Highly efficient conversion of aldehydes to carboxylic acid in the presence of platinum porphyrin sensitizers, air and sunlight

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ABSTRACT: A variety of aromatic and aliphatic aldehydes were oxidized to the corresponding carboxylic acids in the presence of platinum porphyrin, sunlight and air in acetonitrile solvent under mild conditions. Nitrobenzaldehydes were found to be very efficient $^1O_2$ scavengers that quench the formation of acids from any aldehyde in the presence of free-base porphyrin sensitizers. However, nitrobenzaldehydes were converted to the corresponding acids in the presence of platinum porphyrins. The platinum porphyrins are very good and efficient catalysts for a wide range of applications in the aerobic conversion of aldehydes to acids.

KEYWORDS: photooxidation, platinum porphyrin, carboxylic acid, sunlight, aldehyde.

INTRODUCTION

Numerous works have been concentrated on the oxidation of organic compounds in the last century, owing to their importance in organic synthesis and in the industry [1]. The popular conventional method for the conversion of aldehydes to their corresponding carboxylic acids involves the use of Jones' reagent [2]. The Jones reagent however has two disadvantages; highly acidic media and the stoichiometric generation of Cr-based hazard material. Other efficient reagents have also been reported such as oxone [3], calcium hypochlorite [4] and 2-hydroperoxyhexafluoro-2-propanol [5]. Hydrogen peroxide has also been used as an oxidant under severe basic conditions [6], or in combination with other reagents such as formic acid [7], sodium chlorite [8], benzene selinic acid [9], magnesium monoperoxyphthalate (MMPP) [10] and other transition metal mediated reactions [11–17]. However, all of these methods have some limitations such as the requirement of strong acidic or basic conditions,

stoichiometric or super stoichiometric amounts of costly or hazardous oxidizing agents, or elevated temperatures. Therefore, mild, catalytic, economic and efficient alternative methods are required.

An extensive effort has also focused on metalloporphyrins which are efficient biomimetic catalysts for hydrocarbon oxidation using molecular oxygen and various oxygen transfer reagents [18, 19]. Unfortunately, metalloporphyrins catalysts usually require use of stoichiometric oxidation for thermal oxidation of the substrates. Therefore, finding a catalytic system for the oxidation of hydrocarbons by O_2 under mild conditions is still a challenging issue [20, 21]. A few examples of photochemical oxidations using O_2 and a metalloporphyrins catalyst have been reported [22, 23]. Their reactivities are found to be dependent upon the central metal, the substituents on the porphyrin ring, and the axially coordinated ligands. Platinum porphyrins have also been investigated as oxygen sensing probes, photosensitizer, potential antitumor agents [24], molecular conductors and components of molecular devices [25]. Platinum porphyrins in high oxidation states are also known, but studies of these higher oxidation state derivatives are limited [26].

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Although a synthetic reaction using solar energy was reported about 50 years ago, the rate was very slow and the yield of product was poor. Sunlight has recently been applied as a sustainable light source [27]. To alleviate these problems, strong UV light (*e.g.* from a high pressure mercury lamp) has been used to accelerate the reaction. If solar radiation can be used to efficiently mediate the oxidation of alcohols, an environmentally benign process will be established. This concept leads back to the origin of organic photochemistry in the late 19th century [28]. In this works we first investigate the photocatalytic oxidation of aldehydes by sunlight then we describe the effects of solvent, time, metal, mechanism and the structure of sensitizers in these reactions.

EXPERIMENTAL

Chemicals and reagents

Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a BRUKER DRX-300 AVANCE spectrometer at 300.13 and 75.47 MHz NMR spectra were obtained on solution in DMSO-d_6 using TMS as internal standard. Light intensity determined with light meter [(LT lutron model YK-2500LX). The chemicals used in this work were purchased from Merck and Fluka Chemical Companies. The conversion and selectivity of products were monitored by Agilent and Finnigan TRACE gas chromatographs.

Preparation of catalyst

The *meso*-substituted porphyrins were synthesized from the reaction of related aldehydes and pyrrole [29]. The reaction was carried out in the boiling propionic acid with the addition of 10 vol.% acetic anhydride. The purification of porphyrins was carried out using the crystallization from different organic solvents. To introduce the platinum ion into a macrocycle molecule the benzonitrile method with divalent platinum salts was used [30]. The solvents were boiled down in vacuum, and the residue was recrystallized from the chloroform-methanol mixture.

