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Tony Cousin, Gregory Chatel, Bruno Andrioletti, Micheline Draye. Oxidative cleavage of cycloalkenes using hydrogen peroxide and a tungsten-based catalyst: towards a complete mechanistic investigation. *New Journal of Chemistry*, 2021, 10.1039/D0NJ03592K . hal-03084823

HAL Id: hal-03084823

<https://hal.science/hal-03084823>

Submitted on 2 Apr 2021

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Oxidative cleavage of cycloalkenes using hydrogen peroxide and a tungsten-based catalyst: towards a complete mechanistic investigation

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

Tony Cousin,^{a,b} Gregory Chatel,^a Bruno Andrioletti^{b*} and Micheline Draye^{a*}

The identification of the intermediates and by-products produced during the oxidative cleavage of cycloalkenes in the presence of H₂O₂ and a tungsten-based catalyst for the production of dicarboxylic acids has been carried out under various experimental conditions. On the basis of this mechanistic investigation and previous studies from the literature, a complete reaction scheme for the formation of reaction products and by-products is proposed. In this hypothesis of mechanism, the production of a hydroperoxyalcohol intermediate accounts for the two pathways proposed by Noyori and Venturello for the formation of the targeted dicarboxylic acid. In addition, a Baeyer-Villiger oxidation of the mono-aldehyde intermediate allows explaining the formation of short chain diacids observed as by-products during the reaction. Hence, the proposed mechanism constitutes a real tool for scientists looking for a better comprehension and heading to set up environmentally-friendly conditions for the oxidative cleavage of cycloalkenes.

Introduction

The oxidative cleavage of C=C bonds has witnessed a growing interest for several decades as a key transformation to access value-added mono- and dicarboxylic acids from olefins.^{1–5} More specifically, dicarboxylic acids are major intermediates for the manufacture of important polyesters and polyamides materials but also for the production of daily products found in a wide range of applications such as lubricants, fibers, cosmetics, pesticides, pharmaceuticals and plasticizers.^{6,7} In the chemical industry, this class of compounds is mainly obtained by oxidative cleavage of unsaturated carboxylic acids and cycloalkenes.^{6,7} One of the oldest oxidative cleavage process was patented by DuPont in the 50s for the production of adipic acid. Since, this dicarboxylic acid is still manufactured *via* the aerobic oxidation of cyclohexane to cyclohexanol and cyclohexanone followed by the oxidative cleavage of either one or a mixture of both (ketone + alcohol = KA Oil) with nitric acid.⁸ This industrial process leads to the formation of adipic acid in 95% yield with an annual production of 4 million tons.^{7,9} Adipic acid production is mainly dedicated to the synthesis of nylon 6,6 but also to plasticizers, lubricants and polyurethane resins.^{7,10}

Despite the major importance of adipic acid for key

applications, the DuPont process results in the production of large volumetric amounts of nitrous oxide. Actually, up to 400,000 metric tons of N₂O arise from the oxidative cleavage of KA Oil by nitric acid, representing 8% of the total anthropogenic production of this greenhouse gas.^{11,12} Nitrous oxide is particularly harmful towards the environment as it causes ozone depletion, smog, acid rains and its global potential warming is 300 times higher than CO₂.^{13–16} Even if efforts to reduce the amount of released N₂O through recycling, thermal and catalytic decomposition^{10,14,16,17} have been done, the energy consumption for adipic acid production remains high because this multi-step reaction is performed at temperatures reaching up to 160 °C.^{7,8,13}

These observations have prompted researchers to develop more environmentally-friendly routes for the production of dicarboxylic acids through cycloolefin oxidative cleavage. In this context, hydrogen peroxide has been considered to replace commonly used oxidants. Indeed, H₂O₂ presents many advantages for the development of greener oxidation reactions: it is a widely available oxidant with 47% of active oxygen content, non-toxic, only releases water as theoretical by-product and does not require temperatures above 100 °C to perform oxidations.^{18,19} The H₂O₂-mediated oxidative cleavage of cycloalkenes has been widely documented in the literature. The last trends in the development of sustainable catalytic systems for this reaction have been recently reviewed.⁵ In particular, the use of hydrogen peroxide in association with tungsten-based catalysts has shown to be a promising combination to decrease the environmental impact of the cycloalkene oxidative cleavage. Indeed, compared to other transition metals used for this reaction, tungsten-based catalysts are low cost,^{20,21} non-toxic^{22,23} and react with H₂O₂ to

^aLCME, Univ. Savoie Mont Blanc, 73000 Chambéry, France.

