Scientific
Research

Dimerization of 1-Phenyl-1*H*-tetrazole-5-thiol over Metalloporphyrin Catalysts

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ABSTRACT

In an alkaline methanol solution, dimerization of 1-phenyl-1*H*-tetrazole-5-thiol (HL) was carried out over metalloporphyrin catalysts under mild conditions. The dimer product, 1,2-bis(1-phenyl-1*H*-tetrazol-5-yl) disulfane (L-L), was characterized by determinations of infrared (IR), HPLC, NMR and elementary analysis respectively. *In situ* UV-Vis spectroscopic analysis and cyclic voltammetric (CV) determinations suggested that the active intermediate for L-L formation is an axially ligated complex, RS-Mn^{III}THPP, which decomposes into a Mn^{II}THPP molecule and a stable radical (·SR) for coupling to form the disulfane. Meanwhile Mn^{II}THPP molecule can be oxidized easily to form Mn^{III}THPP species again by oxygen from the air for using in next catalytic circle.

Keywords: Disulfane; Dimerizatoin; Catalytic Conversion; Metalloporphyrin Catalyst

1. Introduction

Metalloporphyrins have been extensively studied because their excellently catalytic functions in organic preparations [1-4]. Meanwhile their catalytic activities were dramatically enhanced by halogen substitutions in the conjugated porphyrin planes [5-8]. Recently, porphyrin molecules were anchored on the surfaces of silica and polymer for easy separation from the catalytic systems [9,10]. Furthermore, cobalt porphyrin molecules supported on pyrolysed carbon exhibited high activity in catalytic conversion from hydrogen sulfides to S_8 circle molecules [11]. Catalytic conversion of organic substrates provides wide research fields in biomimetic oxidations. Oxidation of 2-substituted quinolines over metalloporphyrin catalysts showed that biomimetic oxidation can replace the biological approach, thus allowing access to large quantities of metabolites [12]. A series of ruthenium porphyrin catalysts promoted the oxidations of organic substrates such as styrenes, cycloalkenes, α,β-unsaturated ketones, steroids, benzylic hydrocarbons and arenas [13]. N_4 macrocyclic complex catalysts for the electrochemical oxidation of thiols exhibited high efficiency, and their activities were adjusted dramatically by tuning the redox properties of the macrocyclic molecular electrodes [14]. Disulfane analogues are important biochemicals, which are generally produced in the alkali cleavage of insulins [15]. For instance, hydropersulfides have been implicated

as important intermediates in the cell-killing action of the anticancer natural products *leinamycin* and *varacin*. It has been suggested that disulfanes mediate to convert molecular oxygen to reactive oxygen species under physicologically relevant conditions [16]. In 4-thiouridine's biosynthesis, evidences proved that the biological sulfur was transferred via persulfide groups [17]. In the biomimic preparations of [Fe$_4$S$_4$] clusters, RSH compounds were partially converted into RSSR disulfanes [18-20], and these evidences were beneficial for exploring the forming mechanism of [Fe$_4$S$_4$] clusters. As far as we know, there was no disulfane's preparation over metalloporphyrin catalysts has been reported. Above research works encouraged us to investigate the catalytic preparation of 1, 2-bis(1-phenyl-1*H*-tetrazol-5-yl) disulfane (L-L) over metalloporphyrin catalysts. Furthermore *in situ* UV-Vis and CV determinations supplied more kinetic information toward better understanding of the catalytic mechanism in L-L preparation.

2. Experimental

Metalloporphyrin catalysts were synthesized according to literature method [21-23]. As a typical run for catalytic reaction, 0.15 g of 1-phenyl-1*H*-tetrazole-5-thiol (HL) and 1.5 mg of THPPMnCl were dissolved in 20 ml of alkali methanol at 25°C, followed by stirring for 2 h, and a yellow product was deposited. This reaction is described in **Scheme 1**. After filtration, washing with water
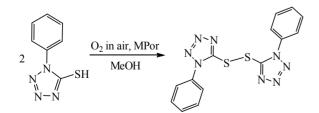
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and drying, the product was characterized by determinations of melting point (144°C - 146°C), ^{1}H-NMR (doublets at 6.65 - 6.72 ppm and triplets at 7.10 - 7.25 ppm with integration areas of 1.2180 and 1.7257), IR (522.4 cm^{-1} assigned to ν_{S-S}) and elementary analysis [Found. (Calc. for $C_{14}H_{10}N_8S_2\%$): C 47.61 (47.44), H 2.79 (2.84), N 31.58 (31.62), S 18.72 (18.60)]. The quantitative analyses were performed by HPLC and UV-Vis techniques. The electrochemical equipment was made from combination of a model JSH-1 potentiostat, a model DCG-2 multipleprogramm-function designator and a Type 3088 function recorder. Before electrochemical determinations, the solvent dimethyl sulfoxide (DMSO) was in turn dried by 5A molecular sieves, refluxed with CaH_2, distilled in vacuum and sealed for later use. Purification of Ar: The gas passed in a row through two gas-washing bottles containing $KMnO_4$ and $K_2Cr_2O_7$-H_2SO_4 solution, three columns of active copper granules (180°C); 5A molecular sieves and silica gel. After these processes the purity of Ar reached 99.99%.

