ELECTROCHEMICAL STUDIES OF THE STABILITY OF COPPER β-DIKETONE CHELATES

Wulfhard MICKLER[1], Anke MONNER[2] and †Erhard UHLEMANN

Universitat Potsdam, Institut fur Anorganische Chemie und Didaktik der Chemie, PF 60 15 53, D-14415 Potsdam, Germany; e-mail: [1] wmickler@rz.uni-potsdam.de, [2] moenner@van-hees.com

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The voltammetric reduction of copper β-diketone chelates was used to get information on their complex stability. 1,1,1-Trifluoropentane-2,4-dione, pentane-2,4-dione, 1-phenylbutane-1,3-dione, 1,3-diphenylpropane-1,3-dione and 2,2,6,6-tetramethylheptane-3,5-dione were chosen as model ligands. The complexes were reduced in two separate steps the first of which proved to be reversible. The experimental data are suitable for calculation of the relative stability constants of corresponding Cu(I) and Cu(II) complexes. The data well correlate with the overall stability constants determined potentiometrically. The results were applied to some new hydrophobic β-diketones which are not accessible to potentiometric measurements.

Key words: Electrochemistry; Voltammetry; Complex stability constants; Copper complexes; β-Diketones; Chelates.

Polarography is a well-known method for determination of stability constants of complexes[1]. The difference of the half-wave potentials ΔE for the reduction of hydrated and complexed metal ion is given by the equation

$$\Delta E = -\frac{RT}{zF}\ln\beta - n\frac{RT}{zF}\ln[\mathrm{L}] \ . \tag{1}$$

The function $E_p = f(\log [\mathrm{L}])$ is accessible by measuring the reduction potentials in dependence on the ligand concentration [L]. If the reaction proceeds reversibly, the slope of this function corresponds to 0.059 n/z. In this way, the number of ligands n and transferred electrons z as well as the overall stability constant β can be determined. If a metal in several valence states forms complexes, then the equation

$$\mathrm{ML}_n + z\,\mathrm{e} \rightleftharpoons \mathrm{ML}_m + (n-m)\,\mathrm{L}^- \tag{2}$$

is valid for the reduction[2].

The half-wave potential is given by

$$E_{1/2} = E^0 - \frac{RT}{zF} \ln \frac{D_{ox}}{D_{red}} - (n - m) \frac{RT}{zF} \ln [\mathrm{L}] \ . \tag{3}$$

In many cases the diffusion coefficients D_{ox} and D_{red} of the oxidized and reduced forms are assumed to be equal. Consequently, the two polarographic reduction steps of copper complexes can be described by the equations[3]

$$\Delta E_1 = -\frac{RT}{zF} \ln \frac{\beta(\mathrm{Cu^{II}L_2})}{\beta(\mathrm{Cu^{I}L})} - (n - m) \frac{RT}{zF} \ln [\mathrm{L}] \tag{4}$$

$$\Delta E_2 = -\frac{RT}{zF} \ln \beta(\mathrm{Cu^{I}L}) - m \frac{RT}{zF} \ln [\mathrm{L}] \ , \tag{5}$$

where $\beta(\mathrm{Cu^{II}L_2})$ and $\beta(\mathrm{Cu^{I}L})$ are the stability constants for the copper(II) and copper(I) complexes.

A very important condition for polarographic determination of stability constants of complexes is the reversibility of the electrode process. This condition is not fulfilled in nonaqueous solvents or in mixtures of aqueous and nonaqueous solvents. Such mixtures are necessary, however, for the study of complexes with organic ligands, but quantitative measurements are scarcely known.

As an example, the complexation of copper by β-diketones was previously studied in dioxane–water mixtures[4–6]. Unfortunately, the reduction was found to be irreversible. Hence, the half-wave potentials could only be used as a measure of the relative stability of complexes[7].

In this paper, former investigations were repeated with the help of modern voltammetric techniques to find relationship between polarographic data and complex stability constants determined potentiometrically.

EXPERIMENTAL

The measurements were carried out with VA processors 646 and 693 (Metrohm, Switzerland) at a hanging mercury drop electrode. An automatic control warrants a reproducible drop size of 0.4 $\mathrm{mm^2}$. The Ag/AgCl/3 M KCl was used as a reference electrode and the platinum bar as an auxiliary electrode. The pulse polarographic and cyclovoltammetric measurements were performed at the scan rate of 20 mV $\mathrm{s^{-1}}$. The period of a potential pulse was 600 ms and the potential step 12 mV.

