Ecl. Quím., São Paulo
6:51-54, 1981.

PRELIMINARY NOTE
PROTONATION CONSTANTS OF p-SUBSTITUTED BENZYLIDENEPYRUVIC ACIDS

C. MELIOS*
A.M. DELSIN*
J.C. TOGNOLLI*
M. MOLINA*

MELIOS, C. **et alii**. Protonation constants of p-substituted benzylidenepyruvic acids. **Ecl. Quím.**, São Paulo, **6**:51-54, 1981. (Preliminary Note).

KEY-WORDS: Benzylidenepyruvic acids, protonation constants, Potenciometry.

INTRODUCTION

In view of the widespread application of carboxylic acids, their salts and metal ion complexes as extractive agents, catalysts, stabilizer, corrosion inhibitors etc., there have been many recent studies aimed at determining the factors that generate and affect these properties [1-4]. As part of our project devoted to the investigation of interactions comprising arylidenepyruvic acids, the present communication deals mainly with the protonation constants of Benzylidenepyruvic acid and five of its p-substituted derivatives, determined in aqueous medium, at 25.°C and 1.00 M ionic strength, adjusted with sodium perchlorate.

LIST OF MAIN SYMBOLS AND ABBREVIATIONS

ABP, p-acetamidobenzylidenepyruvic acid, BP; benzylidenepyruvic acid; C_B concentration of standard sodium hydroxide solution; CBP, p-chloro benzylidenepyruvic acid; C_H, total concentration of dissociable hydrogen ions; C_L, total concentration of ketoacid; C_L^i, total initial concentration of ketoacid; DMBP, p-dimethylaminobenzulidenepyruvic acid, h, concentration of free hydrogen ions; I, ionic strength; IBP, p-isopropylbezylidenepyruvic acid; K_1^H, stoichiometric protonation constant of monoprotic acid HL = [HL] /h. [L]; K_W stoichiometric ionic product of water = h. [OH^-]; MBP, p-methozybenzylidenepyruvic acid; MeBP, p-methylbenzylidenepyruvic acid; pH', pHmeter reading, ph = - log h; σ, standard deviation; V_O, initial volume; Z, average number of hydrogen ions bound to each ketoacid anion.

EXPERIMENTAL

Materials and Solutions: All of the benzylidenepyruvic acids were prepared by condensation of pyruvic acid (or its

* Departamento de Química Analítica, Instituto de Química de Araraquara — UNESP.

sodium salt) with the corresponding aromatic aldehyde, using an alkaline catalyst [5,6]. Solutions of perchloric acid, sodium hydroxide and sodium perchlorate were prepared and standardized as described earlier [7]. Other chemicals used were of analytical purity.

Apparatus: Potenciometric measurements were run on an "Orion" model 701 digital pH/mV meter. The investigation was carried out as a series of potenciometric titracions, performed as described elsewhere [7]. Melting points are uncorrected and were determined in a Mettler FP-2 apparatus with the sample inserted *ca.* 50°C below the m.p.. A heating rate of 2°C/min. was maintained; this was reduced to 0,2°C/min. for temperatures *ca.* 2°C below the m.p..

Methods

(1) Determination of hydrogen-ion concentrations: The pH' values were measured by using the following cell:

$$+\,Hg(l)\,Hg_2(Cl_2(s)\,\Big|\begin{matrix}0.100M\ NaCl(aq)\\ 0.900M\ NaClO_4(aq)\end{matrix}\Big|\ \text{Test solution}\ (1.00M\ ClO_4^-)(aq)\ \Big|\ \begin{matrix}\text{Glass}\\ \text{Electrode}\end{matrix}\ -\ (a)$$

The electrodes were "Orion" 910100 glass and "Corning" 476002 calomel, modified as indicated in cell (a). The measuring assembly was first standardized by using an acetate buffer (0.100 M acetic acid - 0.100 M sodium acetate — 0.100 M sodium acetate - 0.900 M sodium perchlorate, ph = 4.75) whose ph was assigned by taking into account the thermodynamic protonation constant of acetic acid determined by HARNED *et al.* [8] at 25°C and the ionic activity coefficients given by MEITES [9]. The pH' values were converted into ph by means of the calibration factor H'/h experimentally determined as recommended by MCBRYDE [10].

