

Catalytic decomposition of dimethyldioxirane and cyclic acetone triperoxide in presence of polynuclear complexes of cobalt(II,III) and copper(II)

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Abstract

Dinuclear copper and cyclic trinuclear cobalt complexes with pyrazolate and OH⁻ bridges are able to decompose dimethyldioxirane in acetone, triggering radical reactions. Some products of reactions between organic substrates (cyclohexene or ethylbenzene) or acetone with secondary radicals formed from dimethyldioxirane: hydroxyl, methyl and acetomethyl, were identified and quantified. Tested complexes were also able to homolytically decompose cyclic acetone triperoxide and the radicals formed induced homolytic oxidation of cyclohexene producing 2-cyclohexen-1-ol and 2-cyclohexen-1-one at moderate yield.

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1. Introduction

Dioxiranes are well recognized oxidants acting both as oxygen-transfer agents [1–4] and one-electron oxidants [5]. The instability of dioxiranes in presence of transition metal ions has been experienced in many laboratories [2,3]. On the other hand, numerous efforts of using these oxidants in presence of metal ions were reported [5–11]. It has been demonstrated that dimethyldioxirane (DMD, **1**) was able to oxidatively decarbonylate LM(CO)₃ complexes (L = Tp or Cp*, M = Mo(0), Re(I)) with formation of TpMo(IV–VI) and Cp*Re(VII) oxenoids [6]. Metaloporphyrins were reported to form oxenoid forms of Fe(IV,V), Mn(IV), and Cr(IV) upon low temperature treatment with DMD [5,7]. Moreover, iron(III) and manganese(III) porphyrins assisted in chemoselective epoxidations of uracil and its derivatives [8]. Examples of oxidation of metal-coordinated phosphorus and sulfur with DMD were recently reviewed [8]. Typical examples of oxyfunctionalization of ligands in

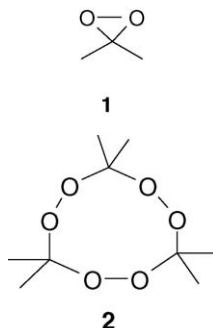
organometallic compounds are epoxidation of allyl and methallyl (R) complexes of TpW(O)₂R [9] and synthesis of epoxyferrocenes by selective oxygen transfer into cyclopentadienyl-appended acyl and allyl substituents [10]. The involvement of Jacobsen's Mn(III)salen catalyst in enantioselective 1a, 7a epoxidation of isoflavones with DMD was also reported [11].

Here, we have described some attempts to use DMD, **1** as oxygen atom transfer agent in presence of polynuclear cobalt and copper complexes of known structure [12,13]. We found that metal ions promoted radical decomposition of **1** instead of oxygen atom transfer to common organic substrates like cyclohexene. The products of radical reactions were analyzed and identified by GC method with MS and FID detections.

Additionally, we have tried to explore the ability of oxygen atom transfer from another oxygen-rich substrate, acetone triperoxide (**2**) in presence of those complexes. **2** was reported to form from DMD [1]. It was obtained for the first time by Wolfenstein [14] and later the structure of the compound was confirmed independently [15,16]. However, we have used another synthetic protocol based on oxidation of acetone by H₂O₂ in presence of sulfuric acid.

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We have found that **2** was partially decomposed in presence of trinuclear $(\text{DBM})_3(\text{pz})_4(\mu^3\text{-OH})\text{Co}_3$ (**3**) [12] and dinuclear $(\text{DBM})_2(\text{pz})(\mu^2\text{-OH})\text{Cu}_2$ (**4**) complexes [13] (DBM = dibenzoylmethanate and pz = pyrazolate anions) with minor oxygen transfer to cyclohexene.



2. Experimental

2.1. Syntheses

2.1.1. Dimethyldioxirane, **1**

1 has been synthesized by the method described in [1] and distilled as azeotrope with parent acetone. In typical procedure, the 0.06 M solutions were obtained based upon iodometric titration and used in oxidation experiment.

