

Multinuclear NMR spectroscopic characterization of Co(III) species: Key intermediates of cobalt catalyzed autoxidation

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Abstract

Using ¹H, ¹³C and ⁵⁹Co NMR spectroscopies, it was shown that, the so-called ‘Co(III) acetate’-reactive intermediate of cobalt acetate catalyzed autoxidation, is the mixture of the oxo-centered trinuclear cations [Co₃O(OAc)₆(AcOH)₃]⁺ (**I**) and [Co₃O(OAc)₅(OH)(AcOH)₃]⁺ (**II**) in 1:3–1:2 ratio. Cations **I** and **II** are the major species in the freshly prepared solutions of Co(III) acetate in CH₂Cl₂ and AcOH. Immediately after dissolving in MeOH, **I** converts into cation [Co₃O(OAc)₅(OMe)(MeOH)₃]⁺ and **II** into cation [Co₃O(OAc)₅(OH)(MeOH)₃]⁺. Reactivity of **I** and **II** towards *p*-xylene was determined. The addition of *p*-xylene to the sample containing **I** and **II** under anaerobic conditions in CH₂Cl₂ (1:3 *p*-xylene/CH₂Cl₂ by volume, 293 K) gave rise to gradual decrease of their concentration. The half-life was 2 h for cation **II** and 1.3 h for cation **I**. © 1998 Elsevier Science B.V.

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1. Introduction

Simple alkanes or alkylbenzenes can be selectively oxidized by molecular oxygen in AcOH with Co(OAc)₂ · 4H₂O as a starting material for the catalyst. It is generally agreed that active species of these oxidations are in situ formed Co(III) complexes formed in situ, so-called ‘cobaltic acetate’ [1,2]. However, despite numerous attempts, the structure of Co(III) acetate in solid or solution remains unknown [3–7].

Multinuclear NMR spectroscopies has opened up new avenues for the detailed characterization of Co(III) acetate in solutions. We have used

the ⁵⁹Co, ¹³C and ¹H NMR spectroscopy to characterize the structure and reactivity of Co(III) complexes, existing in Co(III) acetate ‘cobaltic acetate’ solutions in AcOH, CH₂Cl₂ and MeOH.

2. Experimental

Acetic acid, methanol, *p*-xylene and methylethylketone (MEK) were purified by standard techniques [8]. Commercial Co(OAc)₂ · 4H₂O, CD₃OD, CDCl₃, CD₂Cl₂ and 80% H₂O₂ were used without additional purification. Anhydrous 40% peracetic acid in AcOH was prepared from acetic anhydride and H₂O₂ [9]. Reactivity studies of Co(III) species with *p*-xylene were car-

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ried out under argon directly in NMR tubes at 293 K (CH_2Cl_2) or 373 K (AcOH). To start the reactions, the excess of *p*-xylene was added to the Co(III) acetate solutions to make 1:3 *p*-xylene/ CH_2Cl_2 or 1:1 *p*-xylene/AcOH volume mixtures. Concentration of Co(III) acetate was 50 mg per 1 ml of solution.

2.1. Synthesis of Co(III) acetate complexes

2.1.1. Method 1

2.5 g (10 mmol) of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ was dissolved in 200 ml of glacial acetic acid, and 6 g (30 mmol) of 40% peracetic acid was added dropwise. The color of the solution changed from crimson to green. The solvent was then removed under vacuum and the green solid obtained was used for further investigations. The adequate analysis of elemental analytical data for the samples of Co(III) acetate was complicated by difficult to control admixtures of AcOH and H_2O , greatly depended on the drying regime.

2.1.2. Method 2

The procedure was similar to that of method 1, only 50% HOAc was used instead of glacial acetic acid.

2.1.3. Method 3

The 'Co(III) acetate' species prepared according to methods 1 or 2, were dissolved in H_2O and heated at 383 K for 1 h. The solvent was removed then under vacuum and the green solid obtained was investigated further. The samples of Co(III) acetate prepared by methods 2 and 3, do not give reproducible elemental analytical data.