Reaction procedures

General procedure for the synthesis of carboxylic acids. The aldehydes (0.5 mmol) and a 1 mL CH$_2$Cl$_2$ solution of the PtTMP (0.5 × 10^{-3} mmol) were dissolved in 14 mL of CH$_3$CN in a quartz tube. Air was bubbled through the solution and the sample was irradiated using sunlight 75400 LUX (Intensity determined with light meter LT lutron model YK-2500LX) for 4–24 h. The solvent was removed under vacuum, and the residue was separated by column chromatography (silica gel,

n-hexane/EtOAc, 13:1) to give the corresponding carboxylic acid. The conversion and selectivity of products were measured by GC. The product of entry 12, Table 2 was confirmed from the melting points and ^{1}H and ^{13}C NMR spectra.

Gas-chromatographic method. Analytical methods. Gas-chromatographic determinations were carried out by means of a Finnigan TRACE GC Ultra with an Innowax column (RTX-1) and H$_2$ as the carrier gas. The flow was (1/4 mL/min). The temperature program was 50–180 °C (11 °C/min), 180–270 °C (11 °C/min).

Selected spectral data

Terephthalic acid (12). Colorless crystals; mp > 260 °C. ^{1}H NMR (300.13 MHz, DMSO-d_6): δ, ppm 8.00–8.15 (4H, m, H Ar), 13.31 (2H, br s, CO$_2$H). ^{13}C NMR (75.47 MHz, DMSO-d_6): δ, ppm 129.9, 130.4, 134.9, 139.3, 167.1.

RESULTS AND DISCUSSION

In previous studies, efficient catalytic systems for free-base porphyrins-catalyzed aerobic oxidations of aldehydes have been developed in the presence of visible light and sunlight [31]. In continuation of our studies for aerobic oxidation of organic compounds with porphyrin and using solar energy herein, we would like to report a novel and highly efficient catalytic system for the aerobic oxidation of aldehydes using platinum porphyrins as catalyst, by which aldehydes and its substituted derivatives can be smoothly oxidized to corresponding carboxylic acids. Photo-oxygenation was performed in the oxygenated solutions of acetonitrile under sunlight in the presence of platinum porphyrins under 1 atmosphere pressure of air at room temperature (Scheme 1).

PtTPP: R^1=R^2=R^3=R^4=R^5=H
PtTMP: R^1=R^3=R^5=CH$_3$, R^2=R^4=H
PtTPFPP: R^1=R^2=R^3=R^4=R^5=F
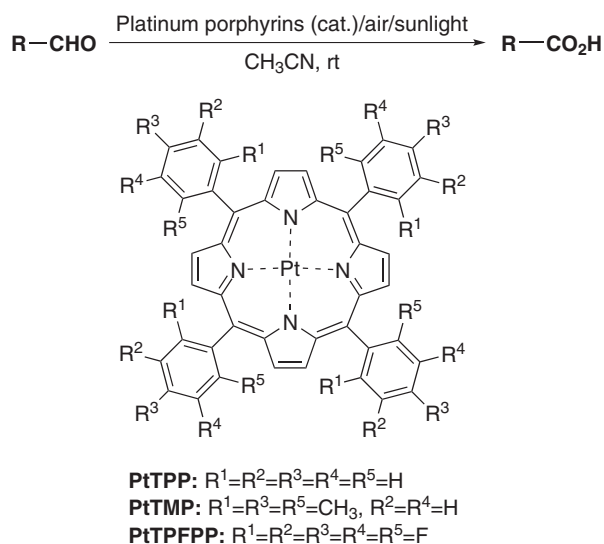
Scheme 1. Reaction scheme and the structure of platinum porphyrins used as catalysts

Initial attempts to optimize the reaction conditions for the oxidation of aldehydes to the corresponding carboxylic acids were performed by a variety of metalloporphyrins with 2-methoxybenzaldehyde as the test substrate. The yields are highest for platinum porphyrins as is indicated in Table 1. All other metals have shown negligible yields, but Pd and Ni porphyrins were slightly reactive. ZnTPP which is relatively reactive for electron-withdrawing substituted aldehydes (59% conversion for 4-bromobenzaldehyde) showed no reactivity for less reactive aldehydes such as 2-methoxybenzaldehyde. The complexes of paramagnetic metal ions of the first row transition metals have a very short triplet lifetime in solution and are not reactive [32]. In contrast, complexes of diamagnetic Pd(II) porphyrins and Pt(II) show both intense fluorescence and pho-sphorescence, with triplet lifetimes in the range of msec [33] and show highest reactivity. The catalytic activity of metalloporphyrins for photooxidation appeared to be dependent on the nature of the ligands as well. PtTMP Showed the best activity among PtTMP, PtTPP and PtTPFPP, and presented excellent catalytic performance for the oxidation of 2-methoxybenzaldehyde under mild reaction conditions. Therefore PtTMP was chosen for further investigations. When the oxidation of 2-methoxybenzaldehyde was conducted in the absence of PtTMP, the yield of 2-methoxybenzoic acid was negligible (Table 1, entry 10). However, the yield showed remarkable increase by adding 1.0×10^{-6} mol of platinum porphyrin to the reaction mixture (Table 1, 91%, entry 8).

