Inorganica Chimica Acta, 28 (1978) L131–L133
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Mechanism of Addition of N-Propylimidazole to Tetraphenylporphinatoiron(III) Chloride

DAVID BURDIGE and D. A. SWEIGART*

Department of Chemistry, Swarthmore College, Swarthmore, Pa. 19081, U.S.A.

Received February 23, 1978

The reaction of tetraphenylporphinatoiron(III) chloride, FeTPPCl, with imidazoles has recently received considerable attention [1–10]. In this reaction, the iron changes from five-coordinate high-spin to six-coordinate low-spin:

$$\mathrm{FeTPPCl + 2\ RIm \rightarrow FeTPP(RIm)_2^+, Cl^-} \qquad (1)$$

The monomidazole adduct is generally not seen because the equilibrium constant for addition of the second imidazole (K_2) is greater than that for the first addition (K_1). No evidence has yet been reported for the existence of six-coordinate FeTPP(RIm)Cl, but LaMar and Walker [4] have indirect NMR evidence for $\mathrm{FeTPP(N\text{-}MeIm)^+, Cl^-}$ in chloroform above 50 °C and Hambright *et al.* [11] claim to have prepared the five-coordinate high-spin complex $\mathrm{FeTPP(Im)^+, Cl^-}$ by heating $\mathrm{FeTPP(Im)_2^+, Cl^-}$ to 200–260 °C.

In view of the associative mechanism of chloride exchange [5] in FeTPPCl, and other kinetic studies of five-coordinate systems [12], we felt that the first species formed in reaction (1) is probably low-spin six-coordinate FeTPP(RIm)Cl which may then dissociate to $\mathrm{FeTPP(RIm)^+, Cl^-}$ and finally form the bis adduct.

Herein we report kinetic data for reaction (1) with N-propylimidazole (PrIm), and demonstrate the rapid reversible formation of an intermediate which we believe to be FeTPP(PrIm)Cl.

Experimental

FeTPPCl was purchased from Strem Chemical Co. and recrystallized from benzene. Purity was verified by comparison to published spectra. N-Propylimidazole was purchased from Chemical Dynamics Corporation and was freshly distilled from KOH before use. Acetone was distilled and dried over molecular sieves.

TABLE I. Rate Data for Reaction (1)[a].

[PrIm], *M*	k_{obs}, s^{-1}
0.0102	0.59
0.0325	1.10
0.0612	1.57
0.0991	2.24
0.1301	2.53
0.1735	2.93
0.2603	3.44
0.3904	3.97
0.5205	4.05

[a] Acetone solvent, 26 °C.

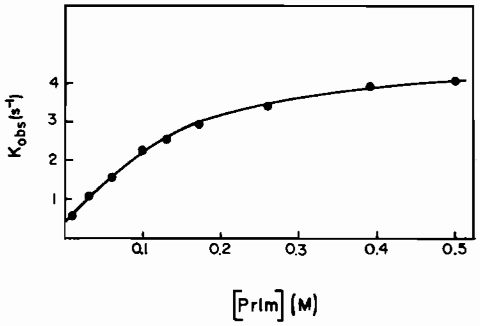

Figure 1. Plot of k_{obs} *vs.* nucleophile concentration for reaction (1) with N-PrIm.

Spectra were recorded on a Perkin-Elmer 323 instrument. Reaction rates were followed using a Durrum stopped-flow machine. The solvent was acetone, the FeTPPCl concentration about 5 × 10^{-5} *M* and the nucleophile concentration was kept in pseudo first-order excess (0.01–0.50 *M*). The rates were followed at a number of wavelengths, most often 555 nm.

Results and Discussion

Table I and Figure 1 contain the kinetic data for reaction (1). At high [PrIm] values, a limiting rate is reached. A plot of $1/k_{obs}$ *vs.* 1/[PrIm] (Figure 2) is linear except for the point at the lowest value of [PrIm] not included in Figure 2). As shown below, this point deviates because reaction (1) does not go to completion.

