Thermochimica Acta, 107 (1986) 371–374
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

THERMODYNAMIC STABILITY CONSTANTS OF BIVALENT METAL COMPLEXES OF 2-HYDROXY-3,4-DIMETHOXYACETOPHENONE

RESH B. BASNET and BHAGWAN S. GARG
Department of Chemistry, University of Delhi, Delhi 110 007 (India)

(Received 18 March 1986)

Metal chelates of substituted hydroxyacetophenone find wide applications and are important analytical reagents. These have great affinity for various biologically active metal ions. The present study has been undertaken to study the thermodynamic stability constants of 2-hydroxy-3,4-dimethoxyacetophenone with bivalent metal ions at different temperatures in 50% v/v dioxan–water medium.

EXPERIMENTAL

2-Hydroxy-3,4-dimethoxyacetophenone was synthesised by the conventional methods and its purity was checked by NMR, IR, UV, MP and TLC. A digital pH-meter (ECIL model PH 5651), with a glass electrode (0–14 pH range) was used for pH measurements. The pH-meter was standardised with potassium hydrogenphthalate and phosphate buffers before performing the actual titrations.

The solution of 2-hydroxy-3,4-dimethoxyacetophenone was prepared in freshly distilled dioxan. All the metal ion solutions were prepared and standardised by conventional procedures. Sodium perchlorate (Riedel) was used to keep the ionic strength constant for all sets. A solution of tetramethyl ammonium hydroxide (TMAH) (Merck) in 50% aqueous dioxan was used as the titrant. It was standardised with oxalic acid. All other chemicals used were of reagent grade. The titrations were carried out in an atmosphere of nitrogen, which was presaturated with 50% v/v aqueous dioxan. The measurements were made at a definite temperature which was kept constant by using an MLW (West Germany) (NBE type) thermostat.

Procedure

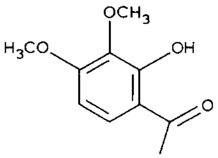
The method of Bjerrum and Calvin, as modified by Irving and Rossotti [1] has been used to determine $\bar{n}$ and pL values. The following solutions (total volume = 19.67 ml instead of 20 ml, due to contraction in volume on mixing dioxan and water) were titrated potentiometrically against standard 0.05 M TMAH, in 50% dioxan (v/v) to determine $\bar{n}$ and pL values for the formation of the complexes:

(i) 2 ml of $HClO_4$ (0.02 M) + 1 ml of $NaClO_4$ (2.0 M) + 0.5 ml of KNO_3/K_2SO_4 (0.02 M) + 6.5 ml of doubly distilled water + 10 ml of dioxan (100%).

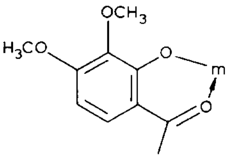
(ii) 2 ml of $HClO_4$ (0.02 M) + 1 ml of $NaClO_4$ (2.0 M) + 0.5 ml of KNO_3/K_2SO_4 (0.02 M) + 5 ml of ligand (0.01 M) + 5.0 ml of dioxan + 6.5 ml of doubly distilled water.

(iii) 2 ml of $HClO_4$ (0.02 M) + 1 ml of $NaClO_4$ (2.0 M) + 0.5 ml of metal nitrate or sulphate (0.02 M) + 5.0 ml of ligand (0.01 M) + 5.0 ml of dioxan + 6.5 ml of doubly distilled water.

During complexation the orthophenolic proton is replaced by an equivalent amount of metal(II) and thus the ligand (I) acts as a monobasic acid. The phenolic group dissociates first and the pK_a value of the ligand will correspond to the dissociation of this group.



(I)



(II)

From the titration curves of solutions (i), (ii) and (iii) the values of $\bar{n}$ and pL have been calculated using an IBM 360 Fortran-IV computer. The corresponding values of stability constants have been calculated using the weighted least-squares method of Sullivan et al. [2]. The weighted least-squares treatment determines that set of β_n which makes the function

$$U, U = \sum_{n=0}^{N} (y - x - nz)\beta_n x^n$$

TABLE 1

Stability constants of bivalent metal complexes of 2-hydroxy-3,4-dimethoxyacetophenone at $\mu = 0.1$ M $NaClO_4$ and temperature = 50 ± 0.5 °C

Metal ion	log K_1	log K_2	log β_2	S_{min}
H^+	11.40	–	–	–
Mg(II)	4.10	3.58	7.68	0.0167
Mn(II)	5.84	5.48	11.32	0.0915
Co(II)	6.10	5.65	11.75	0.0082
Ni(II)	6.20	6.52	12.72	0.0515
Cd(II)	6.67	6.11	12.78	0.0799
Zn(II)	7.99	7.33	15.32	0.0367
Cu(II)	8.28	8.04	16.32	0.1129

