Inorganica Chimica Acta, *107* (1985) 63–66

Cu(II) Binding by Substituted 1,3,5-Triazine Herbicides

P. DECOCK, B. DUBOIS, J. LERIVREY

Laboratoire de Chimie Minérale et Méthodologie Analytique, Université des Sciences et Techniques de Lille, 59-655 Villeneuve d'Ascq, Cedex, France

C. GESSA

Istituto di Chimica Agraria, Università degli Studi di Sassari, 07100 Sassari, Italy

J. URBAŃSKA and H. KOZŁOWSKI*

Institute of Chemistry, University of Wrocław, 14 F. Joliot-Curie Street, 50-383 Wrocław, Poland

Received December 4, 1984

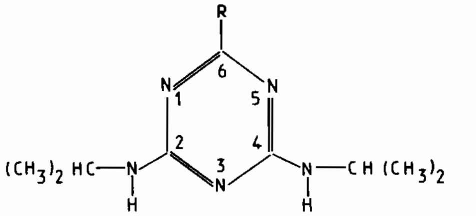
Abstract

s-Triazine herbicides form relatively stable complexes with cupric ions, complexes in which the major binding site was found to be a cyclic nitrogen N5. Polarographic data have shown that cuprous ions also form quite stable complexes with the studied ligands. The stability constants strongly suggest that s-triazines act in solutions as the monodentate ligands, a result which agrees well with earlier X-ray results.

Introduction

Attention has recently been given to studies on a possible mechanism of s-triazine absorption by mineral matter of soil [1–3]. The formation of coordination complexes of herbicides with exchangeable metal ions of the clay minerals could be of critical importance in such a mechanism, and a precise physico-chemical description of the herbicide–metal systems seemed important to us.

Reck *et al.* [4–10] determined several structures of s-triazine–metal coordination compounds showing the structural varieties of s-triazines ligands in the formed complexes. The ring nitrogen (N5) was shown to be a major binding site for most systems studied. The involvement of the other s-triazine donors was found also to be possible, with relatively long metal–ligand bond formation. In order to understand more precisely the stability of the formed metal–s-triazine complexes, as well as to learn their behaviour in solution, we made spectroscopic, potentiometric and polarographic studies of the Cu(II) complexes with prometone (2-methoxy-4,6-bis(isopropylamino)-s-triazine) (PR), hydroxyprometone (2-hydroxy-4,6-bis(isopropylamino)-s-triazine) (PROH), propazine (2-chloro-4,6-bis(isopropylamino)-s-triazine) (PZ) and prometryne (2-methylthio-4,6-bis(isopropylamino)-s-triazine) (PY).



R—O-CH$_3$ (PR), OH (PROH), Cl (PZ), S-CH$_3$ (PY)

Scheme 1

The results of these studies are reported in this paper.

Experimental

Potentiometric studies were performed with the use of analytical potentiometry (F.I.C.S.) [11]. The solutions were prepared in deionized and bidistilled water under argon atmosphere. Carbonate-free 0.1013 M NaOH was prepared in 0.15 M NaCl and standardized against phthalate (National Bureau of Standards). A solution of 0.1 M HCl was standardized with 0.1013 M NaOH. Puratronic cupric chloride was dissolved to a concentration of 0.2 M in 0.003 M HCl solution, checked by titration with EDTA. PR, PZ and PY were used as obtained from CIBA-GEIGY. Purity was checked by C.P.G. PROH was prepared by bubbling dry hydrochloride into a dry solution of PR in ether.

---

*Author to whom correspondence should be addressed.

0020-1693/85/$3.30

The potentiometric titrations were carried out on a Tacussel ISIS 20000 pH-meter at 25 ± 0.03 °C with a TB 10/HA glass electrode and a KCl saturated reference electrode.

Calculations were performed on an Apple II computer. The titrated quantities of Cu(II) and triazines are given in Table I.

TABLE I. Quantity in Micromoles of Copper and s-Triazines used in Titration.

Cu	PR	Cu	PROH	Cu	PY
0 0.5 1	6.25	0 0.6 0.8	6.81	0 1 2	5.72
0.5	4.46 6.25 8.93	0.6	4.87 6.81 9.74	1	3.98 5.72 7.96

EPR measurements were performed with a Varian E 102 instrument operating at X-bond frequency (9.05 GHz). Spectra were recorded at 77 K in methanol. Electronic absorption spectra were taken on a Beckman UV 5270. The Cu(II) concentration used in spectroscopic studies was 10^{-3} M.

