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Epoxidation of alkenes by ozone catalysed by Fe(TMP)Cl

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Abstract

The epoxidation of a number of cyclic and linear terminal alkenes by an O_2–O_3 mixture at room temperatures catalysed by Fe(TMP)Cl is reported. It appears that the alkene forms a primary ozonide which rearranges to a secondary ozonide, and it is the latter which, when catalysed by Fe(TMP)Cl, affects the subsequent alkene epoxidation. A number of other metal complexes were also tested as catalysts, but Fe(TMP)Cl was the most effective. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

There are relatively few examples in the literature of homogeneous organic oxidations effected by ozone in the presence of a transition-metal catalyst. Gross et al. [1,2] have described alkane oxidations catalysed by iron porphyrin complexes, and in a recent communication, Neumann and Khenkin [3] have described alkane oxidations catalysed by the polyoxometalate $Li_{12}[Mn_2^{II}ZnW(ZnW_9O_{34})_2]$ both in conjunction with an O_3–O_2 mixture as co-oxidant. There is also a report on the oxidation of menthol using cobalt (II) acetate and ozone [4].

Campestrini et al. [5] reported in 1991 that an O_3–O_2 mixture could be used to epoxidise alkenes under ambient conditions with the porphyrin complex Mn(Br$_8$-TMP)Cl (Br$_8$-TMP is the dianion of 5,10,15,20-tetramesityl-β-octa-bromoporphyrin), albeit with low efficiency. This is a particularly remarkable reaction since ozone is widely used as an alkene cleavage reagent [6,7]. It was shown that dichloromethane solutions of a variety of alkenes were cleaved, as expected, by an O_3–O_2 mixture to aldehydes or carboxylic acids; however, in the presence of Mn(Br$_8$-TMP)Cl and an axial *N*-donor ligand (pyridine or 4-*tert*-butylpyridine) epoxides were also formed over a 15–40-min period in yields varying from 5% to 40% with catalytic turnovers

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from 5 to 39. Similar experiments using $Fe(Br_8$-TMP)(OAc) in general gave poorer results [5].

The present study was initiated to ascertain whether more widely available metal catalysts could be used to catalyse alkene epoxidation by ozone. We concentrated our efforts on Fe(TMP)Cl (TMP is the dianion of 5,10,15,20-tetramesitylporphyrin), but also investigated the use of a variety of other complexes.

2. Experimental

Starting materials were purchased from Aldrich or BDH and used without further purification. Alkenes were checked for purity by GC. Both Fe(PHTH)Cl and $H_3[PW_{12}O_{40}] \cdot nH_2O$ was obtained from Aldrich and used without further purification.

2.1. Preparations

Both Fe(TMP)Cl and Mn(TMP)Cl were obtained from the reaction of $FeCl_2$ with the free base porphyrin $TMPH_2$, made by Lindsey and Wagner's procedure [8] and metallated by the method used for tetraphenylporphyrinate complexes by Kobayashi et al. [9]. They were checked for purity by electronic spectroscopy. The complexes Ru(TMP)(CO) [10–12], trans-Ru(TMP)(O)$_2$ [10–12], $(({}^nC_6H_{13})_4N)_2[W_2O_3(O_2)_4]$ [13], $(({}^nC_4H_9)_4N)_6[MnW_9O_{32}]$ [14] were prepared by the procedures in cited literatures.

2.2. Epoxidation procedures

The ozoniser was a Model TOG A1 Tri-Ox ozoniser; the ozone content was determined for various oxygen gas flows and applied potentials by titration against thiosulfate solution of the iodine released by ozone from a standard iodide solution [15]. In general, 0.02 g of ozone in 2 dm^3 of O_2/min was used.

2.2.1. With trans-stilbene as precursor

Trans-Stilbene (1.80 g, 10 mmol) was dissolved in CH_2Cl_2 (25 cm^3) and O_3–O_2 was passed through the solution for 30 min. After this time, the O_3 was turned off and replaced by a nitrogen stream for 5 min to remove any dissolved O_3 or O_2. To this solution alkene (10 mmol) and Fe(TMP)Cl (0.048 g, 0.05 mmol) were added in CH_2Cl_2 (25 cm^3) and the mixture stirred at room temperature for 24 h, after which time H_2O (30 cm^3) and zinc dust (1 g) were added. The mixture was then stirred for a further hour. The biphasic mixture was separated and the organic layer reduced in volume. The residue was analysed by GC or GCMS (see Table 1).

