

Potentiometric & Spectrophotometric Determinations of Dissociation Constants of β -Diketoarylazo Compounds

MAMDOUH S. MASOUD*, A. M. KADDAH, A. M. KHALIL & N. I. TAWFIK

King Abdulaziz University, Faculty of Science, Chemistry Department, P.O. Box 1540, Jeddah, Saudi Arabia

Received 30 June 1978; revised 12 December 1978; accepted 2 February 1979

The dissociation constants of some β -diketoarylazo compounds have been determined potentiometrically and spectrophotometrically in 50 vol % ethanol-water medium at $25 \pm 0.1^\circ$ and an ionic strength of 0.1. The behaviour of these compounds is related to the nature of the substituent, based on spectral measurements.

ALTHOUGH biological activity and dyeing properties of some diacyl and/or arylmethane azo dyes have been reported¹⁻⁶, not much work has been reported on their structural chemistry. In the present work we have carried out spectrophotometric (electronic, IR, NMR and mass) and potentiometric studies in order to have deeper insight into the structures of these compounds.

Materials and Methods

A general method of preparation was based on coupling acetylacetone, benzylacetone and dibenzoylmethane with appropriate diazonium salt in cold sodium hydroxide solution⁴. The crude product was recrystallized from ethanol to give the corresponding azo compounds in good yields.

Infrared spectra were taken in KBr on a Pye-Unicam SP 1100 spectrophotometer and electronic absorption spectra on a Pye-Unicam SP 500 spectrophotometer. PMR and the mass spectra were recorded at the Chemistry Department, Austin University, Texas, USA.

A radiometer pH meter type 28 was used to record the pH of the solution with an accuracy of ± 0.01 pH units. The pH meter readings (B) recorded in ethanol-water solutions were corrected for non-aqueous solvent by the method of Van Uitert and Haas⁷. The readings were made on a series of solutions containing known amounts of HCl and NaCl with an ionic strength of 0.1 in 50 vol % ethanol-water medium at $25 \pm 0.1^\circ$. Ligand solution (10 ml, $1 \times 10^{-3}M$) was mixed with NaCl solution ($\gamma = 0.1$) and transferred to the titration cell. A stream of nitrogen gas was passed to remove the traces of O_2 and CO_2 . The titrant ($10^{-2}M$ NaOH) was added in instalments of 0.05 ml and each titration repeated twice to check the reproducibility (± 0.01 pH units).

All the other reagents were made from high-purity materials or purified reagents, and all solutions were prepared in deionized water.

Results and Discussion

Table 1 lists the compounds under investigation

with their m.p.s, colours, λ_{max} , $\log \epsilon_{max}$ and pK_a values.

The electronic spectra of these compounds at different pH values exhibited intense bands corresponding to $\pi \rightarrow \pi^*$ transitions. Different spectrophotometric methods were applied to calculate the dissociation constants of the compounds. The following limiting absorption equation was applied⁸:

$$pK_a = pH + \log \frac{A_b - A}{A - A_a} \quad \dots(1)$$

where A is the absorbance at the corresponding pH, A_b is that in the strongly alkaline solution and A_a is that in the strongly acidic solution. The plot of log absorbance ratio term versus pH was linear from which the pK_a values were obtained. Colleter's method⁹ (Eq. 2) gave similar results.

$$K_a = \frac{[H_2^+] - M [H_3^+]}{M - 1} \quad \dots(2)$$

In Eq. (2) M is given by the expression (3)

$$M = \frac{A_3 - A_1}{A_2 - A_1} \cdot \frac{[H_2^+] - [H_1^+]}{[H_3^+] - [H_1^+]} \quad \dots(3)$$

where A_1 , A_2 and A_3 are the absorbances at the $[H_1^+]$, $[H_2^+]$ and $[H_3^+]$ respectively.

Irving and Rossotti mode of calculation was applied to calculate the pK values from potentiometric data¹⁰. The \bar{n} and pL relation was used for this purpose.

The obtained pK_a values for the compounds, which are of acid-base equilibria type correspond to the overall dissociation constants of different tautomers (I and II) (Scheme 1).

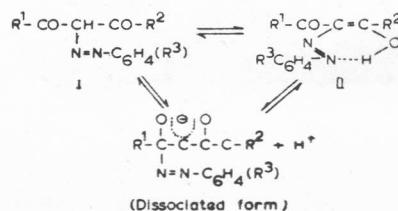


TABLE 1 — CHARACTERIZATION DATA, UV MAXIMUM ABSORPTIONS AND pK_a VALUES AT $25 \pm 0.1^\circ$ OF SOME β -DIKETOARYLAZO COMPOUNDS

