Study of Some Phenylazo Derivatives of 1,1-Dimethyl--3,5-cyclohexadione Operating as Acid-Base Indicators

V. MADAJOVÁ, E. KUCHÁR and M. ŽEMBERYOVÁ

Department of Analytical Chemistry, Faculty of Natural Sciences, Komenský University, Bratislava 1

Received July 18, 1970

In revised form April 1, 1971

 $2 \cdot (p \cdot N \cdot Dimethylaminophenylazo)$, $2 \cdot (p \cdot N \cdot diethylaminophenylazo)$, and $2 \cdot (p \cdot N \cdot ethyl \cdot N \cdot hydroxyethylaminophenylazo) \cdot 1, 1 \cdot dimethyl \cdot 3, 5 \cdot cyclo$ hexadione were prepared and studied spectrophotometrically as acid-baseindicators.

The colour changes of the investigated indicators depending on the hydrogen ion concentration of medium were interpreted on the basis of a comparison with phenylazo-1,1-dimethyl-3,5-cyclohexadione as well as of a study of the relationship between pK_i and temperature. The indicators in fundamental state are internally stabilized by forming a quinoid structure ($\lambda_{max} = 510$ nm). The existence of this form is limited by protonation of nitrogen in the amino group ($\lambda_{max} = 380$ nm) in acidic medium and by formation of an anion having enol form ($\lambda_{max} = 390$ nm) in basic medium.

Some azo derivatives of β -diketones were studied as acid-base indicators. Azo derivatives of 1,3-indandione are intensely orange-red coloured [1-4]. The colour of these solutions depends to a high degree on pH of the medium. From the derivatives of 1,3-indandione, it were 2-phenyl-1,3-indandione, 2-phenyl-5-aza-1,3-indandione [5], 2-(p-N-diethylaminophenylazo)-1,3-indandione-oxime [6], and 2-(p-N-diethylaminophenylazo)-1,3-indandione [7] which were studied as acid-base indicators.

Experimental

Instruments and chemicals

The spectrophotometric measurements were carried out by means of a VUS-1 spectrophotometer (Zeiss, Jena) equipped with a temperature controlled measuring cell space. The temperature was maintained at 20 ± 0.1 °C by means of a thermostat U-3 (VEB--Prüfgeräte Werkstätte, Meidingen-Dresden). A pH-meter PHM 4B (Radiometer, Copenhagen) equipped with a glass electrode G 302 and reference calomel electrode K 100 was used for pH measurements.

Abbreviations:

DMP 2-(p-N-dimethylaminophenylazo)-1,1-dimethyl-3,5-cyclohexadione.

DEP 2-(p-N-diethylaminophenylazo)-1,1-dimethyl-3,5-cyclohexadione.

HEP 2-(p-N-ethyl-N-hydroxyethylaminophenylazo)-1,1-dimethyl-3,5-cyclohexadione.

P phenylazo-1,1-dimethyl-3,5-cyclohexadione.

All chemicals used were anal. grade. The solution of 0.1 N-NaOH was deprived of carbonates and its factor was determined with oxalic acid. Ionic strength was adjusted to $\mu = 0.1$ by means of a solution of KCl.

pilenylazo-1,1-dimetriyi-3,3-cyclonexactones									
Compound	Formula	M	Calculated/found			Yield	M.p.		
			% C	%Н	% N	[%]	[°Ċ]		
DMP	$C_{16}H_{21}N_3O_2$	287.352	66.87 67 10	7.36	14.62 14.68	60 - 65	165 - 166		
DEP	$\mathrm{C_{18}H_{25}N_{3}O_{2}}$	315.404	$68.54 \\ 68.72$	7.99 8.12	$13.32 \\ 13.37$	60	132 - 134		
HEP	${\rm C_{18}H_{25}N_{3}O_{2}}$	244.284	$\begin{array}{c} 65.23 \\ 65.38 \end{array}$	7.60 7.68	$12.68 \\ 12.72$	60	178 - 180		

Table 1

Characterization of the prepared *p*-*N*-substituted phenylazo-1,1-dimethyl-3,5-cyclohexadiones

Melting points (Kofler), yields and analysis results are given in Table 1. The homogeneity of the derivatives prepared was checked by paper chromatography. The most satisfactory solvent system was the mixture butanol—benzene—acetic acid (2:10:2). The prepared derivatives were identified by infrared spectroscopy. The interpretation of infrared spectra of the newly prepared substances will be the subject of the following paper.