(2) Determination of Protonation Constants: The K_1^H values were determined by titrating the ketoacids (C_L^i = 1.79-6.59 mM; V_0 = 125.18 ml) made up to I = 1.00 M by adding sodium perchlorate, with sodium hydroxide solution (C_B = 0.0200-0.0500 M), I = 1.00 M, adjusted with sodium percholorate. For IBP, the sodium salt was employed and the associated K_1^H was analogously determined by using 0.100 M perchloric acid as titrant. The C_L^i values were taken from the end points of the titration curves except for IBP whose values was assessed by direct weighing of its sodium salt. The K_1^H values were derived[11] from C_L, C_H, K_w and h. The pK_W value (13.60 ± 0.01, I = 1.00 M) was previously determined [7].

RESULTS AND DISCUSSION

Some properties of the benzylidenepyruvic acids considered in this work are given in Table I. The protonation constants are listed in Table II. Quite regular titration curves, characteristic of monoprotic acids, were obtained for all the ketoacids. A set of constant K_1^H values for ABP could not be achieved; the results may have been influenced by hydrolytic liberation of acetic acid during the titrations as observed for the analogous p-acetamidobenzoic acid [14]. However, the data associated with the ABP system suggest that the named ketoacid shoud also be relatively strong (log $K_1^H \approx 2$).

TABLE I Properties of Benzylidenepyruvic Acids

Ketoacid	Colour	m. p. (.°C)	lit. m. p. (.°C)	Solubility* (g/l)
BP	pale yellow	57.1 — 58.4	55 — 57 [12]	0.69
MeBP	yellow	126.2 — 127.3	127 — 127.5 [13]	1.15
IBP	canary yellow	201.7 — 203.7	—	—
MBP	canary yellow	129.0 — 129.8	130.5 — 131 [13]	1.36
CBP	pale yellow	137.2 — 137.7	139 — 140 [5]	0.47
ABP	orange-yellow	228.3 — 229.2	—	0.42
DMBP	reddish-brown	142.4 — 143.0	143.2 — 144 [6]	0.72

* — approximate values in aqueons medium at 25.°C and I = 1.00 ($NaClO_4$)

TABLE II — Protonation Constants of Benzylidenepyruvic Acids and Summary of Potentiometric Titration Data.
t = 25.00 0.05.°C I = 1.00 M ($NaClO_4$)

Ketoacid	C_L^i(mM)	useful ph range	useful Z range	R *	log $K_1^H \pm \sigma$
BP	3.90	2.44 — 2.55	0.049 — 0.043	12	1.18 ± 0.02
MeBP	6.02	2.26 — 2.50	0.088 — 0.056	25	1.25 ± 0.02
IBP	4.66	1.94 — 2.18	0.578 — 0.503	8	2.15 ± 0.04
MBP	6.59	2.28 — 2.56	0.185 — 0.096	17	1.59 ± 0.02
CBP	2.67	2.67 — 3.14	0.180 — 0.071	20	1.96 ± 0.04
DMBP	3.29	3.42 — 4.32	0.726 — 0.245	35	3.80 ± 0.02

* — R = number of readings

STECHER et al. [13] determined the protonation constants of BP, MeBP, MBP. 3-methoxy-BP and 3-bromo-BP in water, at 25°C, the ionic strength was not kept constants. The authors found that these are strong acids and show no significant variation of K_1^H with substituent groups, i.e., log K_1^H = 1.96-1.99.

This conclusion is in a marked disagreement with our results in so far as the BP, MeBP and MBP systems are concerned. The experimental conditions adopted by STECHER *et al.* in determining the K_1^H values, e.g., failure in maintaining a constant ionic strength and use of pH' values directly in the calculations, should certinly play an important role in explaining the differences found. Current investigations carried out in this laboratory have shown that the K_1^H values of some benzylidenepyruvic acids are highly sensitive to changes of ionic strength.

The main difficulty found in studying the systems under consideration is connected with the poor solubility of the benzylidenepyruvic acids in aqueous medium and their high degree of ionization. Thus the ph ranges from which the K_1^H values could be derived with reasonable precision are quite restricted, even working with nearly saturated solutions of the ketoacids. The named acids are more soluble in organic solvents, e.g., ethanol. Titration of CBP in 50% w/w ethanol-water, at 25°C and I = 1.00 M ($NaClO_4$) has been perfomed according to a previously outlined procedure[15]. Working with C_L^i = 6.28 mM, the useful Z range could be estended (0.435-0.276; R = 31) giving log K_1^H = 2.35 ± 0.02. This value is consistent with the one found in aqueous medium (Table II):

Further work in mixed media — designed along the lines suggested by BENET *et al.* [16] — is in progress in order to obtain additional confirmation for the constants presently determined in aqueous medium.