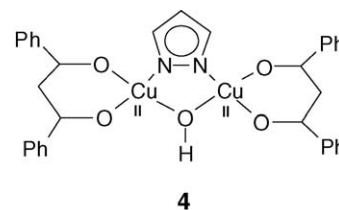
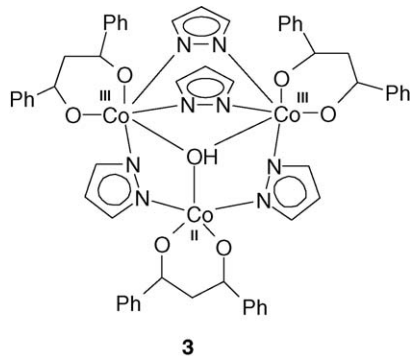
2.1.2. Cyclic acetone triperoxide, **2**

20 cm³ 24.6% aqueous hydrogen peroxide, 72 cm³ 96% H₂SO₄ and 10 cm³ acetone were stirred at room temperature for 24 h. Afterwards acetone was rotary evaporated at 25–30 °C and resulting white crystalline residue was filtered off, washed with water, divided into small portions (100 mg) and dried at room temperature. 4.82 g of **2** was obtained (47.8% yield at conversion of H₂O₂ at the level of 76.2% and selectivity calculated for consumed H₂O₂ equal to 53.7%). mp = 93–93.5 °C (lit.: 97 °C [13], 90–94 °C [14]), mass spectrum (ESI) revealed peak at *m/z* = 222, corresponding to (C₃H₆O₂)₃ (222.24).

Caution: **2** is potentially explosive and therefore it was stored in small portions.

2.1.3. Trinuclear $(\text{DBM})_3(\text{pz})_4(\mu^3\text{-OH})\text{Co}_3$ **3** and dinuclear $(\text{DBM})_2(\text{pz})(\mu^2\text{-OH})\text{Cu}_2$ **4** complexes

3 and **4** were synthesized as described before [12,13]. Schematic views of **3** and **4** are as follows:



2.2. Catalytic tests

Series of experiments of catalytic oxidation of cyclohexene and ethylbenzene with **1** and **2** in presence of trinuclear cobalt complex **3** and dinuclear copper complex **4** and their equimolar mixture were performed under nitrogen atmosphere. For comparison oxidation of cyclohexene with *tert*-butylhydroperoxide, TBHP in presence of **3**+**4** mixture was also tested. In some cases, kinetic runs were monitored by product determination in aliquots of reaction mixture. Products and unreacted substrates were identified by GC–MS method, and afterwards quantified by GC with FID detection and *n*-decane internal standard. Additionally unreacted TBHP, **1** and **2** were determined by iodometric titration. Details of catalytic experiments, including product yield, are collected in Table 1.

Two oxidants were added to reaction mixtures as stock solutions of **1** in acetone (typically 0.06 M, prepared and determined prior to use), 5 M solution of TBHP in decane or 1.4 M solution in chlorobenzene, obtained by extraction of TBHP from 70% aqueous solution into chloroform, addition of chlorobenzene and removal of chloroform on rotary evaporator. **2** was added as solid. Samples for GC–MS determination were obtained by low-temperature bulb-to-bulb distillation. Solid residues after catalytic runs were analyzed for recovery of **3** and **4** by ¹H NMR and UV–vis spectra, respectively, and the recovery was always found to be higher than 75%.

2.3. Instruments

Product analysis was performed on Hewlett-Packard (HP 5890 II) gas chromatograph equipped with flame ionization detector and mass detector (HP 5971 A). The 25 m long HP-5 columns were used in both cases. In some experiments, Agilent Technologies GC–MS instrument was used with 5890N chromatograph and 5973 model mass detector.

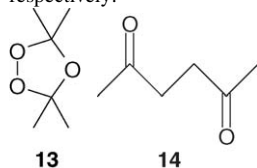
3. Results and discussion

Previously we have demonstrated moderate catalytic activity of trinuclear complex **3** in oxidation of cyclohexene with dioxygen or TBHP with formation of 2-cyclohexene-1-ol, **8** and 2-cyclohexene-1-one, **7** in chlorobenzene (see Chart 1). Here we used the same catalyst and tested its activity in oxygen atom transfer from DMD, **1** and cyclic acetone triperoxide, **2** in acetone. For comparison we have tested **3** with TBHP oxidant in acetone (Table 1, entry 1) and chlorobenzene (entry 2) and found that in acetone the major product of oxidation of cyclohexene with TBHP was **7**, opposite than in chlorobenzene. Moreover, some radical reaction was initiated in the system in acetone,

