The Complexation of Palladium(II) by Chloroacetate

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The complexation of palladium(II) by chloroacetate was studied by spectrophotometry in 1.00 M-(Na, H)ClO$_4$ at (25.0 $\pm$ 0.2) °C. The experimental data were treated numerically by OPIUM program. The stability constant log $\beta_{PdL} = 3.30_9 \pm 0.01_1$ and spectra of individual species were calculated. The calculated stability constant is in good agreement with the value predicted by LFER approach (3.4$_8 \pm$ 0.1$_3$). The thermodynamic parameters of complexation reaction, ΔH = (-10.7 ± 0.7) kJ mol^{-1} and ΔS = ($-26._7 \pm 42._1$) J K^{-1} mol^{-1}, were also estimated by weighted linear least-squares procedure from the dependence of stability constant on temperature in the region 25—44 °C.

Chloroacetic acid is a stronger acid than acetic acid due to halogen derivatization on an aliphatic chain. Generally, it forms less stable complexes with transition metal ions than acetic or other monocarboxylic organic acids nonderivatized on aliphatic chain [1]. The substance is often used as a buffer to study palladium complex equilibria in acidic media [2, 3], because of its low pK_a value. Unfortunately, there is a lack of stability constants for the system palladium(II)—chloroacetate [1] and mostly the complexation of palladium(II) by chloroacetate is neglected.

Recently, an extensive equilibrium and kinetics study of palladium with thirteen organic mono- and dicarboxylic acids was done [4, 5]. The authors determined the stability constants of PdL complex and also the rate constants of formation and dissociation processes. These values correlate very well with protonation constants of the ligands according to Linear Free Energy Relationship (LFER).

As there are no experimental values of stability constants of Pd(II)—chloroacetate available, the aim of this work was to determine the chemical model for palladium(II)—chloroacetate system and to verify experimentally the validity of LFER approach published elsewhere [5].

EXPERIMENTAL

Palladium (anal. grade, ALFA Matthey—Johnson, Germany) and chloroacetic acid (anal. grade, Fluka, Switzerland) were used as received. Other chemical substances (NaClO$_4$, HClO$_4$, etc.) were of anal. grade with trace content of other metal ions lower than 0.0005 %.

The palladium(II) perchlorate was prepared as described earlier [6]. Palladium salt was dissolved in concentrated nitric acid and evaporated to dryness. This procedure was repeated several times with concentrated (70 mass %) perchloric acid to eliminate traces of nitrate.

The palladium content was determined according to the standard procedures (spectrophotometrically as PdBr$_4^{2-}$ and by ICP-AES at λ = 340.458 nm), details can be found elsewhere [7]. The content of acid in the standard solution of palladium(II) perchlorate was determined by alkalimetric titration after addition of KSCN to mask palladium in the form of Pd(SCN)$_4^{2-}$ complex in order to eliminate palladium(II) extensive hydrolysis at low acidity [7, 12].

The absorbance measurements were carried out on the one-beam diode array spectrophotometer HP 8453 A (Hewlett—Packard, USA). The palladium concentration (c_{Pd} = 0.0108 mol dm^{-3}) was fixed for all experiments. The ligand concentration was changed during the experiment in the concentration range 0—0.55 mol dm^{-3} at proton concentrations 1.00 resp. 0.80 mol dm^{-3}. The ionic strength was maintained at the value of I((Na, H)ClO$_4$) = 1.00 mol dm^{-3} by sodium perchlorate additions. The contribution of chlorocetate for higher $-\log\{[H^+]\}$ values was taken into account when calculating the total acidity and ionic strength. The temperature was kept at (25.0 $\pm$ 0.2) °C or at other values as described below.