E-mail: micheline.draye@univ-smb.fr

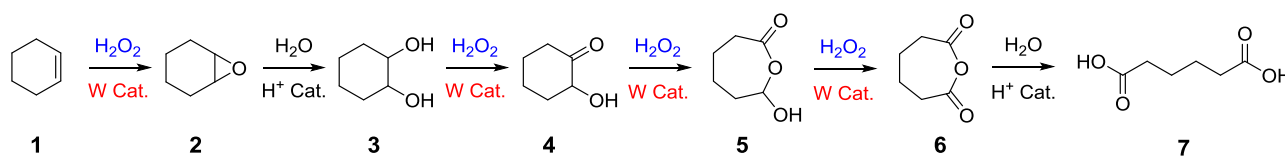
^bUniv Lyon, Université Claude Bernard Lyon 1, INSA-Lyon, CPE-Lyon, ICBMS UMR CNRS 5246, Campus Lyon-Tech la Doua, Bât. Lederer, 43 Boulevard du 11 Novembre 1918, 69622 Villeurbanne, France.

E-mail: bruno.andrioletti@univ-lyon1.fr

† Electronic Supplementary Information (ESI) available.

See DOI: 10.1039/x0xx00000x

produce peroxotungstate compounds highly active toward olefins.^{24,25}



Scheme 1: Oxidative cleavage of cycloalkenes with H_2O_2 and a tungsten-based catalyst according to Noyori.^{11,26}

Among the numerous studies dealing with H_2O_2 -mediated cycloalkene oxidative cleavage with tungsten-based catalysts, a large majority of publications exposes the reaction mechanism suggested by Noyori *et al.*^{11,26} for rationalizing the formation of dicarboxylic acids from cycloalkenes (Scheme 1).

This mechanism involves six reaction steps including an alkene epoxidation, an epoxide hydrolysis, a first alcohol oxidation, a Baeyer-Villiger oxidation, a second alcohol oxidation and a cyclic anhydride hydrolysis (Scheme 1). Even if intermediates **2** to **4** have been unambiguously identified and described in the literature, the production of intermediates **5** and **6** through Baeyer-Villiger enlargement have not been highlighted yet. Their presence in the oxidation mechanism has been so far justified through indirect studies and computational modelling.^{27–29}

No complete mechanism has been established to date to explain the formation of the targeted dicarboxylic acid from the hydroxy-ketone intermediate **4**. Moreover, among studies on the oxidative cleavage of cycloolefins, several by-products are often observed along with the expected dicarboxylic acid. Indeed, from 1 to 5% of additional dicarboxylic acids, shortened by 1 to 3 carbon atoms compared to the targeted one, are observed at the end of the reaction.^{11,30,31} Despite their occurrence in studies, no hypothesis for their formation has been suggested so far.

The accurate comprehension of the reaction pathways for product and by-products formation is of prime interest to determine the conditions favouring the production of the targeted dicarboxylic acid and minimizing the formation of these by-products.

In this study, we aim at confirming and completing the mechanisms proposed in the literature for the oxidative cleavage of cycloalkenes with H_2O_2 and a tungsten-based catalyst through the structural determination of intermediates and by-products of the reaction. Studies of the reaction at different stages and under different experimental conditions allow highlighting the structure and amount of by-products formed during the reaction.

Experimental

All chemicals were used without further purification and purchased from Acros, Aldrich, Alfa Aesar, Honeywell and Fluka.

Gas chromatography was performed on a HP 6890 Series gas chromatograph from Hewlett Packard using a flame-ionization detector and equipped with an Optima-5MS Accent capillary column (dimethylpolysiloxane, 30 m x 0.25 mm x 0.25 μm) from Marcherey Nagel. All analyses were undertaken with helium as carrier gas (24 $\text{mL}\cdot\text{min}^{-1}$) in split mode (split ratio: 1:40) and an injector and a detector both heated at 290 $^\circ\text{C}$.

Mass spectra were recorded on an Agilent 5973 N Mass Selective Detector coupled to an Agilent 6890 GC and equipped with an Optima 5 capillary column (dimethylpolysiloxane 30 m x 0.32 mm x 0.25 μm) from Macherey-Nagel.