3. Results and Discussion

3.1. Activity and Selectivity of Metalloporphyrin Catalysts

Table 1 presents catalytic activities in dimerization of HL under various conditions. Notably, the Mn-porphyrin catalysts are very active for this reaction, and only oxidative coupling products are obtained. For example, THPP-MnCl exhibits the conversion at 57.6% with the selectivity for L-L at 100%. Apparently, high activity and selectivity in oxidative coupling of HL is potentially important for industrial applications in preparing L-L and its intermediated compounds. Furthermore, it is interesting to note that various Mn-porphyrin catalysts exhibit quite different activities (**Table 1**, Runs 1, 17-21). For example, TMOPPMnCl gives rise to the L-L yield at 48.2%, and TNPPMnCl supplies the L-L yield only at 5.6%, which is low as the yield over simple manganese salts. The activity order over these Mn-porphyrin catalysts is as follows: THPPMnCl > TMOPPMnCl > TAPP- MnI$_5$ > TCPPMnCl > TPPMnCl > TNPPFeCl. The Mn-porphyrin catalysts with electron-donating groups, such as -OH, -NH$_2$, and -OCH$_3$, and with large solubility in gives high
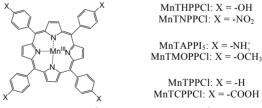
Scheme 1. The dimerization of HL over metalloporphyrin catalyst in the air.

Table 1. Catalytic activities in oxidative coupling of HL (1-phenyl-1*H*-tetrazole-5-thiol) by air under various conditions over Mn-porphyrin and Mn-salt catalysts in the solution with NaOH (0.1 mol/L).

No	Items^a			
	Catalyst^b	Solvent	Conv./%	Yield/%
1	THPPMnCl	Methanol	57.6	57.6
2	THPPMnCl	Ethanol	45.8	45.8
3	THPPMnCl	2-Propanol	36.7	36.7
4	THPPMnCl	1-Propanol	35.2	35.2
5	THPPMnCl	1-Butanol	31.6	31.6
6	THPPMnCl	*t*-Butanol	35.8	35.8
7	THPPMnCl	Glycol	14.6	14.6
8	THPPMnCl	1,4-Butanediol	12.8	12.8
9	THPPMnCl	Water	--	10.6
10	THPPMnCl	Acetone	--	12.3
11	THPPMnCl	*n*-Hexane	--	14.7
12	THPPMnCl	Cyclohexane	--	11.3
13^c	THPPMnCl	Methanol	--	13.6
14	No Catalyst	Methanol	--	3.7
15	MnCl$_2$·4H$_2$O	Methanol	--	5.3
16	MnSO$_4$·H$_2$O	Methanol	--	6.8
17	TNPPMnCl	Methanol	--	5.6
18	TAPPMnI$_5$	Methanol	--	43.6
19	TMOPPMnCl	Methanol	--	48.2
20	TPPMnCl	Methanol	--	10.8
21	TCPPMnCl	Methanol	--	14.3
22	THPPMnCl(Reuse)^d	Methanol	55.7	55.7
23	Recycle for 2 times^d	Methanol	50.3	50.3

^{a}The metalloporphyrin catalyst structures are as below:

MnTHPPCl: X = -OH
MnTNPPCl: X = -NO$_2$

MnTAPPI$_5$: X = -NH$_3^+$
MnTMOPPCl: X = -OCH$_3$

MnTPPCl: X = -H
MnTCPPCl: X = -COOH

^{b}HL:Catalyst = 4.3×10^5/1 for Runs 1-13; 1.2×10^5/1 for Runs 15, 16 and 100/1 for Runs 1-21.
^{c}The system without NaOH added.
^{d}THPPMnCl solution was recovered from the filtration of reaction mixture.

conversions, while those catalysts with electron-withdrawing groups of -NO$_2$, -COOH, and even -H, or with poor solubility in alkali methanol, give low conversions. Possibly, the catalytic activities could be related to both stability and low redox potential of the intermediate of L-MnPor.

