Efficient biomimetic decarboxylation of diphenylacetic acid by [Mn(TPP)X]*n*-Bu_4NIO_4 catalytic systems: effect of anionic axial ligands (X^-)

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Highly efficient decarboxylation of diphenylacetic acid has been performed by tetrabutylammonium periodate in the presence of different [Mn(TPP)X] complexes (X^- = anionic axial ligand) in CH_2Cl_2. In these catalytic systems, diphenylacetic acid was selectively (>97%) converted to benzophenone. The reactivity of manganese porphyrins are markedly influenced by the nature of anionic axial ligands and the efficiency of the catalysts decreases in the order: $CN^- > OCN^- > N_3^- > SCN^- > F^- > OAc^- \sim Cl^- \sim Br^- \sim I^- \sim ClO_4^-$. Marked improvement in reactivities and selectivities has resulted from addition of imidazole and its derivatives to the reaction mixture. π-Bonding interaction in Mn–X moiety and the possibility of distal hydrogen bonding between imidazole and X^- is presented to describe the enhanced catalytic activities observed for Mn(TPP)X (X^- = SCN^-, N_3^-, OCN^-, CN^-). A simple catalytic cycle is also proposed to show the role of X^- in the possible intermediates.

Keywords: diphenylacetic acid, manganese porphyrins, anionic ligands, decarboxylation, catalysis

Metalloporphyrin-mediated reactions using various single oxygen donors such as PhIO, ClO^-, H_2O_2, HSO_5^- and IO_4^- have been reported as model reactions for cytochrome P-450 catalysed oxidations.[1] In these catalytic reactions work was focused on the nature of central metal atoms (M), porphyrin ligands (Por) and axial nitrogenous bases (B), which markedly affected the catalytic activity of metalloporphyrins. Recently we have described the roles of M, Por and B in metalloporphyrin catalysed epoxidation of olefins by tetrabutylammonium periodate using a qualitative molecular orbital diagram.[2] We have shown that the catalytic efficiency of manganese porphyrins is strongly affected by the π-donor ability of a nitrogenous base (*i.e.* imidazole) to the Mn centre.

However, there are a lot of reports showing the dependence of metalloporphyrins actions on the axial anionic ligand (X^-).[3] Evidence for prominence of X^- was provided when Bruice *et al.* used [Mn(TPP)X] and [Mn(CAPTPP)X] (Fig. 1) as catalysts for oxygenating cyclohexene.[3d] Mn(CAPTPP)X, which can only form an O = Mn^V species wherein the Mn moiety is not complexed to X^- as a sixth ligand, was very reluctant to catalyse oxygen transfer.[3d] In the epoxidation of alkenes with [Fe(TPP)X/PhIO], Tatsono *et al.* found that electronegative ($CF_3CO_2^-$ *vs* $CH_3CO_2^-$) and weak coordinating ligands (ClO_4^- and BF_4^-) increase the catalytic activity of the complexes and suggested that the anionic ligands increase the electrophilicity of the oxo-intermediate, leading to a high yield of cyclooctene epoxide.[3e] Effects of anionic ligands on the formation of oxoiron (IV) porphyrin intermediates[3f,g] and their NMR and resonance Raman spectral features,[3h] and electrochemical behaviour of Mn(III) → Mn(II) porphyrins[3i,j] and their NMR shifts[3k,l] have been studied comprehensively.

In this work, decarboxylation of diphenylacetic acid by tetrabutylammonium periodate (*n*-Bu_4NIO_4) in the presence of different manganese (III) tetraphenylporphyrin catalysts (Fig. 2) and nitrogenous bases are studied at ambient temperature. Particular focus of attention was placed in the anionic ligands and their influence on the activity of the catalysts.

Results and discussion

The ability of manganese porphyrins as catalyst in oxidative decarboxylation of carboxylic acids was studied earlier.[4] We also used these kind of catalysts for oxidative decarboxylation of diphenylacetic acid by tetrabutylammonium periodate (Eqn(1)) and studied the role of X^- ligand of manganese porphyrins in these reactions.

