

The Electrochemistry of Iron Porphyrin Nitrosyls in the Presence of Pyridines and Amines

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Abstract

The electrochemistry of Fe(P)(NO) , where P was tetraphenylporphyrin (TPP), tetraphenylchlorin (TPC) and protoporphyrin dimethyl ester (PPDME), was studied in the presence of substituted pyridines and various amines. Both in the presence and absence of the ligand, the first reduction wave of Fe(P)(NO) was reversible. Weak complexes between the iron porphyrin nitrosyls and the pyridines or amines were observed. Upon reduction, the pyridine or amine was lost, and there was no evidence of complexation of the ligand with Fe(P)(NO)^- . There were also no significant differences in the Fe(P)(NO) -ligand formation constants between P = TPP and TPC. The formation constants for the Fe(P)(NO) -ligand complex, $K_{\text{NO-L}}$, varied linearly with the $\text{p}K_{\text{a}}$ of the ligand. The slopes of the $\text{p}K_{\text{a}}$ versus $\log K_{\text{NO-L}}$ curves were 0.22, 0.19 and 0.20 for P equal to TPP, TPC and PPDME, respectively. These slopes were significantly smaller than the values previously observed for $\text{Fe}^{\text{II}}(\text{P})$ and $\text{Fe}^{\text{III}}(\text{P})$, but only slightly smaller than the complexes where NO was replaced by CS or CSe (0.31 and 0.23, respectively).

The visible spectra of Fe(P)(NO) in the presence of the nitrogenous bases were also obtained. With the addition of ligand, the Soret band shifted to longer wavelengths (405 to 419 nm for pyridine), while the long wavelength region shifted to shorter wavelengths (532 to 520 nm for pyridine). Spectra of $\text{Fe(P)(NO)}\text{(L)}$ at high concentrations of L were not stable indefinitely, but slowly lost NO to generate the bis-ligand complex, Fe(P)(L)_2 .

Introduction

The reduction of nitrite is an enzymatic process that is carried out by two major classes of enzymes. One enzyme, the assimilatory nitrite reductases, reduces nitrite to ammonia. A second class, the dis-

similatory nitrite reductases, reduces nitrite to nitric or nitrous oxide. Iron nitrosyls have been found to be intermediates in both these processes. For the first class of enzymes (the assimilatory nitrite reductases), the fifth axial ligand is thought to be a sulfur ligand, such as a cysteine, while the latter class (the dissimilatory nitrite reductases) has histidine as the fifth ligand. It has been the aim of our research in recent years to determine the chemical importance of the axial ligand in the redox chemistry of iron nitrosyls, and to see if these differences relate to the enzymatic process.

The electrochemistry of iron porphyrin nitrosyls has been studied by several workers [1–3]. The oxidation and reduction of Fe(P)(NO) , where P was equal to octaethylporphyrin, chlorin and isobacteriochlorin, was studied by Fujita and Fajer [1] using voltammetry, visible spectroelectrochemistry and EPR. Kadish *et al.* [2, 3] examined the voltammetric behavior and spectroelectrochemistry of Fe(TPP)(NO) and Fe(OEP)(NO) in a wide range of nonaqueous solvents. In all these cases, Fe(P)(NO) , was found to be reduced in a one-electron reversible process to Fe(P)(NO)^- [1–3].

The visible spectroscopy of Fe(TPP)(NO) in the presence of pyridine was also studied [3]. There was essentially no change in the visible spectrum of Fe(TPP)(NO) when the concentration of pyridine was low, and Fe(TPP)(NO) was converted to Fe(TPP)(py)_2 at high pyridine concentrations (when the solvent was methylene chloride). In this work, they concluded that Fe(TPP)(NO)(py) was spectrally quite similar to Fe(TPP)(NO) . This was consistent with an earlier observation by Tonn [4]. An equilibrium constant for the formation of Fe(TPP)(py)_2 from Fe(TPP)(NO)(py) of 0.7 was calculated [3]. Interestingly, they also found that Fe(TPP)(NO) was more likely to form the bis-pyridine ferrous complex in a methylene chloride/pyridine solution than in neat pyridine. Yoshimura studied the same reaction for the protoporphyrin dimethyl ester (PPDME) complex using infrared spectroscopy [5], and found that Fe(PPDME)(NO)(py) was formed only at high concentration of pyridine. Using an atmosphere of NO gas, he was able to obtain the visible spectrum for Fe(PPDME)(NO) -

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(py). This spectrum was significantly different from Fe(PPDME)(NO) [6].