RESULTS AND DISCUSSION

The measurements were done at various, rather high proton concentrations (1.00 mol dm^{-3} and 0.80 mol dm^{-3}) to prevent extensive palladium hydrolysis

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Table 1. Comparison of Stability Constants of Palladium(II) Complexes with Various Simple Organic Acids at 25 °C and at $I((Na, H)ClO_4) = 1.00$ mol dm^{-3}

Ligand Carboxylic acid	Protonation constant $\log\{K_a\}$	Stability constant $\log\{\beta_{ML}\}$	Source
Formic	3.53	3.67 ± 0.03	[5]
Acetic	4.57	4.34 ± 0.02	[4]
Propionic	4.67	4.32 ± 0.05	[4]
Butyric	4.68	4.38 ± 0.02	[5]
Glycolic	3.62	3.81 ± 0.01	[4]
DL-Lactic	3.64	3.79 ± 0.01	[5]
Methoxyacetic	3.40	3.604 ± 0.003	[5]
Malonic	2.60; 5.07	3.40 ± 0.02	[5]
Succinic	3.95; 5.12	4.03 ± 0.07	[5]
L-Malic	3.11; 4.45	3.65 ± 0.01	[5]
Citric	2.80; 4.08	3.46 ± 0.01	[5]
Chloroacetic	2.66^a	$3.4_8 \pm 0.1_3^b$	This paper LFER approach
Chloroacetic	2.66^a	$3.284_8 \pm 0.008_3^c$	This paper
		$\mathbf{3.30_9 \pm 0.01_1^d}$	Exp. value

a) Taken from [9] and [10]; *b)* calculated from LFER: $\log\{\beta_{ML}\} = (0.48 \pm 0.03) \times \{pK_a\} + (2.2 \pm 0.1)$ [5]; *c)* calculated by means of OPIUM program (statistical weight $= 1/s(A)^2$) for all experimental points, where $s(A) = 0.003$; *d)* calculated by means of OPIUM program (varied weight $= 1/s(A)^2$) for all experimental points, where standard deviation of absorbance, $s(A)$, declared by producer Hewlett—Packard is $s(A) = 0.001 + 0.004 \times (A)$.

at $-\log\{[H^+]\} > 2$ [12]. The maximum of broad absorption band of Pd^{2+} ion (380 nm) is slightly shifted towards higher wavelength in comparison to the band of palladium(II) complex PdL^+ (390 nm). The increase of absorbance, which is a consequence of complex formation, was also observed. The formation of palladium(II) complex with chlorocetate can be written as

$$Pd^{2+} + nL^- \Leftrightarrow PdL_n^{(2-n)} \quad \beta(PdL_n^{(2-n)}) \quad (A)$$
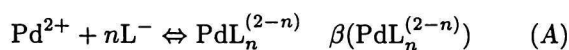
with stability constant $\beta(PdL_n^{(2-n)})$

$$\beta(PdL_n^{(2-n)}) = \frac{[PdL_n^{(2-n)}]}{[Pd^{2+}][L^-]^n} \quad (1)$$

Absorbance matrix data of 45 solutions ($[H^+] = 1.00$ mol dm^{-3} and 0.80 mol dm^{-3}) $\times$ 39 wavelengths (260—450 nm, each 5 nm) were used for the stability constant determination of species present in solution by OPIUM software package [8]. The protonation constant of chloroacetate was taken from literature or calculated for given temperature using published data $\Delta H° = 3.1$ kJ mol^{-1} [9, 10]. Several models were tested. The simple model involving only PdL^+ complex was found to be viable. The same statistical parameters for evaluation of correct chemical model were used as in [15]. The models taking into account PdL_2 species formed or hydrolytic palladium(II) species for correction of calculated stability constant β_{PdL} were also tested. It was found that neither PdL_2 nor hydrolytic mixed species was formed since almost the same stability constants for different proton concentrations ($\log\{\beta([H^+] = 1.00$ mol dm$^{-3})\} = 3.279 \pm$

0.005 and $\log\{\beta([H^+] = 0.80$ mol dm$^{-3})\} = 3.257 \pm 0.004$) were obtained. The models including mixed species do not give better fit for experimental data, therefore the formation of single PdL^+ complex was considered as the best explanation of experimental data (Table 1). This fact is also in good agreement with the results obtained for other transition metal ions forming weak complexes with chloroacetate [1].