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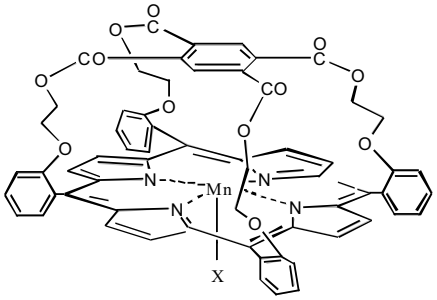


Fig.1 Mn(CAPTPP)X.

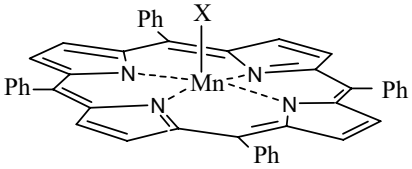


Fig. 2 Manganese(III) *meso*-tetraphenylporphyrin catalysts used in this study: Mn(TPP)X; X^-= F^-, Cl^-, Br^-, I^-, $ClO4^-$, OAc^-, N_3^-, OCN^-, SCN^-, CN^-.

$$Ph_2CHCOOH \xrightarrow[ImH/CH_2Cl_2]{Mn(TPP)X/n\text{-}Bu_4NIO_4} Ph_2C{=}O \qquad (1)$$

We first tested oxidative decarboxylation by Mn(TPP)OAc/*n*-Bu_4NIO_4 catalytic system and found that these single phase catalytic decarboxylations are highly retarded in the absence of nitrogenous bases. As seen in Table 2 (runs 11 and 12) small amounts of carbonyl product are formed in the absence of imidazole. Furthermore, in the presence of imidazole, 97–100% of the products are benzophenone (Table 2; data in the parentheses for selectivities).

The influence of nitrogenous base on the rate of reactions increases in the order: imidazole > 4(5)-methylimidazole > benzimidazole > 1-methylimidazole (Table 1). This trend is nicely consistent with the steric and electronic effects of the imidazoles described in our previous work.[2]

Among CH_2Cl_2, $CHCl_3$, CH_3CN, EtOH, DMF and their selected mixtures, CH_2Cl_2 was chosen as an expedient solvent in which higher carbonyl yield was observed (Table 1).

As shown in Table 2, manganese porphyrins bearing weak coordinating ligands such as Cl^-, Br^-, I^-, ClO_4^- and OAc^- show similar activities, and give low yields (runs 2–6).

Table 1 Effect of solvents and axial nitrogenous bases (imidazoles) on the oxidative decarboxylation of diphenylacetic acid by [Mn(TPP)OAc]/*n*-Bu_4NIO_4 catalytic system[a,b]

Solvents	BzPhen.(%) in the presence of			
	ImH	4(5)-MeImH	BzImH	1-MeIm
CH_2Cl_2	69	47	28	13
$CHCl_3$	41	23	20	9
CH_3CN	58	35	23	9
EtOH	8	3	–	–
DMF	Trace	–	–	–
$CH_2Cl_2/CHCl_3$ (1: 1)	45	–	–	–
$CH_2Cl_2/CHCl_3$(2: 1)	53	29	14	6
CH_2Cl_2/CH_3CN(1: 1)	61	–	–	–
CH_2Cl_2/EtOH(1: 1)	17	–	–	–

[a] The reactions were performed with similar molar ratios (within 60 minutes) as in the Experimental section.
ImH, imidazole; 4(5)-MeImH, 4- or 5-methylimidazole (tautomeric); BzImH, benzimidazole; 1-MeIm, 1-methylimidazole; BzPhen, Benzophenone.

Comparisons of yields (%) in runs 2–8, show significant decarboxylations acquired by manganese porphyrins containing the anionic ligands SCN^- and N_3^-. However, when the reactions were carried out in the presence of [Mn(TPP)X] complexes containing OCN^- and CN^- the highest efficiencies were obtained and decarboxylations were completed in less than ~30 minutes (runs 9 and 10). So, the nature of X^- has an important influence on the catalytic activity of the porphyrin complexes.