Figure 1 shows the of formation percent of 2-methoxybenzoic acid *vs.* time in an oxygenated solution in acetonitrile under sunlight irradiation in the presence of PtTMP. The Soret band of PtTMP was monitored at 398.5 nm using a UV-vis method. This method showed
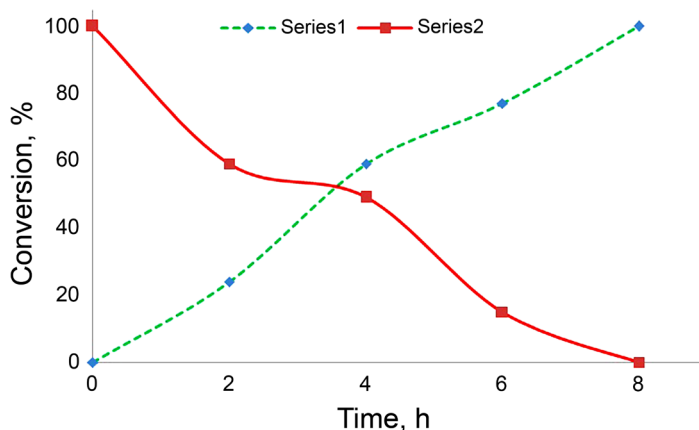

Fig. 1. Formation of 2-methoxybenzoic acid *vs.* time of irradiation in acetonitrile (Series 1); Percent of remaining PtTMP *vs.* time (Series 2)

that sensitizer bleaching for PtTMP was complete in 8 h under our conditions. After the disappearance of the porphyrin Soret band, the formation of the oxidation products stopped, and the reaction conversion remained constant. Therefore, the end point of the reaction can be controlled by the change of color of the reaction medium (Fig. 1).
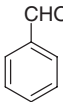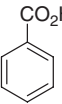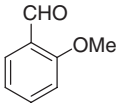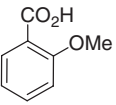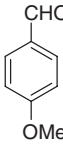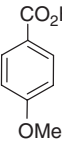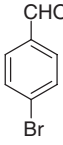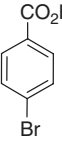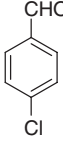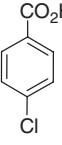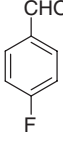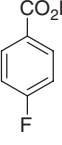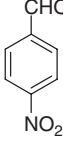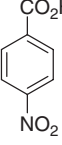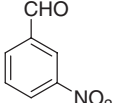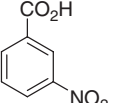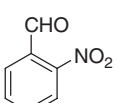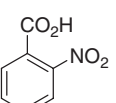
To check the generality of this method, the oxidation of a variety of aromatic and aliphatic substrates was studied under sunlight. As shown in Table 2, this catalytic system was applicable to a wide range of aromatic and aliphatic substrates. The aldehydes were converted into the corresponding carboxylic acids in high percentages within reasonable times with a high turnover number. Aromatic aldehydes possessing electron-withdrawing groups on the phenyl ring (Table 2, entries 4–9) were more reactive than those with electron-donating substrates (Table 2, entries 2, 3). Porphyrin degradation was also accelerated in the presence of less reactive substrates.

Table 2 also shows that PtTMP is more reactive than H_2TMP and the patterns of reactivity for different substrates are somehow different for PtTMP and H_2TMP.

To find a clue to the mechanism, the aerobic oxidation of 2-methoxybenzaldehyde in various solvents and singlet oxygen scavengers has been investigated and the results are summarized in Table 3. The engaged solvents for the oxidation reactions are dimethylformamide, acetonitrile, dimethylsulfoxide, NaN_3/Na_2SO_3/acetonitrile and H_2O. NaN_3/Na_2SO_3 is known as a singlet oxygen scavenger in the literature science it produces N_3^- in the presence of light which N_3^- compete with $^1O_2$ [34]. Acetonitrile is a good solvent for oxidation reactions since it is relatively inert toward oxidation, and its tendency toward coordination and interaction with coordination compound is low. In addition acetonitrile is usually enough polar to dissolve the substrates, products and the catalyst.

