INVESTIGATION OF THE CONDITIONS OF EXTRACTION OF ION-ASSOCIATES OF 3-QUINUCLIDINYL BENZILATE WITH ACIDIC DYES

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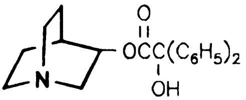
Ion-associates of 3-quinuclidinyl benzilate (BZ) with thirteen acidic dyes were examined after their extraction into chloroform. Based on spectrophotometric measurements, the optimum pH of the aqueous phase was established and the extraction yields, distribution ratios, conditional extraction constants and limits of detection were calculated. Bromocresol green and metanil yellow are suggested as reagents for the analysis of BZ.

3-Quinuclidinyl benzilate, conventionally denoted BZ (ref.[1]), is among the most efficacious psychoactive substances in the glycolate group[2]. Electrochemical[3], spectrometric[4] as well as TLC[5] methods have been used to quantitate BZ. Spectrophotometric methods are based on the formation of characteristically coloured condensation products or ion pairs with the anions of a suitably chosen dye.



Reactions of aromatic compounds with concentrated sulfuric acid give stable red carbonium ions[6]. These condense with additional reagents to give characteristically and markedly coloured compounds. The Marquis reagent[7], which is a formaldehyde solution in sulfuric acid, is usually prepared; this reagent has been applied to the determination of six benzilates based on the formation of dark blue solutions[8]. The blue reaction product has been found to arise by condensation of two molecules of BZ linked through a methyne bridge[9]. Formaldehyde can be replaced with compounds from which it is formed on the action of sulfuric acid, such as paraformaldehyde, hexamethylenetetramine[10], the iron acetate complex[11,12], etc. Benzilic acid as well as BZ forms with 1-naphthol in sulfuric acid a purple-red condensation product exhibiting an absorption maximum at 558 nm (ref.[13]).

Protonation of the tertiary heterocyclic nitrogen in 3-quinuclidinyl benzilate dissolved in an acid solvent enables association of the (3-benziloyloxy)quinuclidinium cation with the anion of a suitable dye to an ion pair which is extractable into nonpolar solvents. The ion pair formation has been used as the basis for an extraction photometric method of determination of BZ with methyl orange[3].

The aim of the present work was to examine the formation of ion-associates of 3-quinuclidinyl benzilate with some anionic dyes from the groups of azo compounds, sulfophthaleins, anthraquinones and nitrophenols, using the spectrophotometric technique after extraction with chloroform.

EXPERIMENTAL

Chemicals and Apparatus

3-Quinuclidinyl benzilate (99.5%) was prepared at the Military Repair Shop No. 072 in Zemianské Kostolany, and its purity was checked by titration with perchloric acid in a mixture of glacial acetic acid and acetic anhydride using crystal violet as the indicator[14]. The anionic dyes, viz. alizarin black S (*I*) (C.I. 67430), naphthol blue black (*II*) (C.I. 20470), bromopyrogallol red (*III*) (5,5-dibromopyrogallolsulfonephthalein), cresol red (*IV*), Xylidine Ponceau 2R (*V*) (C.I. 16150), 2,6-dinitrophenol (*VI*), bromophenol blue (*VII*), bromothymol blue (*VIII*) (3,3-dibromothymolsulfonephthalein), bromoxylenol blue (*IX*), thymol blue (*X*), Orange II (*XI*) (C.I. 15510), bromocresol green (*XII*) (3,3,5,5-tetrabromo-*m*-cresolsulfonephthalein) and metanil yellow (*XIII*) (C.I. 13065) were products of Merck, Darmstadt. Chloroform after extraction of the ion-associate was shaken twice with water and distilled at 60 °C. Citrate and borate buffers at pH 1.0 to pH 8.0 in 0.1 pH unit steps were prepared following ref.[15] and checked with an MV 870 pH-meter (Präcitronic Dresden). Spectrophotometric measurements were carried out on a Spekol 11 single-beam spectrophotometer (Carl Zeiss, Jena).

Procedures

To measure the absorption spectrum of the ion-associate and the dependence of the extracted ion pair on the pH of the reaction medium, 2 ml volumes of buffer solutions with pH 1.1 to 7.0 in 0.1 pH unit steps were mixed with 0.1 ml of the dye solution (c_L = 5 mmol l^{-1}) and 0.1 ml of the BZ solution (c_{BZ} = 0.5 mmol l^{-1}). The mixture was extracted for 2 min into 2 ml of chloroform, the aqueous phase was drained, and the $A = f(\lambda)$ and $A = f(\mathrm{pH})$ at λ_{max} dependences were measured (Table I).