To compare the acid-base properties, we prepared phenylazo-1,1-dimethyl-3,5-cyclohexadione according to *Gudriniece* and *Vanag* [1]. Further derivatives were also prepared by this method.

2-(p-N-Dimethylaminophenylazo)-1,1-dimethyl-3,5-cyclohexadione (DMP)

0.12 mole of N-dimethyl-p-phenylenediamine sulfate was dissolved in 36 ml of concentrated hydrochloric acid and 72 ml of water. After cooling the solution to the temperature of -2° C or -5° C, we diazotized with 0.12 mole of sodium nitrite under constant stirring and cooling. 0.12 mole of 1,1-dimethyl-3,5-cyclohexadione dissolved in 20 ml of 15% NaOH was added to the formed diazonium salt. After adjusting pH to the value of 8-8.5, the mixture was allowed to stand for two hours at the above temperature. The mixture was acidified with hydrochloric acid to pH 4 and the precipitate was filtered off. After repeated crystallization from ethanol the reaction product was obtained in the form of dark red crystals with metallic gloss, which are well soluble in acetic acid, ethyl alcohol, acetone, ether, and chloroform but little soluble in water.

2-(p-N-Diethylaminophenylazo)-1,1-dimethyl-3,5-cyclohexadione (DEP)

The diazotization of N-diethyl-p-phenylenediamine sulfate and copulation with 1,1-dimethyl-3,5-cyclohexadione was carried out as described above. After crystallization from acetone green crystals with metallic gloss were obtained. These crystals are well soluble in acetic acid, ethyl alcohol, and acetone but little soluble in water.

2-(p-N-Ethyl-N-hydroxyethylaminophenylazo)-1,1-dimethyl--3,5-cyclohexadione (HEP)

The diazotization of N-ethyl-N-hydroxyethyl-p-phenylenediamine sulfate and copulation with 1,1-dimethyl-3,5-cyclohexadione was performed in the same manner as in preceding cases. After crystallization from acetone violet-blue crystals with metallic shine were obtained. These crystals are well soluble in acetic acid, ethyl alcohol, and acetone but slightly soluble in carbon tetrachloride and water.

Results and Discussion

For spectrophotometric measurements the indicators were dissolved in 50%. aqueous solution of ethyl alcohol and 2×10^{-3} m stock solutions of these indicators were prepared. 0.6-0.8 ml of the stock solution and 6 ml of ethyl alcohol were used for each measurement. The solution was filled up to 25 ml with ethyl alcohol. Actual concentrations of the indicators are quoted in relevant plots.

The spectrophotometric investigation of p-N-substituted phenylazo-1,1-dimethyl--3,5-cyclohexadione has shown that these substances are in contrast to non-substituted phenylazo-1,1-dimethyl-3,5-cyclohexadione available as acid-base indicators with two colour changes. The existence of different colour forms of indicators established by different electron distributions is due to thea cid-base transformations of indicators depending on pH of the medium.

As evident from Figs. 1 and 2, DEP occurs in a bright yellow form in acidic medium up to pH 4, turns red in the pH interval between 6-8.5, and becomes deep yellow provided the basicity of solution exceeds pH 10.5. Two isosbestic points $(\lambda = 425 \text{ nm}, \lambda = 440 \text{ nm})$ prove the existence of two simple acid-base equilibria. Colour changes take place in the pH intervals between 4-6 (yellow-red) and between 8-10.5 (red-yellow). These changes can be observed in Fig. 3 which expresses the relationship A = f(pH) on the basis of the absorption curves presented in Figs. 1 and 2 at characteristic wave lengths. The p K_i values calculated according to [5] are given in Table 2. These values are in good agreement with the values found graphically.



