*Contribution from the Naval Postgraduate School, Monterey,
California 93940, U.S.A. and the Chemistry Department,
King's College, Strand, London, W.C. 2, United Kingdom*

Isosbestic Points and Consecutive Reactions Schemes: The Reaction of Tetra-amminepalladium(II) Ion with Chloride in Acid Solution

R. A. Reinhardt[*] and J. S. Coe

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In studies of the spectrophotometric course of a reaction isosbestic points are often observed, and these may be present during the whole course of the reaction or during only part of it. In the latter case a particular ambiguity in interpretation arises for consecutive reactions of the type $A \rightarrow B \rightarrow C$. This ambiguity is discussed in some detail and is illustrated for the particular case of the reactions of the tetraamminepalladium(II) ion with hydrochloric acid.

In spectrophotometric studies of reactions proceeding by consecutive steps, the problem exists, when the intermediate is not isolable, in deciding which of the two determined rate constants applies to the first step and which to the second. Thus, in two recent studies[1,2] on the kinetics of interaction of $[Pd(NH_3)_4]^{2+}$ with aqueous hydrochloric acid, opposite conclusions were reached regarding which step was the faster. Each paper, in supporting its conclusions, made use of the term « isosbestic point »; we wish therefore to examine here the use of this concept in connection with consecutive reaction schemes, particularly as applied to the reaction mentioned above.

Cohen and Fischer[3] have considered conditions for the existence of isosbestic points, defined as wavelengths at which absorbance remains constant during the entire course of a reaction. They have shown the utility of the concept for one-step and simultaneous reactions; but they also point out the nonoccurrence of isosbestic points, as so defined, for consecutive reactions in which the rate constants of the consecutive steps are similar in magnitude.

However, the term isosbestic point is commonly used (when discussing the spectrophotometric course of a reaction) to describe a point at which several spectra intersect, irrespective of whether the constant absorbance is observed during the entire reaction or during only part of it. We wish here to examine in more detail the interpretations that may be given to the observation of isosbestic points when these occur only during the later part of the spectrophotometric course of a reaction, *i.e.* « delayed » isosbestic points. Many such cases have been reported in the literature.[4] Thus, Figure 1a shows the results of Coe *et. al.*[1] for the $[Pd(NH_3)_4]^{2+}$—Cl^- reaction, wherein delayed isosbestics appear at about 275 and 340 mm.

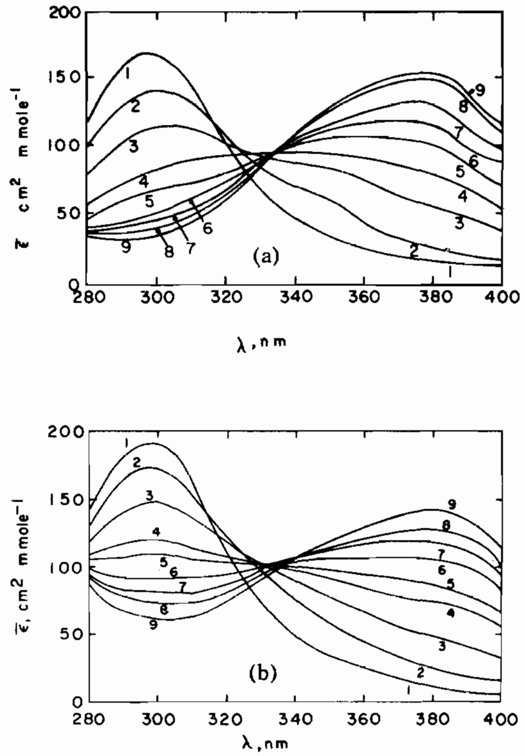

Figure 1. Change in absorption spectra during the reaction of $[Pd(NH_3)_4]^{2+}$ with Cl^-: a) experimental (Coe, Hussain and Malik); b) computed. Successive times are at 30, 120, 240, 390, 480, 630, 780, 900 and 1200 sec. $[Cl^-] = 0.10\,M$, $\mu = 0.25\,M$, 25°

(*) To whom inquires should be addressed: Code 5411, Naval Postgraduate Scool, Monterey, California 93940, U.S.A.