Two calculation strategies in experimental data treatment by OPIUM program were used. The first approach uses nonweighted general regression ($\log\{\beta_{PdL}\} = 3.284 \pm 0.008$) while the second one employs weighted general regression ($\log\{\beta_{PdL}\} = 3.31 \pm 0.01$) (Table 1). Calculated numerical values of stability constants of PdL complex are also in good agreement with the value predicted by LFER [5] ($\log\{\beta_{PdL}\} = (0.48 \pm 0.03) \times 2.66 + (2.2 \pm 0.1) = 3.5 \pm 0.1$). The molar absorptivities calculated by OPIUM program are shown in Fig. 1. Molar absorptivity at absorption maximum 390 nm is equal to 125 which is lower than molar absorptivity of PdL complex of other simple acids (acetic: $\log\{\beta_{PdL}\} = 4.34$, ε (390 nm) $= 186$ dm^3 mol^{-1} cm^{-1}; propionic: $\log\{\beta_{PdL}\} = 4.32$, ε (390 nm) $= 209$ dm^3 mol^{-1} cm^{-1}; glycolic: $\log\{\beta_{PdL}\} = 3.81$, ε (390 nm) $= 166$ dm^3 mol^{-1} cm^{-1}) [4, 5].

The formation of unique PdL^+ complex was confirmed by other experiment. The change of absorbance of solution for different proton concentration in solution ($c_L = 0.5$ mol dm^{-3}, $1.4 < -\log\{[H^+]\} < 4.0$) was observed. At $-\log\{[H^+]\} < 3.0$, the absorbance at 380 nm was constant and was equal to $0.489_5 \pm 0.005_4$ (average numerical value of the molar absorptivity was estimated $122._4 \pm 1._4$). This value is in good agreement with the value calculated by OPIUM program,
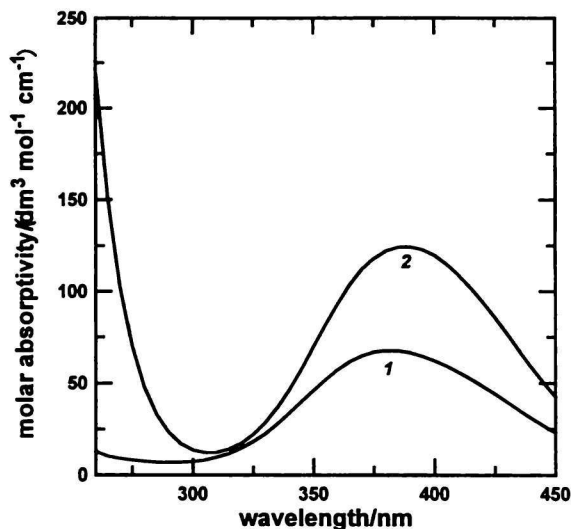
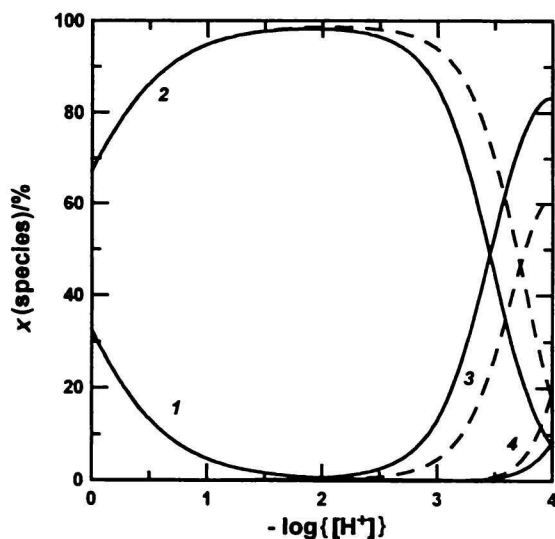**Fig. 1.** Calculated spectra of individual species. *1.* Pd^{2+}; *2.* PdL^+.