2.2.2. Direct epoxidation of alkenes

The alkene (10 mmol) and Fe(TMP)Cl (0.048 g, 0.05 mmol) were dissolved CH_2Cl_2 (50 cm^3) and O_3–O_2 was passed through the solution for 5 min, after which the ozone supply was turned

Table 1

Alkene epoxidations catalysed by Fe(TMP)Cl with trans-stilbene/O_3

Conditions: Trans-stilbene (1.8 g, 10 mmol) in CH_2Cl_2 (50 cm^3) was ozonised for 30 min, then Fe(TMP)Cl in CH_2Cl_2 (one equivalent in 25 cm^3) added with alkene (200 equivalents) and stirred at room temperature for 24 h.

The combined turnover for the data referred by footnotes b and c is 16.

Alkene	Conversion to epoxide[a] (%) [Turnover]
Cyclooctene	42 [84]
Cyclohexene	21 [42]
trans-Stilbene	10 [20]
Cis-stilbene	6[b]
	2[c]
Styrene	31 [62]
Cyclododecene	26 [52]
1-Hexene	15 [30]

[a] Remainder unconsumed alkene.
[b] Yield of cis-stilbene oxide.
[c] Yield of trans-stilbene oxide.

Table 2
Epoxidation of cycloalkenes catalysed by Fe(TMP)Cl
Conditions: The alkene (200 equivalents) with Fe(TMP)Cl (one equivalent) in CH_2Cl_2 (50 cm^3) was ozonised for 5 min at room temperature at 1 g/h of O_3, the mixture stirred for a further 8 h at room temperature without ozone, filtered through a pad of silica to remove Fe(TMP)Cl, and analysed by GCMS.

Alkene	Product ratio[a]		
	Unreacted alkene	Epoxide [TO][b]	Cleavage products[c]
Cyclopentene	0	0 [0]	100
Cyclohexene	40	20 [40]	40
Cycloheptene	60	10 [20]	30
Cyclooctene	20	40 [80]	40
Cyclododecene	100	0 [0]	0
1-Hexene	85	10 [20]	5
1-Heptene	85	10 [20]	10
1-Octene	50	25 [50]	25
1-Nonene	60	15 [30]	25
1-Decene	60	20 [40]	20
1-Undecene	50	20 [40]	30
1-Dodecene	90	10 [20]	0

[a] Determined by GCMS.
[b] [TO] = turnover number.
[c] Aldehyde and/or acid formed by alkene cleavage.

off and the solution stirred at room temperature overnight. Water (30 cm^3) and zinc dust (1 g) were then added and the solution stirred for a further hour. The biphasic mixture was separated and the organic layer reduced in volume. The residue was analysed by GC or GCMS (see Section 3 and Table 2).

2.3. Instrumentation

^{1}H NMR spectra were measured on a Jeol EX-270 spectrometer and microanalyses were carried out by the Imperial College Microanalytical Service. The GCMS data were obtained by Mr. John Barton on a Micromass AutoSpec, fitted with a Hewlett-Packard 5890 gas chromatograph with an SGE BPX5 column. The GC data were measured on a Perkin-Elmer Autosystem instrument using a Perkin-Elmer 2m stainless steel column packed with 5% Carbowax on Chromosorb WHP AW. Response factors were checked with standard samples.

3. Results and discussion

Here, we show that an ozone–oxygen (O_3–O_2) gas mixture, generated by a normal commercial ozoniser, can be used to epoxidise various alkenes catalytically in conjunction with the porphyrin complex Fe(TMP)Cl and other complexes in homogenous solution under ambient conditions.

3.1. Using trans-stilbene / ozone as an epoxidising agent

The use of the porphyrin complex Fe(TMP)Cl as a catalyst for the epoxidation of trans-stilbene under the conditions of Campestrini et al. [5] was investigated. The catalyst was dissolved in CH_2Cl_2 and 200 equivalents of the alkene added. The O_3–O_2 mixture was then passed through this solution for periods of 1, 5, 10, 20 and 30 min and the reaction mixture immediately analysed by GC. No epoxide formation was detected, with only the product of olefin cleavage (benzaldehyde) being formed. Addition of pyridine or 4-tert-butylpyridine to the reaction mixture made no difference.