2.2. Methyl ethyl ketone (MEK) autoxidation

0.37 g (1.5 mmol) of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ was dissolved in 40 ml of glacial acetic acid and 5 ml MEK was added as a promoter. The solution was stirred in a flask equipped with a reflux condenser at 340 K while the oxygen gas was slowly bubbled through the solution. The color of the solution gradually turned dark green.

After 10 h of the oxidation the solution was cooled, the solvent and unreacted MEK (conversion was less than 30%) were removed under vacuum and the green solid was dissolved in AcOH and investigated by ^{59}Co NMR. The main product of MEK oxidation was acetic acid. Traces of the co-product $\text{CH}_3\text{COCH}_2\text{COOH}$ were also detected by ^1H NMR spectroscopy.

2.3. Nuclear magnetic resonance measurements

^{59}Co , ^{13}C and ^1H NMR spectra were recorded at 96.125, 100.58 and 400.13 MHz, respectively, using the pulsed FT NMR technique on a Bruker MSL-400 spectrometer. ^1H and ^{13}C spectra were obtained in 5 mm and 10 mm standard cylindrical tubes, respectively. ^{59}Co spectra were obtained with 10 mm cylindrical tubes (1.5–2.0 ml sample volume). To increase the sensitivity of the ^{59}Co NMR measurements, a high power probe head was used. The operating conditions were as follows: 400 kHz sweep width, 50 Hz spectrum accumulation frequency, 3000–60 000 number of scans. The data were accumulated with 512 data points in the time domain and were transformed with the optimal exponential multiplication of 100–500 Hz. Chemical shifts were calculated in ppm with positive values in the low-field direction with respect to the references: external $\text{Co}(\text{acac})_3$ in CHCl_3 for ^{59}Co (no correction for magnetic susceptibility was done), internal TMS for ^1H and ^{13}C . To obtain ^{59}Co chemical shifts with respect to commonly used reference $\text{Co}(\text{CN})_6^{3-}$, 12 500 ppm should be added to our values. The error in ^{59}Co chemical shift values was ± 10 ppm for the line width around 5 kHz and ± 100 ppm for the line width around 50 kHz.

3. Results and discussion

3.1. Co(III) acetate in MeOH

Using ^{59}Co and ^1H NMR spectroscopies, three main types of the diamagnetic Co(III) com-

plexes (A, B, C) were observed in solutions of Co(III) acetate in methanol. 5 min after dissolving Co(III) acetate (prepared by method 2) in MeOH, complexes A and B were observed in ^{59}Co and ^1H NMR spectra. Complex B slowly converts with time into complex A ($t_{1/2}$ about 15 min at 293 K) (Fig. 1). The concentration of complex C was low in the freshly prepared samples. Heating Co(III) acetate samples (prepared by method 1 or 2) for 5 min at 323 K gave rise to disappearance of ^{59}Co resonances of complexes A and B and to increase of that of complex C at 1250 ppm ($\Delta\nu_{1/2} = 3$ kHz). Complex C is not the sole product of complexes A and B decomposition. A number of paramagnetically shifted resonances different from those of Co(II) acetate were observed in the ^1H NMR spectrum of Co(III) acetate after heating the sample in MeOH. These paramagnetically shifted resonances probably belong to mixed valence Co(III)–Co(II) species. The structures

of these species and that of complex C are still unclear.

3.1.1. Complex A, $[\text{Co}_3\text{O}(\text{OAc})_5(\text{OMe})(\text{MeOH})_3]^+$

Two resonances (at 850 ppm ($\Delta\nu_{1/2} = 5$ kHz) and 680 ppm ($\Delta\nu_{1/2} = 10$ kHz)) with relative intensities 2:1 correspond to complex A in the ^{59}Co NMR spectrum (Fig. 1). These resonances belong to two equivalent and one unique cobalt atoms.

