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Characterization with ^{95}Mo, ^{17}O, ^{1}H NMR and EPR of alkylperoxo, alkoxo, peroxo and diolo molybdenum(VI) complexes formed in the course of catalytic epoxidation of cyclohexene with organic hydroperoxides

E.P. Talsi*, O.V. Klimov and K.I. Zamaraev*

Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, Prospekt Akademika Lavrentieva, 5, Novosibirsk 630090 (Russian Federation); tel. (+7-383)2355750, fax. (+7-383)2355756/5757/5766

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Abstract

Using ^{95}Mo, ^{1}H, ^{17}O NMR and EPR, we have characterized molybdenum(VI) complexes formed in the course of catalytic epoxidation of cyclohexene with *tert*-butyl and cumene hydroperoxides. Dioxobis(acetylacetonato)molybdenum(VI) and hexacarbonyl molybdenum(0) were used as starting materials for the catalysts. Six new molybdenum(VI) complexes (I-VI) were detected. Complexes I, II and III are formed when ROOH is added to solutions of $MoO_2(acac)_2$ in pure benzene. In benzene:cyclohexene:hydroperoxide mixtures complexes I-III are observed only at the initial stage of the epoxidation process. Then they are gradually replaced by complexes IV-VI that drive the catalytic cycle of epoxidation. NMR spectra of complexes IV-VI are the same, irrespective of whether $MoO_2(acac)_2$ or $Mo(CO)_6$ have been used as the starting material for the catalysts. On the basis of the ^{95}Mo, ^{1}H, ^{17}O NMR, EPR spectra and reactivity studies, the following compositions for I-VI are suggested: I is the alkylperoxo complex $MoO_2(OOR)_2$, II the alkoxo complex $MoO_2(OR)_2$, III the monoperoxo complex $MoO(O_2)(acac)_2$, IV and V are two types of MoO_2(1,2-diolo)$_2$ complexes (where 1,2-diolo is *trans*-cyclohexane-1,2-diol), and VI the alkylperoxo complex MoO_2(1,2-diolo)(OOR). The latter complex serves as the active particle of epoxidation.

Key words: alkylperoxo complexes; epoxidation; EPR; ^{1}H NMR; hydroperoxides; molybdenum; ^{95}Mo NMR; ^{17}O NMR

Introduction

Selective epoxidation of olefins with organic hydroperoxides catalyzed by molybdenum complexes (Halcon process) is an important industrial reaction [1,2]. Based on convincing kinetic data, alkylperoxo complexes of molybdenum(VI)are supposed to serve as active species of epoxidation [3-6]. However, in spite of numerous attempts, these species have been neither isolated,

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*Corresponding authors.

nor observed spectroscopically. In this work we report on the first spectroscopic detection and characterization with ^{95}Mo, ^{1}H, ^{17}O NMR and EPR of alkylperoxo complexes of Mo(VI). These complexes were detected and characterized *in situ* in the course of epoxidation of cyclohexene with *tert*-butyl and cumene hydroperoxides in the presence of dioxobis(acetylacetonato) molybdenum(VI) $MoO_2(acac)_2$ and hexacarbonyl molybdenum(0) $Mo(CO)_6$ as starting materials for the catalyst. Peroxo-, alkoxo- and diolo molybdenum(VI) complexes were also identified spectroscopically in the reaction solutions.

Experimental

Cyclohexene and benzene were purified according to the standard methods [7]. Benzene-d_6 and dioxane-d_8 were dried over sodium metal. Cumene and *tert*-butyl hydroperoxides were purified as described in ref. 8a. *trans*-Cyclohexane-1,2-diol was prepared according to ref. 8b. Butane-2,3-diol of pure grade was used without purification. $MoO_2(acac)_2$ was synthesized as described in ref. 9, dioxobis(diethyldithiocarbamato)molybdenum(VI) as described in ref. 10. $Mo(CO)_6$ of a pure grade was used without purification. Reactions were carried out by addition of pure ROOH to solutions of molybdenum complexes in benzene or benzene:cyclohexene mixtures. Experiments were carried out at 293–353 K either in closed vessels in air or directly in NMR tubes. Mixing of solutions of molybdenum complexes with organic hydroperoxides can cause vigorous heating which can eject solutions from the tubes in which they are mixed. To avoid this, hydroperoxides were added gradually in small portions. Oxidation products were identified according to their ^{1}H NMR spectra.