(1) J. S. Coe, M. D. Hussain, and A. A. Malik, *Inorg. Chim. Acta, 2,* 67 (1968).

(2) R. A. Reinhardt and R. K. Sparkes, *Inorg. Chem., 6,* 2190 (1967).

(3) M. D. Cohen and E. Fischer, *J. Chem. Soc.,* 3044 (1962); see also H. Mauser, *Z. Naturforschg., 23b,* 1021 (1968).

(4) Ref. 1 and also: A. J. Poë and D. H. Vaughan, *Inorg. Chim. Acta, 1,* 255 (1967); L. Cattalini, A. Orio, and M. Nicolini, *J. Amer. Chem. Soc., 88,* 5734 (1966); L. Cattalini, A. Orio, and M. L. Tobe, *ibid., 89,* 3130 (1967); L. Cattalini and M. L. Tobe, *Inorg. Chem., 5,* 1145 (1966).

Consider the reaction scheme:

$$A \xrightarrow{k_A} B \xrightarrow{k_B} C \qquad (1)$$

where k_A and k_A are first-order rate constants.

Putting $\alpha = [A]_t/[A]_o$, $\beta = [B]_t/[A]_o$ and $\gamma = [C]_t/[A]_o$ (where $[A_o]$ is the initial concentration of A, and $[X]_t$ the concentration of species X at time t) we have[5]

$$\alpha = e^{-k_A t} \qquad (2)$$

$$\beta = x(e^{-k_A t} - e^{-k_B t}) \qquad (3)$$

where $x = k_A/(k_B - k_A)$.

Also,

$$\bar{\varepsilon} = \varepsilon_A\alpha + \varepsilon_B\beta + \varepsilon_C\gamma \qquad (4)$$

and

$$\alpha + \beta + \gamma = 1, \qquad (5)$$

where, at a given wavelength, $\bar{\varepsilon}$ is the average extinction coefficient (absorbance per cm divided by total concentration) and ε_X is the molar extinction coefficient of species X.

From equations (2) - (5):

$$\bar{\varepsilon} - \varepsilon_C = [(\varepsilon_A - \varepsilon_C) + x(\varepsilon_B - \varepsilon_C)]\, e^{-k_A t} - x(\varepsilon_B - \varepsilon_C)e^{-k_B t} \qquad (6)$$

For a reaction such as (1), therefore, the general condition for the appearance of a delayed isosbestic point is that, at a given wavelength, $(\bar{\varepsilon} - \varepsilon_C)$ must become practically zero before the total reaction is complete.

This can only occur (in non-trivial situations) if each of the two terms on the right-hand side of (6) becomes zero at one wavelength whilst, at most other wavelengths, at least one term is non-zero. During the later part of the reaction the first term will become negligible compared with the second at all wavelengths if $k_A > k_B$, and conversely if $k_A < k_B$. There are, therefore, two possible conditions giving rise to delayed isosbestic points:

(i) when $k_A > k_B$ a delayed isosbestic will occur at a wavelength for which $(\varepsilon_B - \varepsilon_C) = 0$,

(ii) when $k_A < k_B$ a delayed isosbestic will occur at a wavelength for which $(\varepsilon_A - \varepsilon_C) + x(\varepsilon_B - \varepsilon_C) = 0$.