It will be the purpose of this work to investigate the voltammetry of Fe(P)(NO) in the presence of substituted pyridines and amines in order to measure the formation constants of Fe(P)(NO) and Fe(P)(NO)⁻ with these ligands. In addition, we will investigate whether there are any systematic differences between the chlorin and porphyrin macrocycle in regards to iron-nitrosyl coordination and voltammetry. Visible spectroscopy will be used to characterize the Fe(P)(NO) complex, as well as to provide an independent method for calculating the formation constants between Fe(P)(NO) and pyridines or amines. Because of the ease of displacement of NO by ligands, care was taken to investigate this reaction and to carry out the work under conditions that minimized this problem. In this way, it was possible to determine the effect of nitrogen base coordination on the stability and redox chemistry of the iron nitrosyl.

Experimental

Equipment

Cyclic voltammograms were obtained either with an ECO Instruments 553 potentiostat and EG&G Princeton Applied Research 175 universal programmer or an IBM Instruments EC/225 voltammetric analyzer. The waveforms were recorded on a Hewlett-Packard 7045A X-Y recorder. A three electrode IBM cell was used for the voltammetric work, with platinum electrodes as the working and auxiliary electrodes, and an SCE as the reference electrode. The reference electrode was separated from the porphyrin solution by a salt bridge. Visible spectra were obtained with a Perkin-Elmer 320 spectrophotometer with a P-E 3600 data station. Infrared spectra were obtained with an Analect Instruments FX-6200 FT-IR spectrometer.

Chemicals

Reagent grade chemicals were used for all experiments without further purification except for the liquid pyridine ligands which were distilled prior to use. Tetraphenylporphyrin (H₂TPP), ethylene chloride, aniline, pyridine, 3,4-lutidine, benzylamine, 4-dimethylaminopyridine (DMAP), 3-cyanopyridine, and 4-picoline were obtained from Aldrich Chemical Co. Tetra-n-butylammonium perchlorate (TBAP) was obtained from GFS Chemical Co. Alumina, sodium borohydride, and sodium hydrosulfite were obtained from Fisher Scientific Co., while anhydrous ferrous chloride was obtained from Alfa Products. Nitric oxide was obtained from Matheson Gas Products and purified by passing the gas over potassium hydroxide pellets. Protoporphyrin dimethyl ester was obtained from Sigma Chemical Co.

Tetraphenylchlorin (H₂TPC) was synthesized by the diimide reduction of H₂TPP [7]. Fe(TPP)(Cl), Fe(TPC)(Cl) and Fe(PPDME)(Cl) were synthesized by the FeCl₂/DMF method [8]. Fe(TPP)(NO), Fe(TPC)(NO) and Fe(PPDME)(NO) were obtained from their respective ferric chloro complexes [9, 10].

Procedure

The following procedure was used to obtain the voltammetric data. A known volume of ethylene chloride and the desired pyridine or amine with TBAP was added to the voltammetric cell. The solution was then degassed with pre-purified nitrogen, which had been saturated with ethylene chloride. Once the oxygen had been purged, a known amount of Fe(P)(NO) was then added. Bubbling continued for about 1 min until the porphyrin was completely dissolved and the solution was mixed. The voltammograms were then obtained, with the solution being mixed by bubbling between voltammetric scans.

Results

Electrochemistry of Fe(P)(NO) in the Presence of Pyridine Derivatives and Amines

The voltammetric behavior of Fe(P)(NO), where P = TPP, TPC and PPDME, in the presence of pyridine and amines (L) was studied in order to measure the Fe(P)(NO)(L) and Fe(P)(NO)(L)⁻ formation constants in a noncoordinating solvent such as ethylene chloride. In the absence of an added ligand, two reversible one-electron reduction waves were observed, as had been previously reported [2, 3]. The $E_{1/2}$ for the first wave was found to be -0.93 V versus SCE. When pyridine was added, the $E_{1/2}$ of the first wave shifted to more negative potentials, as is shown in Table I. The slope of the $E_{1/2}$ versus $\log [\text{py}]$ curve was generally less than the theoretical Nernstian slope of 59 mV, except for high concentrations of pyridine. This indicated that a weak complex was formed between Fe(TPP)(NO) and pyridine. In addition, these results indicate that the ligand (pyridine) was lost upon reduction. In the presence of pyridine, the wave remained reversible, and the peak current function was independent of pyridine concentration (Table I). Finally, no waves were observed at the potential that corresponded to Fe(TPP)(py)₂, both prior to and after scanning through the Fe(TPP)(NO) wave.

