Thermochimica Acta, 149 (1989) 199–204
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

COMPLEXING ABILITY OF PESTICIDES AND RELATED COMPOUNDS. THERMODYNAMIC PARAMETERS FOR THE FORMATION OF COPPER(II) COMPLEXES OF PHENOXYACETATE, 2-PHENOXYPROPIONATE AND 2-PHENOXYBUTYRATE IN AQUEOUS SOLUTION AT DIFFERENT TEMPERATURES AND IONIC STRENGTHS

LORENZO ABATE, RICCARDO MAGGIORE and CARMELO RIGANO

Dipartimento di Scienze Chimiche dell'Università, Viale A. Doria 6, 95125 Catania (Italy)

CONCETTA DE STEFANO

Istituto di Chimica Analitica dell'Università, Salita Sperone 31, 98166 S. Agata di Messina (Italy)

(Received 16 December 1988)

ABSTRACT

The formation constants of copper(II) complexes of phenoxyacetate, 2-phenoxypropionate and 2-phenoxybutyrate were determined potentiometrically, using an (H^+)–glass electrode at 10, 25, 37 and 45 °C, at different ionic strengths in the range $0.05 \leq I \leq 0.3$ mol l^{-1}. Values for $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ were estimated from the temperature coefficients. Using the formation constants obtained, together with literature results for low molecular weight monocarboxylate ligands, a simple linear relationship between formation and protonation constants was obtained.

INTRODUCTION

Copper is an element which is present only in small quantities in plants, but is necessary for some of their vital functions. The amount of copper present in the soil is of the order of 10 ppm (with high variability, of as much as one order of magnitude), whereas in plants it is present in amounts of the order of 100 ppm. This difference of one order of magnitude between the quantities present in the soil and in plants clearly indicates selective absorption by the latter. In fact, it is well known that significant copper deficiency causes serious illness in plants. Since absorption of the metal ions from soil to plant is governed by the transference of these ions as complexes, it is extremely interesting to investigate the thermodynamic parameters for the formation of species between the ligands present in the soil and the metal ions essential for the life of the plant. In the soil, apart from ligands

0040-6031/89/$03.50

'congenial' to the life of plants, there also occur toxic types of ligand, such as pesticides. A thorough investigation of the copper-complexing capacities of pesticides would therefore be interesting to those involved in studying and protecting plant environments. In previous works in this series [1,2] studies have been made of the protonation and stability constants of phenoxyacetic and 2,4-dichlorophenoxyacetic acids with the alkali and alkaline-earth metals. In the present work we report on the results of a study of complexes of copper with some phenoxy derivatives. The study was carried out potentiometrically at various temperatures and ionic strengths, simulating the different conditions of hypothetical soils, in order to discover the conditions in which copper transference can occur via complex formation with pesticides.

EXPERIMENTAL

Materials

Phenoxyacetic (Fluka), 2-phenoxypropionic (EGA-Chemie) and 2-phenoxybutyric (Aldrich) acids were used without further purification. Alkalimetric titrations gave > 99.5, > 98.2 and > 99% purity for the three ligands, respectively. Copper nitrate (C. Erba RD) was standardized by EDTA titration [3]. Potassium hydroxide solutions were prepared by diluting concentrated Merck ampoules, and then standardized against potassium hydrogenphthalate (Fluka, puriss.). Nitric acid solutions were prepared by diluting concentrated Merck ampoules, and then standardized against KOH.

Apparatus

Potentiometric measurements were performed using a Metrohm 654 pH-meter coupled with glass–saturated calomel electrodes supplied by Orion, the instrumental resolution being ±0.1 mV. The titrant solution (KOH) was delivered by a Metrohm model 654 dispenser (minimum reading 0.01 cm^3). An IBM PC XT and a Honeywell printer were coupled with the pH-meter and the dispenser in order to add pre-established volumes of titrant and print the corresponding e.m.f. values. The measurement cells (25 cm^3) were thermostatted at $T \pm 0.2°C$. All titrations were carried out by stirring magnetically and bubbling purified N_2 through the solution.