The characteristic pattern (at 2.38 (s, 3H), 2.33 (s, 6H) and 2.05 (s, 6H), δ , CD_3OD) attributed to complex A in the ^1H NMR spectrum (Fig. 1) is similar to that of the acetate ligands of trinuclear cation $[\text{Co}_3\text{O}(\text{OAc})_5(\text{OMe})(\text{Py})_3]^+$ with the known structure [10]. The corresponding resonances of $[\text{Co}_3\text{O}(\text{OAc})_5(\text{OMe})(\text{Py})_3][\text{PF}_6]$ in CD_3CN from two sets of two equivalent acetate ligands and one unique acetate ligand were observed at 2.19 (s, 3H), 2.17 (s, 6H), 1.89 (s, 6H) [10]. Note that the differences in chemical shifts between the resonances of complex A (0.05 and 0.28 ppm) are close to the differences of those of $[\text{Co}_3\text{O}(\text{OAc})_5(\text{OMe})(\text{Py})_3][\text{PF}_6]$ (0.02 and 0.28 ppm) [10].

Three additional resonances appear in the ^1H NMR spectrum of complex A when CH_3OH was used instead of CD_3OD as a solvent. They belong to one bridging OMe-group (at 1.33 (s, 3H)), two equivalent (at 3.52 (s, 6H)) and one unique (at 3.76 (s, 3H)) axial methanol molecules. In agreement with this assignment, the unusually low value of chemical shift for μ -OMe group (0.76 ppm) was observed for $[\text{Co}_3\text{O}(\text{OAc})_5(\text{OMe})(\text{Py})_3][\text{PF}_6]$ [10].

Thus, complex A is a trinuclear cation $[\text{Co}_3\text{O}(\text{OAc})_5(\text{OMe})(\text{MeOH})_3]^+$. The role of a counter ion can be played by, OAc^- , which is in fast exchange with AcOH liberated from the sample in MeOH. The ^1H NMR resonance of OAc^-/AcOH is highly broadened by paramagnetic Co(II) impurities and is not observed in Fig. 1.

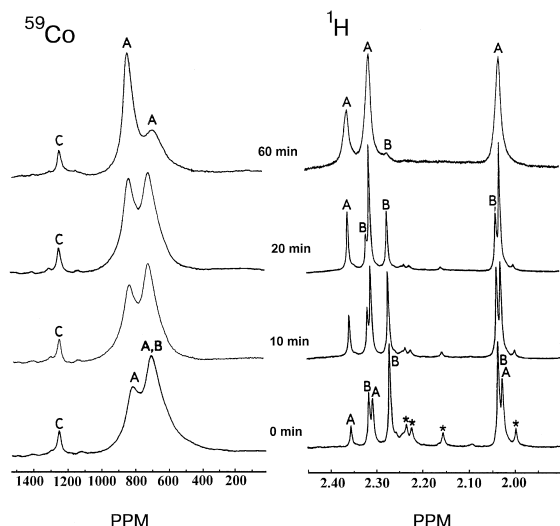


Fig. 1. ^{59}Co and ^1H NMR spectra of Co(III) acetate (method 2) in CD_3OD at various lengths of time after the dissolving of 30 mg of Co(III) acetate in 1 ml of CD_3OD . ^{59}Co NMR spectra were recorded at 96.12 MHz, spectrum accumulation frequency 50 Hz, sweep width 400 kHz, number of scans 10000, chemical shifts were calculated with respect to $\text{Co}(\text{acac})_3$.

3.1.2. Complex B, $[Co_3O(OAc)_5(OH)(MeOH)_3]^+$

Complex **B** exhibits a characteristic pattern (at 2.34 (s, 3H), 2.29 (s, 6H) and 2.06 (s, 6H), δ , CD_3OD) in the 1H NMR spectrum (Fig. 1). The ^{59}Co resonance of complex **B** (≈ 700 ppm ($\Delta\nu_{1/2} = 7$ kHz)) is close to that of complex **A** (Fig. 1). Complex **B** converts to complex **A** in CH_3OH with time (Fig. 1). Probably, complex **B** is a cation $[Co_3O(OAc)_5(OH)(MeOH)_3]^+$, and conversion of complex **B** to complex **A** is caused by the displacement of OH^- by OMe^- . The substitution of $\mu-OH$ group by $\mu-OR$ in ROH was reported for $[Co_3O(OAc)_5(OH)(Py)_3]^+$ [11,12]. We could not observe two separate resonances in the ^{59}Co NMR spectrum of complex **B** as in the case of complex **A**. Probably, the 2:1 ^{59}Co resonances of complex **B** are too close to be distinguished at the existing line widths.