To explain the effect of X^- on the catalytic activities of [Mn(TPP)X] complexes, a simple catalytic cycle for the possible interactions, is presented in Fig. 3. Under the reaction conditions, [Mn(TPP)X] complexes (**1**) bearing weak coordinating anionic ligands of Cl^-, Br^-, I^-, ClO_4^- and OAc^- interact with an excess amount of *n*-Bu_4NIO_4, leading to exchange of X^- with IO_4^- and formation of six coordinate [(ImH)Mn(TPP)IO_4] (**2**).

For instance, addition of *n*-Bu_4NIO_4 and imidazole into a CH_2Cl_2 solution of Mn(TPP)I (Soret λ_{max} = 496 nm)[3d] as the starting manganese porphyrin caused a drastic change in the position of its Soret band, indicating the exchange of I^- with IO_4^- and formation of [ImHMn(TPP)IO_4](**2**) (Soret λ_{max} = 478 nm)[2] under reaction molar ratio (Fig. 4). Here, imidazole is bound to the Mn centre as a nucleophilic ligand.[5] Then, [ImHMn(TPP)IO_4](**2**) is converted to a high valent manganeso oxo-species, (**3**), as the reactive oxidant.[6] This conclusion is nicely supported by UV-visible spectra taken from the reactions mixture containing [Mn(TPP)I] catalyst after 30 minutes (Fig. 5) and also by the literature.[2,7]

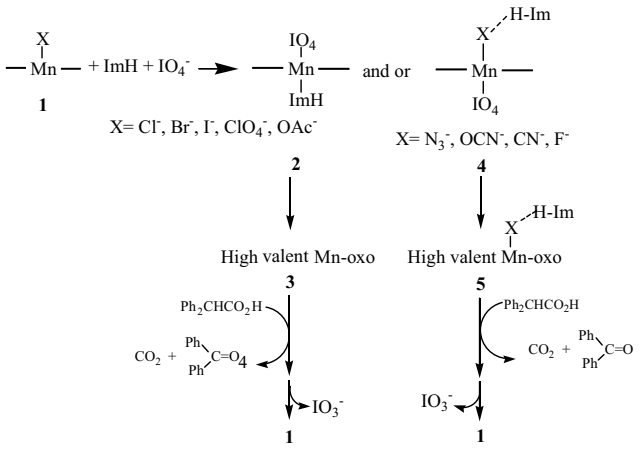


Fig. 3 A simplified mechanism for [Mn(TPP)X] catalysed decarboxylation of diphenylacetic acid by *n*-Bu_4NIO_4.

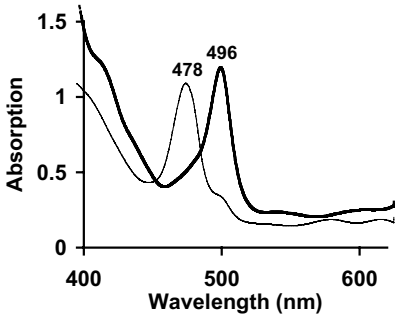


Fig. 4 Immediate conversion of [Mn(TPP)I] (Soret λ_{max} = 496 nm) into [ImHMn(TPP)(IO_4)] (species **2**; λmax = 478 nm), in the presence of *n*-Bu_4NIO_4 and ImH in CH_2Cl_2 under catalytic molar ratios.

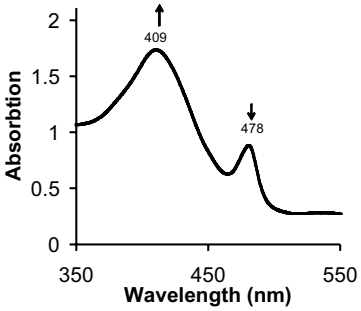


Fig. 5 Conversion of [HImMn(TPP)(IO_4)] (λ_{max} = 478) to high valent manganese oxo species (**3**) (λ_{max} = 409 nm) in the reaction mixture.

