Thermochimica Acta, 157 (1990) 365–368
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

EVALUATION OF THERMODYNAMIC PARAMETERS OF BIVALENT METAL COMPLEXES OF 2-HYDROXYACETOPHENONETHIOSEMICARBAZONE (2-HATS)

BHAGWAN S. GARG *, SUDIPTA GHOSH, VINOD K. JAIN
and PRAMOD K. SINGH

Department of Chemistry, University of Delhi, Delhi-110007 (India)

(Received 13 June 1989)

ABSTRACT

Thermodynamic parameters (ΔG, ΔH and ΔS) and stability constants of complexes of 2-hydroxyacetophenonethiosemicarbazone (2-HATS) with Mg(II), Mn(II), Cd(II), Pb(II), Ni(II) and Cu(II) have been determined pH-metrically in 50% (v/v) aqueous dioxan. The formation constants (log β_n) have been calculated using the weighted least-squares method.

INTRODUCTION

Domagk et al. [1] reported for the first time the antitubercular activity of *p*-acetamidobenzaldehydethiosemicarbazone, which is found to be enhanced by the presence of a small amount of copper ions [2]. Recently [3] we have reviewed the analytical applications of thiosemicarbazones and semicarbazones. Chumatkov et al. [4] reported the antitumour activity of the thiosemicarbazone derivative of 2-pyridinecarboxaldehyde. Keeping in view the wide analytical applicability and biological activity of thiosemicarbazones, the present study has been undertaken to study the complexing ability of 2-hydroxyacetophenonethiosemicarbazone towards bivalent metal ions at different temperatures in 50% (v/v) dioxan–water medium.

EXPERIMENTAL DETAILS

Instrumental

A digital pH meter (ECIL model pH 5651) with a single glass–calomel electrode assembly was used for the pH measurements.

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* Author to whom correspondence should be addressed.

0040-6031/90/$03.50

Chemicals and reagents

2-Hydroxyacetophenonethiosemicarbazone (2-HATS) was prepared by condensing equimolar quantities of thiosemicarbazide and 2-hydroxyacetophenone in presence of a few drops of glacial acetic acid. The purity of 2-HATS was checked by thin layer chromatography, elemental analysis, IR and ^{1}H NMR spectroscopy, and melting point $\approx 195\,^\circ\mathrm{C}$. All metal ion solutions were prepared from the corresponding sulphates or nitrates (AR, BDH) in double distilled water, and were standardised by conventional methods. Sodium perchlorate (Riedel) was used to maintain constant ionic strength. Tetramethylammonium hydroxide (TMAH, Merck), 0.1 M in 50% aqueous dioxan, was used as titrant. The solution of ligand was prepared in dioxan; the dioxan used was purified according to the procedure described by Weissberger et al. [5]. The titrations were carried out in a nitrogen atmosphere (N_2 purity $\approx 99.9\%$) which was presaturated with 50% (v/v) aqueous dioxan before passing through the reaction mixture.

Potentiometric titrations

The method of Bjerrum and Calvin as modified by Irving and Rossotti [6,7] was used to determine $\bar{n}$ and pL values. The experimental procedure involves the potentiometric titration of the following solutions against 0.1 M TMAH in 50% (v/v) dioxan–water medium: (i) $HClO_4$ (2.5×10^{-3} M); (ii) $HClO_4$ (2.5×10^{-3} M) + 2-HATS (5.0×10^{-3} M); (iii) $HClO_4$ (2.5×10^{-3} M) + 2-HATS (5.0×10^{-3} M) + M^{2+} (5.0×10^{-4} M).

In order to determine thermodynamic parameters such as ΔG, ΔH and ΔS, the titrations were repeated at various temperatures (15, 30 and $50 \pm 0.5\,^\circ\mathrm{C}$) and at constant ionic strength of 0.1 M $NaClO_4$. The experimental temperature was kept constant within $\pm 0.5\,^\circ\mathrm{C}$ by using an MLW (F.R.G.) NBE type thermostat. The pH values in aqueous organic mixtures were corrected using the method of van Uitert and Hass [8], and correction to the volume was also performed according to the method of Rao and Mathur [9].