3.2. Co(III) acetate in CH_2Cl_2 ($CHCl_3$)

^{59}Co , ^{13}C (CH_2Cl_2) and 1H ($CDCl_3$) NMR spectra of the freshly prepared sample of Co(III) acetate (method 1) show that two types of the diamagnetic Co(III) complexes (**I** and **II**) predominate in solution (Fig. 2). For most samples

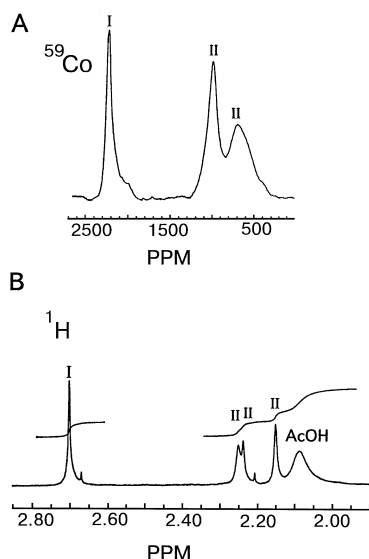


Fig. 2. ^{59}Co and 1H NMR spectra of Co(III) acetate in CH_2Cl_2 and $CDCl_3$, respectively.

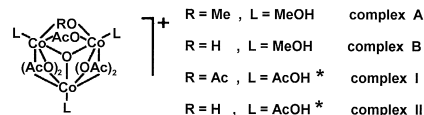


Fig. 3. The structures of Co(III) trinuclear cations **A**, **B**, **I** and **II**.

the ratio $[I]/[II]$ was 1:2–1:3. The choice of solvents for recording of ^{59}Co , ^{13}C and 1H NMR spectra was determined by good solubility of Co(III) acetate in CH_2Cl_2 and by good resolution of the 1H resonances of complex **II** in $CDCl_3$. There was no fundamental difference between 1H NMR spectra of Co(III) acetate in CD_2Cl_2 and $CDCl_3$. However, in $CDCl_3$ the 1H NMR lines of complex **II** were resolved better.

The sample prepared by method 2 was insoluble in CH_2Cl_2 or $CDCl_3$ and was further studied in AcOH (see below).

Complex **I** exhibits one resonance in both ^{59}Co (at 2200 ppm ($\Delta\nu_{1/2} = 5.2$ kHz)) and 1H (at 2.71 ppm) NMR spectra (Fig. 2). $^{13}C\{^1H\}$ NMR spectrum of complex **I** exhibits two resonances at 191.97 ppm (COO) and 27.05 ppm (CH_3).

Complex **II** exhibits two resonances in the ^{59}Co spectrum (at 1000 ppm ($\Delta\nu_{1/2} = 10$ kHz) and 700 ppm ($\Delta\nu_{1/2} = 22$ kHz)) and three resonances with relative intensities 2:1:2 (at 2.25, 2.23, 2.14 ppm) in the 1H NMR spectrum (Fig. 2).

$^{13}C\{^1H\}$ NMR spectrum of complex **II** consists of two sets of three resonances. One set with relative intensities 2:1:2 (at 191.27, 190.44, 190.26 ppm) belongs to COO^- groups, another with relative intensities 2:2:1 (at 26.76, 24.31, 23.96 ppm) to CH_3 groups of bridging acetate ligands.

Most probably, complex **I** is the trinuclear cation $[Co_3O(OAc)_6(AcOH)_3]^+$ with equivalent bridging acetate ligands and complex **II** is the trinuclear cation $[Co_3O(OAc)_5(OH)(AcOH)_3]^+$ with two sets of two equivalent bridging acetate ligands and one unique bridging acetate ligand (see also Fig. 3). The role of counter ions can be played by AcO^- anions. Alternatively, one of the axial ligands could be the OAc^- -anion. In