In each case a plot of $\log(\bar{\varepsilon} - \varepsilon_C)$ *vs.* time for measurements at the wavelength of the isosbestic point gives the value of the rate constant for the faster step. However, it is necessary to have some information concerning the spectrum of B before it can be decided whether the first or second step is faster, *i.e.* whether (i) or (ii) is the condition giving rise to the isosbestic. If, for example, it is known that, at a given wavelength, $\varepsilon_B = \varepsilon_C$, then a plot of $\log(\bar{\varepsilon} - \varepsilon_C)$ *vs.* time will give k_A (irrespective of the relative values of k_A and k_B and irrespective of whether an isosbestic occurs at this wavelength). Similarly, if ε_B is known at a wavelength where $\varepsilon_A = \varepsilon_C$, values of β may be calculated using (4) and (5). Then x may be determined from:[5]

$$\beta_{max} = \left(1 + \frac{1}{x}\right)^{-(1+x)}$$

and the relative values of k_A and k_B found. Finally, if both ε_B and ε_A are known at any particular wavelength, the value of k_A may be determined from the initial rate of change of absorbance,

$$\left(\frac{d\bar{\varepsilon}}{dt}\right)_0 = k_A(\varepsilon_B - \varepsilon_A)$$

This method has been used by Colvin *et. al.*[6]

Some of the foregoing points may now be illustrated by reference to the reactions of $[Pd(NH_3)_4]^{2+}$ with aqueous hydrochloric acid. The spectra in Figure 2 show that $(\varepsilon_B - \varepsilon_C) = 0$ at 355 nm (where rate plots are indeed linear,[2] and give k_A) and not at ~340 nm which is the observed isosbestic point.[1] Further, at the observed isosbestic point, values of x can be calculated from the values of the extinction coefficients, read from the spectra in Figure 2, and application of the equation: $(\varepsilon_A - \varepsilon_C) + x(\varepsilon_B - \varepsilon_C) = 0$. Excellent agreement is found between the calculated values of x and those found if the assignments of Coe *et. al.* are reversed. (See Table I). This analysis also explains why the observed isosbestic point occurs at slightly different wavelengths with different values of $[Cl^-]$, since x is a function of $[Cl^-]$.

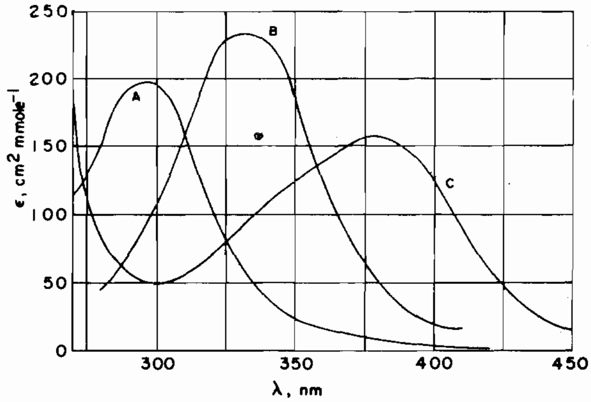

Figure 2. Absorption spectra of $[Pd(NH_3)_4]^{2+}$ (Curve A), $[Pd(NH_3)_3Cl]^+$ (Curve B), and $Pd(NH_3)_2Cl_2$ (Curve C).

Table I.

$[Cl^-]$ (*M*)	λ (nm)	ε_A [a]	ε_B [a]	ε_C [a]	x_{calc}	x_{obs} [b]
0.20	336	47	224	99	0.45	0.42
0.15	337	44	222	101	0.50	0.47
0.10	338	41	220	103	0.58	0.53
0.05	342	36	207	108	0.79	0.73

[a] Interpolated from Figure 2, values in cm² mmole⁻¹. [b] From Ref. (1), reversing the assignments of k_A and k_B.

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(5) A. A. Frost and R. G. Pearson, « Kinetics and Mechanism », 2nd Ed., Wiley, New York, (1961) p. 166 ff.

(6) C. B. Colvin, R. C. Gunther, L. D. Hunter, J. A. McLean, M. A. Tucker, and D. A. Martin, Jr., *Inorg. Chim. Acta, 2,* 487 (1968).

We conclude from the preceding arguments that, for the reaction considered, $k_B > k_A$. In final support of this proposition we have computed, using equation (6), spectral scans over the range 280 - 400 nm for the experiment, carried out at 25°, 0.1 *M* Cl^-, $\mu = 0.25\,M$. For the computation we have used extinction coefficients from Figure 2 and the rate constants of Coe *et. al.*, with assignment reversed: *i.e.* $k_A = 0.0022$ sec^{-1} and $k_B = 0.0062$ sec^{-1}. The computed scans are shown in Figure 1b and may be compared with the experimental[1] scans of Figure 1a.