Dye No.	R^3	m.p. $^\circ\text{C}$	Colour	λ_{max} nm	pK_a	
					Potentiometry*	Spectrophotometry†
$R^1 = R^2 = \text{CH}_3$						
1	H	87	Yellow	365	3.88 ± 0.02	—
2	<i>o</i> -NO ₂	187	Deep yellow	390	2.96 ± 0.03	10.02 ± 0.20
3	<i>m</i> -NO ₂	146	Beige	350	3.08 ± 0.02	—
4	<i>p</i> -NO ₂	237	Pale yellow	380	3.04 ± 0.01	—
5	<i>o</i> -OCH ₃	145	Pale orange	395	4.02 ± 0.02	11.32 ± 0.02
6	<i>m</i> -OCH ₃	89	Reddish brown	370	3.91 ± 0.01	11.13 ± 0.03
7	<i>p</i> -OCH ₃	104	Brownish red	400	4.10 ± 0.01	11.54 ± 0.02
$R^1 = \text{CH}_3; R^2 = \text{C}_6\text{H}_5$						
8	H	103	Yellow	315	4.36 ± 0.02	—
9	<i>o</i> -NO ₂	150	Lemon yellow	395	3.69 ± 0.03	11.27 ± 0.02
10	<i>m</i> -NO ₂	121	Cream	350	4.42 ± 0.01	9.36 ± 0.06
11	<i>p</i> -NO ₂	152	Brownish yellow	385	4.29	11.46 ± 0.04
12	<i>o</i> -OCH ₃	132	Golden yellow	400	4.02 ± 0.08	12.04 ± 0.08
13	<i>m</i> -OCH ₃	115	Brownish yellow	375	5.03	10.32 ± 0.06
14	<i>p</i> -OCH ₃	73	Yellow	405	5.08	11.82 ± 0.04
$R^1 = R^2 = \text{C}_6\text{H}_5$						
15	H	158	Orange	350	5.22 ± 0.10	4.01 ± 0.10
16	<i>o</i> -NO ₂	195	Deep yellow	410	2.40 ± 0.12	5.60 ± 0.01
17	<i>m</i> -NO ₂	201	Yellow	370	3.66 ± 0.02	8.60 ± 0.05
18	<i>p</i> -NO ₂	182	Brownish yellow	390	3.06	7.71 ± 0.09
19	<i>o</i> -OCH ₃	161	Orange	415	3.02	—
20	<i>m</i> -OCH ₃	166	Reddish brown	400	4.01 ± 1.03	—
21	<i>p</i> -OCH ₃	152	Brownish orange	420	3.32	7.56 ± 0.07

*For protonation-deprotonation equilibrium.

†For deprotonation-ionization equilibrium.

TABLE 2 — UV DATA OF DIACYL AND/OR AROYLMETHANE AZO DYES IN DIFFERENT SOLVENTS

Dye No.*	CCl ₄		CHCl ₃		Dioxan		Acetone		Ethanol	
	λ_{max}	$\log \epsilon_{\text{max}}$	λ_{max}	$\log \epsilon_{\text{max}}$	λ_{max}	$\log \epsilon_{\text{max}}$	λ_{max}	$\log \epsilon_{\text{max}}$	λ_{max}	$\log \epsilon_{\text{max}}$
2	385	4.28	390	4.25	385	4.231	390	4.176	390	3.74
7	395	4.255	402	4.30	390	4.415	400	4.279	400	4.328
9	395	3.123	397	3.215	400	3.17	397	3.225	395	3.255
10	363	4.267	360	4.199	355	4.231	355	4.176	355	4.225
11	395	3.552	430	3.387	395	3.584	395	3.471	395	3.519
14	405	4.297	405	4.322	402	4.246	403	4.279	—	—
16	405	4.29	410	4.243	395	4.255	410	4.19	405	4.114
18	390	4.47	396	4.568	390	4.532	390	4.579	390	4.362

*Sl nos. refer to the dyes listed in Table 1.

The data show that the magnitudes of the pK_a values depend on the nature of the substituents where inductive and conjugative effects are operative. There are some indications that azo containing groups may behave as +R as well as -R groups, depending on the electronic requirements of the reaction. The arylazo group is sufficiently polar for proximity effects to become significant in the *ortho*-position, where its inherent behaviour may be masked by field effects and by even more direct interaction with the sidechain¹¹. The compounds gave characteristic band near 310 nm at pH lower than 7 and in the wavelength range 375-425 nm in alkaline solutions, indicating the presence of acid-base equilibria. The difference in pK_a values for methyl and phenyl substituted compounds can

be attributed to the nature of each substituent. The electron donor methyl group with the hyperconjugative effect facilitates the ionization of the proton. The phenyl group is more bulky than the methyl leading to a slight decrease in the ionization. The pK_a values of the *m*-NO₂ derivatives are higher than those of the *p*-NO₂ derivatives, due to increased conjugation in the latter compounds, thereby facilitating ionization.