The parameters $\bar{n}_H$, the average number of protons bound to ligand, $\bar{n}$, the average number of ligand molecules bound per metal ion, and pL, the free ligand exponent, were evaluated using the expression described by Irving and Rossotti [6,7]. Using these parameters, the pK_a values of the ligand and stability constants of its complexes were then calculated. The stability constants were computed on an Uptron PC+ computer using a weighted least-squares program designed after that of Sullivan et al. [10]. Using this method, the set of β_n which makes the function

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

nearest to zero was determined by minimizing the function S

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

with respect to variation in β_n. In the above equations, y is the total ligand concentration, x is the total concentration of unbound ligand, z is the total metal ion concentration and β_n denotes stability constants.

$S_{\min}$ has the same statistical distribution as χ^2 with K degrees of freedom and with weights defined in accordance with Rydberg and Sullivan [11]. $S_{\min}$ can be equated to χ^2.

RESULTS AND DISCUSSION

The order of formation constants of the metal complexes of 2-HATS has been found to be Mg(II) < Mn(II) < Cd(II) < Pb(II) < Ni(II) < Cu(II). This

TABLE 1

Stability constants of complexes of bivalent metals with 2-HATS at $\mu = 0.1$ M $NaClO_4$ at different temperatures and their thermodynamic parameters at $\mu = 0.1$ M $NaClO_4$ and 30 ± 0.5 °C

System	Stability constant	Temperature (°C)			$-\Delta G$ (kJ mol^{-1})	$-\Delta H$ (kJ mol^{-1})	$-\Delta S$ (kJ K^{-1} mol^{-1})
		15	30	50			
2-HATS	log K_1^H	10.70	10.40	10.19	–	–	–
Mg–2-HATS	log K_1	3.30	3.03	2.92	17.57	20.45	0.0088
	log K_2	–	–	–	–	–	–
	$S_{\min}$	0.01752	0.00135	0.00233	–	–	–
Mn–2-HATS	log K_1	5.00	4.51	4.32	26.15	39.07	0.0426
	log K_2	3.52	3.05	2.92	–	–	–
	$S_{\min}$	0.00067	0.00218	0.00135	–	–	–
Cd–2-HATS	log K_1	5.59	4.83	4.74	27.99	50.75	0.0751
	log K_2	4.20	3.24	3.16	–	–	–
	$S_{\min}$	0.01390	0.00145	0.00906	–	–	–
Pb–2-HATS	log K_1	5.74	5.01	4.90	29.03	56.81	0.0916
	log K_2	4.37	3.41	3.35	–	–	–
	$S_{\min}$	0.01365	0.00715	0.00762	–	–	–
Ni–2-HATS	log K_1	5.94	5.31	5.14	30.79	58.32	0.0908
	log K_2	4.44	3.53	3.49	–	–	–
	$S_{\min}$	0.09156	0.01635	0.02433	–	–	–
Cu–2-HATS	log K_1	6.84	5.91	5.81	34.26	69.99	0.0912
	log K_2	5.12	4.08	4.00	–	–	–
	$S_{\min}$	0.00113	0.0320	0.02308	–	–	–

order is in good agreement with that observed by several other workers [12–14].

In all cases except for Mg(II), log K_1 and log K_2 values were obtained and reported. In the case of Mg(II), the 1 : 1 complex initially formed was extensively hydrolysed subsequently. In all cases, it was observed that log $K_1 >$ log K_2. The values of the stability constants, reported in Table 1, reveal that the stability constants decrease with increasing temperature, as do the pK_a values of 2-HATS.

The thermodynamic parameters (ΔG, ΔH and ΔS) were calculated using the following relationships

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

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

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

The overall free energy, enthalpy and entropy changes at 30 ± 0.5 °C are reported in Table 1. These results indicate that ΔG and ΔH are negative, which shows that the complex formation reactions are favourable at ordinary temperatures.

ACKNOWLEDGEMENT

One of the authors (S.G.) is grateful to U.G.C., New Delhi for providing financial assistance.

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