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Registry No. U(COT)$_2$, 11079-26-8; U(Cp)$_3$, 54007-00-0; U(TFA)$_4$, 32627-13-7.

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Contribution from the Department of Chemistry,
Boston University, Boston, Massachusetts 02215

Kinetics of Chloride Substitution into Bis(oxalato)platinate(II) Ion

Jeffrey Hoch and Ronald M. Milburn*

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Kinetic studies on platinum complexes have received new impetus since discovery[1] that certain of these substances exhibit extraordinary biological activity. Oxalato and malonato complexes are among those exhibiting such activity, and where marked differences for analogous complexes are observed, as in the case of [Pt(en)C_2O_4] and [Pt(en)mal],[2] the relative labilities of the carboxylato ligands may be involved.[3] In order to investigate some of these matters we are extending our earlier work[4] on platinum(II) complexes.

We report here on the reactivity of $Pt(C_2O_4)_2^{2-}$ in aqueous chloride media. The solvent is of interest because of its relevance to biologically important fluids, especially blood plasma. Our main observations, which have been for 1 M chloride in the pH range 5–8, are consistent with a simple reaction sequence leading to quantitative production of $PtCl_4^{2-}$.

Some studies were carried out on more strongly acidic solutions (pH <2; 1 M Cl^-). For these conditions a marked oxygen dependence was observed, and even when attempts were made to exclude all dissolved oxygen, complications remained.

In the pH range 5–8 we find no evidence for an influence from dissolved oxygen or for polynuclear species. For these pH conditions the kinetic results are consistent with a sequence of consecutive first-order reactions leading to $PtCl_4^{2-}$. Our results are compared with those obtained by Giacomelli and Indelli[5] for NCS^- substitution into $Pt(C_2O_4)_2^{2-}$.

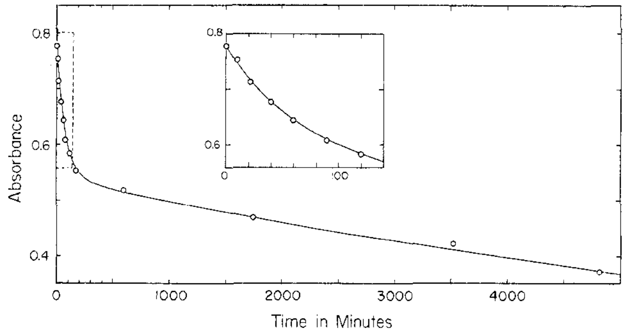

Figure 1. Absorbance vs. time for experiment 1: $[Pt(C_2O_4)_2^{2-}]_0 = 2.00 \times 10^{-4}$ M, [NaCl] = 1.00 M, $T = 35.0$ °C, λ 285 nm. Points are experimental values and the line is calculated from eq 2 with $k_1 = 0.21 \times 10^{-3}\ s^{-1}$, $k_2 = 1.28 \times 10^{-6}\ s^{-1}$, $\epsilon_I = 3850$, and $\epsilon_{III} = 40$. The smaller graph, in insert, is an expansion of the part of the larger graph enclosed within dashed lines.

Experimental Section

Potassium bis(oxalato)platinate(II) dihydrate was prepared by the method of Vèzes[6] and was purified as previously described.[4a] Water was doubly distilled and exhibited negligible UV absorption above 220 nm; other materials were of reagent grade. Phosphate buffers, used for reactions in the pH range 5.5–7.5, were prepared by established procedures.[7]

Kinetic runs were initiated by mixing, at the appropriate temperature, equal volumes of a $K_2[Pt(C_2O_4)_2]$ solution (freshly prepared) with a solution containing chloride (NaCl, and for experiments at low pH, also HCl). For a few runs where $[Cl^-] < 1$ M, $NaClO_4$ was included to maintain constant ionic strength. For reactions in the pH range 5.5–7.5, phosphate buffer, at total phosphate concentrations of up to 10^{-2} M, was generally included, although some experiments were conducted in which the buffer was omitted. In the latter case pH measurements were made at the beginning and completion of reaction. The total platinum(II) concentration in reaction solutions was (1.0–4.0) × 10^{-4} M while the chloride concentration was 1.00 M in all but a few cases (which are specified). The ionic strength was constant for each run and was always in the range 1.00–1.03 M. Temperatures were held constant to ±0.1 °C.