It was thought that the secondary ozonide formed during alkene cleavage might act as the effective epoxidant (see Scheme 1), such ozonide formation being a key step in the Criegee mechanism for alkene cleavage [16,17]. To test this hypothesis, a solution of trans-stilbene (10 mmol in 50 cm^3 of CH_2Cl_2) was ozonised for 30 min at room temperature and ozonolysis then stopped. The Fe(TMP)Cl (0.05 mmol) and cyclooctene (10 mmol) were then
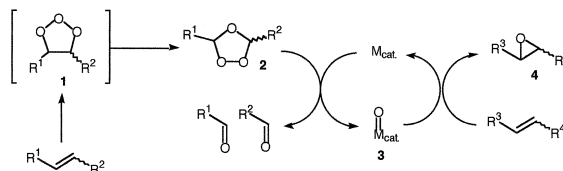
Scheme 1. Proposed diagrammatic mechanism for epoxidation of alkene catalysed by Fe(TMP)Cl.

added, the mixture stirred at room temperature for 24 h and then water and zinc dust were added to reduce any unreacted ozonide. The organic layer was separated, dried over anhydrous $MgSO_4$, concentrated and analysed by GC.

Cyclooctene oxide was formed in a 42% yield, which suggested the ozonide of *trans*-stilbene may indeed be the effective co-oxidant rather than ozone itself. A blank experiment, in which exactly the same procedure was followed but without Fe(TMP)Cl produced a yield of 5% epoxide, showing that there is indeed some catalytic effect. The only other product formed according to GC–MS was benzaldehyde, which is a necessary cleavage side-product of the ozonolysis of *trans*-stilbene.

Further oxidations were carried out using a 20-fold excess of *trans*-stilbene over cyclooctene to compensate for any decomposition to benzaldehyde during the reaction, but no increase in yield of epoxide was observed; such ozonolysis was carried out, as before, for 30 min. When the reaction was carried out at 0°C and −78°C following the initial ozonolysis, the yields of cyclooctene oxide fell to 12% and 2%, respectively.

To test the versatility of the reaction, alkenes other than cyclooctene were epoxidised (Table 1). The system is effective for both linear and cyclic alkenes although the yields are moderate. There is a substantial variation in yields and catalytic turnovers for the alkenes studied. The highest are with cyclooctene, but this is expected since it is well known to be a high-yielding substrate in metal-catalysed epoxidations; indeed the general sequence of yields is remarkably similar to those found in earlier work with epoxidations catalysed by polyperoxotungstates [13,18]. In the case of *cis*-stilbene, the loss of stereochemical integrity could be indicative of a stepwise oxygen-transfer mechanism.

In order to test the time-dependence of the reaction between cyclooctene and O_3–O_2 in the presence of Fe(TMP)Cl, aliquots of the reaction solution were removed (and analysed by GC) at

intervals of 1, 2, 5, 10, 20, 30 and 45 min for the first hour and then at hourly intervals for the next 11 h. It appears that there is an induction period of ca. 1 h before which time, no epoxide is formed. After an hour, epoxide is formed at a reasonably constant rate until ca. 7 h, after which time, no further epoxide formation was detected. The reaction profiles (Fig. 1), i.e., the percentage ratio of cyclooctene oxide to cyclooctene vs. time, were plotted. The induction period was presumed to be due to the formation of the active catalyst (see later section) and, hence, Fe(TMP)Cl is a precursor to the actual catalyst.