The base electrolyte consisted of 75% (v/v) dioxane and 25% (v/v) acetate buffer (pH 5.5). The buffer also served as a supporting electrolyte. Solutions were deoxygenated by vigourous bubbling with pure nitrogen for 15 min. A temperature of 23 ± 2 °C was maintained.

The model compounds **1**–**5** (Table I) were commercially available. The other β-diketones were synthesized by Claisen condensation of acetophenone with corresponding esters following literature methods[8]. The physicochemical properties and the extraction behaviour of these compounds were reported elsewhere[9]. The ligands studied are given in Table I.

RESULTS AND DISCUSSION

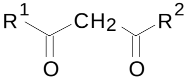
The potential for the reduction of copper ions is 62 ± 5 mV as found by means of the differential pulse method. The reduction of copper chelates with β-diketones proceeds in two steps, the first one being reversible.

$$Cu^{II}L_2 + e + H^+ \rightleftharpoons Cu^{I}L + HL \qquad (6)$$

$$Cu^{I}L + e + H^+ \rightarrow Cu^0\,(Hg) + HL \qquad (7)$$

Typical cyclovoltammograms for the copper(II) complex of **4** are given in Fig. 1. Figure 2 shows reduction peaks in dependence on the ligand concentration. It can be seen that the reduction peak according to Eq. (*6*) decreases with increasing concentration of the ligand, whereas the second peak (Eq. (*7*)) simultaneously increases. For the first step the ratio of anodic and cathodic peak currents is approximately unity with the peak

TABLE I
β-Diketones used as ligands in copper chelates



Compound	Name	R^1	R^2
1	1,1,1-Trifluoropentane-2,4-dione	CF_3	CH_3
2	Pentane-2,4-dione	CH_3	CH_3
3	1-Phenylbutane-1,3-dione	C_6H_5	CH_3
4	1,3-Diphenylpropane-1,3-dione	C_6H_5	C_6H_5
5	2,2,6,6-Tetramethylheptane-3,5-dione	$(CH_3)_3C$	$C(CH_3)_3$
6	1-Phenyldecane-1,3-dione	C_6H_5	$n\text{-}C_7H_{15}$
7	1-(4-Hexylphenyl)butane-1,3-dione	$p\text{-}C_6H_{13}–C_6H_4$	CH_3
8	1-Cyclohexyl-3-phenylpropane-1,3-dione	C_6H_{11}	C_6H_5
9	1-Cyclohexyl-4-phenylbutane-2,4-dione	$C_6H_{11}–CH_2$	C_6H_5
10	1-Cyclohexyl-5-phenylpentane-3,5-dione	$C_6H_{11}–CH_2–CH_2$	C_6H_5
11	1-Cyclopentyl-5-phenylpentane-3,5-dione	$C_5H_9–CH_2–CH_2$	C_6H_5

separation of 65 mV, indicating the reversibility of the reaction. On the other hand, the second reduction step is irreversible (Eq. (*7*)). For all the studied compounds and the first reduction step the plot of the potential *vs* logarithm of the ligand concentration gives straight line with the slope of 60 ± 10 mV, assuming to $(n - m)/z = 1$.

On the basis of reversibility of the first reduction step, the relationship of stability constants of Cu(II) and Cu(I) complexes can be evaluated (see Eq. (*4*)). Table II gives a survey of the measured potentials and calculated stability data. In Fig. 3, these data are correlated with stability constants β_2 determined potentiometrically in the same solvent mixture.

The linear relationship

$$\beta_2 = a\ (\log \beta(\mathrm{Cu^{II}L_2})/\beta(\mathrm{Cu^{I}L})) + b \tag{8}$$

with $a = 6.57$ and $b = -14.07$ (correlation coefficient $r = 0.995$) enables to evaluate the stability constants of β-diketones because potentiometry is not applicable due to their