Fig. 1. Dependence of the absorbance curves on pH for the solutions of DEP. $c = 6.4 \times 10^{-5}$ M; d = 1.000 cm.

pH: 1. 2.05; 2. 4.21; 3. 4.72; 4. 5.40; 5. 6.52; 6. 7.55.



Fig. 2. Dependence of the absorbance curves on pH for the solutions of DEP.
c = 6.4 × 10⁻⁵ M; d = 1.000 cm.
pH: 1. 7.56; 2. 8.40; 3. 9.21; 4. 9.93; 5. 10.60; 6. 11.50.

For DEP the dependence of $pK_{i(1)}$ on temperature is presented in Fig. 4. This relationship complies with the following equation

$$pK_i = A - BT$$

where A and B are constants and T is absolute temperature [8]. Similarly, the $pK_{i(2)}$ value of DEP also decreases with increasing temperature.



Fig. 3. Relationship A = f(pH) for DEP (from Figs. 2 and 3). 1. $\lambda = 380$ nm; 2. $\lambda = 510$ nm.

HEP and DMP were studied analogously and their characteristic constants are given in Table 2. All three studied p-N-substituted derivatives show qualitatively equal behaviour. Only the pK_i values are different because of the different inductive effect of varying substituent. The dependence of pK_i on temperature is also descending linearly in both acidic and alkaline regions.

In order to interpret the individual colour forms, we compared DMP, DEP, and HEP to P in addition to the mentioned measurements. The only colour change of the P derivative in the pH interval between 8.7 and 11.6 is not suited for the indication of equivalence point in acid-base titrations. Enol anions of the forms of all three indicators show little distinct yellow-orange colour. The absorption curves of the P indicator depending on pH are presented in Fig. 5.

Tal	ble	2

Characteristic values of the studied indicators Indi-Colour change £380 nm £510 nm £390 nm $pK_{i(2)}$ $pK_{i(1)}$ [pH] cator (pH 2.05) (pH 7.5) (pH 11.5) DMP 2.15×10^4 2.30×10^4 2.01×10^{4} 3.67 + 0.03 9.97 + 0.18 bright yellow-red 3.5 - 5.5red - yellow9.5 - 10.8DEP 1.17×10^{4} 1.38×10^{4} 1.15×10^4 5.40 \pm 0.18 9.80 \pm 0.18 bright vellow-red 4.5 - 6red-yellow 9.3 - 10.5bright yellow-red HEP 2.63×10^4 $2.93 imes 10^4$ $2.29 imes 10^4$ 4.05 ± 0.10 9.55 ± 0.19 3.8 - 4.6red-yellow 9.5 - 10.5

Chem. zvesti 25, 343-349 (1971)



Fig. 4. Variation of $pK_{i(1)}$ with temperature for DEP.



Fig. 5. Dependence of the absorbance curves on pH for the solutions of P. c = 4.8 × 10⁻⁵ M; d = 1.000 cm. pH: 1. 1.90; 2. 8.70; 3. 9.20; 4. 9.50; 5. 11.58.

With respect to the results of the spectrophotometric study of DMP, DEP, and HEP and to their comparison to P, the acid-base equilibria may be described as follows:



The existence of the red "quinoid" form by which the fundamental molecule is internally stabilized is possible neither in acidic medium in which the nitrogen of amino group is protonized nor in alkaline medium where this stabilization is not allowed by the anion structure of the enol form. In acidic medium there cannot

¢

be excluded a protonation of the nitrogen atom of azo group adjacent to amino group instead of the protonation of amino group because the colour effect should be equal. The interpretation of the colour change of methyl orange involves protonation of the azo group. In this case opposite to the derivatives studied, the protonated form is more coloured, that is, the molecule thus protonated is able to be stabilized by quinoid structure.

