Autocatalytic Reduction of dichloro 5, 10, 15, 20 tetraphenylporphinatoplatinum(IV) by 1-Methylimidazole*

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It was observed that in toluene solution, excess 1-methyl-imidazole (MeIm) reduces dichloro 5, 10, 15, 20 tetraphenyl-porphinatoplatinum(IV) (PtTPPCl$_2$) to tetraphenylporphinato-platinum(II) (PtTPP) autocatalytically (Fig.1). There was no Pt(III) intermediate or 1-methylimidazole radical detected by Electron Resonance Spectroscopy (ESR) at 25°C. The reaction was found to be autocatalyzed by the PtTPP product when the 1-methylimidazole to PtTPPCl$_2$ concentration ratio is about 10^4 or more. From the data obtained it is reasonable to suppose that aggregation of the PtTPP product with PtTPPCl$_2$ plays an important role in this reduction process.

Introduction

Porphyrins and porphyrin derivatives play an important role in the biochemistry of all living systems. They form the main structure of pigments like chlorophyll and heme that are involved in electron transfer processes of life. In hemoglobin the Fe(II) ion is surrounded by the imidazole group of the aminoacid histidine[1,2]. In order to understand the biological processes there has been great interest in the reactions of simpler synthetic Fe(III) porphyrins with cyclic amines as a model for more complex systems.

The reduction reaction of dichloro 5, 10, 15, 20 tetraphenyl-porphinatoiron(III) by cyclic amines such as piperidine and imidazole was detected by Moesbauer spectroscopy and the piperidine reaction mechanism was proposed to be an autoreduction where the rate of the reaction strongly depended on the concentration of the excess piperidine[3,4]. In another report, the mechanism of N-methyl-imidazole reduction was assumed to involve the rapid formation of a mono(imidazole) complex followed by a rate limiting chloride ionization[5]. To our knowledge there is no report on the reduction of platinum porphyrins by this group of compounds. In this context we report the reduction of dichloro 5, 10, 15, 20 tetraphenylporphinatoplatinum(IV) with excess 1-methylimidazole in toluene (Fig. 1). The reactions were followed and the changes in one of the visible Q bands of PtTPPCl$_2$ which is at 572.8 nm were recorded.

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* In memory of the Professor Dr. S. I. Shupack of the Chemistry Department Villanova University Pa. U.S.A. where this research was carried out

Experimental

PtTPPCl$_2$ and PtTPP were prepared according to the methods described in the literature[6−8]. They were purified by dry column chromatography. Their identification was done by UV-Visible and NMR Spectroscopy in accordance with the values in the literature[9].

A Beers' Law study was performed to detect any self aggregation of PtTPPCl$_2$ or PtTPP and to calculate the molar extinction coefficients of PtTPPCl$_2$ at 572.8 nm and PtTPP at 509.8 nm in toluene. Absorbance measurements were done on the diluted solutions of porphyrins. The linear behavior of the absorbance versus concentration plots tell us that there is no aggregation within the concentration ranges studied. The absorbance values were plotted against concentrations to obtain the molar absorption coefficients for PtTPPCl$_2$ (ϵ=4897.7) and PtTPP(ϵ=24547.1) from the slopes.

1- Methylimidazole was stirred with KOH pellets and distilled on bariumoxide under nitrogen. The distillate was then stored over molecular sieves and stored in the refrigerator. The purity of it was confirmed by Gas Chromatography and Mass Spectroscopy.
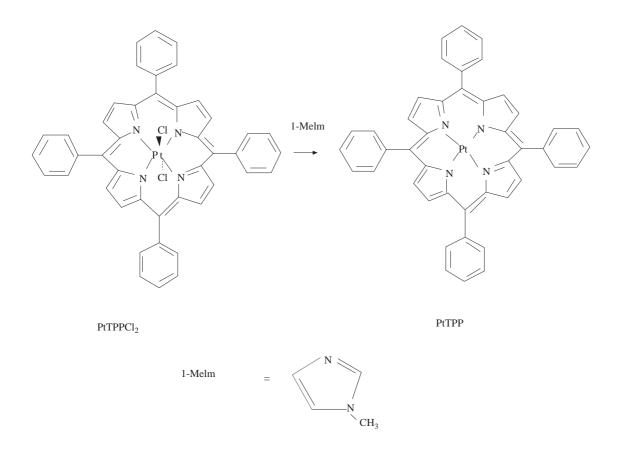