The shift in the $E_{1/2}$ with pyridine concentration is plotted in Fig. 1. The best fit for the observed potential shifts is obtained by the following equation:

$$(E_{1/2})_L = (E_{1/2})_{un} - 0.059/n \log(1 + K_{NO-L}[L]) \quad (1)$$

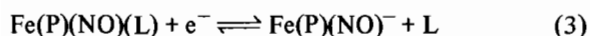
where K_{NO-L} is the equilibrium constant for reaction (2) below, and $(E_{1/2})_{un}$ and $(E_{1/2})_L$ are the $E_{1/2}$ values in the absence (uncomplexed) and presence of

TABLE I. Cyclic Voltammetry of Fe(TPP)(NO) in the Presence of Pyridine^a

[pyridine] (M)	[Fe(TPP)NO] (mM)	$E_{1/2}$ (V vs. SCE)	i_p (μ A)	$i_p/v^{1/2}C^b$
0	0.20	-0.934	38	600
0.12	0.12	-0.943	27	710
0.31	0.12	-0.943	19	500
0.43	0.15	-0.944	25	530
0.62	0.13	-0.948	25	610
1.24	0.18	-0.951	40	700
1.85	0.15	-0.957	33	700
2.47	0.15	-0.962	31	650
3.1	0.12	-0.970	23	610
3.7	0.16	-0.973	32	630
4.3	0.18	-0.976	34	600
4.9	0.19	-0.983	32	530
				610 \pm 70

^aScan rate = 0.10 V/s; solvent = ethylene chloride; temperature = 23 °C. ^b μ A/(V/s)^{1/2} mM.

pyridine (or amines), respectively. Equation (1) is consistent with the following electrochemical mechanism:



From the shifts in half-wave potentials, it is apparent that the reduction product, Fe(P)(NO)^- , does not coordinate with pyridine. Similar behavior was observed for other pyridines and amines, and for Fe(TPC)(NO) and Fe(PPDME)(NO) . The formation constants are summarized in Table II. The Fe(PPDME)(NO) results are in agreement with an earlier infrared study [5].

Visible Spectroscopy of Fe(P)(NO) in the Presence of Nitrogen Ligands

The changes in the visible spectrum, as pyridine was added, was complicated by the tendency of

TABLE II. $K_{\text{NO-py}}$ Values for Fe(P)(NO) in Ethylene Chloride

Base	pK_a	Fe(TPP)(NO)^a	Fe(TPC)(NO)	Fe(PPDME)(NO)^b
3-cyanopyridine	1.40	<0.1 (0.16)	<0.1	<0.1
4-acetylpyridine	3.51	(0.6)		
aniline	4.63	0.4		0.4
pyridine	5.28	0.7 (0.62)	1.1	0.8 (1.1)
4-picoline	5.98	1.6 (1.4)	1.2	0.8 (0.8)
3,4-lutidine	6.46	1.8 (2.8)	1.1	1.7 (0.9)
benzylamine	9.33	3.8	5.8	2.9 (3.2)
4-DMAP	9.71	8.8	6.1	6.4 (7.6)

^aValues in parenthesis obtained in this work by visible spectroscopy. ^bValues in parenthesis obtained by infrared spectroscopy from ref. 5.