With respect to the shift of the colour change of DMP, DEP, and HEP indicators into less acidic region in comparison with the colour change of methyl orange a protonation of the nitrogen atom in amino group may be supposed because it is more basic than the nitrogen atom in azo group. With increasing temperature the values of pK_1 decrease what is caused by increasing deprotonation in weak acidic medium or increasing dissociation in alkaline medium. The characteristic values of the indicators under investigation are summarized in Table 2.

It is interesting to compare the molar absorptivities of the indicators studied. DEP is less coloured than DMP or HEP. This fact can be interpreted in accordance with [9] by hyperconjugation in the case of DMP and interaction of the free electron pairs of nitrogen and oxygen in the case of HEP.

The visual determination of colour changes of the indicators studied was performed by potentiometric titration. 20 ml of 0.1 n-HCl was used as titrated solution while 0.1 n-NaOH was applied as titrating agent. 0.10 ml of 1% alcoholic solution of indicator was added into the titrated solution. The equivalence point was indicated by the colour change of indicator from bright yellow to red. The colour changes of DMP, DEP, and HEP in acidic region may be visually observed in a narrow pH range (Table 2). An addition of 0.03 ml of 1% solution of methylene blue makes the colour change more contrast and involves the change from yellow--green to red-violet.

Furthermore, the alkalimetric and acidimetric titrations with 0.1; 0.05; and 0.01 n solutions of strong acids and bases were carried out. The colour changes in these titrations are distinct so that DMP, DEP, and HEP can be used as acid-base indicators for the determination of strong acids, bases, and ammonia. Some results are presented in Table 3. The quoted consumptions of 0.1; 0.5; and

Table 3

Consumption of NaOH in the titration of 10 ml of 0.1; 0.05; and 0.01 N-HCl for the use of different indicators

N-NaOH ·	Consumption ml NaOH							
	methyl orange	methyl red	DMP	DEP	HEP			
0.1 0.05 0.01	$\begin{array}{c} 10.065 \pm 0.010 \\ 10.010 \pm 0.001 \\ 10.030 \pm 0.010 \end{array}$	$\begin{array}{c} 10.043 \pm 0.004 \\ 10.092 \pm 0.001 \\ 10.217 \pm 0.005 \end{array}$	$\begin{array}{c} 10.041 \pm 0.003 \\ 10.090 \pm 0.002 \\ 10.120 \pm 0.004 \end{array}$	$\begin{array}{c} 10.045 \pm 0.002 \\ 10.091 \pm 0.002 \\ 10.183 \pm 0.010 \end{array}$	$\begin{array}{c} 10.015 \pm 0.002 \\ 10.071 \pm 0.002 \\ 10.200 \pm 0.005 \end{array}$			

0.01 N-NaOH are the average values of 10 titrations for which methyl orange, methyl red, DEP, DMP, and HEP were used as indicators.

The second colour change in alkaline region of the investigated indicators is not suited even for the determination of weak acids because it is not sharp enough and takes place at a higher pH than that of the equivalence point.

References

- 1. Gudriniece E. J., Vanag G. J., Ž. Obšč. Chim. 28, 58 (1958).
- 2. Gudriniece E. J., Vanag G. J., Žuk R., Izv. Akad. Nauk Latv. SSR 11, 185 (1959).
- 3. Hunig S., Boes O., Justus Liebigs Ann. Chem. 28, 579 (1953).
- 4. Bülow G., Scholotterbeck F., Ber. 35, 2187 (1902).
- 5. Hrnčiar P., Zacharová D., Acta Facult. Rer. Natur. Univ. Comenianae (Chimia), Tom. VIII, Fasc. X, 587 (1964).
- 6. Kuchár E., Stankoviansky S., Zacharová D., Chem. Zvesti 20, 423 (1966).
- Kuchár E., Stankoviansky S., Zacharová D., Acta Facult. Rer. Natur. Univ. Comenianae (Chimia), Tom. XII, 199 (1968).
- 8. Pekkarinen A., Suomen Kemistilehti B38, 63 (1965).
- 9. Baker J. W., Nathan W. S., J. Chem. Soc. 1844, 1935.

Translated by R. Domanský