Polarographic studies were performed on HP 05 and Tacussel PRG5 polarographs. In the latter case a three electrode system was used: a dropping mercury electrode as a working electrode, and a platinum wire as a counter electrode, and a saturated calomel electrode as a reference electrode. Polarograms were recorded at 25 °C under argon in 0.15 M $NaClO_4$ electrolyte.

Results and Discussion

PR may be considered as a LH ligand, with a protonation site on a cyclic nitrogen in the vicinity of C6 (N5 or N1). Our results indicate a pK value for the ligand equal to 4.39, which is relatively close to that found earlier by spectroscopic methods [12].

Potentiometric results indicate the formation of two major species, CuL_2 and $CuH_{-1}L_2$ (Table II). At higher pH than 7.5, even for 20-fold excess of ligand, the formation of cupric hydroxide is observed and therefore all studies were performed below pH 7.5. The β value of CuL_2 ($\log \beta = 7.6$) is very close to that found for $Cu(NH_3)_2$ species [13, 14], suggesting a monodentate character of the metal–prometone binding in CuL_2 species. The absorption spectra strongly suggest two nitrogens being involved in a cupric ion binding showing 670 nm d–d transition with $\epsilon = 80$ M^{-1} cm^{-1} [15]. The EPR measurements have indicated the presence of one major species at pH range 4–6 ($g_{\parallel} = 2.389$, $A_{\parallel} = 150$ Gs), besides a Cu(II) aquoion.

TABLE II. Logarithm Stability Constants ($\log \beta pqr$) of Complex Species $M_pH_qL_r$ (M = Cu(II), L = PR, PROH, PZ or PY) in 0.15 M NaCl at 25 °C. K_1 is in Relation with $Cu + 2LH_{n-1} \rightleftarrows CuH_{2n-2}L_2$ and K_2 with $CuH_{2n-2}L_2 \rightleftarrows CuH_{2n-3}L_2$.

L	p	q	r	$\log \beta pqr$	$\log K_1$	$\log K_2$
PR	0	1	1	4.39		
	1	0	2	7.06	7.06	
	1	−1	2	1.15		−5.91
PROH	0	1	1	11.16		
	0	2	1	16.53		
	1	2	2	29.08	6.76	
	1	1	2	23.07		−6.01
	1	−1	2	7.66		
PZ	0	1	1	1.85		
PY	0	1	1	4.29		
	1	0	2	6.90	6.90	
	1	−1	2	1.51		−5.39

This major complex formed at pH 4–6 is a species in which two PR molecules being deprotonated bind Cu(II) ion via N5 (or N1) nitrogens. It corresponds very closely to the solid state structure of the complexes reported earlier [4–7]. The low β value of CuL_2 species, showing a monodentate rather than a chelate binding of the ligand, indicates that ether oxygens (which form very long bonds with Cu(II) ion in the solid state complex) are not competitive in the solution with solvent molecules or Cl^- ions in the metal ion binding. The latter ion is, in fact, bound to metal ion in the solid state complex. The increase of pH above 6 leads to the deprotonation of CuL_2 complex and the $CuH_{-1}L_2$ species becomes a major species at pH ≃ 7. The pK value of this deprotonation (6.05), though relatively low, may be attributed to one of metal bound H_2O molecule. The low value of pK may derive from the fact that both ligands are uncharged and monodentately bound to the Cu(II) ion.

Hydrolyzed prometone molecule, PROH, has two measurable deprotonation constants $pK_1 = 5.37$ and $pK_2 = 11.16$ (Table II). The former value, similarly to prometone, corresponds to protonation of cyclic nitrogen around C6 carbon and the latter value to deprotonation of C6–OH group. Both values were estimated earlier by spectroscopic methods [12] and they correspond roughly to the values obtained in this work.