Figure 1. Reduction of dichloro 5, 10, 15, 20 tetraphenylporphinatoplatinum(IV) to 5, 10, 15, 20 tetraphenylporphinatoplatinum(II)
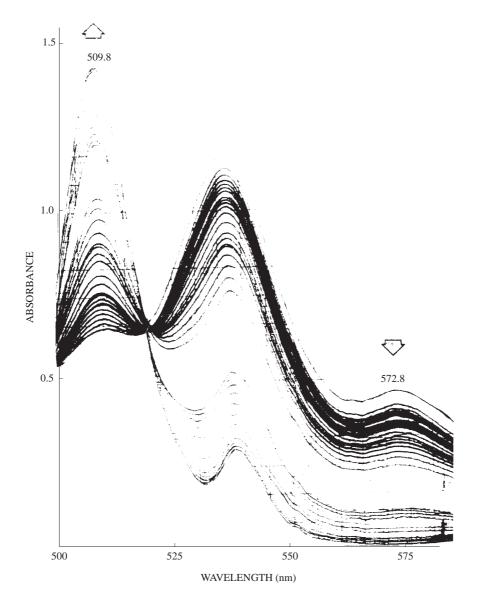
Figure 2. The Reduction of Pt(IV)TPPCl$_2$ to Pt(II)TPP The Visible Spectrum

The reaction solvent toluene was purified and dried by distilling over sodium benzophenone ketyl under nitrogen. Gas-tight syringes were used for the transfer of solutions in all reactions. The PtTPPCl$_2$ concentrations were taken within the range 0.01-0.1 mM. MeIm concentrations were between 300 and 4000 mM. Toluene solutions PtTPPCl$_2$ were prepared under nitrogen and left in and ultrasonic bath to ensure dissolution. The solutions were then transferred to a constant temperature cuvette held at 25°C. MeIm was also kept at this temperature prior to the reaction. MeIm was added to the porphyrin solution by a syringe and the contents of the cell were shaken well to avoid fluctuations in the initial absorbance readings due to mixing. Right after this, the timing and scanning were started. The 600-500 nm region was scanned every 200 seconds by a Varian Cary 219 UV-Visible spectrophotometer controlled by an Apple computer. The absorbances at 572.8 nm (due to PtTPPCl$_2$) were recorded. The reactions were followed for 15-20 hours until they were at least 75% complete. The final readings were taken 2 days later. The reaction of MeIm with PtTPP was also carried out the same way, scanning the 500-300 nm region every 10 minutes. PtTPP

concentrations were 0.001-0.01 mM. The reaction of $PtTPPCl_2$ with 1-methylimidazole in the presence of PtTPP was carried out under the same conditions except that a known amount of PtTPP was added to the $PtTPPCl_2$ solution. For this reaction $[PtTPPCl_2]$=0.132 mM and [PtTPP]=0.064 mM, the [Melm] to $[PtTPPCl_2]$ ratio being 3.4×10^4.

ESR was run on a Varian E12 ESR spectrophotometer at room temperature at the University of Pennsylvania using 2,2,6,6 tetramethyl 4- hydroxypiperidiniumoxide (THPO) as a trapping radical. The reaction was run in the presence of THPO for three weeks.

Results and Discussion

Toluene solution of $PtTPPCl_2$ can be reduced to PtTPP in the presence of excess 1-methylimidazole as evidenced by the visible spectrum (Fig. 2). The peak in the visible region due to $PtTPPCl_2$ at 572.8 nm decreased and a new band belonging to PtTPP at 509.8 nm increased continuously. No other peak, which could be an indication of bond formation between 1-methylimidazole and Pt, was observed. There was no detectable change in 1-methylimidazole spectrum. The changes on the Melm cannot be observed because of the large excess of 1Melm with respect to the low concentration of $PtTPPCl_2$. Any change would be negligible compared with the initial Melm concentration which was at least 1000 times more than that of $PtTPPCl_2$. However, Melm is expected to be oxidized to 1-Methylimidazolidinium radical cation which in turn captures a chloride from the $PtTPPCl_2$ to form a 1-Methylimidazolidinium chloride salt. This type of very short-lived radical cation of imidazoles was reported to be observed by ESR[10].

