Iron(III) porphyrin catalyzed epoxidation of 1,4-diphenyl butadiene

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Received 27 December 2002

The meso-tetrakis (pentfluorophenyl) porphyrinatoiron (III) chloride (F20TPPFeCl) catalyzed mono epoxidation of 1,4-diphenyl butadiene (DPBD) has been achieved by tert-butylhydroperoxide in methanol. This reaction does not proceed in dichloromethane. The most significant observation is that the reaction is inhibited at higher diene concentration. In order to understand the nature of the reactive intermediate in this reaction the same oxidation reaction has been conducted by authentically generated oxo-iron (IV) porphyrin cation radical and by the tert-BuO· radical. Unlike F20TPPFe(III) Cl/t-BuOOH oxidizing system, oxoiron (IV) porphyrin cation radical reacts smoothly with DPBD to produce the monoepoxide in dichloromethane. The yield of the epoxide in the oxidation reaction by oxo-iron (IV) porphyrin cation radical, however, drops drastically when the reaction is conducted in methanol. The results have indicated that in the F20TPPFe (III) Cl catalyzed oxidation of DPBD by tert-BuOOH the oxo-iron (IV) porphyrin cation radical is not the actual reactive intermediate. In the oxidation of DPBD by the tert-BuO· radical the maximum yield of the epoxide has been achieved in neat dichloromethane and the yield goes down in methanol, the trend is just opposite to those observed in the hydroperoxide reactions. The catalyst-hydroperoxide adduct is believed to be the major reactive intermediate in this oxidizing system.

Introduction

The iron (III) porphyrin catalyzed oxidation reactions of organic substrates and their potential application in industry has brought considerable attention to these reactions. Most of these studies have employed oxidants such as iodosylbenzenes and peracids, although hypochlorites and monopersulfuric acid have also been used. There have been limited success in these reactions where hydroperoxides are used as oxidants. The basic reason for this unsuccessful reaction is still unclear. Several studies have claimed initial homolytic cleavage of the peroxy bond and the involvement of oxo-iron(IV) porphyrin and RO· radical intermediates as potential oxidants. However heterolytic cleavage of the same peroxy bond and the involvement of oxo-iron(IV) porphyrin catalysis in this oxidation reaction has also been claimed by others. In the present study 1,4-diphenyl butadiene(DPBD) has been chosen as the diagnostic probe, meso-tetrakis (pentfluorophenyl) porphyrinatoiron (III) chloride (F20TPPFeCl) as the catalyst and tert-butylhydroperoxide as the terminal oxidant. The results demonstrate that the reactive intermediate responsible for this oxidizing system is certainly not the oxo-iron(IV) porphyrin cation radical. The probable structure of the reactive intermediate has been proposed.

Materials and Methods

Dichloromethane was dried over CaO for 12 h and then distilled. The distilled methanol was treated with Mg iodine followed by distillation. Absolute methanol thus obtained contained basic impurities of magnesium oxide, so it was redistilled again over sulphanilic acid (ca 5g/0.5l) under nitrogen to obtain conductivity quality methanol. Pentafluoroiodosylbenzene (C4F3 IO, caution! potential explosive) was prepared according to the literature procedure. The F20TPPH2 and F20TPPFe(III) Cl were synthesized by reported methods. The tert-butyl hydroperoxide(90% in water) and 1,4-diphenyl butadiene were purchased from Aldrich chemical company and were used without further purification. Purity of the oxidants were determined by iodometric analysis as described earlier.

Instrumentation

UV-visible spectra and kinetic measurements were recorded with a Perkin Elmer Lambda 2S-spectrophotometer interfaced with a digital computer. The cell holder of the spectrophotometer was connected with a Julabo F-30 temperature regulator.

General reaction conditions

All the reactions were performed at least in duplicate at 25±1°C under argon atmosphere and the data reported represent the average of these results. The epoxidation of DPBD at higher concentrations were generally performed in a screw-cap vial of 5 ml capacity, fitted with a sure-seal teflon septum. Aliquot
Results and Discussion

In the attempted oxidation of the diene (1,4-diphenyl butadiene) by tert-BuOOH it has been observed that DPBD was not oxidized by tert-butyl hydroperoxide alone in either of the two solvents investigated such as dichloromethane or methanol. In the presence of meso-tetrakis (pentafluorophenyl) porphyrinatoiron (III) chloride (F20TPPFeCl), however, the diene was oxidized by tert-BuOOH. The most significant observation was that this oxidation was very sensitive towards the solvent polarity and on the reagent concentrations. A different kind of solvent effect has been observed in the oxidation reactions of oxo-iron (IV) porphyrin cation radical and in case of the tert-butyl hydroperoxy radical. The details are given under the following subheadings.