^{95}Mo, ^{17}O and ^{1}H NMR spectra were recorded at 26.026, 54.043 and 400.13 MHz, respectively, using the pulsed FT NMR technique, with a Bruker MSL-400 NMR spectrometer. Compounds with the natural abundance of ^{95}Mo (15.70%) and ^{17}O (3.7×10^{-2}%) were used in the ^{95}Mo and ^{17}O NMR studies. Deuterated solvents (benzene-d_6, dioxane-d_8) were used in the ^{1}H NMR studies. ^{1}H spectra were obtained in standard cylindrical 5 mm tubes. ^{95}Mo and ^{17}O spectra were obtained with cylindrical 10 mm tubes (1.3–1.5 cm^3 sample volume). A high power probe head was used for ^{95}Mo and ^{17}O NMR measurements to increase sensitivity [11]. The field homogeneity was adjusted by shimming on the ^{2}H resonance of $^{2}H_2O$. The homogeneity was not less than 10 Hz. Minor modification of standard probe head described in ref. 12 allowed us to work with liquid samples when gas is evolved during the measurements.

The following operating conditions were used for ^{95}Mo and ^{17}O NMR measurements: sweep width 80000 (^{17}O) and 50000 Hz (^{95}Mo); spectrum accumulation frequency 100 Hz (^{17}O) and 50 Hz (^{95}Mo); number of scans 3000–60000 (^{95}Mo), 60000–200000 (^{17}O); 90° radio frequency pulse at 13 (^{17}O) and

12 μs (^{95}Mo). The data were accumulated with 2K data points in the time domain and were transformed with optimal exponential multiplication (^{17}O, 50–100 Hz; ^{95}Mo, 10–50 Hz). Chemical shifts were calculated in ppm with positive values in the low-field direction with respect to the reference: TMS for ^{1}H, H_2O for ^{17}O, 2 M Na_2MoO_4 solution in D_2O for ^{95}Mo. The errors in measuring the ^{17}O and ^{95}Mo chemical shift values are ±1 ppm for a line width below 500 Hz, and that for measuring a line width is ±20 Hz for line widths between 100 and 400 Hz. The EPR spectra were recorded using a Bruker-ER-200D spectrometer. The concentration of paramagnetic centers was measured by comparing the second integrals of the EPR spectra of the sample of interest and the reference: a 0.1 mg crystal of $CuCl_2 \cdot 2H_2O$.

Results

Reaction of $MoO_2(acac)_2$ with tert*-butyl and cumene hydroperoxides in benzene*

^{95}Mo nuclear magnetic resonance

For mononuclear diamagnetic species, the ^{95}Mo NMR chemical shift varies with the oxidation state of molybdenum atom in the following way: Mo(VI), from 3200 to −200 ppm; Mo(IV), from −300 to −3000 ppm; Mo(II), from −100 to 2072 ppm; Mo(0), from −770 to −2200 ppm [13a].

The initial complex $MoO_2(acac)_2$ in benzene exhibits an ^{95}Mo spectrum that is a singlet line with $\delta = 6$ ppm and a width at half of the height $\Delta\nu_{1/2} = 130$ Hz. After adding pure Me_3COOH (to make its concentration $[Me_3COOH] = 0.1$ M) to the 0.05 M solution of $MoO_2(acac)_2$ in benzene at 293 K, two weak additional signals become observed. One of them at $\delta = 31$ ppm, $\Delta\nu_{1/2} = 150$ Hz, corresponds to complex **I**, and the other at $\delta = 42$ ppm, $\Delta\nu_{1/2} = 200$ Hz, to complex **II** (see Fig. 1a). Upon addition of a further portion of pure Me_3COOH (to make $[Me_3COOH] = 0.3$ M*) to the sample of Fig. 1a, the intensity of line **I** increases while line **II** disappears (Fig. 1b). Upon subsequent keeping of the sample at 293 K, the concentration of complex I diminishes with time (Fig. 1b–d). When the next portion of pure Me_3COOH (to make $[Me_3COOH] = 1$ M*) is added to the sample of Fig. 1d, the signal of complex I reappears and the signal of the new complex, **III** ($\delta = -116$ ppm, $\Delta\nu_{1/2} = 100$ Hz), becomes observed (Fig. 1e).