Cyclohexene oxidative cleavage

The reactions were performed following the procedure described in the reference study.^{11,26} Hydrogen peroxide (35 wt.%, 2.6–525 g, 4.4 eq.) was added to a mixture of tungsten-based catalyst (1 mol%) and Phase Transfer Catalyst (PTC: Aliquat 336[®] or Oct₃MeN⁺HSO₄⁻, 1 mol%) into a round bottom flask. The solution was vigorously stirred with a magnetic stirring bar at room temperature for 10 min to solubilize as much of catalyst as possible. After addition of cyclohexene (0.5–100 g, 1 eq.), the round bottom flask was equipped with a condenser and successively heated to 75 $^\circ\text{C}$ for 30 min, 80 $^\circ\text{C}$ for 30 min, 85 $^\circ\text{C}$ for 30 min, and 90 $^\circ\text{C}$ for 6 h 30 min while stirring at 1,000 rpm. After 8 h, the reaction medium was cooled to room temperature before being placed at 5 $^\circ\text{C}$ overnight. Then, the resulting white precipitate was separated from the aqueous solution by filtration, washed 3 times with cold deionized water and dried under reduced pressure. Sodium sulphite was added portion-wise to the aqueous filtrate until complete decomposition of remaining hydrogen peroxide. After acidification with sulfuric acid to pH = 1, water was then evaporated under reduced pressure and 20 mL acetone was added to the solid residue. After separation of the organic solution from inorganic salts by filtration, acetone was eliminated under reduced pressure. Solid residues from the aqueous filtrate and precipitated adipic acid were analyzed by gas chromatography for quantification of all reaction products by internal standard method (dodecane used as internal standard) after derivatization with N-O-bis(trimethylsilyl)trifluoroacetamide for 2 h at 50 $^\circ\text{C}$. Reaction by-products were identified by GC/MS (characterization is available in ESI⁺).

Cycloalkene epoxidation

The cyclopentene, cyclohexene and cyclooctene epoxidations were performed as follows. Into a 250 mL round bottom flask, an aqueous solution of hydrogen peroxide (280 mmol, 26.90 g, 1.5 eq., 35 wt.%) was added to a mixture of H_2WO_4 (1.4 mmol, 0.346 g, 0.75 mol%) and Aliquat 336® (1.4 mmol, 0.56 g, 0.75 mol%). The aqueous solution was stirred at room temperature with a stirring bar for 10 min before adding the cycloalkene (185 mmol). The round bottom flask was equipped with a condenser before stirring the biphasic mixture at 80 °C without any incubation period at 1,000 rpm for 30 min.

At the end of the reaction, the aqueous phase was separated from the organic layer, thoroughly extracted by CH_2Cl_2 or diethyl ether (3 x 30 mL) in order to recover remaining cycloalkene and newly formed products, and concentrated under reduced pressure. Isolation and analysis of non-extracted epoxidation by-products contained into the aqueous phase were undertaken according to the same procedure as previously. Reaction by-products were identified by GC/MS (characterization is available in ESI†).

Results and discussion

Within the scope of our study, we decided to limit our investigations to cyclohexene, cyclopentene and cyclooctene for the epoxidation and to cyclohexene for the oxidative cleavage. Indeed, the oxidative cleavage of cycloolefins is well-described in the literature on these small-sized cycloalkenes and affords the dicarboxylic acids with over 75% yields.⁵ Besides, the reaction performed on larger rings such as cyclooctene and cyclododecene results in low yields, generally below 30% because of transannular reactions occurring on the epoxide derivatives of these medium-sized cycloalkenes.^{5,32} Among the studies on the oxidative cleavage of cyclic alkenes with H_2O_2 and a tungsten-based catalyst, those from Noyori and co-workers are still a reference in terms of green chemistry. Indeed, the reaction conditions involve 4.4 equivalents of 30% H_2O_2 , 1 mol% of Na_2WO_4 and $\text{Oct}_3\text{MeN}^+\text{HSO}_4^-$ as a Phase Transfer Catalyst (PTC). These conditions allow to perform the oxidative cleavage of 100 g of cyclohexene from 75 to 90 °C in 8 h and without any organic solvent. Adipic acid is isolated in 93% yield.^{11,26}

During our studies, the oxidative cleavage of cyclohexene was investigated under the conditions described by Noyori and co-workers. The production of adipic acid as well as the by-products was followed by gas chromatography (GC). At first, the reaction was studied under the conditions used for the oxidative cleavage of 100 g of cyclohexene, corresponding to 600 mL of reaction volume,^{11,26} and on 8 and 3 mL scales in order to decrease the amounts of reactants used per run. The obtained results are gathered in the Table 1.