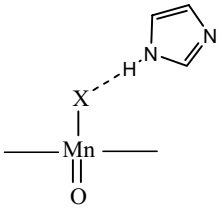
Thus, it seems that a subsequent conversion of [Mn(TPP)I] (Soret λ_{max} = 496 nm) into [HImMn(TPP)IO_4] (Soret λ_{max} = 478 nm)[2] and then into the species **3** (Soret λ_{max} = 409 nm) was achieved in the reaction mixture. Parallel results were also obtained (not shown) with [Mn(TPP)X] (X^- = Cl^-, Br^-, ClO_4^-) in terms of the formation of species (**2**) and (**3**).

It is notable that the nature of Mn–X bond in these complexes is important. Thus the similar activities observed for [Mn(TPP)X] with X^- of Cl^-, Br^-, I^-, $ClO_4^-$and OAc^- (Table 2, the data in 30 min) indicate that these ligands were similarly exchanged by IO_4^- prior to the formation of (**2**), and consequently have not any contribution to the active oxidant (**3**). Thus, X^- does not participate directly in the oxygen transfer step.

Table 2 Effect of anionic axial ligands of [Mn(TPP)X] catalysts on the oxidative decarboxylation of diphenylacetic acid by *n*-Bu_4NIO_4 in the presence and absence of ImH[a]

Run	X^- in [Mn(TPP)X]	BzPhen. (%) after 30 min	BzPhen. (%) after 60 min[c]
1	F^-	73	96 (99)
2	Cl^-	49	58 (99)
3	Br^-	47	55 (99)
4	I^-	47	55 (98)
5	ClO_4^-	45	52 (97)
6	OAc^-	50	69 (99)
7	SCN^-	70	94 (100)
8	N_3^-	85	100 (100)
9	OCN^-	98	100 (100)
10	CN^-	100	100 (100)
11	Cl^-	11[b]	32 (54)
12	OCN^-	21[b]	48 (63)

[a]See Experimental section for detailed reaction procedures. All reactions were run at least in duplicate and the data represent the average of these reactions. ImH, imidazole; BzPhen benzophenone.
[b]BzPhen. (%) in the absence of ImH.
[c]Selectivity (%): the percentage of ratio of benzophenone *vs* converted diphenylacetic acid (data in parentheses).



$X^- = N_3^-, OCN^-, CN^-, F^-$

Scheme 1

However, SCN^-, N_3^-, $OCN^-$and CN^- are able to form both σ- and π-bonding with the Mn centre in manganese tetraphenylporphyrins. Apparently, displacement of these strong coordinating ligands by IO_4^- was severely limited.

In order to explain the improvements observed by imidazole (Table 2) we propose that the active species herein is [ImH---XMn-oxo] (**5**) which is generated from **4** (except for $X^- = SCN^-$ that can not form H-bonding with ImH; *vide infra*). Here, X^- occupies the sixth position of the complex *trans* to the oxo ligand (Scheme 1).

The much better catalytic activities of manganese tetraphenylporphyrins with X^- ligands of N_3^-, OCN^-, CN^- than those of Cl^-, Br^-, I^-, ClO_4^-, OAc^- are presumably due to the attendance of the former in the suggested oxidant (**5**) (Scheme 1). It is plausible to assume that SCN^-, N_3^-, OCN, and CN^- donate electron density to the Mn centre through X-Mn π-bondings. In line with the arguments described for π-bonding interactions in ImH→Mn(Por),[2] X-Mn π-bonding also provides a driving force for oxygen atom transfer to diphenylacetic acid in (**5**). Furthermore, the occurrence of decarboxylations only in the presence of the nitrogenous bases may suggest an intermolecular hydrogen bondings[5c,8] between the coordinated N_3^-, OCN^- and CN^-, and nitrogenous base H-imidazoles (Scheme 1). However, SCN^- is bound to the Mn centre through its nitrogen atom,[9] so it cannot construct hydrogen bonding with ImH and give a lower yield than N_3^-, OCN^- and CN^- (Table 2, run 7). Such distal hydrogen bonding serves to favour the π-bonding in the X-Mn moiety and facilitate the oxygen atom transfer from [ImH---XMn-oxo] (**5**) to the substrate. To examine the importance of this hydrogen bonding in enhancing the π- ability of X^-, we added 0.01 mmol of 1-methylimidazole to the [Mn(TPP)CN]/*n*-Bu_4NIO_4 catalytic system, and obtained 36% of benzophenone in 60 minutes. Similar experiments using [Mn(TPP)CN]PhIO system showed again a little amount (43%) of the carbonyl product. These findings suggest that H-imidazoles can form a hydrogen bond with X^- through these N-H group, thus increasing the donor ability of X. Whereas 1-MeIm is structurally incapable of such bonding.