The half-lives of this reaction with changing $PtTPPCl_2$ and Melm concentrations can be seen in Table 1. The half-life of the reaction decreases as the ratio of Melm to $PtTPPCl_2$ concentration increases, meaning the reduction of Pt(IV) to PT(II) is faster for higher ratios. With a ratio of less than 10^2 the half-life exceeds a day.

Table 1. The change in half-lives with the change in $[Melm]/[PtTPPCl_2]$ ratio

$[PtTPPCl_2]$mM	[Melm] mM	$[Melm]/[PtTPPCl_2]$	$t_{1/2}$(hrs)
0.024	0.072	3.0	-
0.048	0.901	18.7	-
0.032	7.2	225.0	-
0.065	360	5.5×10^3	11.11
0.106	3610	3.4×10^4	6.66
0.091	3610	3.9×10^4	6.11
0.065	3610	5.5×10^4	4.16

The data were treated kinetically. There was no simple relationship (like 0, 1st or 2nd order) between the rate and the $PtTPPCl_2$ concentration. The $PtTPPCl_2$ concentrations (calculated from absorbance values) versus time were plotted for each reaction. The shape of the curve obtained from experimental data points, changed dramatically as the $[Melm]/[PtTPPCl_2]$ ratio increased. A ratio above 10^4 gave curves like in Figure 3. However, this behavior was not observed in the plots for $[1Melm]/[PtTPPCl_2]$ ratios below 10^4. As the former curves suggest, the conversion of $PtTPPCl_2$ of PtTPP proceeded at a slow rate during the initial periods of the reaction where there was practically no PtTPP in solution. As the PtTPP concentration increased however, the rate of reduction increased considerably giving a straight line. This situation is typical for an autocatalytic process where the PtTPP product is accelerating the reaction[11].

The sigmoidal shape of product growth curves of PtTPP for $[Melm]/[PtTPPCl_2]$ ratios of 10^4 or more are also in agreement with this suggestion (Figure 4). For lower ratios the curves are hyperbolic.
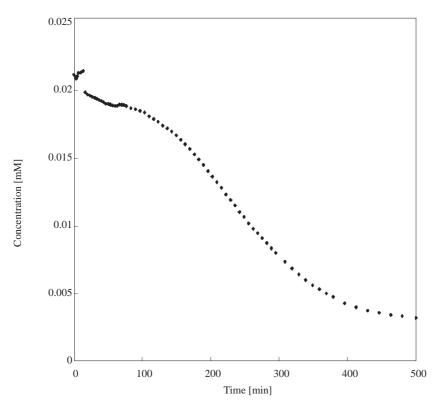

Figure 3. $PtTPPCl_2$ Concentration vs. Time Plot for $[Melm]/[PtTPPCl_2] \geq 10^4$

Autocatalysis kinetics was applied to the data of the former type of reactions according to the methods described in the literature[11]. If it is assumed that a pure autocatalyzed and an uncatalyzed reaction are taking place simultaneously the following expression can be derived:

In $[PtTPPCl_2] = k_c ([PtTPPCl_2]_0 + k_0/k_c)t$ + constant where $[PtTPPCl_2]_0$ is the initial concentration of $PtTPPCl_2$ and k_c and k_0 are the catalyzed and uncatalyzed reaction rate constants respectively. The plot or the nautral logarithm of $PtTPPCl_2$ concentrations versus time gives curves which change into a straight line for the final stages of the reaction. The regression for the straight line is 0.998 for the final data points. For a reaction where purely catalyzed and uncatalyzed paths are taking place simultaneously the slope of this straight line becomes

$$slope = k_c[PtTPPCl_2]_0 + k_0$$

In such a case when the slope is plotted against initial $[PtTPPCl_2]_0$ concentrations, the resulting straight line is expected to intersect the ordinate to give a k_0 value, the gradient being k_c. If this straight line with a slope of k_c passes through the origin, the reaction is a pure catalyzed one with $k_0 = 0$. The former case applies to our reaction where the pseudo order rate constants are $k_0 = 4 \times 10^{-5} \sec^{-1}$ and $k_c = 6.6$ $L.mol^{-1}.\sec^{-1}$ in which

$$k_0 = k'_0[Melm]^a \quad and \quad k_c = k'_c[Melm]^a.$$

k_0 and k_c values are expected to increase as the Melm concentration increases. The order of the reaction with respect to Melm concentration could not be calculated.