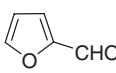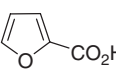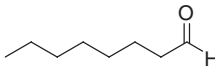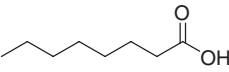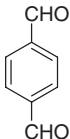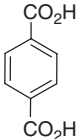It could be observed from Table 3 that the reaction medium played an important role in the oxidation system. It seems that acetonitrile and NaN_3/Na_2SO_3/acetonitrile were

Table 1. Effect of various metalloporphyrins on the photooxidation of 2-methoxybenzaldehyde[a]

Entry	Catalyst	Conversion into 2-methoxy-benzoic acid, %
1	ClMnTPP	trace
2	ClFeTPP	trace
3	ClCoTPP	trace
4	ClNiTPP	6
5	ZnTPP	trace
6	PdTPP	27
7	PtTPP	75
8	PtTMP	91
9	PtTPFPP	71
10	no catalyst	—

[a] 0.5×10^{-6} mol porphyrins, 0.5×10^{-3} mol 2-methoxybenzaldehyde, 8 h.

Table 2. Oxidation of aldehydes to carboxylic acids in the presence of (a) PtTMP and (b) H$_2$TMP under sunlight irradiation

Entry	Aldehyde	Acid	Time, h	Conversion, %		TON[c]
				Sunlight[a]	Visible light[b]	
1	CHO (benzaldehyde)	CO$_2$H (benzoic acid)	4	95	87 (72 h)[31b]	950
2	CHO, OMe	CO$_2$H, OMe	8	91	71 (72 h)[31b]	910
3	CHO, OMe (para)	CO$_2$H, OMe (para)	8	81	95 (48 h)[31b]	810
4	CHO, Br	CO$_2$H, Br	4	100	100 (16 h)[31b]	1000
5	CHO, Cl	CO$_2$H, Cl	4	100	89 (72 h)[31b]	1000
6	CHO, F	CO$_2$H, F	4	100	74 (48 h)[31b]	1000
7	CHO, NO$_2$	CO$_2$H, NO$_2$	24	69	Trace	690
8	CHO, NO$_2$ (meta)	CO$_2$H, NO$_2$ (meta)	24	57	Trace	570
9	CHO, NO$_2$ (ortho)	CO$_2$H, NO$_2$ (ortho)	24	83	Trace	830
10	furan-CHO	furan-CO$_2$H	8	100	100 (48 h)[31b]	1000
11	octanal	octanoic acid	8	85	96 (48 h)[31b]	850

(*Continued*)

Table 2. (*Continued*)

Entry	Aldehyde	Acid	Time, h	Conversion, %		TON[c]
				Sunlight[a]	Visible light[b]	
12	CHO / CHO (benzene ring)	CO$_2$H / CO$_2$H (benzene ring)	4	100	100 (16 h)[31b]	2000
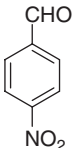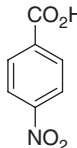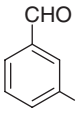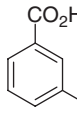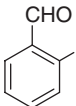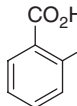
[a] 0.5×10^{-6} mol PtTMP and 0.5×10^{-3} mol aldehydes as substrates, air (1 atm) and sunlight (75400 LUX). [b] 1.0×10^{-6} mol H$_2$TMP and 1.0×10^{-3} mol aldehydes as substrates, air (1 atm) and fluorescent circular lamp, six 22 W lamps (32400 LUX). [c] Turnover number of the PtTMP catalyst.

Table 3. Effect of solvent and ^{1}O$_2$ on the conversion of 2-methoxybenzaldehyde to 2-methoxybenzoic acid

Entry	Solvent	Conversion
1	acetonitrile	91[a]
2	dimethyl formamide	trace[a]
3	dimethyl sulfoxide	trace[a]
4	NaN$_3$/Na$_2$SO$_3$/acetonitrile	65[a]
5	H$_2$O	trace[a]
6	NaN$_3$/Na$_2$SO$_3$/acetonitrile	trace[b]

[a] 0.5×10^{-6} mol PtTMP, 0.5×10^{-3} mol 2-methoxybenzaldehyde after 8 h. [b] 0.5×10^{-6} mol H$_2$TMP, 0.5×10^{-3} mol 2-methoxybenzaldehyde after 8 h.