Pasternack and Stahlbush [10] have recently reported kinetics for reaction (2). They found the rate to be second order

$$\mathrm{FeTPP(DMSO)^+ + 2Im \rightarrow FeTPP(Im)_2^+ + DMSO} \quad (2)$$

in Im. We have studied reaction (1) (in acetone) with imidazole, 4-phenylimidazole, and 2-methylimidazole and, likewise, find the reaction to be second order in nucleophile. However, replacement of the imidazole

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*To whom correspondence should be addressed.

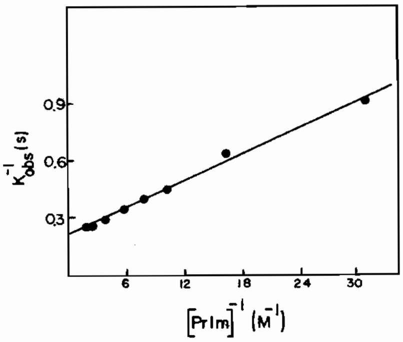

Figure 2. Reciprocal plot of data from Table I. The point at [PrIm] = 0.0102 *M* is not included.

hydrogen with an alkyl group such as methyl or n-propyl changes the observed rate constant from second order to that shown in Figure 1.

The mechanism we propose to account for this behavior is:

$$\mathrm{FeTPPCl + PrIm \overset{K}{\rightleftharpoons} FeTPP(PrIm)Cl}$$

$$\mathrm{FeTPP(PrIm)Cl \underset{k_2}{\overset{k_1}{\rightleftharpoons}} FeTPP(PrIm)^+, Cl^-}$$

$$\mathrm{FeTPP(PrIm)^+, Cl^- + PrIm \underset{k_4}{\overset{k_3}{\rightleftharpoons}} FeTPP(PrIm)_2^+, Cl^-}$$

The first step is a pre-equilibrium to form the low-spin six-coordinate intermediate that then dissociates to yield high-spin FeTPP(PrIm)$^+$, Cl$^-$. Then this reacts to give the low-spin bis adduct. Using the steady state approximation for the five-coordinate intermediate, k_{obs} is found according to equation (3).

$$k_{obs} = \frac{k_1 k_3 K[\mathrm{PrIm}]^2}{(1 + K[\mathrm{PrIm}])(k_2 + k_3[\mathrm{PrIm}])} + \frac{k_2 k_4}{(k_2 + k_3[\mathrm{PrIm}])} \qquad (3)$$

If $k_3[\mathrm{PrIm}] \gg k_2$, the equation simplifies to equation (4).

$$k_{obs} = \frac{k_1 K[\mathrm{PrIm}]}{(1 + K[\mathrm{PrIm}])} + \frac{k_2 k_4}{k_3[\mathrm{PrIm}]} \qquad (4)$$

Except at the lower values of [PrIm] the second term, which is due to the reverse reaction, is not important. Under these conditions, equation (5) follows:

$$\frac{1}{k_{obs}} = \frac{1}{k_1} + \frac{1}{k_1 K}\,\frac{1}{[\mathrm{PrIm}]} \qquad (5)$$

TABLE II. Absorbance Data for Reaction (1) Showing the Formation of an Intermediate.[a]

λ, nm	A_o	A_∞	$A_\infty - A_o$	ΔA_{obs}	A_{INT}[b]
480	0.98	0.94	−0.04	−0.26	1.28
490	1.07	0.77	−0.30	−0.45	1.27
500	1.29	0.72	−0.57	−0.59	1.32
510	1.36	0.70	−0.66	−0.54	1.20
520	1.17	0.72	−0.44	−0.46	1.19
530	0.86	0.81	−0.05	−0.46	1.41
535	0.69	0.88	+0.19	−0.36	1.43
535	0.69	0.88	+0.19	−0.04[c]	1.41
540	0.58	0.97	+0.39	−0.18	1.35
540	0.58	0.97	+0.39	+0.22[d]	1.35
545	0.50	1.02	+0.52	+0.02	1.18
550	0.45	1.05	+0.60	+0.24	0.94
555	0.46	1.02	+0.56	+0.38	0.70
560	0.47	0.95	+0.48	+0.38	0.61

[a] Measured on stopped-flow instrument, solvent acetone, 20 °C; [PrIm] = 0.3 *M* unless otherwise indicated. [b] See text for explanation. [c] [PrIm] = 0.05 *M*. [d] [PrIm] = 0.03 *M*.