Fig. 2. Distribution diagram of Pd complexes in solution under experimental conditions ($c_{Pd} = 0.004$ mol dm^{-3}, $c_L = 0.500$ mol dm^{-3}, $I = 1.00$ mol dm^{-3}, $t = 25.0\,°C$). *1.* Pd^{2+}; *2.* PdL^+; *3.* $Pd(OH)_2$; *4.* $Pd(OH)_4^{2-}$.
—— Calculated for palladium hydrolytic complexes ($\log\{K(Pd(OH)^+)\} = -2.0$, $\log\{K(Pd(OH)_2)\} = -4.0$); – – – calculated for palladium hydrolytic complexes ($\log\{K(Pd(OH)^+)\} = -2.0$, $\log\{K(Pd(OH)_2)\} = -4.5$).

which supports our hypothesis that only PdL^+ complex species was formed. At $-\log\{[H^+]\} > 3.0$, the absorbance increased probably due to palladium(II) hydrolysis as shown in Fig. 2. The distribution diagram shows how the hydrolysis of palladium(II) is shifted towards higher $-\log\{[H^+]\}$ (the formation of $Pd(OH)_2$ species is primarily influenced by the formation of PdL^+ species). The hydrolytic constants of $Pd(OH)^+$ and $Pd(OH)_2$ species ($\log\{K_1\} = -2.0$,

$\log\{K_2\} = -4.0$ for $I(HClO_4) = 1.00$ mol dm^{-3} taken from [12]) were roughly estimated from the behaviour of palladium in the presence of chlorides or bromides in solution [12] because there are large discrepancies in the rare literature data of hydrolytic constants determined by means of different experimental techniques (potentiometry and spectrophotometry [13], solubility measurement [14], *etc.*). The precipitate of $Pd(OH)_2$ species in solution has influence on precision of hydrolytic constants obtained as it was pointed out in [12, 13]. It can be seen from the distribution diagram (Fig. 2) that the estimated values ($\log\{K_1\} < -2.0$, $\log\{K_2\} \approx -4.5$) should be in good agreement with the experimental ones ($\log\{K_1\} = -2.3 \pm 0.1$, $\log\{K_2\} = -4.8 \pm 0.2$ for $I(NaClO_4) = 0.1$ mol dm^{-3} at $17\,°C$ [14]).

We verified if protonated species are formed. The following chemical reaction was considered

$$M + nHL \xrightleftharpoons{K} ML_n + nH^+ \qquad (B)$$

where K is the equilibrium constant of chemical reaction mentioned above defined as (for the sake of clarity the charges of complex species were omitted)

$$K = \frac{[ML_n][H^+]^n}{[M][HL]^n} \qquad (2)$$

We transformed measured variable absorbance A, which is a function of analytical ligand concentration (in case when $c_L \gg c_M$, $A = \varepsilon_M \times [M] + \varepsilon_{ML} \times [ML]$)

$$\log\left\{\frac{A - A_{0M}}{\varepsilon_{ML} c_M - A}\right\} = n \times \log\{c_L\} + $$
$$+ n \times (-\log\{[H^+]\}) + \log\{K\} \qquad (3)$$

where A_{0M} is absorbance of solution without ligand, n is the number of bound ligand molecules with the number of protons splitted-off of chelating ligand [11]. Knowing ε_{ML} measured as mentioned above and keeping $-\log\{[H^+]\}$ constant ($[H^+] = 1.00$ mol dm^{-3}), one obtains the following parameters by linear regression for wavelength 380 nm ($n = 1.003 \pm 0.005$ and $\log\{K\} = 0.566 \pm 0.003$). Using the following relationship

$$\log\{\beta_{ML}\} = \log\{K_a\} + \log\{K\} \qquad (4)$$

one can calculate $\log\{\beta\} = 0.566 + 2.661 = 3.227$, which is in good agreement with the value calculated by means of OPIUM program.