Table 4. Oxidation of nitrobenzaldehydes with free-base porphyrin and PtTMP[a]

Entry	Aldehyde	Acid	Time, h	Conversion, % (PtTMP)	Conversion, % (H$_2$TMP)
1	CHO / NO$_2$ (para benzene ring)	CO$_2$H / NO$_2$ (para benzene ring)	24	69	trace
2	CHO / NO$_2$ (meta benzene ring)	CO$_2$H / NO$_2$ (meta benzene ring)	24	57	trace
3	CHO / NO$_2$ (ortho benzene ring)	CO$_2$H / NO$_2$ (ortho benzene ring)	24	83	trace

[a] 0.5×10^{-6} mol porphyrins and 0.5×10^{-3} mol aldehydes as substrates, air (1 atm), and sunlight (75400 LUX).

and H$_2$O as solvents. Highly coordinated solvents such as dimethylsulfoxide inhibit the formation of an active intermediate by preventing oxygen coordination with the platinum porphyrin formed in the solution and also quench carboxylic acid formation. The reaction did not quench in the presence of NaN$_3$/Na$_2$SO$_3$/acetonitrile which is known as a singlet oxygen scavenger (Table 3, entries 4) and this proves that, singlet oxygen generation is not the main mechanism in the oxidation of aldehydes with PtTMP sensitizers.

We found that nitrobenzaldehydes are the most effective ^{1}O$_2$ scavengers. They are much more effective than NaN$_3$/Na$_2$SO$_3$ systems. The formations of carboxylic acids from the corresponding aldehydes are completely quenched in the presence of nitrobenzaldehydes (Table 4). Therefore we recommend nitrobenzaldehydes as an effective ^{1}O$_2$ scavenger (Scheme 2).

Table 4, however, shows the photooxidation of nitrobenzaldehydes in the presence of PtTMP and H$_2$TMP. Nitrobenzaldehydes were effectively converted to the corresponding acids in the presence of PtTMP, but not H$_2$TMP. This observation accompanied with the observation brought in entry 6 in Table 3 rules out the ^{1}O$_2$ path as the only path for acid formation by PtTMP.

The production of platinum(IV)porphyrin from Pt(II) porphyrin during the reaction period was confirmed by UV-vis study for the photooxygenation of 2-methoxybenzaldehyde, as demonstrated in Fig. 2. Series 1, 2, 3 and 4 in Fig. 2 show the solution spectra of PtTMP in the beginning and after 5, 10 and 15 min of light irradiation, respectively. The strength of the Soret band of PtTMP at 398.5 nm decreased and a new signal gradually increased again at 417.5 nm which was assigned to the Pt(IV) formation. Kadish and co-workers recently reported the first example for electrogeneration of a Pt(IV) porphyrin [35] and the chemical production of high valent Pt porphyrins has been recently reported

effective in the aerobic oxidation of 2-methoxybenzaldehyde to 2-methoxybenzoic acid, in the presence of PtTMP, but not H$_2$TMP.
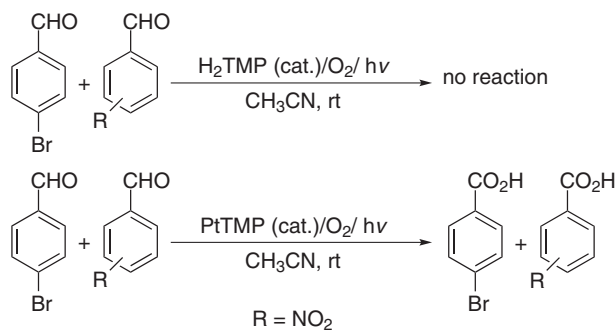
Meanwhile, according to Table 3 (entry 2, 3 and 5), it was found that the reaction was completely inhibited when we used dimethylsulfoxide, dimethylformamide