The $A = f(c_L)$ dependence where c_L is the dye concentration in the reaction mixture was established. For this, 1.8 ml of buffer solution at the optimum pH ($\mathrm{pH_{opt}}$), 0.01 to 0.1 ml of the dye solution (c_L = 5 mmol l^{-1}) in 0.01 ml steps, and 0.02 ml of BZ solution (c_{BZ} = 0.5 mmol l^{-1}) were mixed, the mixture was extracted for 2 min with 2 ml of chloroform, and the absorbance of the extract was measured at the λ_{max} value. The composition of the ion-associate was studied by measuring the dependence of absorbance on the mole fraction of the dye, $A = f(x_L)$. Volumes of 0.01 to 0.1 ml of the dye solution (in 0.01 ml steps) were pipetted and diluted to 0.1 ml with BZ solution ($c_L = c_{BZ}$ = 5 mmol l^{-1}), and 2 ml of buffer solution at $\mathrm{pH_{opt}}$ were added. The whole was extracted with 2 ml of chloroform, and the absorbance of the extract was measured at λ_{max}.

For the calculation of the molar absorptivities of the ion-associates in conditions of quantitative extraction of the dye, 0.01 to 0.1 ml of the dye (c_L = 0.5 mmol l^{-1}) in 0.01 ml steps were pipetted and diluted to 1 ml with the buffer at $\mathrm{pH_{opt}}$, and 1 ml of BZ solution (c_{BZ} = 10 mmol l^{-1}) in the buffer at $\mathrm{pH_{opt}}$

was added. The whole was extracted with chloroform for 2 min, and the absorbance of the extract was measured at λ_{max}.

The molar absorptivity of the ion-associate of BZ was established by measuring the $A = f(c_{BZ})$ dependence. Volumes of 1.8 ml of the buffer at pH_{opt}, 0.1 ml of the dye solution at a concentration corresponding to the c_L/c_{BZ} ratio (Table I), and 0 to 0.1 ml of BZ solution (c_{BZ} = 0.5 mmol l^{-1}) in 0.01 ml steps were pipetted into test tubes. The mixtures were extracted for 2 min with chloroform, the aqueous phase was drained, and the absorbance of the extract was measured at λ_{max}.

The ion-associate distribution ratio D for equal volumes of the aqueous and organic phases ($V_{aq} = V_{org}$) was calculated as

$$D = R/(1 - R) = \varepsilon'/(\varepsilon - \varepsilon'), \qquad (1)$$

where R is the extraction recovery, ε is the molar absorptivity in conditions of quantitative extraction of the ion-associate, and ε' is the molar absorptivity of the ion-associate calculated from the $A = f(c_{BZ})$ dependence. The conditional extraction constant of the ion-associate K'_{ex} was calculated according to ref.[17] as

$$K'_{ex} = D/\{c_L x_{L^-} - (A - A_0)/(\varepsilon' l)\}, \qquad (2)$$

where c_L is the analytical concentration of the dye, x_{L^-} is the mole fraction of the dye in the L^- form, A and A_0 are the absorbances of the ion-associate of the base with the dye and of the blank solution, respectively, and l is the cell thickness.

RESULTS AND DISCUSSION

3-Quinuclidinyl benzilate, which protonates in acid solutions to give (3-benziloyloxy)quinuclidium, combines with anions of the dyes giving rise to ion-associates which are extractable into chloroform. The λ_{max} value was read for them from the $A = f(\lambda)$ dependence. The effect of solution pH on the ion-associate formation is documented by Fig. 1. The optimum pH values of citrate buffers for the formation and