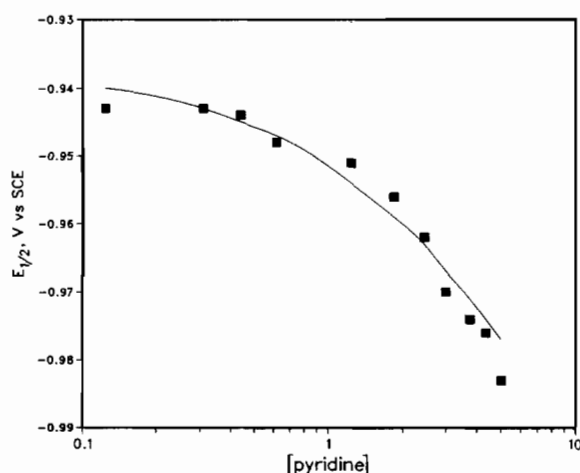
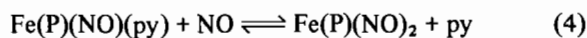


Fig. 1. Variation of the $E_{1/2}$ of Fe(TPP)(NO) as a function of the pyridine concentration. Solvent: ethylene chloride; electrolyte: TBAP; working electrode: platinum; reference electrode: SCE; temperature: 23 °C. Points are the experimental $E_{1/2}$ values obtained from the average of the scan rates from 20–200 mV/s. The line is the theoretical line obtained from eqn. (1), with a $K_{\text{NO-L}}$ value of 0.7.

ferrous porphyrins to form bis-complexes. As was done in the voltammetric study, the visible spectra were taken soon after the mixing of reagents in order to prevent the formation of bis-pyridine complexes. The only exception to this was a series of experiments to determine how stable the Fe(TPP)(NO)(py) solutions were and to verify that Fe(TPP)(py)_2 was formed at long times. An attempt was made to use the procedure of Yoshimura and Ozaki [6] to carry out the reaction under 1 atm of NO. For Fe(TPP)(NO) , it was found that Fe(TPP)(NO)_2 was formed, even in the presence of a high concentration of pyridine.



In the presence of a sufficient amount of pyridine, spectral changes were observed in both the Soret and the 500–600 nm region. The Soret band shifted from 405 to 419 nm, while the 532 nm band shifted to

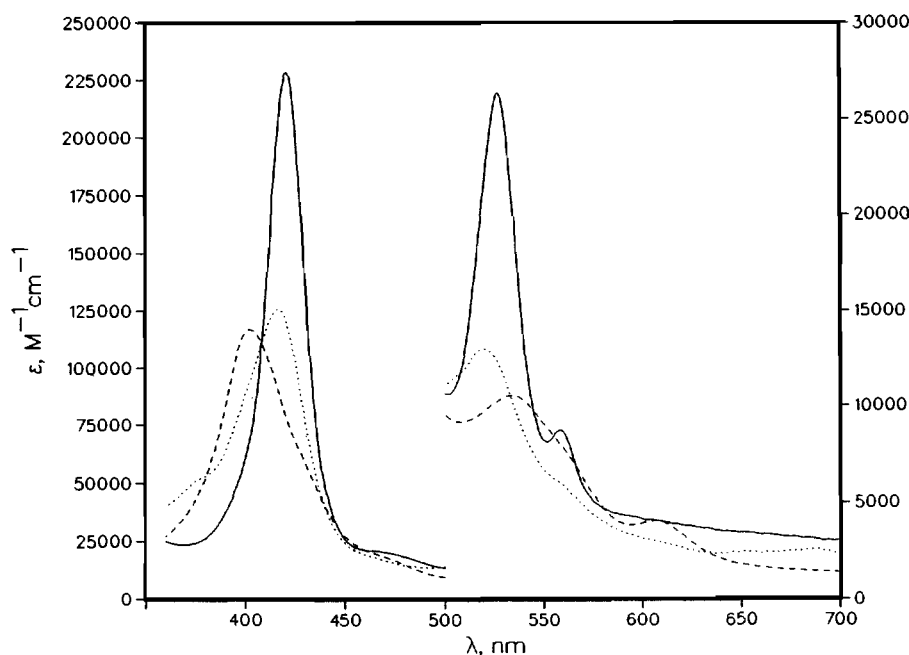


Fig. 2. Visible spectra of Fe(TPP)(NO) in ethylene chloride in the absence of pyridine (dashed line), in the presence of 0.42 M pyridine soon after mixing (dotted line), and in the presence of 4.2 M pyridine after the reaction had been allowed to proceed to completion (12 h) (solid line).