At 600 mL reaction scale, the oxidative cleavage of cyclohexene leads to 83% adipic acid yield (Table 1, Entry 2) instead of the 93% published in the literature (Table 1, Entry 1). These results can be ascribed to the formation of 1,2-

cyclohexanediol, 2-cyclohexanone and glutaric acid observed in 0.5 to 4.5% yields. Moreover, the reaction performed under Noyori's conditions revealed the formation of by-products that were not described in the original work. Thus, little amounts (< 0.5%) of 5-hydroxypentanoic, 5-oxopentanoic and succinic acid were detected during our study. When the reaction volume was decreased from 600 mL to 8 mL and 3 mL, the yield of adipic acid decreased from 83% to 47% and 39% respectively (Table 1, Entries 2, 3 and 4). However, the same by-products were produced in similar yields than with 600 mL reaction volume, leading to an unsatisfactory mass balance. Hence, the oxidative cleavage yields and selectivities lower than 50% observed with reaction volumes below 10 mL can be explained by a cyclohexene loss by volatilization during the 8 h of reaction. Indeed, despite the experimental care, some of the solution has been volatilized. This would explain the choice of 100 g of starting cycloalkene chosen in the reference study,^{11,26} that ensure a minimum impact of volatilization of the reactant on the yield of the reaction. A reaction volume of 8 mL was chosen for the rest of the study, guaranteeing a reasonable yield and the use of a minimum amount of reactants (Table 1, Entry 3).

Table 1 Oxidative cleavage of cyclohexene in the presence of H_2O_2 , Na_2WO_4 and $\text{Oct}_3\text{MeN}^+\text{HSO}_4^-$ at different reaction volumes




Entry ^a	Reaction volume (mL)	Mass of cyclohexene (g)	Conv. ^b (%)	Yield ^c (%)	Main by-products (%) ^d
1	600	100	100 ^e	93 ^e	 (2.5 ^e) (4 ^e)
2	600	100	100	83	 (1-4) (0.5-1) (< 0.5)
3	8	1.3	100	47	 (< 0.5) (3-4.5) (< 0.5)
4	3	0.5	89	39	 (< 0.5)

^a Experimental conditions: cyclohexene, H_2O_2 (35%, 4.4 eq.), Na_2WO_4 (1 mol%), $\text{Oct}_3\text{MeN}^+\text{HSO}_4^-$ (1 mol%), 75-90 °C, 1,000 rpm, 8 h. ^b Based on the amount of converted cyclohexene and calculated by GC with internal standard method. ^c Based on the initial amount of cyclohexene and calculated by GC with internal standard method. ^d By-products detected by GC/MS†. ^e Results from the reference publication.^{11,26}

Then the oxidative cleavage of cyclohexene was studied with different associations of tungsten-based catalysts and PTC

to compare their performance with the $\text{Na}_2\text{WO}_4/\text{Oct}_3\text{MeN}^+\text{HSO}_4^-$ system developed by Noyori, while following the formation of by-products. In addition, $\text{H}_2\text{WO}_4/\text{Aliquat 336}^\circ$ was chosen as catalytic system as it affords yields above 80% for the oxidative cleavage of cyclohexene and cyclopentene in the literature.^{30,33} Different combinations of W-based catalyst and PTC were studied in order to reach a pH < 3 in the reaction medium. Indeed, a pH below 3 is required to ensure the formation of the active catalytic species^{26,34–36} and to prevent H_2O_2 from catalytic and thermal decomposition.^{18,19,37} Thus, the combination $\text{Na}_2\text{WO}_4/\text{Aliquat 336}^\circ$ was not selected as it affords a pH of 6 in the reaction medium. The results obtained with the different catalytic compositions are summarized in the Table 2.