Table 1
Catalytic results

Entry	Catalyst (conc.)	Solvent	Temperature (°C)	Time of reaction (min)	Oxidant	Substrate	Products (% yields)
1	3 (5×10^{-4})	(CH ₃) ₂ CO	56	1360	TBHP (0.3 M)	5 (1.0 M)	7 (35); 9 (18); 6 (8); 8 (3)
2	3 (5×10^{-4})	PhCl	80	120	TBHP (0.3 M)	5 (1.0 M)	8 (33); 7 (17)
3	4 (5×10^{-4})	PhCl	80	120	TBHP (0.3 M)	5 (1.0 M)	No conversion
4	3 and 4 (5×10^{-4})	PhCl	80	120	TBHP (0.3 M)	5 (1.0 M)	9 (45); 7 (28)
5	3 (1.5×10^{-3})	(CH ₃) ₂ CO	25	15	1 (0.015 M)	5 (0.06 M)	7 (34)
6	4 (1.5×10^{-3})	(CH ₃) ₂ CO	25	15	1 (0.015 M)	5 (0.06 M)	8 (32)*
7	3 and 4 (1.5×10^{-3})	(CH ₃) ₂ CO	25	15	1 (0.015 M)	5 (0.06 M)	7 (34)*
8	None	(CH ₃) ₂ CO	25	15	1 (0.015 M)	5 (0.06 M)	6 (65)
9	3 (1.5×10^{-3})	(CH ₃) ₂ CO	25	120	1 (0.016 M)	10 (0.06 M)	11 (20); 12 (7); 13 ^a (17)
10	4 (1.5×10^{-3})	(CH ₃) ₂ CO	25	120	1 (0.016 M)	10 (0.06 M)	11 (22)
11	3 and 4 (1.5×10^{-3})	(CH ₃) ₂ CO	25	120	1 (0.016 M)	10 (0.06 M)	11 (24); 12 (7)
12	None	(CH ₃) ₂ CO	25	120	1 (0.016 M)	10 (0.06 M)	11 (21)
13	3 (5×10^{-4})	(CH ₃) ₂ CO	56	180	2 (0.3 M)	5 (1.0 M)	7 (50); 8 (18); 14 (20) ^b
14	4 (5×10^{-4})	(CH ₃) ₂ CO	56	180	2 (0.3 M)	5 (1.0 M)	7 (25); 8 (6); 14 (23) ^b
15	3 (5×10^{-4})	PhCl	80	180	2 (0.3 M)	5 (1.0 M)	No conversion
16	4 (5×10^{-4})	PhCl	80	180	2 (0.3 M)	5 (1.0 M)	7 (4); 8 (2); 14 (16) ^b
17	None	PhCl	80	180	2 (0.3 M)	5 (1.0 M)	No conversion

Yields of products were calculated in % of initial amount of oxidant. Superscript letters (a and b); **13** and **14** were found as product of conversion of **1** and **2**, respectively:



* Products of DMD decomposition were additionally found (see Section 3).

which resulted in formation of **9**. In order to enhance the radical pathway we applied also dicopper(II) catalyst **4**, which itself was not active in chlorobenzene (entry 3), but together with **3** it triggered the radical pathway, in which major product was **9** and only 28% of oxygen from TBHP was transferred into cyclohexene.

With these comparative results in hand we have tested **1** and **2** in acetone for oxygen transfer to cyclohexene (entries 5–8) and to ethylbenzene (entries 9–12). **1** is known to chemoselectively convert cyclohexene into epoxide [1–4]. On the other hand, **1** decomposes very fast in presence of “naked” transition metal ions, including cobalt(II) acetate. This powerful oxygen transfer agent converted **5** to **6** at room temperature within 15 min, while in presence of **3** and **4** the chemoselectivity was different to give **7** and **8** as major products, respectively. Mixture of **3** and

4 directed reaction towards **7** as product. When **4** was involved in those reactions (entries 6 and 7) the side-reactions took place and many products of methyl radical transfer into substrate (**15**) or solvent (**16**) and products of acetone addition to substrate (**17**) were identified based on GC–MS (at the level below 1% yield):

