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On a Dissociative Pathway in the Anation of Aquadiethylenetriamineplatinum(II) Ion

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In the original investigation [1] of the anation of aquadiethylenetriamineplatinum(II) ion

$$\mathrm{Pt(dien)H_2O^{2+} + Cl^- \underset{k_r}{\overset{k_f}{\rightleftharpoons}} Pt(dien)Cl^+ + H_2O} \qquad (1)$$

the kinetics were described by the customary two-term rate law for substitution on platinum(II), *i.e.* $k_{obs} = k_1 + k_2\ (Cl^-)$. The usual interpretation of k_1 as the rate of solvent attack is not applicable in the case of the solvent complex, so that k_1 was interpreted as representing an unusual dissociative pathway.

This exceptional behaviour for a platinum(II) amine complex has been the subject of two recent reinvestigations published in this journal [2, 3]. Both failed to observe the k_1 term in the rate law and dismissed the original report as due to experimental error. The purpose of this letter is to point out that the original observations are probably correct but can be interpreted in a different way which does not require postulating a dissociative mechanism.

The alternative explanation is that reaction (1) did not go to completion under the conditions of the original study. In such a case the observed rate constant for the approach to equilibrium is

$$k_{obs} = k_f + k_r\ (Cl^-) \qquad (2)$$

Hence the equilibrium constant for reaction (1) can be evaluated from the ratio of intercept to slope of the original data: $K_1 = k_f/k_r = 3 \times 10^3\ M^{-1}$. This equilibrium constant is available independently from the work of Martin and Bahn [4] who measured equilibrium constants for reactions (3) and (4).

$$\mathrm{Pt(dien)Br^+ + H_2O \rightleftharpoons Pt(dien)H_2O^{2+} + Br^-} \qquad (3)$$

$$\mathrm{Pt(dien)Br^+ + Cl^- \rightleftharpoons Pt(dien)Cl^+ + Br^-} \qquad (4)$$

Although they did not do so, these equilibrium constants can be combined to give a value for K_1 in good agreement with that obtained from the kinetics work: $K_1 = K_4/K_3 = 0.26\ M^{-1}/9.6 \times 10^{-5} = 2.7 \times 10^3\ M^{-1}$.

Hence the two-term rate law observed in the original work arises from the approach to equilibrium of reaction (1) in the presence of low concentrations of chloride ($\leqslant 4 \times 10^{-3}\ M$). In the two more recent studies the availability of stopped-flow instrumentation allowed higher concentrations of chloride to be used. This drove the reaction to completion and no chloride independent term (k_1 or k_f) was observed. All three sets of data are consistent with a single associative pathway for the anation reaction. There is no need to postulate a dissociative mechanism for reactions of this class of platinum(II) complexes [5, 6].

References

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