Procedure

HNO_3 solution (about 0.1 mol l^{-1}) and $Cu(NO_3)_2$ solution (about 0.5 mol l^{-1}) were prepared. Each solution to be investigated was obtained by mixing in a volumetric flask (250 cm^3) a weighed quantity of the acid under study, 20 cm^3 of HNO_3 solution and a suitable volume of $Cu(NO_3)_2$

solution, so that the concentration of organic ligand was approximately 0.005 mol l^{-1} and that of salt was in the range 0.005–0.1 mol l^{-1}. The solutions obtained in this way were titrated with standard KOH until 90% neutralization. Similar measurements were performed (without $Cu(NO_3)_2$) in order to determine the protonation constants.

Calculations

Calculations to determine the protonation constants and the purity of the ligands were performed using the ESAB2M computer program [4]. Formation constants were calculated using the STACO computer program [5]. Concentrations and thermodynamic parameters are expressed in the molar scale. Protonation and formation constants are expressed using L = ligand, c = free concentrations.

$$K^{H} = c_{HL} c_{H}^{-1} c_{L}^{-1} \qquad K^{Cu} = c_{CuL} c_{Cu}^{-1} c_{L}^{-1} \qquad (1)$$

RESULTS AND DISCUSSION

The protonation constants of phenoxypropionic and phenoxybutyric acid are reported in Table 1. A corresponding table for phenoxyacetic acid has been reported previously [1].

TABLE 1

Protonation constants of phenoxypropionate and phenoxybutyrate

t(°C)	I (mol l^{-1})	log K^{H} [a]	
		phenoxy-propionate	phenoxy-butyrate
10	0.05	2.80	2.99
	0.1	2.78	2.97
	0.15	2.78	2.97
	0.3	2.79	2.98
25	0.05	2.90	3.02
	0.1	2.88	2.99
	0.15	2.87	2.98
	0.3	2.87	2.99
37	0.05	2.97	3.10
	0.1	2.94	3.07
	0.15	2.93	3.06
	0.3	2.94	3.07
45	0.05	3.01	3.18
	0.1	2.98	3.16
	0.15	2.97	3.15
	0.3	2.97	3.15

[a] $3\sigma(\log K^{H}) = 0.005 - 0.015$.

TABLE 2

Formation constants of copper(II) complexes of phenoxyacetate, phenoxypropionate and phenoxybutyrate

t(°C)	I (mol l^{-1})	log K^{Cu}		
		phenoxy acetate [a]	phenoxy propionate [b]	phenoxy butyrate [c]
10	0.05	1.43		1.33
	0.1	1.41		1.22
	0.15	1.41		1.15
	0.3	1.48		1.0
25	0.05	1.55	1.2	1.45
	0.1	1.51	1.1	1.34
	0.15	1.50	1.1	1.27
	0.3	1.53	1.1	1.14
37	0.05	1.62	1.19	1.54
	0.1	1.57	1.16	1.44
	0.15	1.55	1.17	1.37
	0.3	1.55	1.25	1.24
45	0.05	1.66	1.29	1.60
	0.1	1.60	1.26	1.50
	0.15	1.58	1.27	1.43
	0.3	1.57	1.35	1.30

[a] $3\sigma(\log K^{Cu}) = 0.02 - 0.05$.

[b] $3\sigma(\log K^{Cu}) = 0.1 - 0.2$.

[c] $3\sigma(\log K^{Cu}) = 0.05 - 0.1$.