The most common explanation of the origin of delayed isosbestic points in reactions such as (1) is that they occur where $\varepsilon_B = \varepsilon_C$. However, in reactions of transition metal complexes involving the successive replacement of ligands, the spectra of the species corresponding to A, B and C are likely to be related in a similar manner to that shown in Figure 2 for the palladium complexes. When this is so the condition $(\varepsilon_A - \varepsilon_C) + x(\varepsilon_B - \varepsilon_C) = 0$ is likely to be fulfilled in at least one wavelength region. Thus, although the ambiguity of interpretation revealed here has been illustrated in only one particular case, it may be more commonly present than has hitherto been recognised.

Experimental Section

Absorption spectra of $[Pd(NH_3)_4]^{2+}$, $[Pd(NH_3)_3Cl]^+$, and $Pd(NH_3)_2Cl_2$.

The spectrum of $[Pd(NH_3)_4]^{2+}$ was obtained by measurement on a solution of $Pd(NH_3)_4Cl_2$ in 1 *M* NaCl to which excess ammonia was added (to repress formation of $[Pd(NH_3)_3Cl]^+$).

Two methods were used to obtain the spectrum of $Pd(NH_3)_2Cl_2$. For the first, *trans*–$Pd(NH_3)_2Cl_2$, prepared as described previously,[7] was dissolved in 1 *M* NaCl and the spectrum was scanned at once. Although satisfactory spectra are obtained this way, extinction coefficients cannot be found, since the rate of solubility does not permit a reliable knowledge of the concentration. For the second method, excess HCl was added to $[Pd(NH_3)_4]^{2+}$ in 1 *M* Cl^- and the spectrum was scanned after 15 minutes. Except for the region below 300 m, where formation of $[Pd(NH_3)Cl_3]^-$ obscured the results in the second method, agreement between the methods was good.

The spectrum of $[Pd(NH_3)_3Cl]^+$ was reconstructed as follows: each run was carried out by adding a small portion of aq HCl or NH_3 to $[Pd(NH_3)_4]^{2+}$ in 1 *M* NaCl. The spectrum was scanned after the solution had stood at 25° for 40 min, sufficient time to allow equilibrium for the first two steps of reaction. Abount a dozen such runs were carried out. Absorbance at 330 nm was used as a means of analysis. At this wavelength, extinction coefficients of the three species are 88.2, 233.4, and 61.6 cm^2 mmole^{-1}, respectively, and from the reported[7] equilibrium constants may be computed that for the disproportionation of $[Pd(NH_3)_3Cl]^+$: $\alpha\gamma/\beta^2 = 0.348$.

For each value of $\bar{\varepsilon}$, this last relation, combined with equation (3) - (5) permits computation of α, β, and γ as solutions to a quadratic equation. Points near the maximum in $\bar{\varepsilon}$ (where $d\beta/d\bar{\varepsilon}$, and thus the uncertainty in β, is large) were not considered; for the remainder, the root ambiguity could always be resolved from knowledge of the approximate quantity of acid or ammonia added. Then at each wavelength (other than 330 nm) ε_B may be computed from equations (4) and (5).

Absorption spectra were measured in 10 cm cells. Those for $[Pd(NH_3)_4]^{2+}$ and $Pd(NH_3)_2Cl_2$ were obtained with a Beckmann Model DKIA recording spectrophotometer at ambient temperature; those for $[Pd(NH_3)_3Cl]^+$ with the Beckmann Model DU spectrophotometer, using thermostatted cell holders at 25°. Results are shown in Figure 2.

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[7] R. A. Reinhardt, N. A. Brenner, and R. K. Sparkes, *Inorg. Chem.*, 6, 254 (1967).