Progress of the reaction was followed spectrophotometrically by repetitive scanning through the range 220–340 nm, with particular focus on 285 nm (a maximum for $Pt(C_2O_4)_2^{2-}$, where $PtCl_4^{2-}$ absorbs almost negligibly) and on the 235–245-nm region (in which an isosbestic point exists during the earlier stages of reaction). Oxygen was excluded for some experiments by sweeping reactant solutions with nitrogen prior to mixing by syringe techniques.

Results and Discussion

The chloride concentration (usually 1 M) was in all cases in very large excess to the platinum(II) ((1–4) × 10^{-4} M). For 1 M chloride at pH 5.5–7.5 and 35–65 °C, final spectra were consistent with >98% conversion of $Pt(C_2O_4)_2^{2-}$ to $PtCl_4^{2-}$ in accord with expectations.[8] Replacement of oxalate by chloride undoubtedly involves consecutive steps, and our observations reveal that at least two of these are slow. This feature is illustrated by absorbance vs. time profiles (Figure 1), by nonlinearity of first-order rate plots, and by the absence of an isosbestic point at 242 nm.[9] For this middle pH region the presence or exclusion of oxygen had no apparent effect on the rate or on other aspects of reaction.

The simplest kinetic scheme which can accommodate our observations involves two consecutive first-order processes.

$$\mathrm{I} \xrightarrow{k_1} \mathrm{II} \xrightarrow{k_2} \mathrm{III} \qquad (1)$$

Here I, II, and III are, respectively, $Pt(C_2O_4)_2^{2-}$, an intermediate, and $PtCl_4^{2-}$, while k_1 and k_2 are first-order rate constants. Values of k_1, k_2, and ϵ_{II} (the absorbancy coefficient for the intermediate) were evaluated using a nonlinear least-squares program[10] to minimize differences between observed absorbances (A) at 285 nm (1 cm path) and those

Table I. Pseudo-First-Order Rate Constants at pH 6.5[a]

expt no.	temp, °C	$10^{-3}\epsilon_{II}$ (285 nm)	10^3k_1, s^{-1}	10^6k_2, s^{-1}
1	35.0	2.68	0.21 (±0.01)	1.28 (±0.05)
2	44.9	2.46	0.52 (±0.06)	4.6 (±0.3)
3	55.0	2.98	1.0 (±0.2)	8.3 (±0.3)
4	55.0	3.08	1.4 (±0.3)	8.1 (±0.2)
5	65.0	3.03	1.9 (±0.5)	21 (±1)

[a] Error limits are standard deviations.

calculated from theoretical expression[11] 2, with $\epsilon_I = 3850$[12]

$$A = C_0\{(e^{-k_1t})\epsilon_I + [k_1/(k_1 - k_2)](e^{-k_2t} - e^{-k_1t})\epsilon_{II} + [1 + (k_2e^{-k_1t} - k_1e^{-k_2t})/(k_1 - k_2)]\epsilon_{III}\} \quad (2)$$

and $\epsilon_{III} = 40$[13] [C_0 = initial $Pt(C_2O_4)_2^{2-}$ concentration].

Resulting values[14] of k_1, k_2, and ϵ_{II} for 1 M chloride and pH 6.5 are given in Table I. From these data we obtain $\Delta H_1^\ddagger = 15.0\ (\pm 1.5)$ kcal mol^{-1}, $\Delta S_1^\ddagger = -27\ (\pm 5)$ cal mol^{-1} K^{-1}, $\Delta H_2^\ddagger = 17.7\ (\pm 1.5)$ kcal mol^{-1}, and $\Delta S_2^\ddagger = -28\ (\pm 5)$ cal mol^{-1} K^{-1}.