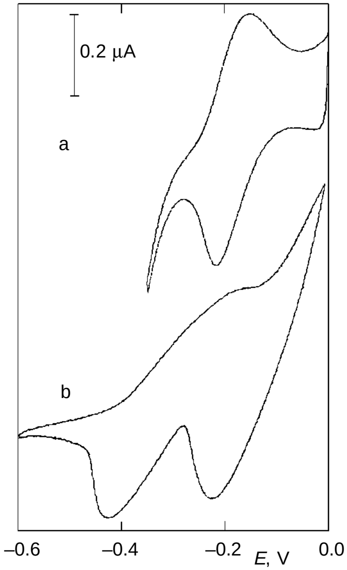


FIG. 1

Cyclovoltammograms for the reduction of copper(II) chelate **4**; reversible reduction Cu(II)⇌Cu(I) (a), irreversible reduction Cu(II) → Cu(I) → Cu(0) (b)

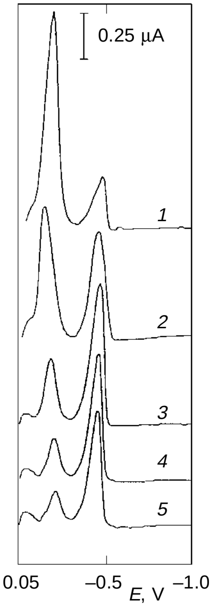


FIG. 2

Polarograms for the reduction of copper(II) chelate **3** in dependence on various concentrations of the ligand: *1* 0.5 . 10^{-3} mol l^{-1}, *2* 1 . 10^{-3} mol l^{-1}, *3* 2.5 . 10^{-3} mol l^{-1}, *4* 5 . 10^{-3} mol l^{-1}, *5* 7.5 . 10^{-3} mol l^{-1}; $[\mathrm{Cu^{2+}}]$: 5 . 10^{-5} mol l^{-1}

limited solubilities. These compounds are, however, interesting as extractants. Table II contains measured reduction potentials which, for the first step, are close to E = –160 mV. Because of their small differences, also the values of stability constants are similar (log β is in the range of 5.6–5.9) and fit well between the values found for the compounds **3** and **4**.

TABLE II
Reduction potentials and stability data of copper β-diketone chelates

Compound	E_p, mV		$\log(\beta(Cu^{II}L_2)/\beta(Cu^{I}L))$	β_2
	Cu^{II}/Cu^{I}	Cu^{I}/Cu^{0}		
1	–76	–157	4.34	14.55[a]
2	–150	–454	5.59	22.69[a]
3	–158	–379	5.73	23.00[a]
4	–170	–403	5.93	24.98[a]
5	–181	–727	6.11	26.42[a]
6	–163	–459	5.81	24.27[b]
7	–160	–449	5.76	23.94[b]
8	–167	–444	5.88	24.73[b]
9	–154	–457	5.66	23.28[b]
10	–152	–444	5.63	23.08[b]
11	–163	–462	5.81	24.27[b]

[a] Ref.[10]; [b] calculated by Eq. *(8)*.

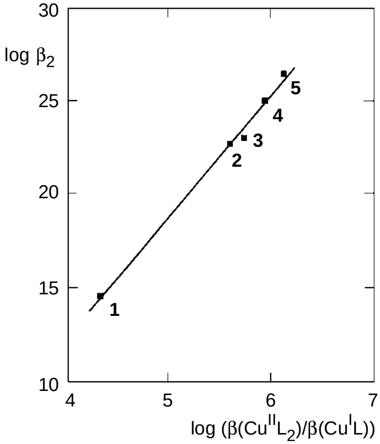


FIG. 3
Correlation of potentiometrically determined log β values with the voltammetric data on the relative stability between copper(I) and copper(II) chelates (for the meaning of numbers, see Table I)

Potentials of second reduction step of copper β-diketone complexes show no unequivocal dependence on the ligand concentration. This finding agrees with the irreversibility of the reaction. Consequently, these potentials are not suitable for the calculation of stability constants. The reduction potentials in the second step as they were determined in this work approximately correspond to data of Holtzclaw[6]. But in the latter case one-step reaction was assumed:

$$CuL_2 + 2\,e + Hg \rightarrow Cu^0\,(Hg) + 2\,HL\ . \qquad (9)$$

Therefore, only qualitative interpretations are possible at present. Only the relation between the stability constants of Cu(I) and Cu(II) complexes can be calculated; the electrochemical data show a linear correlation with the overall stability constants determined potentiometrically in the same solvent. Thus, the stability data can be evaluated for complexes where potentiometric method is not applicable.

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