It is notable that, among halogens, this hydrogen bonding is effective only with the most electronegative fluoride axial ligand which causes the respective oxidant (Scheme 1) very efficient, leading to formation of high carbonyl product (Table 2, run 1). These behaviours are, in fact, nicely consistent with the proposed hydrogen bonding. Possible distal hydrogen bondings between the coordinated periodate and one ImH should also be considered.[2,8] Such interactions are expected to facilitate oxygen atom transfer to diphenylacetic acid. These results may suggest the importance of both hydrogen bonding between ImH and X^- (= N_3^-, OCN^-, CN^- F^-), and the π-bonding interactions of X^- with Mn centre in oxygen atom transfer from the reactive oxidant (**5**) to diphenylacetic acid.

Conclusion

We have shown that the single phase [Mn(TPP)X]*n*-Bu_4NIO_4/ImH catalytic system is a very efficient for oxidative decarboxylation of diphenylacetic acid and the nitrogenous base (*i.e.* ImH) has an essential role in these catalytic reactions. We have also demonstrated that the nature of anionic axial ligands bound to the [Mn(TPP)X] complex is an important factor in evaluating the activity of the catalysts. An appropriate catalyst could be simply selected to obtain desired reaction pathways and used for decarboxylation of the other carboxylic acids. [Mn(TPP)X] complexes containing X^- of SCN^-, N_3^-, $OCN^-$and CN^-, with capability of Mn–X π-bondings, display higher reactivities than those containing Cl^-, Br^-, I^-, ClO_4^- and OAc^-.

Further, these catalytic systems are operative only in the presence of ImH and its derivatives, suggesting the occurrence of ImH---X-Mn hydrogen bondings as shown in Scheme 1.

Finally, our results are consistent with the active species responsible for the oxidation being a high valent manganese oxo porphyrin.

Experimental

Materials

The free base porphyrin, H_2TPP, and [Mn(TPP)OAc] complex were prepared by the methods of Adler.[10] [Mn(TPP)X] complexes ($X^- = F^-$, Cl^-, Br^-, I^-, SCN^-, OCN^-, N_3^-, ClO_4^-) were obtained using [Mn(TPP)OAc] and corresponding NaX salts by a ligand exchange reaction according to the procedure of Ogoshi *et al*.[11]

[Mn(TPP)CN] was synthesised in a manner similar to that described by Scheidt.[21] Diphenyl acetic acid and nitrogenous bases were obtained from Merck or Fluka and used without further purifications (except for benzimidazole which was recrystallised before use).[13]

General procedure for decarboxylation

Stock solutions of metalloporphyrin catalysts (0.001 M) and ImH nitrogenous base (0.2 M) in CH_2Cl_2 were prepared.

In a 10 ml round-bottom flask were added in the order: diphenylacetic acid (0.1 mmol, 0.0212 g), [Mn(TPP)X] (0.002 mmol, 2 ml), ImH (0.01 mmol, 50 µl) and tetrabutylammonium periodate (0.14 mmol, 0.06 g) to achieve the desired ratio. This 2 ml reaction mixture was stirred thoroughly for the required time at ambient temperature in the air. The resulting solution was directly analysed by GLC. Similar results were obtained under Ar.

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