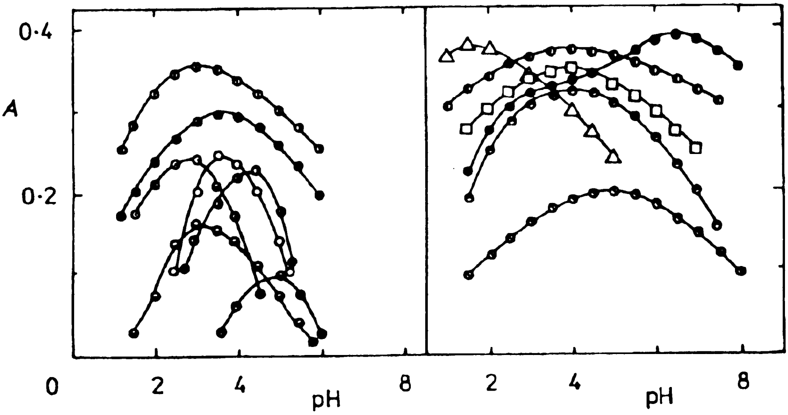


FIG. 1

Dependence of absorbance in the absorption maximum on pH for ion-associates of 3-quinuclidinyl benzilate with dyes. Dye, wavelength (nm): ○ *I*, 520; ⊙ *II*, 623; ◑ *III*, 542; ◒ *IV*, 410; ⊕ *V*, 500; ⊖ *VI*, 428; ⦶ *VII*, 410; ● *VIII*, 415; ◐ *IX*, 412; ⊘ *X*, 415; △ *XI*, 480; □ *XII*, 415; ◓ *XIII*, 415; c_L = 250 μmol l^{-1}, c_{BZ} = 25 μmol l^{-1}

TABLE I
Parameters of 3-quinuclidinyl benzilate ion-associates with various dyes

Dye	Parameter^a										
	λ_{max}	pH_{opt}	c_L/c_{BZ}	k	q	ε	R	$\log D$	$\log K'_{ex}$	L_d	L_D
I	520	3.6	14	14 300	0.0	15 570	0.936	1.05	6.44	0.18	0.25
II	623	2.8	12	11 920	-0.070	50 190	0.238	-0.51	1.81	2.24	2.62
III	542	4.4	8	9 200	-0.030	35 230	0.261	-0.45	1.62	1.59	1.95
IV	410	3.0	10	6 190	0.037	15 580	0.397	-0.18	3.77	2.32	3.05
V	500	3.0	10	14 690	0.021	17 520	0.838	0.72	2.64	0.18	0.34
VI	428	4.9	6	3 630	0.024	6 720	0.540	0.07	5.25	0.65	1.47
VII	410	3.0	8	21 970	0.0	23 280	0.944	1.22	5.15	0.25	0.33
VIII	415	6.5	16	19 360	0.019	19 530	0.991	2.05	6.13	0.28	0.36
IX	412	4.0	18	19 400	0.0	19 640	0.988	1.91	7.76	0.44	0.56
X	415	5.0	12	7 390	0.028	15 870	0.465	-0.06	4.75	0.37	0.48
XI	480	1.6	16	18 800	0.020	21 380	0.880	0.86	5.26	0.39	0.63
XII	415	3.9	5	18 070	0.017	18 200	0.992	2.11	7.12	0.18	0.24
XIII	415	4.0	14	23 330	0.023	24 620	0.948	1.26	5.46	0.29	0.37

[a] λ_{max} is the absorption maximum position (nm), pH_{opt} is the optimum pH value, c_L/c_{BZ} is the optimum dye excess in aqueous phase, k (l mol^{-1}) and q are parameters in the equation $A = kc + q$, where A is absorbance and c is ion-associate concentration, ε (l mol^{-1} cm^{-1}) is the molar absorptivity in conditions of quantitative extraction of the ion-associate, R is the extraction recovery, D is the distribution ratio of the ion-associate, K'_{ex} is the conditional extraction constant, L_d is the limit of detection (mg l^{-1}), and L_D is the limit of determination according to ref.[16] (mg l^{-1}).

extraction of the ion-associates are given in Table I. The composition of the ion-associates of BZ with the dyes was determined by the continuous variations method by measuring the $A = f(x_L)$ dependence where x_L is the mole fraction of the dye. BZ forms ion-associates with Naphthol Blue Black and with Xylidine Ponceau 2R in the ratio 2 : 1; with the remaining dyes, in the ratio 1 : 1.

The chloroform extracts of the coloured ion-associates of 3-(benziloyloxy)quinuclidinium ions with the acidic dyes obeyed the Lambert–Beer law; the correlation coefficient of the least favourable measurement was 0.9936. Well suited are particularly dyes exhibiting low limits of detection L_d and low limits of determination L_D, high extraction recoveries, and high molar absorptivities, such as bromocresol green (*XII*) or metanil yellow (*XIII*).

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