3.2. Influences of the Reaction Media

Moreover, it is also observed that NaOH is a necessary

agent for the catalytic conversion (**Table 1**, Runs 1 and 13). Without sodium hydroxide, only 13.6% of the product could be prepared. Possibly, this catalytic reaction could be promoted by the alkali media to help the mercapto ionization in HL molecules, and therefore the produced L^- anions were easy to coordinate the center metals to form the active intermediates of RS^--Mn(III)- porphyrin.

It is worth noting that the solvents strongly influence the catalytic activities over THPPMnCl catalyst (**Table 1**, Runs 1-12). Notably, by using both the solvents with strong polarity such as H_2O, glycol, and 1,4-butanediol and with weak polarity such as *n*-hexane and acetone, THPPMnCl is catalytically inactive for oxidative coupling of HL. However, the use of the solvents with medium polarity including methanol, ethanol, 1-propanol, 1-butanol, *tert*-butanol, and 2-propanol shows high activities for the reaction (conversions at 31.6% - 57.6%). Particularly, methanol gives the highest conversion at 57.6%. Obviously, the selection of solvents with suitable polarity is important for the reaction.

3.3. Reuse of Active Catalyst

More importantly, a recycle of THPPMnCl catalyst also shows high activity (**Table 1**, Runs 22 and 23). For ex-

ample, the reuse of the catalyst exhibits the conversion at 55.7%, and the recycled catalyst for 2 times gives the activity at 50.3%. However, the recycled catalyst for 5 times gives the catalytic activity at 11.6%, which is reasonably assigned to the loss of the catalyst during the separation of the catalyst with the product. Because the catalyst for the first run is only 1.5 mg, and the separation of the catalyst with the product for 5 times resulted in the loss of the catalyst significantly. If the catalyst used in the reaction are 10 mg for the first run, the recycled catalyst for 5 times still gives the catalytic activity at near 45%. Obviously, the catalyst losing should not be ignored in a system with larger amount of the catalyst.

3.4. *In Situ* UV-Vis Determinations

The *in situ* UV-Vis spectra for the catalytic conversion systems under various conditions were given in **Figure 1**. Generally, $Mn^{III}THPP$ exhibited a Soret band at 472 nm. However, after mixing with HL under flowing nitrogen, the band at 472 nm reduced, and a new Soret band from $Mn^{II}THPP$ species appeared gradually at λ_{max} = 423 nm. In contrast, without HL, the Soret band from $Mn^{III}THPP$ species kept changeless. These results suggest that Mn^{III}-THPP species can be easily reduced by HL to form $Mn^{II}THPP$ species. After exposing the mixture to the air
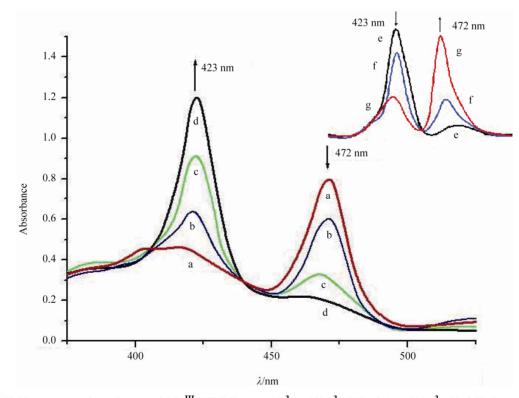

Figure 1. UV-Vis spectra of a mixture of $Mn^{III}THPPCl$ (1×10^{-3} mol/dm^3), HL (0.1 mol/dm^3), NaOH (0.1 mol/dm^3), and methanol treated by nitrogen for (a) 0 min; (b) 20 min; (c) 50 min; (d) 80 min, after d, exposure air for (e) 0 min; (f) 10 min; (g) 20 min. For removing the dissolved oxygen, a mixture of $Mn^{III}THPPCl$, NaOH, and methanol treated by nitrogen for 20 min. All experiments were done at room temperature (25$^\bullet$C) in 20 mL methanol solution containing 0.1 mol/L of NaOH.

within enough time, the band at 472 nm appeared again, while the band at 423 nm reduced gradually. These results suggest that $Mn^{II}THPP$ species was gradually oxidized by oxygen from the air, and $Mn^{III}THPP$ species was obtained again.