The reaction of PtTPP with excess Melm gave no significant change in the UV-Visible spectrum of PtTPP and Melm. Also, the blank runs of PtTPPCl$_2$ without 1-Melm in toluene failed to give any reduction.

The autocatalytic effect was checked by reacting 1-methyl-imidazole with a mixture of PtTPPCl$_2$ and PtTPP. The half-life of the reaction was almost halved in the presence of PtTPP (Table 2). This mixture reaction also showed that the PtTPPCl$_2$ and PtTPP interacted with each other. As the two were mixed, prior to the addition of 1-methylimidazole, a broadening and a sudden drop in the intensity of the Soret bands was observed. The Soret band, which results from the π to $\pi^\star$ transitions of the highly conjugated aromatic porphyrin ring that has a very high molar absorption coefficient for PtTPP at 408 nm(ϵ=295120.9), and for PtTPPCl$_2$ at 419 nm(ϵ=588843.6) became even less intense than the Q bands which have almost one tenth of the Soret molar absorptivity constants. These observations are usually seen when the porphyrins aggregate[12]. Although we have shown by the Beers' Law study that neither PtTPP nor PtTPPCl$_2$ aggregate by themselves in toluene, it is possible to suppose that PtTPP and PtTPPCl$_2$ are aggregating or interacting in some way with each other to affect the $\pi - \pi^\star$ transitions caused by the conjugated system of the porphyrins. Unfortunately no new band, which can be a charge transfer band in the UV-Visible spectrum, was observed, but it is also possible that these charge transfer bands were hidden under the intense Soret bands.
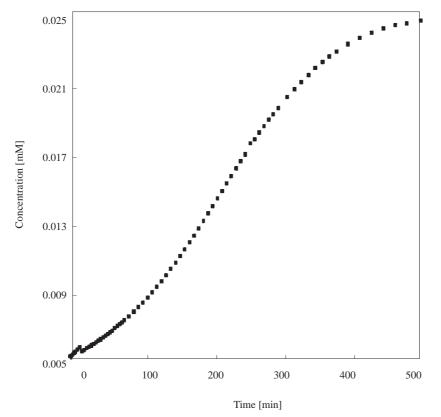

Figure 4. PtTPP Product Growth Curve for [Melm]/[PtTPPCl$_2$]$\geq 10^4$

Table 2. The change in half-life of the reaction in the presence of PtTPP

[PtTPPCl$_2$]mM	[PtTPP] mM	[MeIm]/[PtTPPCl$_2$]	t$_{1/2}$(hrs)
0.132	0.064	3.4×10^4	2.67
0.091	-	3.9×10^4	6.11

Another possibility is the formation of chloro bridged Pt(II) and Pt(IV) porphyrins as such structures exist between hexachloro and tetrachloroplatinates[13].

The interaction of PtTPP with PtTPPCl$_2$ is most likely the cause of autocatalysis. The effect of charge transfer complex formation on autocatalysis has been described in the literature. For such mechanisms usually paramagnetic intermediates are involved[14]. The possibility of formation of a paramagnetic intermediate in our case was investigated by ESR at room temperature. However there was no detectable paramagnetic species at 25°C, but a low temperature ESR measurement would help us to clarify the presence or absence of a paramagnetic species throughout the reaction.

Conclusion

PtTPPCl$_2$ can be reduced to PtTPP with a large excess of 1-methylimidazole by two paths simultaneously. One of them is the autocatalytic reduction path. The PtTPP product, once formed, interacts with PtTPPCl$_2$ and accelerates the reduction reaction by helping the chloride dissociation probably through a π interaction. It is a fast reaction with a psuedo rate constant of 6.6 sec^{-1}. The second path is a very slow reaction which takes place uncatalytically having a pseudo rate constant of 4×10^{-5} L mol^{-1}.sec^{-1}. It is too early to suggest a mechanism for the autocatalysis but it would be interesting to find out how the two platinum compounds interact.

Acknowledgement

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