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Determination of ionisation constants of nitrobenzidines

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Abstract. The ionisation constants of 2-nitrobenzidine, 2,2′-dinitrobenzidine and 2,3′-dinitrobenzidine were determined spectrophotometrically in 33·3% (w/w) methanol. The low pK value obtained for 2,3′-dinitrobenzidine when compared to that of 2-nitro and 2,2′-dinitrobenzidines is explained on the basis of electron withdrawing nature of the nitrogroup and intramolecular hydrogen bonding.

Keywords. Ionisation constant ; spectrophotometry ; nitrobenzidines.

1. Introduction

Nitrobenzidines particularly, 2-nitrobenzidine (2-NB) and 2, 2′-dinitrobenzidine (2, 2′-DNB) have considerable importance in the preparation of azo-dyes (Kuhn 1959) and polycylic cinnoline derivatives (Braith Waite *et al* 1958). It is well-known that organic electrode processes are pH dependent (Kolthoff and Lingane 1952) and in order to study the variation of polarographic half-wave potential ($E_{1/2}$) of an electro-active material (depolariser) with the pH of the medium, the determination of ionisation constant (pK) of the depolariser becomes necessary. The importance of pK determination towards the elucidation of electro-reduction of organic compounds is well-known (Holubek and Volke 1962; Laviron 1962). Hence, in this paper we describe a spectrophotometric method for the determination of ionisation constants of 2-NB, 2, 2′-DNB and 2, 3′-dinitrobenzidine (2, 3′-DNB) in methanol-water mixtures. It may be pointed out that pK values for these nitrobenzidines have not been reported earlier.

2. Experimental

2-Nitrobenzidine (4, 4′-diamino-2-nitro biphenyl, Kovar 1964), 2, 2′-dinitrobenzidine (4, 4′-diamino-2, 2′-dinitro biphenyl, Porai *et al* 1945) and 2, 3′-dinitrobenzidine (4, 4′-diamino-2, 3′-dinitro biphenyl, Lefevre and Turner 1926) were prepared according to the literature procedure. Their purity was checked by melting points (141° C for 2-NB, 204° C for 2, 2′-DNB and 236° C for 2, 3′-DNB), TLC,

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infrared spectra and mass spectrometry. Methanol was purified by the standard procedure before use.

The ionisation constants of 2-NB, 2,2′-DNB and 2,3′-DNB were determined by a spectrophotometric method in 33·3% (w/w) which corresponds to 40% (v/v) methanol-water mixtures (Chattanathan 1971). Solutions of different pH values were prepared in 33·3% (w/w) methanol-water mixture according to the procedure given by Bates *et al* (1963). Solutions of lower pH values were prepared from perchloric acid of different molalities. The pH of various solutions were measured using a KNICK precision pH meter (accuracy ± 0·01 pH unit). The ultraviolet absorption data were obtained with a Carl-Zeiss (ZFM4) spectrophotometer for a definite concentration of each of the nitrobenzidines at different pH values. In the case of 2,3′-DNB, the pK determination was carried out in perchloric acid of different molalities since it was found that no appreciable change in the absorption was noticed for 2, 3′-DNB in the pH range 0·4–2·3.

3. Results and discussion

The ionisation constant (pK_{BH^+}) of a base (B) for the equilibrium $BH^+ \leftrightharpoons B + H^+$ can be calculated from the relation (Bates *et al* 1963),

$$pK'_{BH^+} = \log (C_{BH^+}/C_B) - \log C_{H^+}, \quad (1)$$

where the apparent ionisation constants, pK'_{BH^+} tends to pK_{BH^+} as the molar concentration of the acid in the solvent tends to zero. In the present work, the ionisation ratios (C_{BH^+}/C_B) of various nitrobenzidines were measured spectrophotometrically. Using these and the equilibrium concentration of H^+ ions, the apparant ionisation constants (pK'_{BH^+}) for 2-NB, 2,2′-DNB and 2,3′-DNB were calculated from equation (1). pK_{BH^+} for the nitrobenzidines were obtained by plotting pK′ against the acid concentration and extrapolating the linear plot to infinite dilution. A typical plot is shown in figure 1. The spectral data are presented in

