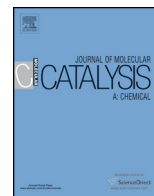




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Oxidation of olefins with H₂O₂ catalyzed by gallium(III) nitrate and aluminum(III) nitrate in solution

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This article is dedicated to Prof. Dr. Ulf Schuchardt, our good colleague and friend, on the occasion of his 70th birthday.

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ABSTRACT

Soluble gallium and aluminum nitrates (simple salts of non-transition metals) are good catalysts for the epoxidation of olefins (cyclooctene, dec-1-ene) including terpenes (carvone, limonene) with hydrogen peroxide in ethyl acetate or tetrahydrofuran (THF). Typically, the gallium salt is more efficient in comparison with the aluminum derivative. Products are formed in yields up to 93%, turnover numbers (TONs) attained 40. Addition of trifluoroacetic acid or pyrazine-2-carboxylic acid (PCA) accelerates the reaction and improves the yield. In striking contrast, added 2,2'-bipyridine or phenanthroline dramatically inhibit the oxidation.

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1. Introduction

Valorization of natural products including biomass is a very attractive task of contemporary chemistry [1]. Many natural compounds, for example, terpenes, contain double bonds and their epoxidation leads to the preparation of valuable product. Usually epoxides are prepared by metal-catalyzed oxygenation of compounds containing double bonds [2]. In recent decades, heterogeneous [3–11] and soluble [12–14] derivatives of non-transition elements aluminum and gallium have been reported by Schuchardt, Sheldon, Mandelli, Rinaldi and Pescarmona to catalyze olefin epoxidations with hydrogen peroxide. The interaction of hydrogen peroxide with soluble derivatives of aluminum, gal-

lium and some other non-transition metals leads to the formation of hydroxyl radicals which induce the oxidation of alkanes [13,15–20]. Goldsmith and co-workers described epoxidation of olefins with peroxyacetic acid catalyzed by gallium complexes with N-donor ligands [21–23]. It is noteworthy that H₂O₂ was not effective in that reaction.

In the present work we have discovered, for the first time, that gallium nitrate in ethyl acetate (as well as in tetrahydrofuran, THF) efficiently catalyzes epoxidation of certain olefins with H₂O₂. Aluminum nitrate [12,13,15] was used for comparison. A remarkable accelerating effect of pyrazine-2-carboxylic acid (PCA) was found in the present study. Finally, we were able to epoxidize dec-1-ene by the Ga/PCA system. Terminal olefins can be epoxidized with difficulty by usual reagents.

2. Results and discussion

2.1. Oxidation of cyclooctene and dec-1-ene

In the first part of this work we carried out a detailed study of cyclooctene oxidation with H₂O₂ catalyzed by nitrates of gal-

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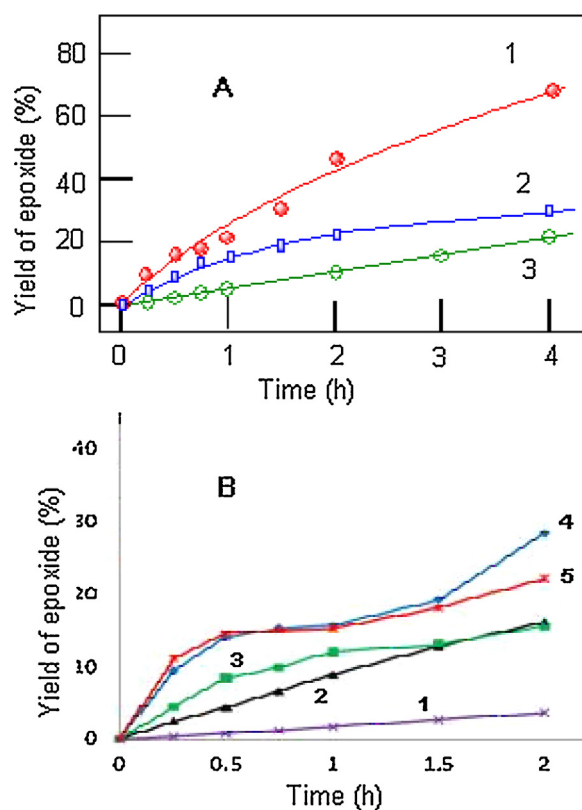