The situation changes dramatically when $PhMe_2COOH$ is used instead of Me_3COOH. After the addition of pure $PhMe_2COOH$ (to make $[PhMe_2COOH] = 0.1$–1 M) to the 0.05 M solution of $MoO_2(acac)_2$ in benzene at 293 K, almost all the initial $MoO_2(acac)_2$ transforms gradually into complex **III** (Fig. 2a–c). The rate of this transformation increases with the increase of

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*The previously added portion of this reagent is not taken into account when calculating this concentration.

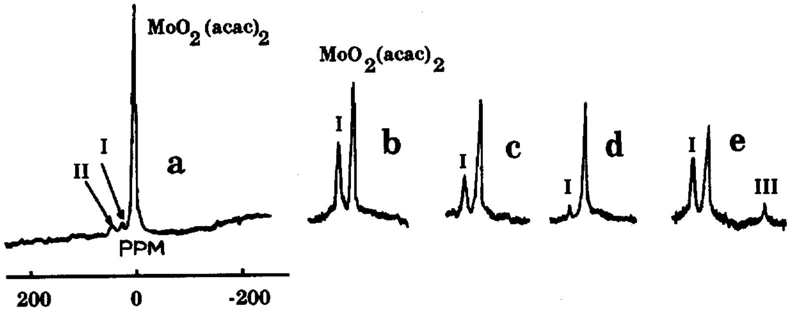


Fig. 1. (a) ^{95}Mo NMR spectrum of 0.05 M $MoO_2(acac)_2$ in benzene recorded 3 min after pure Me_3COOH (to make $[Me_3COOH]=0.1$ M) was added at 293 K. (b-d) Spectra of sample in (a) recorded after various lengths of time after the addition at 293 K of a fresh portion of pure Me_3COOH (to make $[Me_3COOH]=0.3$ M*): (b) 3, (c) 6, (d) 17 min. (e) Spectrum of sample in (d) 3 min after the addition at 293 K of a further portion of Me_3COOH (to make $[Me_3COOH]=1$ M*). All spectra were recorded at 293 K. Spectra accumulation frequency 50 Hz; number of scans 5000.

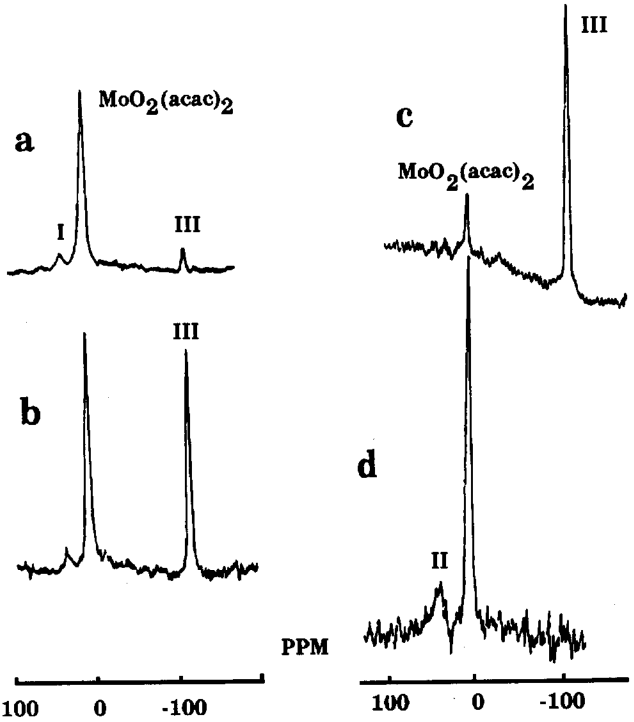


Fig. 2. (a-c) ^{95}Mo NMR spectra of 0.05 M $MoO_2(acac)_2$ in benzene recorded after various lengths of time after the addition at 293 K of pure $PhMe_2COOH$ (to make $[PhMe_2COOH]=0.7$ M): (a) 2, (b) 7, (c) 20 min. (d) ^{95}Mo NMR spectrum of 0.05 M $MoO_2(acac)_2+3$ M C_6H_{10} in benzene, recorded 10 min after the addition at 293 K of pure $PhMe_2COOH$ (to make $[PhMe_2COOH]=1$ M). All spectra were recorded at 293 K. Spectra accumulation frequency 50 Hz; number of scans 5000.