F20TPPFe(III)Cl catalyzed oxidation of DPBD by tert-BuOOH in CH2Cl2

The reaction of DPBD with tert-BuOOH in the presence of F20TPPFeCl was performed in a screw-capped vial. In a typical experiment DPBD (3.12 mg) and a small magnetic stir-bar were taken in a small vial. Solid F20TPPFeCl (1.24 mg) was placed in another small vial. Dry degassed dichloromethane (2.5 ml) was then added to the vials through a gas tight syringe and the contents of the vials were stirred. Required volume of the catalyst solution was added to the diene solution. An aliquot of the reaction mixture was withdrawn, diluted in CH2Cl2 (1.5 ml) in a quartz cuvet and the spectrum was recorded from 300-500 nm. The initial concentration of the diene was calculated from the known extinction coefficient of the diene at 319 nm. Concentrated tert-BuOOH (4 μl, 86.5%) was added to the vial through a gas tight syringe and the solution was magnetically stirred. The progress of the reaction was monitored spectrophotometrically with time by withdrawing an aliquot (10 μl) from the vial and diluting it to dichloromethane (1.5 ml) in the quartz cell. There was no change in the absorbance at 327 nm for at least 24 hours and there was no catalyst degradation as well. The fate of the oxidant has not been determined.

F20TPPFe(III)Cl catalyzed oxidation of DPBD by tert-BuOOH in MeOH.

The reaction of DPBD with tert-BuOOH in presence of F20TPPFeCl was performed in the quartz cell. In a typical experiment the reagent concentrations were DPBD (29.7 μM), F20TPPFeCl (8.41 μM) and oxidant (2.74 mM). The reaction was over within 13 minutes of the addition of the oxidant. The yield of the epoxide was 15.6% with respect to the substrate. Variation of oxidant or catalyst concentration in this range has no effect on the yield of the epoxide. In a separate reaction having F20TPPFeCl (12 -12.5 μM) and tert-BuOOH (2.88 mM), 15% of the DPBD (6.25 mM) was oxidized if the diene was added in the steps of 2.5 x 10⁻⁵ M. However, addition of 6.25 mM of the diene in a single step resulted in no epoxidation. The most interesting observation was that when DPBD (3.78 mM) was reacted with a large excess of tert-BuOOH (172.8 mM) in the presence of F20TPPFeCl (0.42 mM) almost quantitative epoxidation was achieved during the mixing time. These results are given in Table 1.

These results suggest that methanol certainly helps the catalyst to activate the hydroperoxide and we believe the possible competitive coordination of the diene and the oxidant with the catalyst is very crucial in this oxidizing system. Thus at the higher diene concentration the catalyst site is blocked for coordination of the oxidant and this might be the reason of no epoxidation at relatively higher diene concentration.

Oxidation of DPBD by oxo-iron (IV) porphyrin cation radical in CH2Cl2

An unequivocal sample of oxene was generated by the reaction of F20TPPFeCl and C6F3IO in the presence of DPBD in CH2Cl2 solvent18. The change in absorbance of DPBD was monitored with time and the yield of epoxidation was measured. In a typical experiment DPBD (3.15 mg) was dissolved in degassed CH2Cl2 (2.5 ml) in a small vial. In a separate
vial F<sub>20</sub>TPPFeCl (2.07 mg) was dissolved in degassed dichloromethane (2.5 ml). An aliquot (10 μl) of this catalyst solution was withdrawn from the vial and was diluted in CH<sub>2</sub>Cl<sub>2</sub> (1.5 ml) in a low volume quartz cell of 1 cm path length. The absorbance of the soret maxima was measured at 410 nm from where the concentration of the catalyst was determined. The concentration of the diene was calculated from the measured absorbance at 319 nm in CH<sub>2</sub>Cl<sub>2</sub>. Solid C<sub>6</sub>F<sub>5</sub>IO (4.46 mg, 90.9%) was added to the diene solution and the solution was magnetically stirred till the suspension was cleared (ca. 3-4 minutes). After 5 minutes of the addition of the oxidant an aliquot (10 μl) of the reaction mixture was withdrawn from the vial, diluted in CH<sub>2</sub>Cl<sub>2</sub> (1.5 ml) in a quartz cell and the spectrum was recorded. The change in the absorbance at 319 nm was used to calculate the amount of the epoxide produced. The reaction was over in 5 min has been confirmed by the fact that no change of absorbance was observed even after 30 min. The yield of the epoxide was 67.73% with respect to the total oxidant added assuming that the mono epoxide is the only product. The concentrations of the reagents were: DPBD (6.12 mM), C<sub>6</sub>F<sub>5</sub>IO (5.23 mM) and F<sub>20</sub>TPPFeCl (0.78 mM). It has been noted that in those experiments where PFIB was not added as solid but added as a solution in trifluoroethanol (TFE), the yield of epoxide was decreased from 67.73% to about 10%. In the latter experiment the reagent concentrations were DPBD (6.16 mM), C<sub>6</sub>F<sub>5</sub>IO (0.061 mM) and F<sub>20</sub>TPPFeCl (0.89 mM) and the reaction time was 10 min.