According to equation (5), the slope and intercept of Figure 2 are $1/k_1K$ and $1/k_1$, respectively. A least-squares fit yields $k_1 = 5.0 \pm 0.3$ s^{-1} and $K = 8.3 \pm 0.8$ M^{-1}. The infinity absorbance reading showed that the reaction did not go to completion at the lowest value of [PrIm] meaning that the second term in equation (4) was important. Accordingly this point was not included in the plot in Figure 2.

Walker *et al.* [5] attempted to evaluate K_1 for the addition of one mol of base (K_1 is K in the kinetic scheme). In the absence of any spectral evidence for the 1:1 adduct, they assumed that the 1:1 and 2:1 adducts have similar spectra and calculated a value of 9 ± 2 for K with N-MeIm. We show below that their assumption of identical spectra for the 1:1 and 2:1 adducts is adequate at some wavelengths and grossly in error at others. Accordingly, the agreement between K values may be fortuitous.

Strong evidence in support of our assertion that FeTPP(PrIm)Cl is formed in a pre-equilibrium is given by the data in Table II. The calculated ($A_\infty - A_o$) and observed (ΔA_{obs}) absorbance change for the reaction in general do not agree. Indeed, at some wavelengths (535, 540 nm) $A_\infty - A_o$ shows that the products absorb more than the reactants, yet an absorbance *decrease* is observed experimentally. Furthermore, the discrepancy between ΔA_{obs} and $A_\infty - A_o$ itself depends on the PrIm concentration. This is clear evidence for a pre-equilibrium. The data at 535 and 540 nm were used to calculate the equilibrium constant for the formation of the observed intermediate. Using equation (6) [13] K is calculated to be 9.5 M^{-1}, in excellent agreement with the

$$A = -\frac{1}{K}\frac{(A - A_o)}{[PrIm]} + A_o \qquad (6)$$

K calculated from the curvature in the rate constant plot (Figure 1). (In eqn. (6) $A = A_\infty - \Delta A_{obs}$).

The data in Table II can be used to construct the optical spectrum of FeTPP(PrIm)Cl. The absorbance spectrum of the intermediate (A_{INT} in Table II) was calculated using equation (7), where $x = K[PrIm]/(1 + K[PrIm])$ is the fraction of the iron com-

$$A_{INT} = \frac{A - (1 - x)A_o}{x} \qquad (7)$$

plex present as FeTPP(PrIm)Cl. K was taken to be 9.5 M^{-1}. The absorption maxima occur at 500 and 535 nm. In order to obtain a more accurate and continuous spectrum over a broader wavelength range, experiments using a rapid scanning monochromator are being planned.

One example of a $FeTPP^+$ adduct containing a neutral nitrogen donor and an anion as bases has been reported by Scheidt [14]: $FeTPP(py)N_3$. This complex is low-spin [15]. We believe that FeTPP(PrIm)-Cl is also most likely low-spin, meaning that three spin changes (HS → LS → HS → LS) occur during reaction (1).

Kinetic studies using other imidazoles, especially those not substituted at the nitrogen (see above) are in progress. The mechanism given above can accommodate the results for both N-H and N-R imidazoles provided that $k_3[RIm] \gg k_2$ for N-alkyl but $k_3[RIm] \ll k_2$ for N-H imidazoles. This will be discussed in a future paper.

Acknowledgements

The authors are grateful to Professor Judith Hempel and Dr. John Jones for informative discussions. Part of this work was supported by a Dreyfus Teacher-Scholar Grant to D.A.S.

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