The electronic spectra of the compounds are affected by the nature of the solvents, leading to a change in the band positions and their intensities (Table 2). The IR spectra of all the compounds in KBr exhibited two carbonyl bands at 1660 and 1690 cm^{-1} and the absence of νOH and νNH . Also the azo stretching frequency appeared at 1550

cm⁻¹. These findings show that these compounds are predominantly in their keto-form (I)¹². All these compounds absorb ~220 nm due to $\pi \rightarrow \pi^*$ transition (¹L_a—¹A) of the phenyl ring. The following observations and conclusions can be derived from the electronic spectral data: (i) the red shift of the *p*-OCH₃ compounds 7 and 14 is due to the high donor character (mesomeric and inductive effects) of the methoxy group. The electron density on the oxygen atom of the carbonyl group assists the electron migration from the highest occupied orbital of the methoxy group to the vacant orbital on the carbonyl group; (ii) the substituted nitro compounds give electronic spectra mainly due to the $\pi \rightarrow \pi^*$ transitions of the chromophoric groups influenced by charge migration from the O—H group i.e. this interaction assumes that the intramolecular hydrogen bond remains unaffected by non-polar solvents and the charge transfer occurs mainly due to the electron attracting property of the nitro group. Red shift in the maximum absorption in *ortho*-nitro compounds is noticed on increasing the bulk of R₁ and R₂; (iii) the polar solvent molecules are oriented to the polar sites of the solute in the ground state and on excitation the solvent molecules are in a position to solvate the more stabilized polar excited state; (iv) the groups in *ortho* position lead to shift in the maximum absorption due to intramolecular hydrogen bonding, favouring the formation of coplanar chelate ring; (v) the azo group can act as a proton acceptor in hydrogen bonds and the carbonyl oxygen as a proton acceptor in protic solvents. The sole interaction with acetone will be the hydrogen bonding between the hydrogen of the OH— group and the oxygen of the solvent molecules, leading to a decrease in electron density on the oxygen atom. The same trend occurs in chloroform with slight increase in the strength of the intramolecular hydrogen bonding; and (vi) in all the compounds, the solute-solvent interaction is of moderate importance.

Four compounds, viz. Sl. nos. 3, 9, 10 and 12 of Table 1 were chosen for the NMR studies in CDCl₃ (chemical shift in δ , ppm with respect to TMS as internal reference). The signals for the aromatic protons of compound 3 are shifted downfield

(7.7-8.3) due to the deshielding effect of the nitro group. This compound shows two signals (2.5 and 2.6) for the two methyl groups indicating that these groups differ in their electronic environment due to the formation of the enol-isomer in solution. The upfield shift of OH— proton is unexpected. This proton appears to be highly shielded (0.4 ppm) probably due to its involvement in hydrogen-bonding and formation of a stable six-membered ring. The other signals for compound 3 are slightly shifted due to the electron attracting property of the nitro group. Compounds 9, 10 and 12 show two types of signals for aromatic protons i.e. four protons for the arylazo group and five protons for the phenyl group respectively. The arylazo group signals are shifted downfield and appear at 8.2 and 8.8 respectively in the case of compounds 3 and 9. The corresponding signal appears at 7.0 in compound 12, where the electron density of the aromatic ring increases. All signals appear as singlets, except for aromatic protons that appear as multiplets due to spin-spin coupling. The compounds 3, 9, 10 and 12 show in their mass spectra parent ion peaks at *m/e* 249, 311, 311 and 296 respectively which are consistent with the assigned structures.

References

1. HEPPARD, S. E., *Rev. mod. Phys.*, **14** (1942), 303.
2. PRAKASH, A. & GAMBHIR, I. R., *J. Indian chem. Soc.*, **41** (1964), 849; **43** (1966), 529.
3. ZSOLNAI, T., *Biochem. Pharmacol.*, **14** (1965), 1323.
4. ELGUERO, J., JACQUIER, R. & TARAGO, G., *Bull. Soc. chim. Fr.*, (1966), 2990.
5. HOFFMAN, M., McDOWELL, W. & WEINGARTEN, A., *J. Soc. Dyer.*, **84** (1968), 814.
6. TAWFIK, N. *et al.*, *Ind. Tex. J.*, **87** (1977), 117.
7. VANUITERT, L. & HAAS, C. G., *J. Am. chem. Soc.*, **75** (1953), 451.
8. MASOUD, M. S., SALEM, T. M. & ELESSAWY, M. M., *J. chem. engng Data*, **23** (1978), 12.
9. COLLETER, J. C., *Ann. Chim.*, **5** (1960), 415.
10. IRVING, H. & ROSSOTI, H. S., *J. chem. Soc.*, (1953), 3397; (1954), 2904.
11. SHAW, Z. S., FISHER, A. & HAPPER, D. A., *J. chem. Soc. (B)*, (1971), 1818.
12. RAO, H. C., *J. org. Chem.*, **29** (1964), 2959.
13. PATAL, S., *The chemistry of the hydrazo, azo and azoxy groups* (John Wiley, New York), 1975, 109.