3.5. Electrochemistry

The electrolyte is a dimethyl sulfoxide (DMSO) solution containing 2.0×10^{-3} mol/L $Mn^{III}TPPCl$ and 0.1 mol/L $(But)_4NClO_4$ (tetrabutylammonium perchloride, TBAP) in which the O_2 is removed by flowing argon. Under argon protection and at scan rate of 200 mV/s, the cyclic voltammetric experiments are carried out, and the cyclic voltammograms (CV) are seen in **Figure 2**. The CV of MnTPPCl (**Figure 2(a)**) presents three pair of current peaks around −0.72 (omitted), −1.77 and −2.28 V, reflecting the redox processes of Mn(VI)TPP-Mn(III)TPP, Mn(III)TPP-Mn(II)TPP, and the redox process of porphyrin ring (Mn(II)TPP-Mn(II)TPP⁻) respectively. After HL adding, the p_a around −1.77 V disappears, and a new

p_c appears around 1.90 V (**Figure 2(b)**). The new p_c must be caused by the oxidation of a new species containing MnTPP and HL, an active species in L-L forming process.

3.6. Possible Mechanism in HL's Dimerzation

Based on the *in situ* UV-Vis and electrochemical determinations, a possible mechanism for catalytic dimerization of HL was described as **Scheme 2**. Step 1 axial coordination: After dehydrogenation of HSR, the produced ⁻SR anion coordinated with Mn(III)TPP molecules at the axial position. Step 2 chemical reduction and hemolytic cleavage: The electron in ⁻SR was transferred to the central metal and Mn(III)TPP species was reduced to Mn-(II)TPP species, and the cathodic current peak from Mn-(III)TPP to Mn(II)TPP species around −1.77 V (**Figure 2(a)**) therefore was not observed (**Figure 2(b)**). This is a typical chemical-electrical (CE) process. Meanwhile RS-Mn(II)TPP was quickly homolyzed to form Mn(II)TPP molecule and ·SR radical. Owing to their conjugating
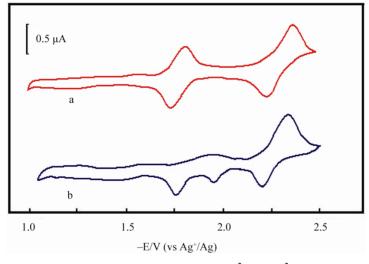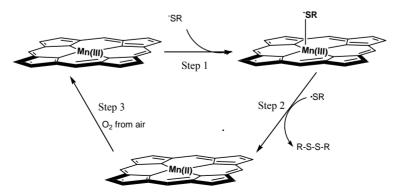

Figure 2. The cyclic voltammetric curves of Mn（III）THPPCl (1×10^{-3} mol/dm³) in DMSO with HL (0.1 mol/dm³) (b) and without HL (a). Supporting electrolyte: $(But)_4NClO_4$ (0.1 mol/L); scan rate: 200 mV/s; reference electrode: luggin capillary, $Ag/AgNO_3$ in MeCN (0.1 mol/L).

Scheme 2. The proposed mechanism for the catalytic dimerization of HL based on *in situ* UV-Vis and CV determination.

configurations, the ·SR radicals were stable enough to collide with each other, and as a result the coupling disulfane products were generated. By the way, in the CV of Mn(III)TPP with HL in DMSO system, the anodic current peaks (i_{pa}) from RS-Mn(II)TPP and Mn(II)TPP to Mn(III)TPP were clearly monitored (**Figure 2(b)**). Step 3 catalyst recovery: Actually, in this catalysis the deactive Mn(II)TPP was oxidized by O_2 from air to form the active species of Mn(III)TPP. The *in situ* UV-Vis determinations also indicated the interconversion between Mn-(III)TPP and Mn(II)TPP (**Figure 1**).

4. Conclusion

In conclusion, an organic compound of 1,2-bis(1-phenyl-1*H*-tetrazol-5-yl) disulfane (L-L) has been synthesized by catalytic dimerization of 1-phenyl-1H-tetrazole-5-thiol (HL) over metalloporphyrin catalysts in alkaline methanol solutions. Experimental results indicate that Mn-porphyrin catalysts with electron-donating groups and with enough solubility in alkaline solvents give high conversions of HL. Meanwhile, a possible mechanism for catalytic dimerization of HL was proposed based on *in situ* UV-Vis and electrochemical determinations. This catalytic dimerization is useful in research on sweetening of fuel oil [24] and biodegradation [25].

5. Acknowledgements

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