The reaction was further examined at 45 °C over the pH range 5.5–7.5 for possible dependence of k_1 on pH; no discernible trend was observed (corresponding values of pH and k_1 (in s^{-1}) are 5.5, 5.5×10^{-4}; 6.2, 7.0×10^{-4}; 6.8, 5.8×10^{-4}; 7.1, 5.6×10^{-4}; and 7.5, 6.5×10^{-4}). The influence of varying the chloride ion concentration was also examined. Values of k_1 were found to be proportional to [Cl^-], within experimental limits of error, as seen by the following result for 35 °C and pH 6.5 (ionic strength held at 1.00 M with $NaClO_4$; paired values are for [Cl^-] and k_1, respectively): 1.00 M, 2.3×10^{-4} s^{-1}; 0.50 M, 1.08×10^{-4} s^{-1}; 0.25 M, 0.67×10^{-4} s^{-1}. A linear least-squares plot of k_1 vs. [Cl^-] provides an intercept of $k_1 = 0.04 \times 10^{-4}$ s^{-1} at [Cl^-] = 0, which can be considered to be zero within the experimental limits, and here we find no evidence for a chloride-independent path. On the other hand, k_2 appears to exhibit little if any dependence on [Cl^-] (for the above runs at 35 °C and pH 6.5, for 1.00 M Cl^-, $k_2 = 1.03 \times 10^{-6}$ s^{-1}; for 0.50 M Cl^-, $k_2 = 0.92 \times 10^{-6}$ s^{-1}) although some uncertainty is introduced for results at lower chloride concentrations because of possible interference from the increasing importance of aquo complexes.

As indicated above, some studies were carried out in strongly acidic media (0.025–0.100 M H^+). The rate of change in absorbance increased with hydrogen ion concentration, yet it was apparent that effects in addition to acid catalysis were occurring. Thus we observed markedly greater rates for reactions from which oxygen was not excluded. Also, even when attempts were made to exclude all oxygen, values of $(dA/dt)/[Pt]_t$ were dependent on the total platinum concentration, $[Pt]_t$ (initial values for 4×10^{-4} M solutions were about half of those for 2×10^{-4} M solutions). The scheme of two consecutive first-order processes, which was adequate to describe the data in neutral solution, would not accommodate the data for these strongly acidic solutions, whether or not oxygen had been excluded. In consequence we were unable to reproduce the simple observations described by Banerjea and Banerjee[15] for 0.02–0.50 M HCl. However, the existence of complications at low pH is consistent with our earlier observations[4a] and with the detailed work of Krogmann and Dodel[16] on oxidation and polymerization reactions of $Pt(C_2O_4)_2^{2-}$.

No such complications are observed for the middle pH region, where a twofold change in platinum concentration resulted in values of $(dA/dt)/[Pt]_t$ which were the same (within ~10%), and here our results are consistent with the simple reaction sequence summarized in Figure 2. According to this view, entry of the first chloride (pseudo-first-order rate constant k_1') is followed by significantly faster entry of the second chloride (k_1'') trans to the first, consistent with the kinetic trans effect of Cl^- exceeding that of oxalate.[17] Similarly, slow entry of the third chloride (pseudo-first-order rate constant k_2') is followed by significantly faster entry of the fourth (k_2''). Consequently the experimental k_1 values will provide a reasonable measure of k_1', and the experimental k_2 values a reasonable measure of k_2'.

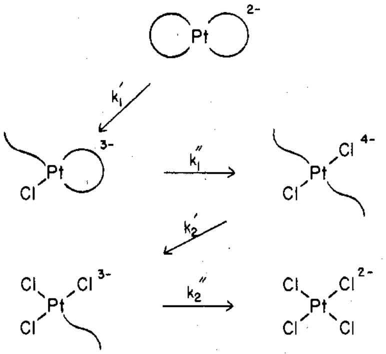

Figure 2. Consecutive reaction scheme leading to $PtCl_4^{2-}$. Closed loops represent chelated oxalate and wavy lines represent monodentate oxalate; pseudo-first-order rate constants are shown.

The chloride ion concentration was constant for each experiment, and accordingly each k_1' and k_2' value should provide a composite measure of chloride and solvent dependent paths. Bimolecular reaction between solvent H_2O and $Pt(C_2O_4)_2^{2-}$ is extremely slow,[4,5] however, and k_1' at 1 M chloride should be numerically equal to the second-order rate constant for bimolecular reaction between Cl^- and $Pt(C_2O_4)_2^{2-}$. Our results on chloride dependency of k_1 support this view. The k_2' values, on the other hand, probably come close to a measure of the solvent dependent path, by analogy to the results of Giacomelli and Indelli with NCS^- as a nucleophile. Indeed, at 45 °C our measured value k_2 is 4.6×10^{-6} s^{-1} compared to the value of 1.6×10^{-5} s^{-1} determined[5] for the reaction of the four-coordinate $Pt(C_2O_4)_2(SCN)_2^{4-}$ with H_2O.

Registry No. $Pt(C_2O_4)_2^{2-}$, 36444-17-4; Cl^-, 16887-00-6.

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