$PhMe_2COOH$ concentration. The small line of complex **I** is also observed at the initial step of the reaction (Fig. 2a–b) but disappears with time (Fig. 2c). Note, that the recording of ^{95}Mo NMR spectra of $MoO_2(acac)_2$ in benzene is complicated by the precipitation of much of the molybdenum complexes after adding ROOH ($R=Me_3C$, $PhMe_2C$) at 293 K. Fortunately, this precipitation was not observed in the presence of the oxidized substrate, cyclohexene, *i.e.* under the conditions of the epoxidation reaction (see below).

^1H nuclear magnetic resonance

The ^1H NMR spectrum of $MoO_2(acac)_2$ in benzene consists of three lines, at 5.116, 1.588, 1.536 ppm with relative intensities 1:3:3, which are attributed to the CH and CH_3 protons of acetylacetonato ligands. After adding pure Me_3COOH (to make $[Me_3COOH]=1$ M) to the 0.01 M solution of $MoO_2(acac)_2$ in benzene at 293 K, the intensity of the lines of $MoO_2(acac)_2$ decreases and new lines appear (Fig. 3). Two lines with relative intensities 1:6 (at 4.91 and 1.578 ppm) can be assigned to the non-coordinated acetylacetone. The intensive singlet line at 2.086 ppm is attributed to complex **I**, since its intensity changes with time in the same way as the intensity of the line of complex **I** in the ^{95}Mo NMR spectra. No other lines whose intensities could correlate with the intensity of the 2.086 line, were observed. Thus, most probably, complex **I** contains only one type of organic ligand, which exhibits a singlet line in the ^1H NMR spectra.

The concentration of complex **II** in pure benzene was too low to identify the lines of this complex in the ^1H NMR spectra. This will be done below for benzene solutions containing cyclohexene, where the concentration of complex **II** is high.

The ^{95}Mo and ^1H NMR spectra of complex **III** are presented in Fig. 4. As can be seen from the ^{95}Mo NMR spectra of Fig. 4A, complex **III** can also be obtained by treating $MoO_2(acac)_2$ solution in benzene with 30–60% H_2O_2 (Fig. 4A-b) or by adding 60% H_2O_2 (to make $[H_2O_2]=0.10$ M) into 0.10 M $MoO_2(acac)_2$ solution in dioxane (Fig. 4A-c). In the ^1H NMR spectrum in

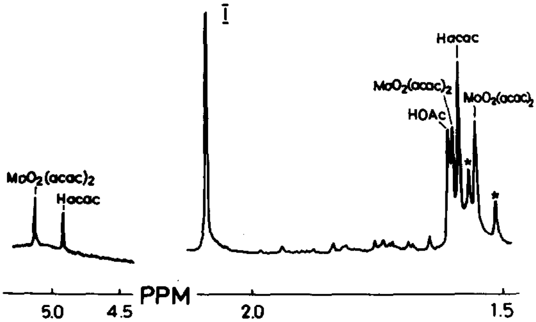


Fig. 3. ^1H NMR spectrum of 0.01 M $MoO_2(acac)_2$ in benzene-d_6 recorded at 293 K 10 min after the addition of pure Me_3COOH (to make $[Me_3COOH]=0.5$ M).