Table 2 Oxidative cleavage of cyclohexene in the presence of different catalytic systems

Entry ^a	Cat. W	PTC	pH ^b	Conv. ^c (%)	Yield ^d (%)	Main by-products (%) ^e
1	Na_2WO_4 . 2 H_2O	Oct_3MeN^+ HSO_4^-	2	100	47 ^e (4) ^f	 (< 0.5)
2	H_2WO_4	Aliquat 336 ^o	3	100	59 ^e (15) ^f	 (0-0.5)
3	H_2WO_4	Oct_3MeN^+ HSO_4^-	< 1	100	45 ^e (5) ^f	 (0.5-3)

^a Experimental conditions: cyclohexene (16.5 mmol), H_2O_2 (35%, 4.4 eq.), Cat.W (1 mol%), PTC (1 mol%), 75–90 °C, 1,000 rpm, 8 h. ^b pH of the aqueous phase during the reaction. ^c Based on the amount of converted cyclohexene and calculated by GC with internal standard method. ^d Based on the initial amount of cyclohexene and calculated by GC with internal standard method. ^e By-products detected by GC/MS⁺. ^f 1,2-cyclohexanediol yield.


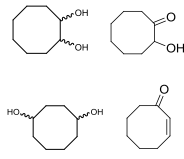

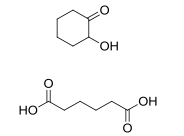

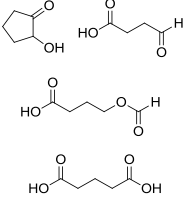
Among the catalytic systems that have been studied, the combination of tungstic acid with Aliquat 336^o led to the highest results with an adipic acid yield of 59% (Table 2, Entry 2).

Under these conditions, the major intermediate is the 1,2-cyclohexanediol with a yield of 15%. The GC/MS analyses of the different runs revealed the formation of by-products of identical structure and in similar amount as previously (Tables 1 and 2). In order to assess a complete mechanism,⁹ the initial alkene epoxidation using H_2WO_4 and Aliquat 336^o has been investigated.

In a very recent study, we showed that this system combined to high frequency ultrasound particularly improved the epoxidation of *cis*-cyclooctene and revealed important mechanistic insights of the studied reaction.³⁸ Hence, under 800 kHz ultrasonic irradiation, in the presence of 0.75%mol of

H_2WO_4 and Aliquat 336^o and 1.5 eq. of 30% H_2O_2 related to the substrate, 96% yield of epoxide was obtained with 98% selectivity within only 30 min. In addition, the non-radical nature of *cis*-cyclooctene epoxidation mechanism has been demonstrated.³⁸ In the present study, under magnetic stirring, the chosen oxidizing system leads to epoxyoctane in 89% yield and 91% selectivity (Table 3, Entry 1). The same conditions have been then used for the epoxidation of cyclohexene and cyclopentene (Table 3, Entries 2 and 3) and the structural identification of the products issued from the oxidation of these three cycloalkenes have been performed (Table 3).

Table 3 Epoxidation of cycloalkenes in the presence of H_2O_2 , H_2WO_4 and Aliquat 336^o

Entry ^a	Olefin	Temp. (°C)	Conv. ^b (%)	Yield ^c (%)	Main-by-products ^d
1		25-85	99	89	
2		25-70*	75	0 (39) ^e	
3		25-50*	48	3 (32) ^e	

^a Experimental conditions: cycloalkene (185 mmol), H_2O_2 (35%, 1.5 eq.), H_2WO_4 (0.75 mol%), Aliquat 336^o (0.75 mol%), 25–80 °C, 1,000 rpm, 30 min. ^b Based on the amount of converted cycloalkene and calculated by GC with internal standard method. ^c Based on the initial amount of cycloalkene and calculated by GC with internal standard method. ^d Determined by GC/MS analysis[†], yields < 2% ^e 1,2-cycloalkenediol yield. * Temperature limited by cycloalkene boiling point.

Unfortunately, in spite of the excellent epoxidation results observed with *cis*-cyclooctene, the oxidizing system was not efficient to selectively convert cyclohexene and cyclopentene to their corresponding epoxides in 30 min. Indeed, while cyclooctene is almost fully transformed to epoxyoctane in 89% yield (Table 3, Entry 1), conversion of smaller cycloalkenes did not exceed 75% and their epoxides were observed in 0 and 3% yields (Table 3, Entries 2 and 3). These results are explained by the higher reactivity of the double bond of cyclooctene toward electrophilic oxidants compared to the one of other cycloalkenes and the strong resistance of its epoxide toward hydrolysis under acidic conditions.^{11,32,39} Indeed, this particular reactivity of medium-sized cycloalkenes such as cyclooctene has been attributed to transannular reactions occurring during solvolysis of their oxides, and which is related to the spatial proximity of the opposite sides of their medium-sized ring.^{32,40}

formyloxobutanoic acids (Table 3, Entry 3). In order to understand the formation of the by-products observed during the different steps of the oxidative cleavage of cycloalkenes, their structure was determined and compared to the results described in the literature.^{11,26,30,41}

The present study on the oxidative cleavage and epoxidation of cyclohexene and cyclopentene allows highlighting the formation of 2 categories of compounds: oxidative cleavage intermediates and by-products.