**Table 1—F<sub>20</sub>TPPFeCl catalyzed oxidation of 1,4-diphenyl butadiene by tert-BuOOH**

<table>
<thead>
<tr>
<th>[DPBD], mM</th>
<th>[F&lt;sub&gt;20&lt;/sub&gt;TPPFeCl], μM</th>
<th>[TBHP], mM</th>
<th>Solvent</th>
<th>% Yield*</th>
</tr>
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<tbody>
<tr>
<td>6.1±1 mM</td>
<td>0.47 mM</td>
<td>13.86</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.00</td>
</tr>
<tr>
<td>29±41 μM</td>
<td>8.41 μM</td>
<td>2.74</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;OH</td>
<td>15±1</td>
</tr>
<tr>
<td>6.5±0.5 mM</td>
<td>12±0.5 μM</td>
<td>2.88</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;OH</td>
<td>0.00&lt;sup&gt;+&lt;/sup&gt;</td>
</tr>
<tr>
<td>6.5±0.5 mM</td>
<td>12±0.5 μM</td>
<td>2.88</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;OH</td>
<td>15±1&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>3.5±0.5 mM</td>
<td>0.42 mM</td>
<td>172.8</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;OH</td>
<td>98±1</td>
</tr>
</tbody>
</table>

* Based on total substrate
+ Batch addition (see text)
\* Single addition

**Table 2—Oxidation of 1,4-diphenyl butadiene by oxo iron (IV) porphyrin cation radical**

<table>
<thead>
<tr>
<th>[DPBD], mM</th>
<th>[F&lt;sub&gt;20&lt;/sub&gt;TPPFeCl], mM</th>
<th>[PFIB], mM</th>
<th>Solvent</th>
<th>% Yield*</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.2±0.1</td>
<td>0.78</td>
<td>5.23</td>
<td>CH&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt;</td>
<td>68±2.0</td>
</tr>
<tr>
<td>6.2±0.1</td>
<td>0.89</td>
<td>0.06</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;Cl-TFE</td>
<td>10.5±0.5</td>
</tr>
<tr>
<td>6.2±0.2</td>
<td>0.89</td>
<td>5.22</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;OH</td>
<td>7.0±1.0</td>
</tr>
</tbody>
</table>

† Based on oxidant.

**Oxidation of DPBD by oxo-iron (IV) porphyrin cation radical in MeOH**

The reaction was performed as has been described above except that C<sub>6</sub>F<sub>5</sub>IO was dissolved in methanol and an aliquot volume was added to the solution containing alkene and F<sub>20</sub>TPPFeCl. The concentrations of the reagents were DPBD (3.17 mg), F<sub>20</sub>TPPFeCl (2.37 mg) and C<sub>6</sub>F<sub>5</sub>IO (4.45 mg) and the total volume of the reaction mixture was 2.5 ml. The yield of the epoxide was 6.92% with respect to the total oxidant added. These results are given in Table 2.

**Reaction of tert-BuOO· radical with DPBD in CH<sub>2</sub>Cl<sub>2</sub>**

An unequivocal sample of tert-BuOO· radical was generated by the known reaction of C<sub>6</sub>F<sub>5</sub>IO with tert-BuOOH. The reactivity of this tert-BuOO· radical with DPBD has been tested by the following procedure.