TABLE III. Visible Spectra of Fe(TPP)(NO)(L) Complexes

Ligand (L)	λ_{\max}	ϵ ($M^{-1} \text{ cm}^{-1}$)
no ligand	405	8.5×10^4
3-cyanopyridine	417	1.13×10^5
4-acetylpyridine	419	1.4×10^5
pyridine	419.5	1.6×10^5
4-picoline	418	1.27×10^5
3,4-lutidine	419	9.4×10^4

520 nm (see Fig. 2). The changes in the Soret region of the visible spectrum were used to measure the formation constant, $K_{\text{NO-L}}$, using the program SPECDEC [11, 12]. Several different models were used in the analysis. The first case considered was that Fe(TPP)(NO), Fe(TPP)(NO)(py) and Fe(TPP)(py)₂ were present. Using the known molar absorptivities of Fe(TPP)(NO) and Fe(TPP)(py)₂, the analysis calculated a value for $K_{\text{NO-L}}$ of 0.6, and made the value for the mono-pyridine/bis-pyridine formation constant negligibly small. The second case assumed that only Fe(TPP)(NO) and Fe(TPP)(NO)(py) were present, and the results were within experimental error of the first case. If the solution was allowed to sit in the presence of high concentrations of pyridine, all the Fe(TPP)(NO)(py) is eventually converted to Fe(TPP)(py)₂ (Fig. 2), as was observed by Lancon and Kadish [3].

Using this approach, the λ_{\max} for the Soret band and the value of their molar absorptivities for a series

of substituted pyridines and amines were determined. These results are summarized in Table III. The formation constants determined by this method are given in Table II. The values obtained by visible spectroscopy are in good agreement with the voltammetric values, where comparisons could be made.

Discussion

The voltammetric and visible spectroscopic results show that Fe(P)(NO) forms weak complexes with pyridines and amines. These formation constants are much smaller than the values observed for other mixed ligand complexes between iron porphyrins, pyridine and diatomic ligands [3, 5, 6, 13–15]. Generally, the formation constants are large: 5500 for CSe [13], and 8300 for CS [14]. The value for CO has not been reported, but it is the major species in pyridine solutions under a CO atmosphere [15]. The formation constants for Fe(PPDME)(NO) agree well with those reported by Yoshimura [5] (Table II). In addition, the identity of the porphyrin (TTP, TPC or PPDME) appears to have no significant effect on the formation constant, $K_{\text{NO-L}}$.

The Soret band for Fe(TPP)(NO) shifted to longer wavelengths when the pyridine or amine complex was formed (404 nm to about 419 nm), and the λ_{\max} did not vary significantly with the pK_a of the ligand. Similar changes in the Soret band were observed in the formation of Fe(PPDME)(NO)(L) complexes [6]. Previous workers [6, 17] have interpreted these

changes as due to a decrease in the interaction of the porphyrin a_{2u} orbital with the iron d_{z^2} orbital, which is induced by a decrease in Fe–Ct distance [17].

The variation in the half-wave potential with pyridine concentration indicates that Fe(P)(NO)^- does not coordinate with pyridines. Assuming that a 5 mV potential shift could be detected at 6 M pyridine, the value of the formation constant for a Fe(P)(NO)(py)^- complex, $K_{\text{NO-L}^-}$, must be less than 0.03. In other words, the $K_{\text{NO-L}^-}$ value is at least 20 times smaller than the $K_{\text{NO-L}}$ value. The decrease in the equilibrium constant might be due to the increased charge density on the iron after reduction. Ligand bonding with iron porphyrin–nitrosyls has been found to be primarily σ in character, even for those ligands that are good π -acceptors [6, 18]. This is due to the strong π -interaction between Fe and NO. In addition, resonance Raman spectroscopy has shown that pyridine and amine ligands significantly increase the electron density at the iron [18]. Therefore, an increase in the electron density on the iron due to the reduction probably weakens the Fe–L bond. The loss of pyridine coordination is similar to what has been observed in the reduction of Fe(P)-(py)_2 , where the pyridine ligation is also lost. The reduction of Fe(P)(CS)(L) and Fe(P)(CSe)(L) has not been reported, but recently, Swistak and Kadish [15] have found that Fe(TPP)(CO)(py)^- was formed upon reduction of Fe(TPP)(CO)(py) , if an atmosphere of CO is maintained. This complex is formally an Fe(I) species, but there was no direct evidence as to its actual oxidation state.