On the one hand, expected reaction intermediates such as epoxide **2**, 1,2-diol **3**, and hydroxy-ketone **4** have been identified (Tables 1, 2 and 3). Despite the different reaction conditions and analyses carried out within the frame of our studies, the hydroxy-lactone **5** and cyclic anhydride **6** proposed by Noyori have never been detected. (Scheme 1).^{11,26}

Pioneering studies reported by Venturello *et al.*⁴² led us to consider other intermediates in this mechanism (Scheme. 1). In particular, the production of a hydroperoxyalcohol intermediate **8** arising from the nucleophilic addition of H₂O₂ on the hydroxy-ketone **4** has been proposed, following the identification of the mono-aldehyde **9** (Scheme 2).⁴² Production of a hydroperoxyalcohol from the addition of H₂O₂ on a ketone has already been justified in earlier examples.^{43,44} Studies of the literature on aldehyde oxidation^{45,46} also support the hypothesis of the formation of the carboxylic acid **7** through the oxidation of the mono-aldehyde intermediate **9**. Interestingly, both mechanisms suggested by Noyori and Venturello are connected *via* the hydroperoxyalcohol **8** intermediate suggested by Venturello. Indeed, compound **8**, also known as the *Criegee intermediate*,^{44,47} is able to rearrange to both the mono-aldehyde **9** and the hydroxylactone **5** *via* a Baeyer-Villiger mechanism (Schemes 2 and 3).^{29,44} Mechanisms proposed by Noyori and Venturello have been combined to complete the reaction scheme suggested by Noyori (Scheme 1).

In their studies on the oxidative cleavage of 1,2-cyclohexanediol derivatives, Fujitani and co-workers⁴¹ proposed the production of a gem-dihydroxy acid (**10** in Scheme 2) to explain the presence of the Baeyer-Villiger product **5** suggested by Noyori, and the formation of the hydroperoxyalcohol **8** and mono-aldehyde **9** suggested by Venturello.⁴² Nevertheless, none of these three intermediates were detected in our studies. It is worth noting that Noyori's hydroxy-lactone **5** is the result of Venturello's mono-aldehyde **9** cyclization.

Thus, regarding the numerous interconnexions existing between the above-mentioned intermediates, both pathways described in Scheme 2 should be considered to rationalize the formation of dicarboxylic acids from cycloolefin oxidative cleavage.

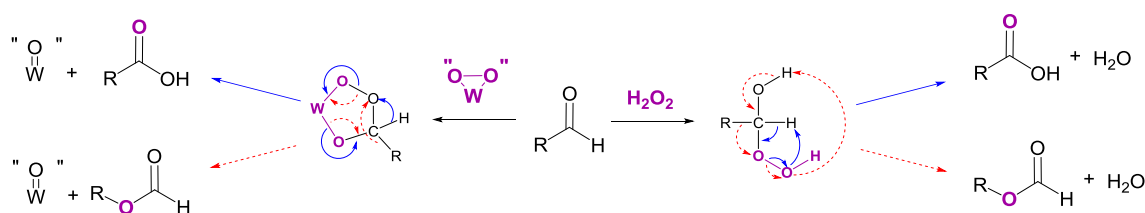
Scheme 3: Hypothesis of acid-catalyzed rearrangement of hydroperoxyalcohol intermediate **8** into hydroxy-lactone **5** or mono-aldehyde **9** (adapted from references 29,31,45).