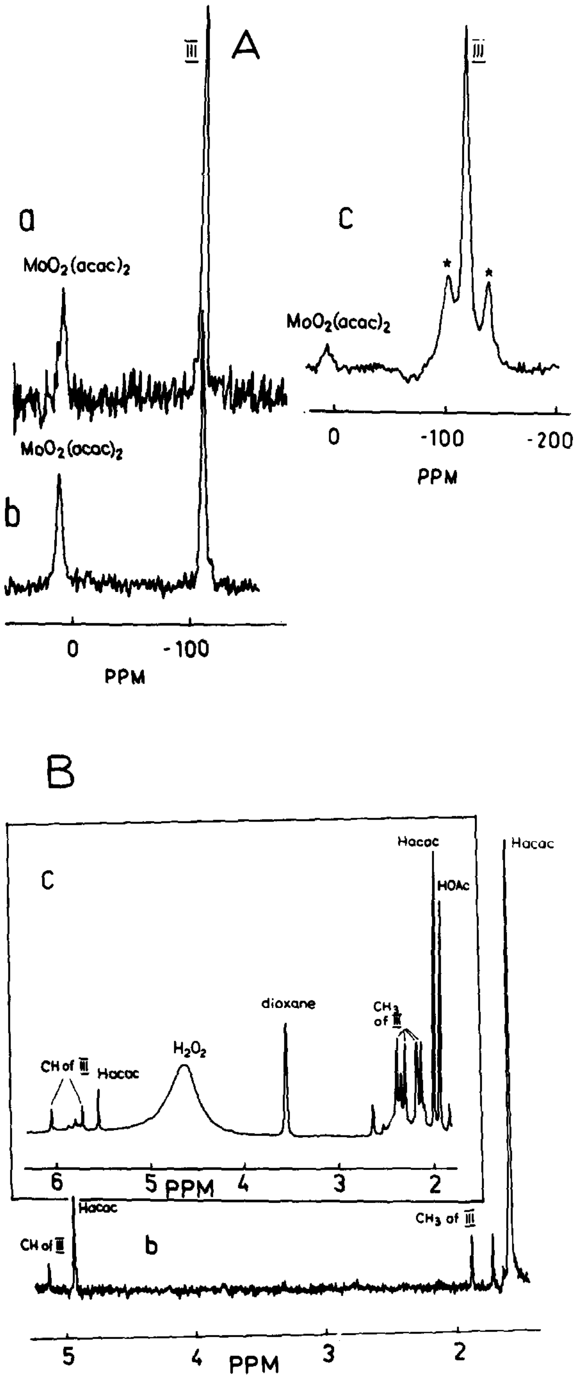


Fig. 4. (A) ^{95}Mo NMR and (B) ^{1}H NMR spectra of complex III prepared by various procedures: (a) 10 min after addition of pure $PhMe_2COOH$ (to make $[PhMe_2COOH]=1$ M) to 0.05 M $MoO_2(acac)_2$ in benzene-d_6 at 293 K; (b) 10 min after treating 1 ml of 0.05 M $MoO_2(acac)_2$ in benzene-d_6 with 0.1 ml of 60% H_2O_2 at 293 K; (c) 10 min after the addition of 60% H_2O_2 (to make $[H_2O_2]=0.1$ M) to 0.1 M $MoO_2(acac)_2$ in dioxane-d_8. All spectra were recorded at 293 K. For ^{95}Mo NMR: accumulation frequency 50 Hz; number of scans 5000.

benzene-d_6, complex **III** exhibits three signals (at 5.13, 1.87 and 1.71 ppm) with the relative intensities 1:3:3 from acetylacetonato ligands (Fig. 4B-b). However in dioxane-d_8 all CH and CH_3 groups of acetylacetonato ligands of complex **III** are non-equivalent, and six lines with relative intensities 1:1:3:3:3:3 are observed (Fig. 4B-c). Thus, complex **III** contains two acetylacetonato ligands.

^{17}O nuclear magnetic resonance

The ^{17}O NMR spectrum of 0.05 M solution of $MoO_2(acac)_2$ in benzene consists of three lines of equal integral intensity. On the basis of its chemical shift [13b], the line at 1037 ppm with $\Delta\nu_{1/2}=200$ Hz can be attributed to the oxygen atoms of two M=O groups, and the lines at 334 and 248 ppm with $\Delta\nu_{1/2}=400$ Hz to the oxygen atoms of acetylacetonato ligands (Fig. 5a). The two other lines are attributable to free acetylacetone in the enol and keto forms.

We have been able to observe two ^{17}O lines in the spectrum of complex **III** obtained by treating a solution of 0.05 M $MoO_2(acac)_2$ in benzene with 60%