this case the protons of the two remaining axial AcOH molecules should be in fast exchange (in the NMR time scale) between all three axial ligands to keep the observed magnetic symmetry. The AcO^- axial ligand or counter ion, and the axial AcOH molecules of complexes **I** and **II** give a broad resonance at 2.09 ppm in the ^1H NMR (Fig. 2) and two broad resonances at 177.5 ppm (COO^-) and 22.7 ppm (CH_3) in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum. The integral intensity of the resonance at 2.09 ppm in Fig. 2 can fit with the expected values for both versions of axial coordination for complexes **I** and **II**. To choose between the alternatives, the conductivity measurements of the CH_2Cl_2 and AcOH solutions of Co(III) acetate (prepared by method 1) were performed. The conductivity was 82 μS for 5.22 mg per 1 ml of CH_2Cl_2 solution (356 μS for 35.04 mg per 1 ml of CH_2Cl_2), and 200 μS for 5.80 mg per 1 ml of AcOH solution. The conductivities of pure solvents CH_2Cl_2 , AcOH, their mixtures, and AcOH– H_2O system (up to 2% H_2O) were negligible and that of 6.80 mg $\text{Co}(\text{OAc})_2 \cdot 4 \text{H}_2\text{O}$ per 1 ml of AcOH solution was as low as 87 μS . The conductivity of well-dissociated $(\text{C}_8\text{H}_{17})_4\text{N}^+\text{Br}^-$ was 6330 μS for 3.05 mg per 1 ml of CH_2Cl_2 solution. All determined values were much lower than those typical for 1–1 electrolytes at the same molar concentration in water solutions, and that is characteristic for non-aqueous solutions. Thus, the conductivity data show that some quantity of ion-pairs dissociating to electric current conducting ions are present in Co(III) acetate solutions. However, the extent of the dissociation of the ion-pairs is difficult to evaluate and thus their concentration could not be calculated.

Note that in contrast to the case of methanol as a solvent, axial AcOH/AcO $^-$ ligands of complexes **I** and **II** are in fast exchange (in ^1H and ^{13}C NMR time scale) with free AcOH in solution. The resulting signals of axial AcOH/AcO $^-$ and free AcOH in the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra shift to the position of uncoordinated AcOH with the increase of AcOH

concentration in the sample. The reason for this variation in exchange behaviour could be the pronounced difference in the coordination strength of AcOH and MeOH as ligands. Besides, the ligand exchange can be catalyzed by Co(II) species always present in solution (via intermediate formation of labile Co(II) complexes [13–15]). The replacement of MeOH for AcOH could change both oxidation–reduction potentials and structural confinement of electron-exchanging Co(II) and Co(III) species.

The analysis of the ^{59}Co NMR spectra of one and the same sample of Co(III) acetate in CH_2Cl_2 and MeOH shows that complex **I** converts into complex **A**, and complex **II** into complex **B** immediately upon dissolving of Co(III) acetate in MeOH.

3.3. Co(III) acetate in AcOH

The sample of Co(III) acetate prepared by method 1 dissolved in AcOH exhibits resonances of complexes **I** and **II** in the ^{59}Co NMR spectrum. However, their ^{59}Co NMR resonances in AcOH ($\Delta\nu_{1/2} \approx 30\text{--}50$ kHz) are broader than those in CH_2Cl_2 . This effect is partially caused by the greater viscosity of AcOH with respect to CH_2Cl_2 . Because of the great linewidths, two ^{59}Co resonances of complex **II** were poorly resolved in AcOH, and one resulting line at ≈ 900 ppm was observed. The sample of Co(III) acetate prepared by method 3 shows an intensive line at 1200 ppm ($\Delta\nu_{1/2} = 15$ kHz) of complex **III** and small resonances of complexes **I** and **II** in the ^{59}Co NMR. Upon dissolution in MeOH, complex **III** converts into complex **C**. **III** is insoluble in CH_2Cl_2 and CHCl_3 . ^1H and ^{13}C NMR measurements were unfruitful for characterization of Co(III) complexes in AcOH because of line broadening. The structure of complex **III** is still unclear.

The growth of water concentration in AcOH would cause the conversion of complex **I** into complex **II**. The experimental data were in agreement with this suggestion. With the increase of water concentration the resonance of

complex **I** decreases and that of complex **II** increases. However, the situation was more complicated. The transformation of complex **I** to complex **II** occurred through the intermediate formation of intermediate complexes with resonances at 1600 and 1900 ppm in the ^{59}Co NMR spectrum. Most probably, this effect is caused by the replacement of axial AcOH ligands by H_2O ligands in the complex **I**. The similar spectra with the lines at 1600 and 1900 ppm were recorded for the sample prepared by method 2, where the substantial part of axial ligands was already H_2O molecules. Detection of the separate resonances at 1600 and 1900 ppm evidences that for complex **I**, the axial AcOH–axial H_2O ligand exchange process is slow in the ^{59}Co NMR time scale, unlike the axial AcOH-free AcOH ligand exchange in the ^1H and ^{13}C NMR time scale (see above).