TABLE 2

Stability constants of bivalent metal complexes of 2-hydroxy-3,4-dimethoxyacetophenone at $\mu = 0.1$ M $NaClO_4$ and temperature $= 40 \pm 0.5°C$

Metal ion	$\log K_1$	$\log K_2$	$\log \beta_2$	S_{min}
H^+	11.43	–	–	–
Mg(II)	4.40	3.97	8.37	0.0040
Mn(II)	5.49	5.04	10.53	0.1247
Co(II)	5.98	5.62	11.60	0.1027
Ni(II)	6.37	5.44	11.81	0.1504
Cd(II)	6.38	6.06	12.44	0.2032
Zn(II)	7.76	7.25	15.01	0.7597
Cu(II)	9.40	8.60	18.00	0.4900

TABLE 3

Stability constants of bivalent metal complexes of 2-hydroxy-3,4-dimethoxyacetophenone at $\mu = 0.1$ M $NaClO_4$ and temperature $= 35 \pm 0.5°C$

Metal ion	$\log K_1$	$\log K_2$	$\log \beta_2$	S_{min}
H^+	11.62	–	–	–
Mg(II)	4.13	3.95	8.08	0.2161
Mn(II)	6.29	4.40	10.69	0.0779
Co(II)	6.29	6.55	12.84	0.4565
Ni(II)	6.52	6.44	12.96	0.6791
Cd(II)	6.76	6.63	13.39	0.3482
Zn(II)	8.49	6.11	14.60	0.1345
Cu(II)	9.58	7.01	16.59	0.2640

nearest to zero, by minimizing

$$S, S = \sum_{i=1}^{I} w_i U^2(x_i y_i z_i)$$

with respect to the variation in β_n. We report the S_{min} values for different metal complexes. S_{min} has the same statistical distribution as χ^2 with K degrees of freedom and with weights defined according to Rydberg and Sullivan [3]. S_{min} can be equated to χ^2, the stability constants thus calculated are given in Tables 1–3.

RESULTS AND DISCUSSION

The order of stability constants of the metal complexes with 2-hydroxy-3,4-dimethoxyacetophenone was found to follow the order:

Mg < Mn < Co < Ni < Cd < Zn < Cu

TABLE 4

Thermodynamic function for the formatioin of bivalent metal complexes of 2-hydroxy-3,4-dimethoxyacetophenone at $\mu = 0.1$ M $NaClO_4$ and temperature = 30 ± 0.5 °C

Metal ion	$-\Delta G$ (kcal mol^{-1})	$-\Delta H$ (kcal mol^{-1})	$-\Delta S$ (kcal K^{-1} mol^{-1})
Cu(II)	13.851	28.56	0.048
Zn(II)	11.425	17.13	0.019
Cd(II)	10.718	37.47	0.088
Ni(II)	10.371	11.42	0.003
Co(II)	8.984	17.13	0.026
Mn(II)	8.083	21.38	0.043
Mg(II)	5.560	19.87	0.047

This order is in good agreement with the order found by Mellor and Maley [4] and Irving and Williams [5,6]. In all cases it has been observed that $\log K_1 > \log K_2$. The values of stability constants in Tables 1–3 reveal that stability constants do not regularly decrease with increasing temperature. On the other hand, the pK_a value does. The thermodynamic parameters (ΔG, ΔH and ΔS) have thus been calculated by using the following relationships:

$$\Delta G = -RT \ln K$$

$$d \log K/d(1/T) = \Delta H/2.303R$$

$$\Delta S = (\Delta H - \Delta G)/T$$

The overall free energy change and enthalpy and entropy changes at 30 ± 0.5 °C are reported in Table 4. The results indicate that ΔG and ΔH are negative which shows that complex formation reactions are favourable at ordinary temperatures.

ACKNOWLEDGEMENTS

One of us (R.B.B.) wishes to thank Tribhuwan University, Kathmandu, Nepal for leave of absence to enable him to spend three years for research at the University of Delhi, India.

REFERENCES

1 H.M. Irving and H.S. Rossotti, J. Chem. Soc., (1954) 2904.
2 J.C. Sullivan, J. Rydberg and W.F. Miller, Acta Chem. Scand., 13 (1959) 2023.
3 J. Rydberg and J.C. Sullivan, Acta Chem. Scand., 13 (1959) 2059.
4 D.P. Mellor and L. Maley, Nature (London), 159 (1947) 370.
5 H.M. Irving and R.J.P. Williams, Nature (London), 162 (1948) 746.
6 H.M. Irving and R.J.P. Williams, J. Chem. Soc., (1953) 3192.