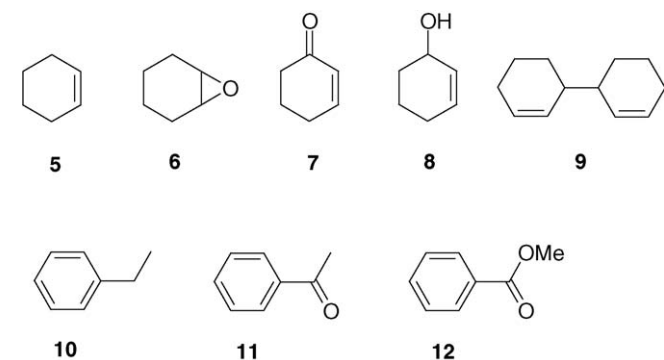
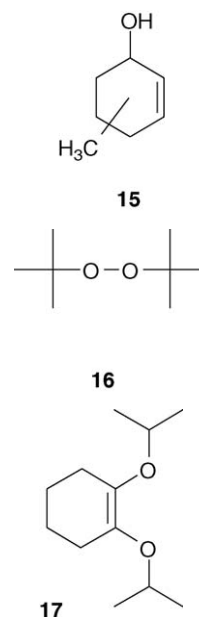
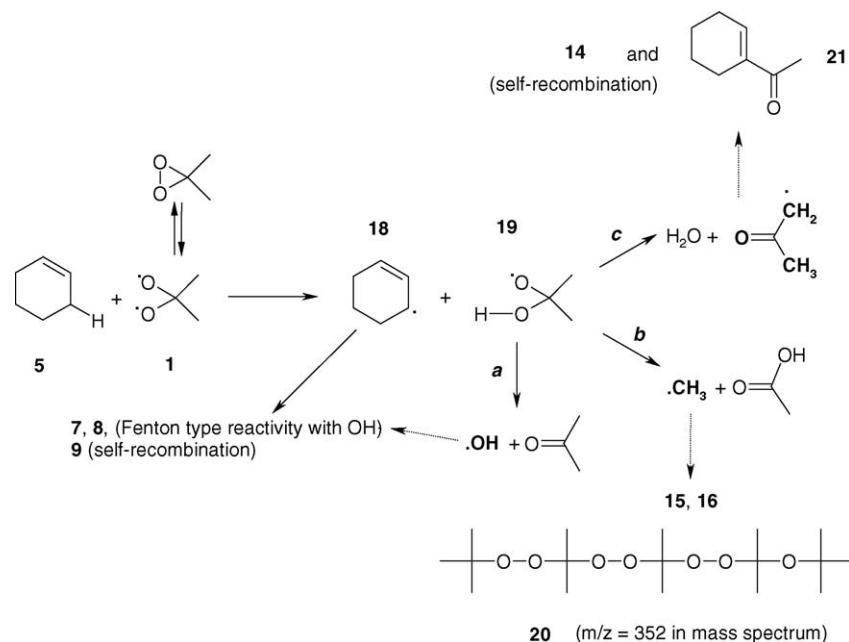


Chart 1.



Formation of those side-products as well as products of radical pathway of oxidation into **15** indicate that reactive species **19** is formed upon hydrogen abstraction from **5**, which is able to diffuse out of cage from cyclohexene radical **18** [17–19] and trigger its own chemistry, before in-cage rebound of **18** takes



Scheme 1.

place. The role of metal ion (both in **3** and **4**) is crucial in the rebound of **18** and in absence of metal ion only epoxide **6** is found. Intermediate **19** decomposes in at least three ways to produce: acetone and OH^\bullet radical (path a, at Scheme 1), CH_3^\bullet radical and acetic acid (path b), or $\text{CH}_3\text{C}(\text{O})\text{CH}_2^\bullet$ radical and water (path c), which are responsible for appearance of identified products: **7** and **8** from hydroxyl radical reactivity with **5** or **18**; **15**, **16**, and polymeric products containing *tert*-butoxy groups, like **20**, which was found in run 7 (entry 7 in Table 1) obtained from methyl radical and **14** as well as **21** (found in run 6)—the product of reaction between $\text{CH}_3\text{C}(\text{O})\text{CH}_2^\bullet$ radical and **5** or rearranged radical **18**.

When ethylbenzene **10** was applied as substrate, the major product was **11** in all cases, including uncatalyzed reaction (entry 12); the yields of substrate conversion were lower than for **5**, and reactive oxygen of **1** was not used to the end; the side-product **13** was found in post-reaction mixtures (entry 9). Generally, expected products of Fenton type reactivity of **10** were found in that series of experiments.

Yet another oxygen-reach substrate **2** was tested in acetone and chlorobenzene using the cyclohexene test (entries 13–17). **2** was stable in both solvents at elevated temperatures. However, it decomposed well in acetone in presence of any of two catalysts, demonstrated slight activity in oxidation of **5** resulting in formation of Fenton-type products **7** and **8**. Additionally, **2** indicated some abilities to abstract hydrogen from methyl group and formation of **14** was noticed.

In conclusion, we have found that dinuclear catalysts induce oxidation of cyclohexene with cyclic acetone triperoxide. The

same catalysts induce various radical pathways of decomposition of dimethyldioxirane.

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