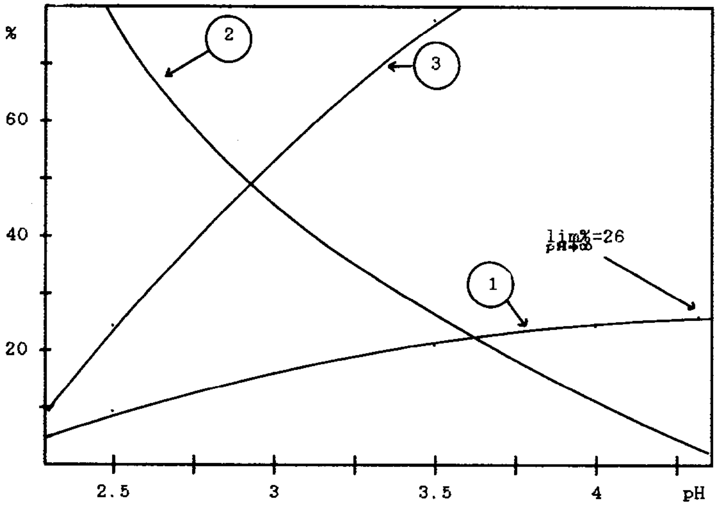

Fig. 1. Distribution of the species in the system Cu^{2+}–H^{+}–phenoxyacetate vs. pH; $T = 25$ °C, $I = 0.05$ mol l^{-1}. Total concentrations: Cu, 1 mmol l^{-1}; phenoxyacetate, 10 mmol l^{-1}. Curve ①, formation percentage of [CuL] with respect to total copper; curve ②, formation percentage of [HL] with respect to total ligand; curve ③, free ligand percentage.

TABLE 3

Thermodynamic parameters at 25 °C and $I = 0.05$ mol l^{-1}

Reaction [a]	$\Delta G^{\ominus}$ (kJ mol^{-1})	$\Delta H^{\ominus}$ (kJ mol^{-1})	$\Delta S^{\ominus}$ (J mol^{-1} deg^{-1})
$H^+ + pop^- \rightleftarrows [H(pop)]^0$	16.55 ± 0.06 [b]	10.2 ± 1.5 [b]	90 ± 6 [b]
$H^+ + pob^- \rightleftarrows [H(pob)]^0$	17.24 ± 0.05	9.2 ± 2.0	89 ± 8
$Cu^{2+} + poa^- \rightleftarrows [Cu(poa)]^+$	8.85 ± 0.15	11 ± 3	67 ± 11
$Cu^{2+} + pop^- \rightleftarrows [Cu(pop)]^+$	6.9 ± 0.7	9 ± 8	54 ± 30
$Cu^{2+} + pob^- \rightleftarrows [Cu(pob)]^+$	8.3 ± 0.3	13 ± 4	71 ± 15

[a] pop = phenoxypropionate; pob = phenoxybutyrate; poa = phenoxyacetate.
[b] $\pm 3\sigma$.

Table 2 gives the formation constants of copper(II) complexes of phenoxyacetate, phenoxypropionate and phenoxybutyrate. By way of example, Fig. 1 shows the distribution diagram for the Cu^{2+}-phenoxyacetate system as a function of pH.

Table 3 gives thermodynamic parameters for both the protonation and formation of complexes with copper of the three acids. As can be seen, the stability of the copper complexes with the ligands studied in this work is very low, and is comparable with that for analogous complexes of acetic acid [6]. Considering the thermodynamic parameters for the protonation and formation of copper complexes of ligands which have only the carboxylic group as coordinating group (formic, acetic, propionic, butanoic, isobutyric, phenylacetic, benzoic, chloroacetic, iodopropanoic and nitroacetic acids), the following linear-type equation can be obtained

$$\log {}^{\mathrm{T}}K^{\mathrm{Cu}} = 0.63 + 0.33 \log {}^{\mathrm{T}}K^{\mathrm{H}} \tag{2}$$

where ${}^{\mathrm{T}}K^{\mathrm{Cu}}$ and ${}^{\mathrm{T}}K^{\mathrm{H}}$ are constants at infinite dilution.