The coordination of Cu(II) with PROH (LH_2) closely resembles that found in the Cu(II)–prometone solutions. The 1:2 complex formed at pH 4–6 has a slightly lower K_1 value ($\log K_1 = 6.76$, see

Table II) than that found for corresponding Cu(II)–prometone species. This suggests the same binding mode in both cases *i.e.* two ligands bound with a metal ion, using almost exactly the same spectroscopic parameters (670 nm, $\epsilon = 80$ M^{-1} cm^{-1}, $g_{\parallel} = 2.389$, $A_{\parallel} = 150$ Gs).

The increase of pH above 6 leads to a deprotonation of a $Cu(LH)_2$ complex with pK = 6.01, very close to that found in the Cu(II)–prometone system (Table II). At pH > 8 a major amount of Cu(II) undergoes hydrolysis to cupric hydroxide. Thus a hydroxyl group of hydroxyprometone being a potential binding site for cupric ion is not effective in a metal ion binding. This derives from the fact that a chelate which could be eventually formed by {N,O} coordination is a rather unfavourable four-membered ring.

Prometryne was found to exhibit the same binding abilities as those described above for PR and PROH. The protonation constant pK = 4.29 is very close to that for PR (4.39). PY also forms two major species, CuL_2 and $CuH_{-1}L_2$. The CuL_2 complex with the d–d transition at 670 nm ($\epsilon = 80$ M^{-1} cm^{-1}) and $g_{\parallel} = 2.388$ and $A_{\parallel} = 153$ Gs is a 2N species with two nitrogens bound to a metal ion. The formation constant (Table II) indicates monodentate binding of both ligands (see discussion above).

For PZ, the protonation constant pK = 1.85, is considerably smaller than those mentioned above for PR, PROH and PY (Table II). The very acidic character of PZ may explain the fact that neither spectroscopic nor potentiometric studies could indicate any complex formation in the aqueous solutions.

Prometone is only polarographically active in its protonated form (PRH^+). In strongly acidic solutions PRH^+ undergoes reduction at –0.965 V (pH = 1). This potential shifts to more negative values when pH increases up to pH ≃ 3.5. The reduction wave of PRH^+ is diffusion-controlled and corresponds to a one-electron reduction process. In the pH range 3.7–5.5 two other irreversible waves are observed, which correspond to the catalytic reduction of hydrogen at –1.26 V (volume wave) and –1.64 V (surface wave [16]) (Fig. 1).

In previous work it was generally assumed that prometone is not active in polarography, though there are data available for the other triazine derivatives [17].

The reduction of Cu(II) aquoions is one-step, and a two-electron process since cuprous ions are very unstable at potentials at which cupric ions are reduced. The reduction of Cu(II) ions in the presence of PR is a complicated process, and polarograms at pH ≃ 6 consist usually of three waves (Fig. 2). The wave at $E_{1/2}$ about 0.17 V corresponds to a one-electron reduction process ($Cu^{2+} \rightarrow Cu^+$). This result clearly shows the stabilization of cuprous ions by prometone ligand. The increase of PR concentration causes the shift of the $E_{1/2}$ value of this process to more positive values (Fig. 2), which indicates that prometone may form quite stable complexes with Cu^+ ions. A similar stabilization effect was found during the reduction of Cu^{+2} ions in the presence of ammonia molecules [18, 19].

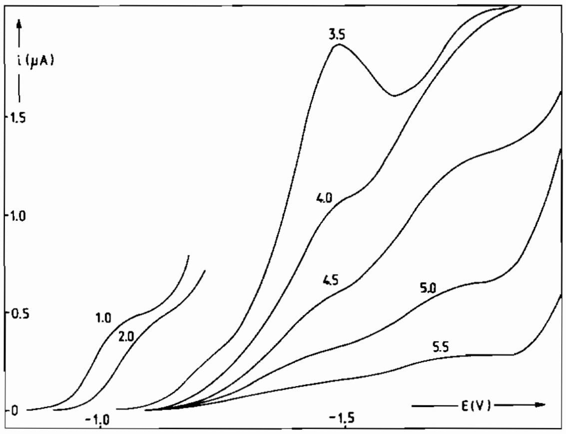


Fig. 1. Polarograms of metal-free prometone solutions at different pH. $c_{PR} = 10^{-3}$ M, $c_{NaClO_4} = 0.15$ M.