We have not detected complexes with the lines at 1600 and 1900 ppm in CH_2Cl_2 as a solvent. Cobalt complexes precipitated upon water addition to CH_2Cl_2 solution. Probably, cobaltic complexes with axial H_2O ligands are insoluble in this solvent.

In the case of complex **II**, we did not observe the new ^{59}Co NMR resonances with the increase of water concentration in AcOH. However the resonance of complex **II** shifted upfield. This shift and the great line width can be explained by the assumption that the line of complex **II** in AcOH is unresolved mixture of the resonances of the type **II** complexes with various sets of axial H_2O or AcOH ligands.

3.4. Reactivity of complexes **I**, **II** and **III** towards *p*-xylene

Complexes **I** and **II** (the sample was prepared by method 1) are rather stable in CH_2Cl_2 . The concentration of complex **II** monitored by ^{59}Co NMR did not change significantly during a 24 h at 293 K. The concentration of complex **I** decreases slowly with a half-life of ca. 10 h.

The first step of the Co(III) acetate reaction with methylbenzenes is generally agreed to be

an electron transfer followed by deprotonation, or H-atom abstraction, to form the organic radical, which then converts into peroxyradical if molecular oxygen is present [1]. Under anaerobic conditions other radical reactions occur, giving usually acetoxy derivative ($\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{OOCCH}_3$ from *p*-xylene) as a main product. The chlorination of the methyl group (via Cl-atom abstraction) is a competitive major pathway in the chlorinated solvents [16].

The addition of *p*-xylene to solution of sample of Co(III) acetate prepared by method 1 in CH_2Cl_2 (1:3 *p*-xylene/ CH_2Cl_2 by volume, anaerobic condition, 293 K) gave rise to gradual decrease of complexes **I** and **II** concentrations. Insoluble $\text{Co}^{\text{II}}(\text{OAc})_2$ participated in the reaction. The products were $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{OOCCH}_3$ and $\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2\text{Cl}$ in 6:1 molar ratio (determined by NMR spectroscopy). The half-life was 2 h for complex **II** and 1.3 h for complex **I**. The observed small difference in the half-lives of complexes **I** and **II** can be explained by the conversion of complex **I** into complex **II** with the increase of water concentration in the course of the *p*-xylene oxidation. Further studies are needed to determine the real difference in reactivities of complexes **I** and **II** towards *p*-xylene.

Complex **III** (the sample prepared by method 3) did not interact with *p*-xylene at noticeable rate at 293 K in AcOH. To determine the reactivity of complex **III** towards *p*-xylene, the reaction was studied under argon at 373 K. The samples in pure acetic acid and in a 1:1 AcOH/*p*-xylene mixture were compared. The characteristic time of the reaction was 2 h at 373 K.

Note, complex **III** prevails among the other diamagnetic Co(III) species at high temperatures (373 K) in AcOH, these are conditions close to those for real oxidation. This does not mean that namely complex **III** drives the catalytic cycle of oxidation. Indeed, the ^{59}Co NMR spectrum of the sample of Co(III) acetate in AcOH, prepared in the course of MEK autoxidation (see Section 2) is very similar to the

spectrum of the sample prepared by method 2, i.e., complexes **I** and **II** were detected, but no signals of complex **III** were observed. Only after a 24 h storage of the solution at 293 K, did the line of complex **III** at 1200 ppm appeared. Thus, complexes **I** and **II** are recovered rapidly by peroxyradicals or peroxides in the course of MEK autoxidation at 340 K. Remember that complex **III** is less reactive towards *p*-xylene than complexes **I** and **II**. Thus, probably, complexes **I** and **II** mainly drive the catalytic cycle of MEK oxidation under these conditions.

Acknowledgements

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