It can be observed from Fig. 2 that the linearity is very good. For these simple ligands, then, the stability constant of the copper complexes can be obtained from the protonation constant alone. As regards dependence on ionic strength, it should be noted that, in agreement with previous observations [7], the Cu^{2+} protonation and formation constants follow the same pattern as a function of ionic strength, independently of the ligand. This dependence can be expressed by the equations

$$\log K^{\mathrm{Cu}} = \log {}^{\mathrm{T}}K^{\mathrm{Cu}} - 2\left[\sqrt{I}/(1+\sqrt{I})\right] + 0.89I \tag{3}$$

$$\log K^{\mathrm{H}} = \log {}^{\mathrm{T}}K^{\mathrm{H}} - \sqrt{I}/(1+\sqrt{I}) + 0.57I \tag{4}$$

Substituting eqns. (3) and (4) into eqn. (2), we obtain

$$\log K^{\mathrm{Cu}} = 0.63 + 0.33\left\{\log K^{\mathrm{H}} - 5\left[\sqrt{I}/(1+\sqrt{I})\right]\right\} + 0.7I \tag{5}$$

Equation (5) can be applied in the ionic strength range $0 \le I \le 0.3$ mol l^{-1} and the temperature range $10 \le t \le 40$ °C. It should be noted that

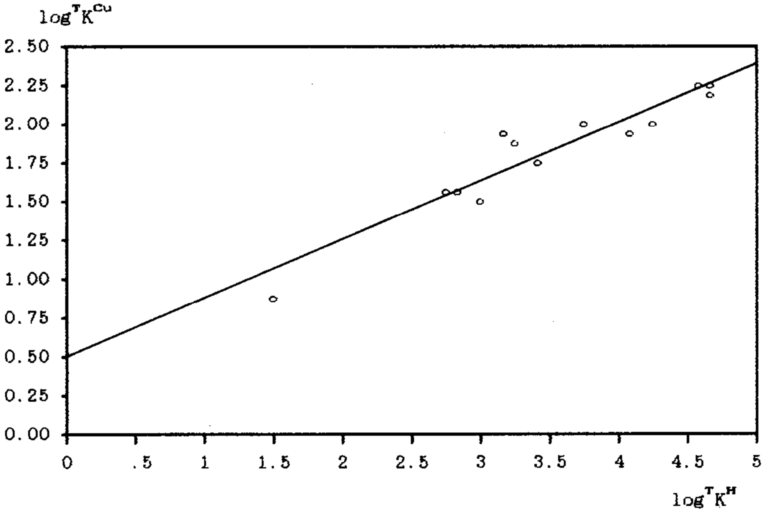

Fig. 2. Log $^TK^{Cu}$ vs. log $^TK^H$ for 13 carboxylic ligands.

since the dependence of log K^{Cu} on temperature is very similar to that of log K^H, in practice they cancel out.

ACKNOWLEDGEMENTS

This work was supported by CNR (Grant 87.02506.74) and the Ministero della Pubblica Istruzione. We thank Prof. S. Sammartano for helpful discussions.

REFERENCES

1 A. Casale, A. De Robertis and S. Sammartano, Thermochim. Acta, 95 (1985) 15.
2 A. Casale, A. De Robertis and C. De Stefano, Thermochim. Acta, 128 (1988) 261.
3 H.A. Flaschka, EDTA Titrations, Pergamon, London, 1959.
4 C. De Stefano, P. Princi, C. Rigano and S. Sammartano, Ann. Chim. (Rome), 77 (1987) 643.
5 C. Rigano and S. Sammartano, unpublished results.
6 A.E. Martell and R.M. Smith, Critical Stability Constants. Vol. 3: Other organic ligands, Plenum, New York, 1977.
7 P.G. Daniele, A. De Robertis, C. De Stefano, S. Sammartano and C. Rigano, J. Chem. Soc., Dalton Trans., 2353 (1985).