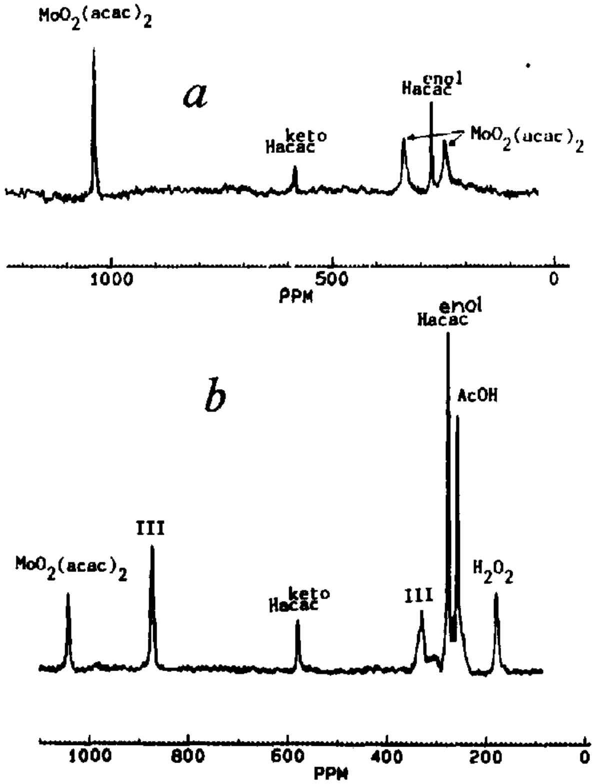


Fig. 5. ^{17}O NMR spectra of: (a) 0.05 M $MoO_2(acac)_2$ in benzene; (b) complex **III** prepared by treating 0.05 M $MoO_2(acac)_2$ in benzene with 60% H_2O_2. The spectra were recorded at 293 K. Spectrum accumulation frequency 100 Hz; number of scans 200000.

H_2O_2 (Fig. 5b). On the basis of its chemical shift [13b], the line at 872 ppm is attributable to the M=O group, whereas that at 328 ppm is attributable to the oxygen atoms of the acetylacetonato ligands of complex **III**. One more line from the oxygen atoms of the acetylacetonato ligands of **III** is, perhaps, masked by the lines of acetylacetone, in the enol form, and acetic acid.

During the reaction between $MoO_2(acac)_2$ and Me_3COOH in benzene at 293 K, the ^{17}O NMR lines from reagents decrease and those from non-coordinated acetylacetone (274 ppm) and *tert*-butanol (63 ppm) increase. The acetylacetone is partly oxidized with time into acetic acid, which exhibits the signal at 263 ppm.

The ^{17}O NMR lines from complexes **I** and **II** were not detected. However, the ^{17}O NMR chemical shifts for both oxygen atoms of Me_3COOH change noticeably in the presence of $MoO_2(acac)_2$. For example, in benzene solutions containing no $MoO_2(acac)_2$ the ^{17}O chemical shifts of the Me_3CO and OH groups are 252 and 200 ppm, respectively. But in the initial stage of the reaction between Me_3COOH and $MoO_2(acac)_2$, in benzene solutions containing 0.05 M $MoO_2(acac)_2$ and 1 M Me_3COOH, the shift of the Me_3CO group decreases to 247 ppm, whereas that of the OH group increases to 207 ppm (the accuracy of the chemical shift measurements is ±1 ppm). This change in the ^{17}O chemical shift is evidence for the coordination of Me_3COOH to $MoO_2(acac)_2$ with the fast (in the ^{17}O NMR time scale) exchange of Me_3COOH molecules between the coordinated-to-molybdenum state and free state in the solution.

Electron paramagnetic resonance

The EPR spectra of 5×10^{-3}–5×10^{-2} M $MoO_2(acac)_2$ in benzene exhibit no signals of paramagnetic centers. After the addition of Me_3COOH (to make $[Me_3COOH]=1$ M) to this solution a weak signal of the $Me_3COO^{\cdot}$ free radical (concentration $(2–3)\times10^{-5}$ M) is observed. The intensity of this signal is consistent with the intensity of the lines of complex **I** in the ^{95}Mo and ^{1}H NMR spectra. This suggests that the $RO_2^{\cdot}$ radical is in an equilibrium with **I**. When Me_3COOH is replaced by $PhMe_2COOH$, the concentration of complex **I** becomes very low, as was described above. In agreement with this, the concentration of the $RO_2^{\cdot}$ radical in the case of $PhMe_2COOH$ is at least 10 times smaller than in the case of Me_3COOH.

Reaction of $MoO_2(acac)_2$ and $Mo(Co)_6$ with tert-*butyl and cumene hydroperoxides in benzene:cyclohexene mixtures*

^{95}Mo nuclear magnetic resonance

The ^{95}Mo NMR spectrum of the solution of $MoO_2(acac)_2$ in benzene:cyclohexene mixtures containing up to 6 M of cyclohexene is the same as in pure benzene. However in contrast to the previous "$MoO_2(acac)_2+Me_3COOH$ in pure benzene" system, in benzene containing 1–2 M cyclohexene, complex **I** is observed only in the early stage of the reaction between $MoO_2(acac)_2$ and Me_3COOH and its concentration is very small.