The variation of the log of the formation constants as a function of the ligand acidity is shown in Table II and in Fig. 3. The slopes of the $\text{p}K_a$ versus $\log K_{\text{NO-L}}$ plots were found to be 0.22, 0.19 and 0.20 for Fe(TPP)(NO) , Fe(TPC)(NO) and Fe(PPDME)(NO) , respectively. The linearity of the data in Fig. 3 indicates that the strength of the Fe–ligand bond is directly related to the σ -bond strength of the ligand. A comparison of these slopes with other ferrous porphyrin complexes with diatomic ligands, as well as with ferric and ferrous porphyrins is shown in Table IV. All of the slopes for iron(II) with diatomic molecules fall in the region from 0.19 to 0.31, with CS being the largest, followed by CSe and NO. Fe(TPP) and Fe(TPC) show considerable scatter due to π -interactions [12]. The ferric complexes all have much larger slopes, with values in the range of 0.6. As was seen for ferric and ferrous bis-pyridine adducts [12], there were no statistical differences between Fe(TPP)(NO) and Fe(TPC)(NO) .

In summary, weak adducts are formed between Fe(P)(NO) and pyridine or amines. While these adducts are weak, significant changes were observed in the visible spectrum. The changes in the visible spectrum and in the half-wave potentials as a function of ligand concentration gave consistent values for the

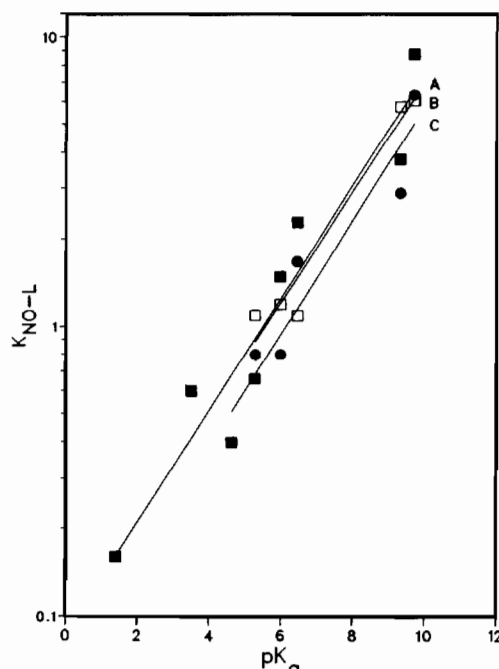


Fig. 3. Variation of the $\log K_{\text{NO-L}}$ values as a function of the $\text{p}K_a$ of the base. Solvent: ethylene chloride, 0.1 M TBAP. Solid squares and line A: Fe(TPP)(NO) ; open squares and line B: Fe(TPC)(NO) ; solid circles and line C: Fe(PPDME)(NO) .

TABLE IV. Log Formation Constant– $\text{p}K_a$ Slopes for Fe(P) with Pyridines and Amines

Complex ^a	Slope	Reference
Fe(TPP)(NO)(L)	0.22 ± 0.03	this work
Fe(TPC)(NO)(L)	0.19 ± 0.02	this work
Fe(PPDME)(NO)(L)	0.20 ± 0.02	this work
Fe(TPP)(L)_2	0.44	16
Fe(TPP)(L)_2^+	1.40	16
Fe(TPC)(L)_2	0.29 ± 0.29	12
Fe(TPP)(CS)(L)	0.31 ± 0.03	14
Fe(TPP)(CS)(L)^+	0.63 ± 0.03	14
$\text{Fe(TPP)(CS)(L)}^{2+}$	0.64 ± 0.05	14
Fe(TPP)(CSe)(L)	0.23 ± 0.02	13
Fe(TPP)(CSe)(L)^+	0.62 ± 0.06	13
$\text{Fe(TPP)(CSe)(L)}^{2+}$	0.70 ± 0.11	13
Fe(TPC)(L)_2^+	1.21 ± 0.16	12

^aL is a pyridine or an amine.

formation constants. The formation constant values depended upon the $\text{p}K_a$ of the ligand, and the iron–ligand bonding is dominated by σ -bonding. Upon reduction, the coordinated pyridine or amine is lost and an uncomplexed Fe(P)(NO)^- species is formed.

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