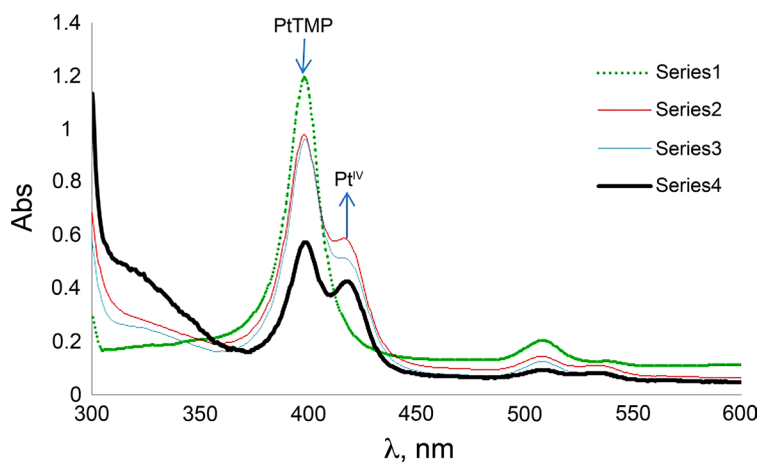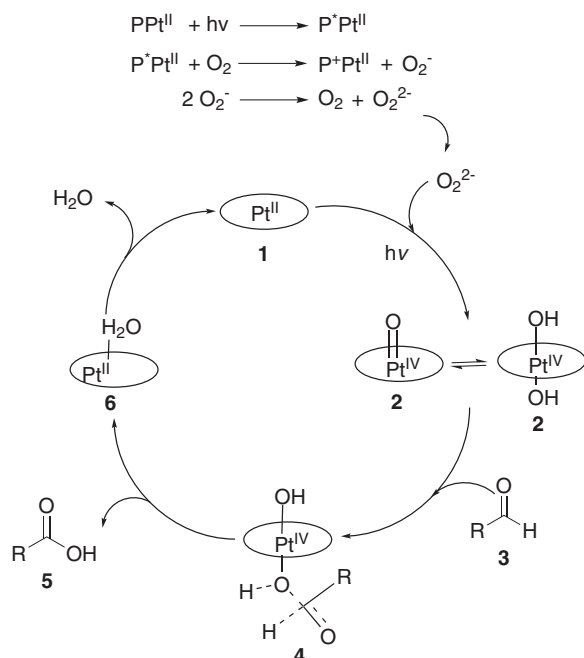**Scheme 2.** Oxidation of different nitrobenzaldehydes in the presence of PtTMP or H$_2$TMP

Fig. 2. Spectral changes, solution A: 2-methoxybenzaldehyde (0.5 mmol) and PtTMP (0.5 × 10^{-3} mmol) (Series 1), solution A 5 min after photoreaction (Series 2), solution A 10 min after photoreaction (Series 3) and solution A 15 min after photoreaction (Series 4)

Scheme 3. A possible mechanism for the formation of the carboxylic acids from aldehydes in the presence of PtTMP

[36]. Our results in UV-vis spectroscopy correlate with the high oxidation of platinum during the photooxidation process.

According to the above discussions, a plausible reaction mechanism for the photooxidation reaction using PtTMP as a catalyst has been proposed as shown in Scheme 3. In the presence of oxygen and sunlight thus, there may be a new photochemical pathway that involves the formation of intermediated **2** as the main oxidant. This oxidant, **2** can oxidize aldehydes to their corresponding acids and reduce itself to reform the starting catalyst [33].

Consequently, platinum porphyrin is a better catalyst than free-base porphyrin since: In $^1O_2$ singlet pathways Pt(II) has high triplet lifetime in the range of msec which result in better generation of $^1O_2$. In the case of platinum another path other than $^1O_2$ path which is formation of active Pt(IV) is involved. This path is more reactive than $^1O_2$ since nitrobenzaldehydes are converted in good yields. In addition electron donating substituent porphyrin such as PtTMP shows highest activity. This is in accord with the mechanism proposed in Scheme 3. Light will induce electron transfer from platinum porphyrin to the O_2. More electron rich porphyrin such as PtTMP is more reactive. Table 1 shows that reactivity is in the other of PtTMP > PtTPP > PtTPFPP. This trend matches with electron donating ability of the porphyrin macrocycles.

CONCLUSION

In conclusion, PtTMP is very effective at photo-oxidation for specific conversions of aldehydes to acids. PtTMP has an advantage over H$_2$TMP for photooxidation in that its reaction time is faster and it is more reactive towards less active aldehydes in comparison with H$_2$TMP. For example PtTMP has the ability to convert nitrobenzaldehydes which is completely inert in the case of H$_2$TMP. However, using precious Pt metals compared to that of free-base porphyrins can be viewed as a disadvantage, however the low amount of catalyst used and its productivity where H$_2$TMP is ineffective makes up for its use.

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