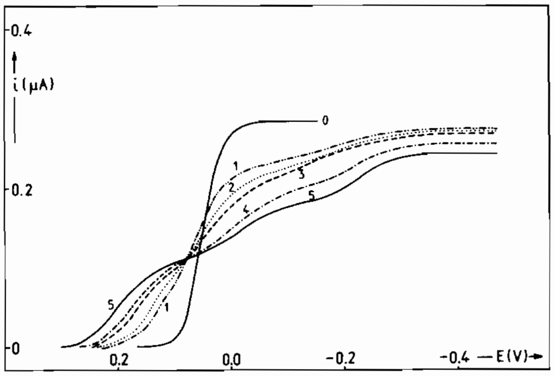


Fig. 2. Polarogram for the Cu(II)–PR solutions for different PR to Cu(II) molar ratios at pH = 6. $c_{NaClO_4} = 0.15$ M; $c_{Cu} = 5 \times 10^{-5}$ M; $c_{PR} = 0$ (0), 10^{-4} (1), 2×10^{-4} (2), 5×10^{-4} (3), 10^{-3} (4) and 2.5×10^{-3} (5).

The second reduction wave at $E_{1/2} \sim 0.02$ V (Fig. 2) is an irreversible wave, corresponding most likely to the reduction of CuL_2 complex which is the only complex species at pH ≃ 6 found for the Cu(II)–PR solutions (see above).

The third wave at $E_{1/2} \simeq -0.24$ V could be assigned as a reduction wave of a Cu(I)–PR complex.

Conclusions

s-Triazine pesticides form relatively stable complexes with Cu^{+2} ions, in which the major binding site is centered on a cyclic nitrogen donor. Polarographic studies have shown that cuprous ions also form stable complexes with s-triazine ligands. The results presented in this work indicate only minor (if any) involvement of other than cyclic donors in metal ion binding, a result which agrees with earlier X-ray studies on similar systems.

Acknowledgement

We thank Dr W. Wilgocki for helpful discussion.

References

1 R. J. Hance, *Can. J. Soil Sci., 49,* 357 (1969).
2 J. B. Weber, *Residue Rev., 32,* 93 (1976).
3 R. J. Hance, *Weed Res., 11,* 106 (1971).
4 G. Reck, A. Kircheiss and R. Baume, *Cryst. Struct. Commun., 10,* 993 (1981).
5 G. Reck, A. Kircheiss and R. Baume, *Z. Anorg. Allg. Chem., 470,* 209 (1980).
6 G. Reck, G. Bannier, A. Kircheiss and R. Baume, *Cryst. Res. Technol., 18,* 1245 (1983).
7 G. Reck, A. Kircheiss, R. Baume and P. Leibnitz, *Cryst. Struct. Commun., 11,* 1997 (1982).
8 G. Reck, R. G. Kretchmer, A. Kircheiss and R. Baume, *Cryst. Struct. Commun., 11,* 1557 (1982).
9 G. Reck, A. Kircheiss and R. Baume, *Cryst. Struct. Commun., 11,* 1147 (1982).
10 A. Kircheiss, A. Bohme, R. Baume and G. Reck, *Wiss. Z. Univ. Halle, XXXII, 83M,* H.5 (1983).
11 P. Decock and B. Sarkar, submitted for publication.
12 J. B. Weber, *Spectrochim. Acta, Part A:, 23,* 458 (1967).
13 R. C. Mercier, M. Bonnet and M. R. Paris, *Bull. Soc. Chim. Fr.,* 2926 (1965).
14 D. Fridman, M. G. Levina and R. I. Sorochan, *Zh. Neorg. Khim., 11,* 1641 (1966).
15 G. Formicka-Kozłowska, H. Kozłowski and B. Jeżowksa-Trzebiatowska, *Inorg. Chim. Acta, 25,* 1 (1977) and refs. therein.
16 S. G. Mairanowskii, 'Catalytic and Kinetic Wavel in Polarography', Plenum, New York, 1968, p. 266.
17 J. Polák and J. Volke, *Cesk. Farm., 32,* 282 (1983).
18 M. von Stackelberg and H. von Freyhold, *Z. Electrochem., 46,* 120 (1940).
19 D. R. Crow, 'Polarography of Metal Complexes', Academic Press, London and New York, 1969, p. 78.