By pretreating the Fe(TMP)Cl this induction period was removed. The Fe(TMP)Cl was dissolved in CH_2Cl_2 with 20 mmol of *trans*-stilbene and ozonised for 5 min. This solution was left stirring for 1 h after which time, 20 mmol of cyclooctene was added and stirred at room temperature for 5 min. When an aliquot of this solution was analysed by GC, cyclooctene oxide was already being formed. The reaction proceeded linearly for a further 5 h after which time, no further epoxide production was seen.
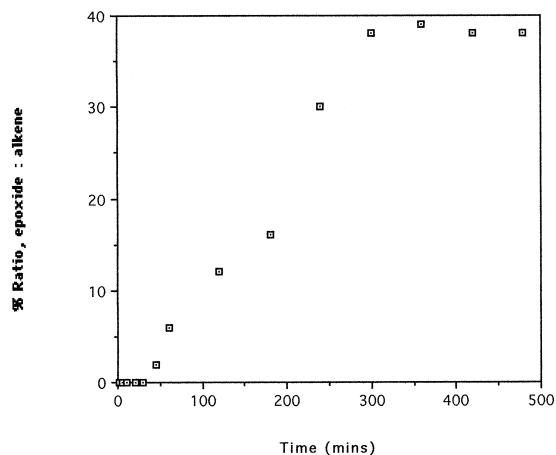

Fig. 1. Plot of the percentage ratio of cyclooctene oxide: cyclooctene vs. time (min). Conditions: Cyclooctene (200 equivalents) with Fe(TMP)Cl (one equivalent) in CH_2Cl_2 (50 cm^3) was ozonised for 5 min at room temperature at 1 g/h of O_3, the mixture stirred for a further 8 h at room temperature without ozone. Samples (1 μl) were withdrawn at regular intervals and analysed by GC.

The yield of epoxide (37%) was similar to that of the non-pretreated Fe(TMP)Cl (42%), showing that the induction period was likely due to the formation of an active catalytic species from Fe(TMP)Cl.

3.2. Direct alkene epoxidation

Having demonstrated the ability of ozonides derived from *trans*-stilbene to act as a sacrificial source of oxygen for catalytic olefin epoxidation, we sought to use a single alkene as ozonide source and substrate. A number of cyclic and straight chain alkenes (200 equivalents in CH_2Cl_2) were ozonised for 5 min, following which ozone was removed from the reaction as described above and Fe(TMP)Cl (one equivalent in CH_2Cl_2) added. The solutions were then stirred at room temperature overnight and after work-up analysed by GC and GC–MS and all products identified. The results are summarised in Table 2.

In all cases, a large percentage of the starting alkene was still present. The highest yields of epoxide for the straight chain alkenes was obtained for *n*-octene and, in most cases, other cleavage products were also observed, i.e., acids or aldehydes, as demanded by our mechanism. In general for the cycloalkenes, the reactivity towards ozone decreases with increasing ring size, i.e., all the cyclopentene reacts to form cleavage products and no epoxide was detected whilst all the cyclododecene remained unreacted. For the terminal alkenes studied there was, unsurprisingly, little deviation in consumption of alkene and corresponding production of epoxide; again, as in Table 1, some correlations can be drawn with epoxide yields obtained with polyperoxotungstates-catalysed [13,18] epoxidations.

The oxidation of cyclooctene gave the highest yield of epoxide, 40%. This is a very significant result as the maximum yield can only be 50%, since for every epoxide molecule formed, one molecule of alkene is consumed in the formation of the ozonide co-oxidant.

The reaction was also repeated using 10% and 20% (v/v) of methanol in CH_2Cl_2 in order to see whether different solvent systems effect the yield of epoxide formed. There was no significant change in the yield of cyclooctene oxide. When the Fe(TMP)Cl catalyst was adsorbed onto silica and used in the same way the yield of epoxide decreased.

The effect of the time of ozonolysis was studied: with Fe(TMP)Cl, significant degradation of the catalyst is observed after 30 min, and it is significantly reduced in its catalytic activity after 1 h.

3.3. Use of other metal catalysts

A variety of other catalysts were also tested using *trans*-stilbene as the primary substrate and cyclooctene as the material to be epoxidised (see Table 3). Those so tested were Mn(TMP)Cl, Ru(TMP)(CO) and *trans*-$Ru^{VI}(TMP)(O_2)$ (known [12] to be effective aerobic epoxidation catalysts), the phthalocyanine complex Fe-(PHTH)Cl, the heteropolyoxo species H_3-$[PW_{12}O_{40}] \cdot nH_2O$ (known to be an effective epoxidation catalyst with H_2O_2 [19,20]), the peroxotungstate dimer $(({}^nC_6H_{13})_4N)_2$-$[W_2O_3(O_2)_4]$, which we have also shown to be

Table 3
Catalytic epoxidation of cyclooctene by various metal catalysts
Conditions: *Trans*-stilbene (1.8 g, 10 mmol) in CH_2Cl_2 (50 cm^3) was ozonised for 30 min, then the metal catalyst in CH_2Cl_2 (0.05 mmol in 25 cm^3) added with alkene (10 mmol) and stirred at room temperature for 24 h.
Turnovers are in square brackets.