Fig. 1. Graph A. Accumulation of epoxide in the oxidation of cyclooctene (1.0 M) with H₂O₂ (4.0 M) containing 3.2 M H₂O in the presence of catalyst (0.02 M): Ga(NO₃)₃ (curve 1), Al(NO₃)₃ (curve 2) and without catalyst (curve 3). Conditions: solvent ethyl acetate, 80 °C. Graph B. Yield of epoxide (subtracting the data for the experiments in the absence of Ga nitrate) for the ratios H₂O₂/cyclooctene 1, 2, 3, 4 and 5 in the reaction catalyzed by Ga(NO₃)₃.

lithium or aluminum which gives rise to the formation of the epoxide and diol (Scheme 1). It should be noted that diol was not detected by GC for the reaction time < 8 h. Diol in a small concentration was found only at time 24 h. For the cases of both catalysts the products were formed predominantly during the first hours of the reaction. Total yield of the epoxide was not changed significantly in aliquots removed at 6, 8 and 24 h reaction. In the case of Ga(NO₃)₃ these values were 71, 77 and 72%, respectively. Some reduction of yield at 24 h reaction time can be due to the formation of over-oxidation products. We measured also the efficiency of hydrogen peroxide usage. This efficiency was calculated taking into account the amount (mol) of remaining hydrogen peroxide in the reaction solution after 24 h, the amount of H₂O₂ initially added to the medium and amount of formed oxidized product. In the case of the reaction catalyzed Ga³⁺ and Al³⁺, efficiency for hydrogen peroxide was 76 and 75%, respectively.

Accumulation of epoxide in the oxidation of cyclooctene is shown in Fig. 1. It can be seen in Fig. 1, Graph B that after 1.5 h some acceleration of the process takes place. It can be assumed that after this time (1.5 h) the system begins to generate hydroxyl radicals. This was totally confirmed by the epoxidation with carvone and it is one of the most interesting features of the work (see Supplementary data, Appendix A).

Fig. 2A demonstrates dependence of the initial reaction rate on initial concentration of cyclooctene. It can be clearly seen that the gallium derivative is noticeably more active than the corresponding aluminum salt. The mode of dependence of W_0 on initial cyclooctene concentration (approaching the limited value when [cyclooctene]₀ grows) indicates that the olefin is epoxidized by an intermediate species which is produced in Ga-catalyzed

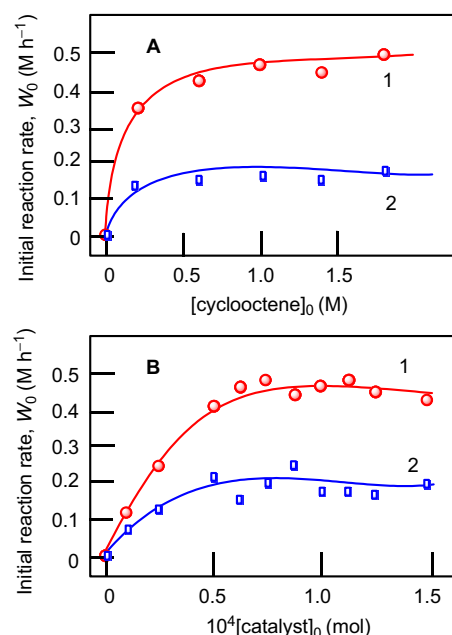


Fig. 2. Epoxidation of cyclooctene with H₂O₂ (4.0 M) containing 3.2 M H₂O in the presence of catalyst: Ga(NO₃)₃ (curves 1), Al(NO₃)₃ (curves 2). Graph A: dependence of initial epoxidation rate W_0 on initial concentration of cyclooctene. Graph B: dependence of initial epoxidation rate W_0 on initial concentration of catalyst. Conditions: solvent ethyl acetate, 80 °C.

decomposition of H₂O₂. Approaching a plateau is in accord with an assumption that catalytically active oxidizing species reacts not only with cyclooctene but also competitively with solvent.