In order to estimate thermodynamic quantities for complexation reaction, the value of stability constant of PdL^+ complex was determined at different temperatures in analogy with that determined at $25\,°C$ (the reagent concentrations, the number of experimental points and their treatment by OPIUM software). The calculated numerical values of the stability constants
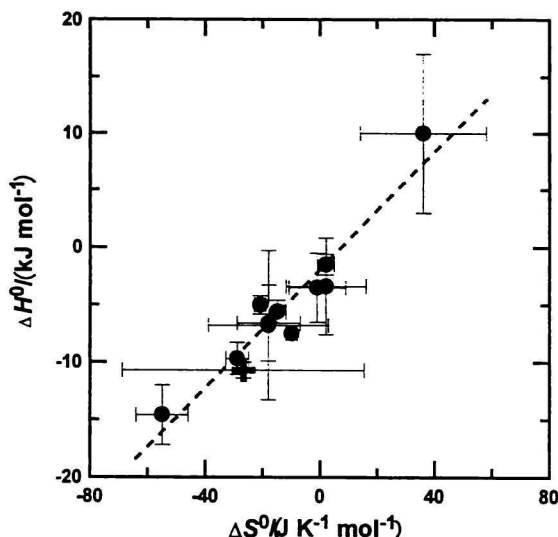
Fig. 3. Compensation effect between ΔH° and ΔS°.

are in good agreement with those obtained for Pd(II) and other simple organic acids, *e.g.* formic acid [4, 5]. As *Elding et al.* pointed out, although the structural differences between the mono-, di-, and tricarboxylic acids are great, the equilibrium constants are not so different as a consequence of the compensation effect between ΔH° and ΔS° (Fig. 3). This was also found in this work for chloroacetic acid. In addition, it can be deduced from the linear relation between ΔH° and ΔS° that the bond between palladium(II) and chloroacetate is of a similar type as that in other carboxylic acids [4, 5].

CONCLUSION

The palladium(II)—chloroacetate system was studied at different ligand (c_L = 0—0.55 mol dm^{-3}) and proton concentrations ([H$^+$] = 1.00 mol dm^{-3} and 0.80 mol dm^{-3}) using spectrophotometry. Experimental data can be explained with a simple model involving PdL$^+$ complex species; respective stability constant and the molar absorptivity of complex in solution were determined. The enthalpic and entropic changes for complexation process were determined as well. Knowledge of the stability constant of Pd(II)—chloroacetate is important to be taken into account when this buffer is used for Pd(II) complex equilibria studies with other ligands.

of PdL$^+$ complex for $I(HClO_4)$ = 1.00 mol dm^{-3} were 3.279 ± 0.005 (25.0 °C), 3.219 ± 0.009 (34.5 °C), and 3.191 ± 0.07 (44.0 °C). Assuming that thermodynamic complexation parameters are independent of temperature within given temperature region, the enthalpy and entropy changes of complexation equilibrium were estimated as slope and intercept obtained from the transformed dependence of stability constant as a function of temperature

$$-R \times \ln(10) \times \log\{\beta\} = \frac{\Delta H}{T} - \Delta S \qquad (5)$$

The estimated thermodynamic parameters ΔH° and ΔS° are given in Table 2 and Fig. 3. The values

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Table 2. Comparison of Thermodynamic Parameters of Palladium Complexes with Simple Organic Acids at 25 °C and at $I((Na, H)ClO_4)$ = 1.00 mol dm^{-3}

Ligand Carboxylic acid	ΔH° kJ mol^{-1}	ΔS° J K^{-1} mol^{-1}	Source
Formic	−9.7 ± 1.4	−29 ± 4	[5]
Acetic	−5.0 ± 0.8	−21 ± 2	[4]
Propionic	−1.5 ± 0.9·	2 ± 3	[4]
Butyric	−14.6 ± 2.6	−55 ± 9	[5]
Glycolic	−5.6 ± 1.0	−15 ± 3	[4]
DL-Lactic	−6.6 ± 3.3	−18 ± 11	[5]
Methoxyacetic	−6.8 ± 6.5	−18 ± 21	[5]
Malonic	−7.5 ± 0.3	−10 ± 2	[5]
Succinic	10 ± 7	36 ± 22	[5]
L-Malic	−3.5 ± 3.0	−1 ± 10	[5]
Citric	−3.4 ± 4.2	2 ± 14	[5]
Chloroacetic	**−10.7 ± 0.7**	**−26.7 ± 42.1**[a]	This paper
Chloroacetic	−8.3 ± 1.6	−34.7 ± 5.1[b]	This paper

a) Calculated by means of weighted linear least-squares procedure from eqn (5); *b)* calculated by means of ordinary linear least-squares procedure from eqn (5).

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