Catalyst	Conversion to cyclooctene oxide[a] (%)
None	5 [10]
Fe(TMP)Cl	42 [84]
Fe(PHTH)Cl	0 [0]
Mn(TMP)Cl	40 [80]
Ru(TMP)(CO)	48 [80]
trans-Ru(TMP)(O)$_2$	8 [16]
$(({}^nC_6H_{13})_4N)_2[W_2O_3(O_2)_4]$	10 [20]
$H_3[PW_{12}O_{40}] \cdot nH_2O$	1 [2]
$(({}^nC_4H_9)_4N)_6[Mn^{IV}W_9O_{32}]$	5 [10]

[a]Remainder, unconsumed cyclooctene.

an effective alkene epoxidant with H_2O_2 [13], and $(^nC_4H_9)_6[Mn^{IV}W_9O_{32}]$, the potassium salt of which we have recently shown may be easily made by ozonolysis [14]. The most effective catalysts were found to be the porphyrin complexes, with $Ru^{II}(TMP)(CO)$ proving to be very slightly superior to $Fe(TMP)Cl$. A curious feature is that *trans*-$Ru^{VI}(TMP)O_2$ is relatively ineffectual; we are unable to suggest a ready explanation for its unreactivity compared with that of $Ru^{II}(TMP)(CO)$.

3.4. A possible mechanism

It may well be that the mechanism of our reaction differs from that operative in the epoxidations of Campestrini et al. [5] catalysed by $Mn(Br_8\text{-}TMP)Cl$; they suggested that a metal oxo intermediate might be involved. Under the conditions of our reactions catalysed by $Fe(TMP)Cl$, we believe that ozone reacts with the alkene to give a primary ozonide **1** (Scheme 1, illustrated here for the reaction with cyclooctene). This then rearranges by the Criegee mechanism [16] to the secondary ozonide **2** [21], and it is this rather than ozone which is the co-oxidant for the epoxidation. Since **2** is in effect an organic peroxide, and $Fe(TMP)Cl$ is known to be an effective epoxidation catalyst with organic peroxides such as *meta*-chloroperbenzoic acid (mpcba) [22], this does not seem unreasonable. Formation of the active catalyst **3** is followed by oxygen transfer to the alkene yielding the epoxide **4**.

The nature of the active species in the epoxidation reaction with $Fe(TMP)Cl$ is likely to be the green oxo-iron(IV) tetramesitylporphyrin cation radical $[Fe^{IV}(TMP^{\cdot+})O]^+$.*Trans*-stilbene was ozonised at room temperature for 5 min forming the secondary ozonide (see Scheme 1), which is thought to be the co-oxidant in such reactions. This solution was then stirred with $Fe(TMP)Cl$ for 30 min at room temperature. The electronic spectrum of the solution was taken after this time and showed a Soret band

(λ_{max} 407 nm) and a Q band (λ_{max} 647 nm). These are in good agreement with those bands previously reported by Groves et al. [22]. This suggests that the step is catalysed by the iron(IV) oxo radical cation $[Fe^{IV}(TMP^{\cdot+})O]^+$. This confirms the earlier observations for our catalytic epoxidation reaction, and is in agreement with the demonstration by Gross and Nimri that styrene is stoichiometrically epoxidised by this species [23,24].

4. Conclusions

We conclude that alkenes may be epoxidised by an O_3–O_2 mixture under ambient conditions with $Fe(TMP)Cl$ as a catalyst. In some cases, the yield of epoxide is close to the theoretical maximum of 50%, given that there is a necessary concomitant formation of cleavage product. We believe that it is the secondary ozonide of the alkene that effects the epoxidation of the remaining alkene substrate and that this step is catalysed by the iron(IV) oxo radical cation $[Fe^{IV}(TMP^{\cdot+})O]^+$.

Acknowledgements

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