The rate dependence of the oxygenation is first order with respect to the initial hydrogen peroxide at [H₂O₂]₀ < 3 M for both catalysts. Dependences of initial rates on concentrations of the catalysts are shown in Fig. 2B. In these cases gallium derivative is also more active. This observation is in accordance with conclusions made on the basis of the DFT calculations [16]. Indeed, a theoretical study demonstrated that the acidity of the gallium and their complexes in aqueous solutions is the highest when compared with the other metals of Group III of the periodic table. It was also argued that the activity of catalysts [M(H₂O)_n]³⁺ in the alkane oxidation with H₂O₂ depends on the stability of the complex and activation of hydrogen peroxide. According to the calculations, this activity in another pathway generating hydroxyl radicals follows the series Al ≈ La < Y ≈ In < Sc < Ga [16]. The dependence of initial epoxidation rate on the amount of catalyst (N , mol) correlates with the catalyst solubility under the studied conditions. Thus, at $N < m_0$ where $m_0 = 0.5 \times 10^{-4}$ mol (that is at catalyst concentration < 10⁻² M) catalyst is completely dissolved in the reaction mixture and the solution is homogeneous. However, at $N > 0.5 \times 10^{-4}$ mol a portion of introduced catalyst ($N - m_0$) is not dissolved and some turbidity of the reaction mixture can be noticed. Assuming that reaction rate is proportional to catalyst concentration in homogeneous solution and that solid catalyst is inactive in the oxidation, that is

$$W_0 = \alpha \frac{N}{V} \text{ at } N \leq m_0 \text{ and}$$

$$W_0 = \alpha \frac{m_0}{V} \text{ at } N > m_0$$

where α are effective pseudo-first order rate constants and V is the reaction solution volume, we will see that given above explanation is in full agreement with experimental results presented in Fig. 2B.

We studied effects of various additives on the yields of products. Figs. S1 and S1a show that addition of acetic acid leads to some

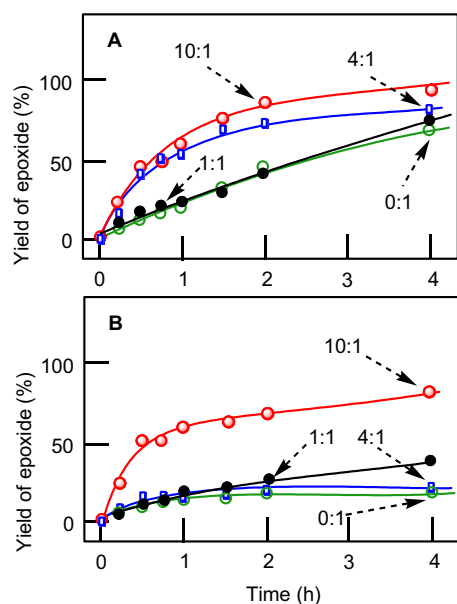


Fig. 3. Accumulation of epoxide in the oxidation of cyclooctene (1.0 M) with H_2O_2 (4.0 M) containing 3.2 M H_2O in the presence of catalyst (0.02 M): $\text{Ga}(\text{NO}_3)_3$ (Graph A), $\text{Al}(\text{NO}_3)_3$ (Graph B) and co-catalyst PCA in the molar ratio PCA:catalyst 0:1, 1:1, 4:1 and 10:1. Conditions: solvent ethyl acetate, 80 °C.

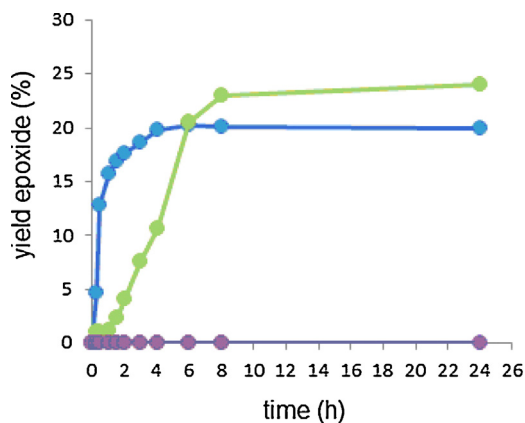


Fig. 4. Accumulation of epoxide in the oxidation of dec-1-ene (1.0 M) with H_2O_2 (4.0 M) containing 3.2 M H_2O in the absence of catalyst (violet curve) in the presence of catalyst (0.02 M): $\text{Ga}(\text{NO}_3)_3$ (green curve) and co-catalyst + PCA in the molar ratio PCA:catalyst 4:1 (blue curve). Conditions: solvent ethyl acetate, 80 °C.