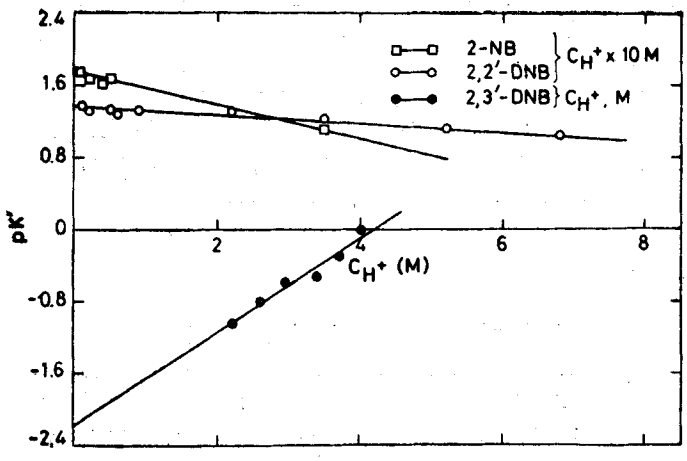

Figure 1. Variation of pK′ with hydrogen ion concentration at $\lambda = 400$ nm for nitrobenzidines.

table 1. The pK_{BH+} values obtained from such a plot for 2-NB, 2,2′-DNB and 2,3′-DNB at the wavelength where the ionisation ratios (C_{BH+}/C_B) between the protonated and unprotonated nitrobenzidines exhibit a large difference (λ = 400 nm in all the cases) were $1{\cdot}76 \pm 0{\cdot}02$, $1{\cdot}34 \pm 0{\cdot}04$ and $-2{\cdot}10 \pm 0{\cdot}04$, respectively. It may be pointed out that pK_{BH+} values calculated at other wavelengths corresponding to $\lambda = 380$ and 390 nm for 2-NB and 2,2′-DNB and $\lambda = 410$ and 430 nm for 2,3′-DNB were found to be independent of the wavelength within the limits of experimental error.

Table 1. Absorbance (D) and molar extinction coefficients (ϵ) for nitrobenzidines at the wavelength ($\lambda = 400$ nm) at various pH values in 33·3% (w/w) methanol-water mixtures. Temperature $30 \pm 0{\cdot}1°$ C.

Substance	pH	D	ϵ	C_{BH+}/C_B	pK′
2-nitrobenzidine					
($6{\cdot}0 \times 10^{-4}$ M)	0·45	0·120	200	4·92	1·14
	0·83	0·155	258	...	...
	1·32	0·205	342	2·22	1·67
	1·45	0·275	458	1·34	1·58
	1·71	0·335	558	0·90	1·66
	1·93	0·380	633	0·66	1·75
	2·11	0·490	817	...	...
2,2′-dinitrobenzidine					
($3{\cdot}0 \times 10^{-4}$ M)	0·17	0·11	367	9·83	1·16
	0·28	0·13	433	7·13	1·14
	0·45	0·14	467	6·22	1·25
	0·65	0·17	550	4·65	1·32
	1·04	0·28	917	1·88	1·32
	1·22	0·35	1167	1·17	1·29
	1·45	0·44	1467	0·67	1·27
	1·92	0·56	1867	0·27	1·36
	2·26	0·63	2100	0·12	1·34
2,3′-dinitrobenzidine					
($2{\cdot}0 \times 10^{-4}$ M)	−0·61	0·31	1550	3·81	−0·03
	−0·57	0·42	2100	1·85	−0·30
	−0·53	0·53	2650	1·03	−0·52
	−0·47	0·62	3100	0·75	−0·60
	−0·41	0·70	3500	0·40	−0·81
	−0·35	0·79	3950	0·20	−1·04

pH values for 2,3′-DNB solutions were calculated from the strength of perchloric acid.

The low pK_{BH^+} values obtained for nitrobenzidines when compared to benzidine (Albert and Serjeant 1971) may be attributed to the electron withdrawing tendency of the nitro group. The low pK_{BH^+} values of 2, 2′-DNB in comparison with 2-NB indicates that 2, 2′-DNB is less basic than 2-NB due to the presence of additional nitro group in the molecule. The negative value of pK_{BH^+} obtained for 2, 3′-DNB ($-2{\cdot}10 \pm 0{\cdot}04$) may be explained on the basis of the fact that the presence of one of the nitro-groups either in 3 or 3′ position would decrease the basic character of the compound due to intramolecular hydrogen bonding with the amino group in 4 or 4′ position of the biphenyl ring.

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