ACKNOWLEDGEMENT

The financial support given by CNPq (Proc. 305632/78) and FAPESP (Proc. 78/1492) is gratefully acknowledged.

MELIOS, C. et alii. Constantes de protonação de ácidos benzalpirúvicos p-substituidos. *Ecl. Quím.*, São Paulo, 6:51-54, 1981. (Nota Previa).

UNITERMOS: Ácidos benzalpirúvicos, constantes de protonação, potenciometria.

REFERENCES

1. MILLER, F. — *Talanta, 1974,* 21, 685 and references therein.
2. TOGNOLLI, J.O. — M. Sci. Thesis, Universidade de São Paulo, 1980.
3. *JOHN, E. — J. Inorg. Nucl. Chem., 1981,* 43, 325.
4. MATUSINOVIC, T.; FILIPOVIC, I. — *Talanta, 1981,* 28, 199.
5. STECHER, E.D.; INCORVIA, M.J.; KERBEN, B.; LEVINE, D.; OEN, M.; SUHL, E. — *J. Org. Chem., 1973,* 38, 4453.
6. MELIOS, C. — PhD dissert., FFCLA. Brazil, 1973, pp. 111-127 and 158-174.
7. MOLINA, M.; MELIOS, C.; TOGNOLLI, J.O.; LUCHIARI, L.C.; JAFELICCI JR., M. — *J. Electroanal. Chem., 1979,* 105, 237.
8. HARNED, H.S.; EHLERS, R.W. — *J. Am. Chem. Soc., 1933, 55,* 65.
9. MEITES, L. — "Handbook of analytical chemistry", McGraw-Hill, N. York, 1963, pp. 1-8.
10. MCBRYDE, W.A.E. — *Analyst, 1969,* 94, 337, *1971,* 96, 739.
11. ROSSOTTI, H.S. — *Talanta, 1974,* 21, 809.
12. REIMER, M. — *J. Am. Chem. Soc., 1926,* 48, 2454.
13. STECHER, E.D.; RYDER, H.F. — *J. Am. Chem. Soc.,* 1952, 74, 4392.
14. ALBERT, A.; Serjeant, E.P. — "The Determination of Ionization Constants"; Chapman and Hall, London 1971; pp. 85.
15. MOLINA, M.; TOGNOLLI, J.O.; MELIOS, C.; SIMÇÕES, R.C. — *Ciênc. e Cult., 1978* (supl.), 30(7), 268.
16. BENET, L.Z.; GOYAN, J.E. — *J. Pharm. Sci., 1967,* 56, 665.

ÍNDICE DE ASSUNTOS

SUBJECT INDEX

ÍNDICE DE AUTORES
AUTHOR INDEX
V. 6

NORMAS

1. A revista "ECLÉTICA QUÍMICA" publica artigos originais e notas prévias escritas num dos seguintes idiomas: português, inglês, francês nas áreas de Química, Física e Matemática.
2. Os artigos originais não poderão exceder 15 folhas datilografadas (25 linhas de 60 espaços) com margem de 3 cm de ambos os lados.
3. As notas prévias não poderão exceder 4 folhas datilografadas nas mesmas condições.
4. Os manuscritos deverão ser enviados em 3 exemplares à

"ECLÉTICA QUÍMICA"
Instituto de Química — UNESP
C.P. 174 — 14800 — Araraquara (SP) — Brasil

5. A apresentação dos originais obedecerá a seguinte ordem:
   a) Título no idioma do artigo e em inglês.
   b) Nome e sobrenome do(s) autor(es) assinalando com asterisco o autor principal para o qual serão mandadas provas e separatas.
   c) Nome e endereço do laboratório.
   d) Resumo de até 200 palavras e sua tradução em inglês.
   e) Os unitermos e suas traduções em inglês.
   f) O texto do trabalho.
   g) Bibliografia obedecendo as leis da IUPAC.
   h) Tabelas, gráficos e fotografias branco e preto, num total geral de 5 por artigo.

   As despesas referentes às tabelas, gráficos e fotografias excedentes assim como as ilustrações a cores correrão por conta dos autores. Os gráficos serão desenhados em papel vegetal e suas legendas serão datilografadas em folha separada.
6. Todo manuscrito será submetido ao Departamento Científico que analisará o valor do trabalho podendo recusá-lo, sugerir modificações ou pedir informações ao(s) autor (es).
7. O relatório do Departamento Científico será anônimo e comunicado aos autores.