increase of the epoxide yield. The epoxidation is not efficient in the absence of the gallium salt although acetic acid is present in the solution (Fig. S1a). Trifluoroacetic acid is also co-catalyst as Fig. S2 demonstrates. The best result has been obtained for $\text{Ga}(\text{NO}_3)_3$ and ten-fold excess of CF_3COOH : yield of the epoxide was 70% after 45 min. A strong accelerating effect has been found for pyrazine-2-carboxylic acid, PCA [24], in the cases of both gallium and aluminum salts (Fig. 3A and B, respectively). The epoxide yield attained 93% in the case of gallium salt after 4 h. Fig. S3 shows that the order of the reaction in PCA is >1 in the case of gallium salt. In contrast to PCA, diamines such as 2,2'-dipyridyl and phenanthroline exhibited inhibiting effects (Figs. S4,S5).

Fig. 4 demonstrates the strong effect of added PCA on initial reaction rate in the dec-1-ene epoxidation. Aluminum nitrate exhibited much less activity under these conditions.

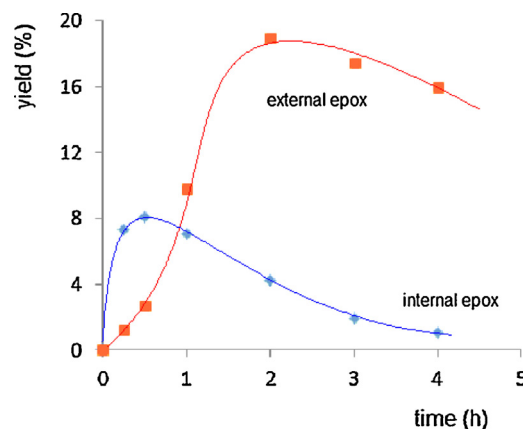


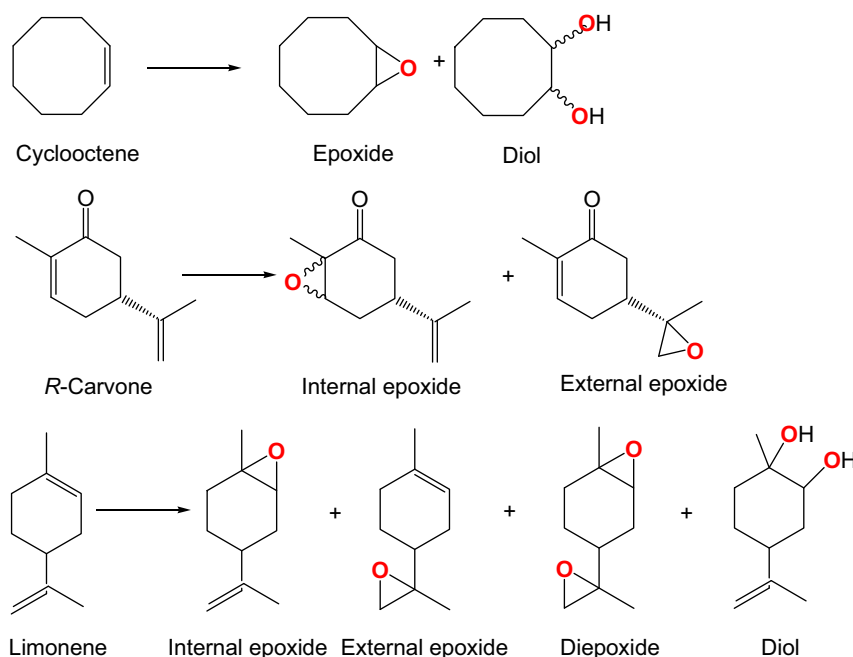
Fig. 5. Accumulation of epoxides in the oxidation of carvone (1.0 M) with H_2O_2 (4.0 M) containing 3.2 M H_2O in the presence of catalyst (0.02 M): $\text{Ga}(\text{NO}_3)_3$ and co-catalyst PCA in the molar ratio PCA:catalyst 4:1. Conditions: solvent ethyl acetate, 80 °C.

