0.23	0.44	—0.21	0.74
V	0.778	0.65	0.12	1.50

TABLE 5 — RESULTS FOR CORRELATION WITH EQ. 2.

Parameter	value	Parameter	value
— α	1.826	S_α	0.02
— β	1.956	S_β	0.03
h	10.743	S_h	0.03
R	0.999		

R = Multiple correlation coefficient
S_α, S_β and S_h are the standard errors of estimate in α, β,
and h respectively; number of points = 5.
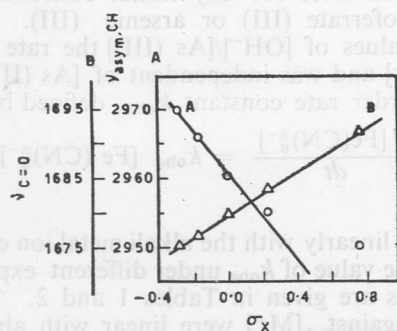
Fig. 5 — Correlations of ν_{as} CH(A) and $\nu_{C=O}$ (B) with the substi-
tuent constants, σ_x.

give rise to two characteristic bands at 2950-2970
and 2855-2880 cm^{-1} corresponding to the in-plane
and out-of-plane vibrations of the hydrogen atoms[31,32].
The plot of Hammett substituent constants, σ_x
versus ν_{as} CH$_2$ (Fig. 5) is linear indicating that the
frequency decreases as the acceptor character of the
substituent increases[33]. This result is in agreement
with the higher acidities of the compounds containing
the acceptor groups. The IR spectra show also two
bands arising from the bending mode of the hydrogen
atom about the carbon atom, the asymmetrical
mode occurring in range 1467-1452 cm^{-1} while
the symmetrical mode occurs in the range 1365-
1380 cm^{-1} (ref. 34). A strong band occurs in the range
1675-1692 cm^{-1} which is associated with the stretch-
ing vibration of the carbonyl group. The plot of
$\nu_{C=O}$ versus the Hammett substituent constant
(Fig. 5) is linear with a positive slope indicating the
direct interaction between the substituted phenyl

ring and the carbonyl group. A strong to medium
intensity band appears near 1040 cm^{-1} and it can be
attributed to the $\nu_{S=O}$ mode[35] while the ν_{C-S} band
is observed as a weak absorption around 660 cm^{-1}
(ref. 35, 36).

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