On the other hand, the by-products formed from side-reactions on oxidative cleavage intermediates have also been

identified in this work during epoxidation and oxidative cleavage of cycloalkenes (Tables 1, 2 and 3). More specifically, dicarboxylic acids with 1 to 3 less carbon atoms compared to the targeted product have been mainly identified during epoxidation and oxidative cleavage studies. This category of by-product is often observed in the literature but no explanation has been brought to date to justify their formation. One reaction pathway that could lead to these shorter diacids could involve a decarboxylation of the desired dicarboxylic acid.⁴ Nevertheless, thermal decarboxylation of dicarboxylic acids mainly occurs at temperatures above 290 °C⁶ and usually leads to the corresponding alkanes. Besides, it was shown in the literature that α -oxoacids can afford diacids shortened by one carbon by decarboxylation in the presence of H₂O₂.⁴⁸

The production of shorter dicarboxylic acids could be explained by a H₂O₂-mediated Baeyer-Villiger oxidation of the mono-aldehyde intermediate **9**. Indeed, while the reaction between an aldehyde and hydrogen peroxide generally leads to the formation of the corresponding carboxylic acid, the nucleophilic addition of H₂O₂ on the aldehyde gives rise to a high-energy hydroperoxyalcohol intermediate that rearranges into formate ester (Scheme 4).^{18,43,44,47} The formation of the carboxylic acid and the formate ester from the rearrangement of the *Criegee intermediate* can take place *via* the nucleophilic addition of either H₂O₂ or peroxotungstate complexes to the mono-aldehyde.⁴⁵ Once formed, the formate ester (Scheme 2, **11**) is next hydrolysed to the alcohol **12** (Scheme 2) that is directly oxidized to the corresponding mono-aldehyde and dicarboxylic acid (Scheme 2, **13** and **14**). The consecutive Baeyer-Villiger oxidations, ester hydrolyses and alcohol oxidations from the oxo-carboxylic acid intermediate **13** (Scheme 2) also lead to dicarboxylic acids with shorter chains (Scheme 2, **15**). In this study on cycloalkenes oxidation, the formate ester **11** has been detected (Table 3, Entry 3) as well as the hydroxy-acid **12** and oxo-acid **13** (Table 1, 2 and 3). In the literature, the formation of intermediates such as **12**, **13** and **15** has been detected during alcohols and aldehydes oxidation using H₂O₂ and phosphotungstic acid.⁴⁵ In addition to the expected carboxylic acids obtained by oxidation of linear and aromatic aldehydes, the presence of formate esters and their alcohol derivatives has been detected, thus supporting the hypothesis of the implementation of a Baeyer-Villiger oxidation.⁴⁵ In addition, Venturello and co-workers also described the presence of this side reaction during the oxidative cleavage of 1-methylcyclohexene. Indeed, 5-acetoxypentanoic acid was shown to be formed as a by-product along with the targeted 6-oxoheptanoic acid.³⁰

Thus, the mechanism disclosed in the Scheme 2 for the production of shorter chain diacids confirms the formation of the mono-aldehyde intermediate **9** as a key intermediate in the oxidative cleavage mechanism of cycloalkenes. Finally, this mechanism also explains the formation of shorter chain diacids observed during linear alkene oxidative cleavage, for which formation of aldehyde intermediates is well-established in the literature.^{3,4,49}



Scheme 4: Competitive oxidation pathways occurring during aldehyde oxidation in the presence of H_2O_2 and a tungsten-based catalyst. In blue: aldehyde oxidation into carboxylic acid. In red dotted lines: Baeyer-Villiger oxidation (adapted from references 18,45).

Conclusions

To summarize, this work proposes a complete mechanism of formation of the products and by-products obtained during the oxidative cleavage of cycloalkenes with H_2O_2 and H_2WO_4 . The reaction has been studied with cyclohexene and cyclopentene under various conditions. The structures and proportions of identified by-products were studied from epoxidation/dihydroxylation and oxidative cleavage stages. The present study shows that, along with targeted compounds, dicarboxylic acids shortened by 1 to 3 carbon atoms compared to the expected ones are mainly formed. The production of these by-products is explained by a Baeyer-Villiger oxidation on a mono-aldehyde intermediate that leads to a formate ester, which is hydrolysed and then oxidized to shorter chain diacids. This hypothesis is supported by the identification of formate esters and hydroxyacids but also by results on H_2O_2 -mediated alcohol and aldehyde oxidation published in the literature, illustrating the formation of a mono-aldehyde intermediate in the cycloalkene oxidative cleavage pathway. The mechanism proposed in this study constitutes a real support for researchers aiming at developing efficient and environmentally-friendly methodologies for the oxidative cleavage of olefins with H_2O_2 and tungsten-based catalysts.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors are grateful to the Région Auvergne Rhône-Alpes for the financial support through an ARC Environnement doctoral research grant (ARC 2016).

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