DPBD (3.35 mg) and a small magnetic stir-bar were placed in a screw cap vial (5.0 ml) and the vial was degassed with argon for 20 min. Degassed dichloromethane (2.5 ml) was then added to the vial through a gas tight syringe and the contents of the vial were stirred. An aliquot (10 μl) was withdrawn from the vial and was diluted in a low volume quartz cell of 1 cm path length cell containing degassed CH<sub>2</sub>Cl<sub>2</sub> (1.5 ml) and spectrum was recorded from 300-500 nm. The initial concentration of the diene was calculated from the known extinction coefficient at 332 nm. Concentrated tert-BuOOH (4 μl, 86.5%) was added to
Table 3—Oxidation of 1,4-diphenyl butadiene by tert-BuOO· radical

<table>
<thead>
<tr>
<th>[DPBD], mM</th>
<th>[TBHP], mM</th>
<th>[PFIB], mM</th>
<th>Solvent</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.2±0.3</td>
<td>13.9</td>
<td>3.3</td>
<td>CH₂Cl₂</td>
<td>35.0±2.0</td>
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<tr>
<td>5.7±0.1</td>
<td>27.7</td>
<td>4.3</td>
<td>CH₂Cl₂-CH₃OH</td>
<td>15.0±2.0</td>
</tr>
<tr>
<td>7.2±0.2</td>
<td>13.9</td>
<td>2.7</td>
<td>CH₃OH</td>
<td>15.0±1.0</td>
</tr>
</tbody>
</table>

*Based on PFIB.

the vial under argon atmosphere followed by the addition of solid C₆F₅IO (2.82 mg, 90.9%). The solution was magnetically stirred till a clear solution was observed (ca 3 min). After 5 min of the addition of the oxidant another 10 µl aliquot was withdrawn from the vial and was diluted in a quartz cuvet and the spectrum was recorded. Rescanning of this solution at longer interval (20-30 min) indicated no change in the absorbance. The yield of the epoxide was 36% with respect to the total C₆F₅IO added. This observation suggests that the catalyst is not destroyed in the oxidation process. At this time scale (5-10 min) tert-BuOOH alone (in the absence of C₆F₅IO) did not produce even 1% of the epoxide.

Reactions of tert-BuOO· radical with DPBD in CH₂Cl₂-CH₃OH (1:3)

This reaction was performed in an identical manner as has been described above but in CH₂Cl₂-CH₃OH solvent. The reagent concentrations used were: DPBD (3.01 mg), freshly distilled methanol (1875 µl), degassed dichloromethane (625 µl). The initial concentration of the alkene was spectrophotometrically determined as described above. Concentrated tert-BuOOH (8 µl, 86.5%) was added to the vial under argon atmosphere and this was followed by the addition of solid C₆F₅IO (3.7 mg). The solution was magnetically stirred and the yield of the epoxide calculated as has been described above was found to be 15% with respect to the total C₆F₅IO added.

Reactions of tert-BuOO· radical with DPBD in CH₃OH

This reaction was performed as has been described above but in neat methanol solvent. The reagent concentrations used were: DPBD (3.76 mg), freshly distilled methanol (2.5 ml). The initial concentration of the alkene was spectrophotometrically determined and then concentrated tert-BuOOH (4 µl, 86.5%) was added to the vial under argon atmosphere. Solid C₆F₅IO (2.32 mg) was added to initiate the reaction. The solution was magnetically stirred and the yield of the epoxide was found to be 15% with respect to the total oxidant added. These results are given in Table 3.

The nature of the solvent dependence on the activity of the hydroperoxide clearly suggest that oxo-iron (IV) porphyrin cation radical cannot be the reactive intermediate in the F₅₀TPPFe (III) Cl catalyzed oxidation of DPBD by tert-BuOOH. The trend in the variation of the yield of the epoxide in the reactions by tert-butyl hydroperoxy radical is also very different with that observed for the F₅₀TPPFe (III) Cl catalyzed hydroperoxide reactions. We believe that well before the formation of either of these two reactive intermediates the catalyst-oxidant adduct is transferring the peroxy oxygen to the substrate. The present results are in agreement with our recent observations.

Conclusion

In the F₅₀TPPFe(III) Cl catalyzed epoxidation of DPBD, the polarity of the solvent plays a major role. The solvent effect observed in this oxidizing system is very different from that observed in the oxidation of the same substrate (DPBD) by oxo-iron (IV) porphyrin cation radical. This observation suggests that in the F₅₀TPPFe (III) Cl catalyzed oxidation reaction the oxo-iron (IV) porphyrin cation radical may not be the actual catalytic species. The effectiveness of this F₅₀TPPFe (III) Cl catalyzed oxidation of DPBD by tert-BuOOH has some interesting relationship with the relative concentrations of substrate, oxidant and the catalyst. At higher substrate concentration the epoxidation reaction was inhibited. We believe that polarity of the solvent helps the catalyst to activate the hydroperoxide by allowing loose coordination of these two molecules. On the other hand at higher concentration the diene also coordinates to the catalyst and the activation of the hydroperoxide is inhibited. The work is in progress to generalize the observations.
Acknowledgement
Financial assistance from Department of Science and Technology (India) and Council of Scientific and Industrial Research (India) is gratefully acknowledged.

References