Thermochimica Acta, 162 (1990) 449–451
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

Note

COMPLEXING ABILITY OF PESTICIDES AND RELATED COMPOUNDS. THERMODYNAMIC PARAMETERS FOR THE FORMATION OF ZINC(II) COMPLEXES (AND OTHER DIVALENT CATIONS) 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 24 October 1989)

Because of the interest in the study of pesticides in connection with environmental problems, we, together with other colleagues, are investigating the complex formation between some classes of ligands used as pesticides and related compounds [1–3]. In this communication we report the determination of the stability constants of zinc(II) with some phenoxycarboxylic ligands (together with the estimation of the stability constants for other divalent metal ions).

The details of the experiment and the calculations are as previously reported for the analogous complexes of copper(II) [3]. Standard $Zn(NO_3)_2$ solutions were prepared from C. Erba RPE solid chemicals, and were titrated with 0.1 M EDTA (C. Erba RPE).

Table 1 lists the formation constants of Zn^{2+}–phenoxyacetate, Zn^{2+}–2-phenoxypropionate and Zn^{2+}–2-phenoxybutyrate complexes. The depen-

TABLE 1

Formation constants of zinc(II) complexes of phenoxyacetate (poa), phenoxypropionate (pop) and phenoxybutyrate (pob)

Complex	$\log K^{Zn}$ ($I = 0.15$ mol l^{-1}) ±3 (std. dev.)			
	10 °C	25 °C	37 °C	45 °C
poa	0.75 ± 0.15	0.73 ± 0.09	0.62 ± 0.12	0.72 ± 0.14
pop	0.7 ± 0.2	0.6 ± 0.1	0.5 ± 0.1	0.6 ± 0.1
pob	0.7 ± 0.2	0.6 ± 0.1	0.4 ± 0.2	0.65 ± 0.15

0040-6031/90/$03.50

dence of these formation constants on ionic strength is independent of the ligand and can be expressed by the following equation (in the range $0 \leq I \leq 0.3$ mol 1^{-1})

$$\log K(I) = \log K(I') - 2G(I, I') + C(I - I') \tag{1}$$

where

$$C = 0.84 - 0.002(T - 25) \qquad T \text{ in } ^\circ\text{C} \tag{2}$$

$$G(I, I') = \left[I'^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})\right] - \left[I'^{\frac{1}{2}}/(1 + I'^{\frac{1}{2}})\right] \tag{3}$$

where I' is the reference ionic strength.

This type of dependence on ionic strength is in agreement with earlier results [3,4]. From the temperature dependence of the formation constants, it is possible, in principle, to obtain $\Delta H^{\ominus}$ and other thermodynamic parameters; but because the constants are affected by rather high errors (owing to the low stability and the relatively low concentration of reagents that have to be used to prevent hydrolysis), it seems better to only use these parameters for the correct speciation of the systems under study at different temperatures in the investigated range. As a general rule for these complexes, the $\Delta H^{\ominus}$ values are quite small and the main contribution to the stability is entropic.

By considering the present results and the literature data for some other monocarboxylic ligands (formic, acetic, propanoic, butanoic, benzoic, chloroacetic, nitroacetic, glyoxylic and 2-methoxybenzoic acids [5]), we obtained a simple relationship between the formation constant of Zn^{II} complexes and the protonation constant of the ligand

$$\log {}^{\text{T}}K^{\text{Zn}} = 0.14 + 0.28 \log {}^{\text{T}}K^{\text{H}} \tag{4}$$

A similar linear equation was obtained for copper(II) complexes [3]. An analysis of the literature data on monocarboxylic complexes of other divalent cations allowed the coefficients of the generic equation

$$\log {}^{\text{T}}K^{\text{M}} = a + b \log {}^{\text{T}}K^{\text{H}} \tag{5}$$

to also be obtained for cobalt(II), nickel(II) and cadmium(II), as reported in Table 2. It was recently reported that Ca^{2+} monocarboxylate complexes show a fairly constant stability, independent of the ligand [2,4].

TABLE 2

Parameters of eqn. (5) for some divalent cations

Cation	*a*	*b*
Cu^{2+}	0.63	0.33
Zn^{2+}	0.14	0.28
Co^{2+}	0.04	0.29
Ni^{2+}	0.15	0.25
Cd^{2+}	0.38	0.32

The results of this and of earlier investigations and, in particular, the tentative generalisations concerning the stability of some classes of ligands, can be useful in the speciation of multi-component natural fluids where pesticides are present. Studies on other classes of ligands (pesticides and related compounds) are in progress.

ACKNOWLEDGEMENTS

We thank the Ministero della Pubblica Istruzione for financial support, and 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 L. Abate, R. Maggiore, C. Rigano and C. De Stefano, Thermochim. Acta, 149 (1989) 199.
4 P.G. Daniele, A. De Robertis, C. De Stefano, S. Sammartano and C. Rigano, J. Chem. Soc., Dalton Trans., (1985) 2353; A. Casale, P.G. Daniele, A. De Robertis and S. Sammartano, Ann. Chim. (Rome), 78 (1988) 249.
5 A.E. Martell and R.M. Smith, Critical Stability Constants, Vol. 3, Other Organic Ligands, Plenum, New York, 1977.