2.2. Oxidation of carvone

We have found the similarity in catalytic behavior of Al^{3+} and Ga^{3+} in epoxidation of (*R*)-carvone. This study was carried out similarly to that performed by Rinaldi, Schuchardt and co-workers [12]. In our case THF was replaced by ethyl acetate because efficiency of the latter was higher for the epoxidation of cyclooctene. Carvone conversion, after 3 h at 80 °C in the case of both metals was ca. 60% (Fig. S6a), but with a mass balance of approximately 65% (Fig. S6b), which indicates that some other volatile products are formed. Internal epoxide was mainly formed in the beginning of the reaction (Fig. S6c). Both systems, Ga and Al, are very fast in generating nucleophilic species OOH which attacks the double internal bond situated closer to the carbonyl group and therefore bearing lower electron density. Thus, within only 0.5 h of the reaction almost all internal epoxide was formed for both catalysts (Fig. S6c). The metals have similar activities and form the same final amount of internal epoxide (13%, after 3 h of the reaction). However, the formation of the species. OOH is faster in the case of Ga^{3+} : after only 15 min there was a 12% yield of the internal epoxide with this metal (with a total yield of 13% i.e. 92% of total yield) whereas yield of the internal epoxide in the case of Al was 9% (and total 13%) or 69% of total yield. The use of carvone as molecule model for understanding the mechanism was useful in one experiment made in the presence of PCA. The results are shown in Fig. 5. PCA favored the formation of external epoxide, probably improving the generation of hydroxyl radicals, the main species responsible for the attack at the external double bond. On the other hand, the protons from carboxylic acid ($\text{p}K_a = 2.9$) could react the OOH^- anions, species responsible for the attack at the internal bond depressing the formation of the internal epoxide. This also confirms the mechanism proposed by Rinaldi et al [12].

2.3. Oxidation of limonene

Like carvone, terpene limonene also contains two double bonds: internal and external ones (Scheme 1). Table 1 summarizes the results on oxidation of limonene with both catalysts in two solvents. It can be seen that internal, external epoxides and diepoxides are produced in approximately equal yields. Yields of isomeric diols are 2–3 times higher than yield of each this product. Total yield of epoxides is lower than in the case of carvone containing electron-withdrawing carbonyl group.

**Scheme 1.** Oxidation of cyclooctene, carvone and limonene.**Table 1**
Oxidation of limonene with H₂O₂ catalyzed by gallium and aluminum nitrates.

Entry	Solvent	Catalyst	Internal epoxide	External epoxide	Diepoxide	Diol
1	Ethyl acetate	Ga(NO ₃) ₃	7	5	7	19
2	Ethyl acetate	Al(NO ₃) ₃	5	4	7	13
3	THF	Ga(NO ₃) ₃	4	5	6	19
4	THF	Al(NO ₃) ₃	3	4	5	9

Yield (%) is given based on starting limonene. Conditions. Limonene, 1.0 M; H₂O₂, 4.0 M; catalyst, 0.02 M. 80 °C, 3 h.

3. Conclusions

In olefin epoxidation with hydrogen peroxide gallium nitrate is more efficient in comparison with aluminum derivative. Additives of trifluoroacetic acid or pyrazine-2-carboxylic acid (PCA) accelerate the reaction. Noteworthy, that in striking contrast, added 2,2'-bipyridine or phenanthroline dramatically inhibit the oxidation.

4. Experimental

The experiments on olefin oxidations were carried out in acetonitrile in thermostated Pyrex cylindrical vessels (total volume 10 mL) with vigorous stirring. In a typical experiment, initially, a portion of the aqueous solution of H₂O₂ (aqueous 70% hydrogen peroxide, Solvay, solution was used as received) was added to the solution of a substrate, catalyst **1** (gallium nitrate) in acetonitrile. Catalyst **1** was used in the form of stock solutions in H₂O₂. (**CAUTION.** The combination of air or molecular oxygen and H₂O₂ with organic compounds at elevated temperatures may be explosive!). After certain periods, the reaction mixture was analyzed by GC using Shimadzu-HP 2010 gas chromatograph equipped with a polyethylene glycol column (Innowax, 25 m × 0.2 mm × 0.4 μm) coupled to the flame ionization detector and an automatic injector measuring concentrations of products. Authentic samples of all oxygenated products were used to attribute the peaks in chromatograms (comparison of retention times was carried out for different regimes of GC-analysis). The quantification of products was accomplished by constructing calibration curves for the products, by using standards of known

concentrations, and CH₃NO₂ as internal standard. The products formed from natural compounds were identified by using a gas chromatography coupled to a mass spectrometer (GC–MS) Shimadzu 2010-plus. The turbidity of the system was monitored using a turbidimeter PoliControl AP2000.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.molcata.2016.03.004>.

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