When concentration of cyclohexene exceeds 3 M, the ^{95}Mo NMR line of complex **I** is not observed at all.

The ^{95}Mo NMR spectrum recorded 15 min after the addition at 293 K of pure Me_3COOH (to make $[Me_3COOH]=0.3$ M) to the 0.05 M $MoO_2(acac)_2$ in benzene containing 1.2 M cyclohexene is presented on Fig. 6a. This spectrum remained unchanged when the sample was kept at 293 K for 1 h.

The signals from complexes **II** and **III** and from two new complexes, *i.e.* **IV** ($\delta=56$ ppm, $\Delta\nu_{1/2}=250$ Hz) and **V** ($\delta=277$ ppm, $\Delta\nu_{1/2}=100$ Hz) are seen in Fig. 6a. Heating the sample of Fig. 6a for 3 min at 353 K gives rise to a significant increase of the concentration of $MoO_2(acac)_2$ and decrease of the concentration of all other complexes (Fig. 6b). This increase of the $MoO_2(acac)_2$ concentration after heating the sample prepared at 293 K is observed only with a rather small initial concentration of Me_3COOH. When the

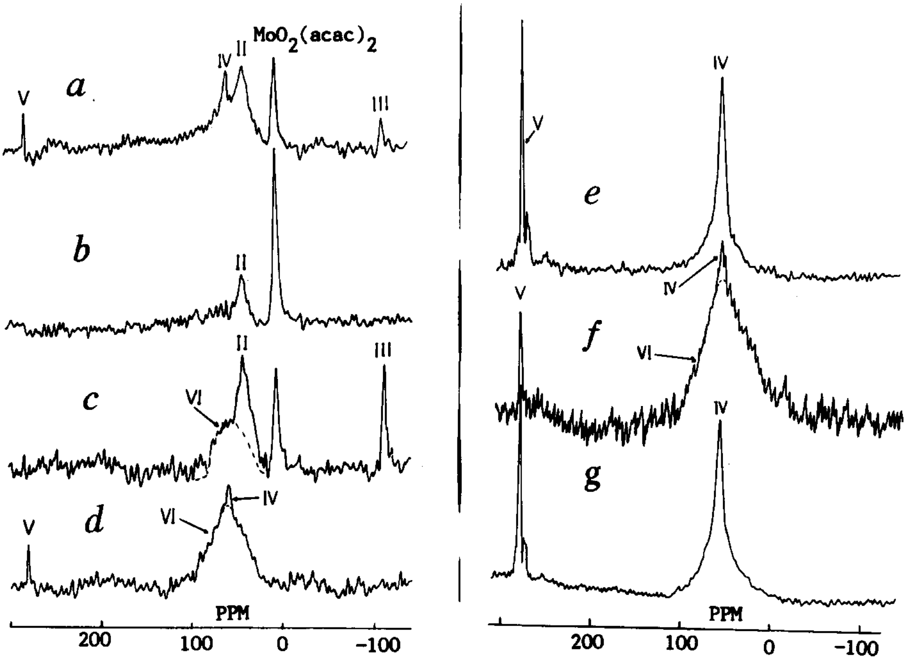


Fig. 6. ^{95}Mo NMR spectra of samples prepared by various treatments of 0.05 M $MoO_2(acac)_2$ in benzene containing initially 1.2 M cyclohexene: (a) Spectrum recorded 15 min after the addition at 293 K of pure Me_3COOH (to make $[Me_3COOH]=0.3$ M); (b) spectrum recorded 5 min after heating sample in (a) at 353 K for 3 min; (c) spectrum recorded 5 min after the addition at 293 K of a further portion of Me_3COOH (to make $[Me_3COOH]=1.5$ M*) to sample in (b). (d) Spectrum recorded 3 min after heating sample in (c) at 353 K for 2 min; (e) spectrum recorded 3 min after the addition of the new portion of cyclohexene (to make [cyclohexene] = 2 M*) to sample (d) and heating at 353 K for 1 min; (f) spectrum recorded 3 min after the addition at 353 K of a further portion of Me_3COOH (to make $[Me_3COOH]=2$ M*) to sample (e); (g) spectrum recorded after heating sample in (f) at 353 K for 3 min. All spectra were recorded at 293 K. Spectrum accumulation frequency 50 Hz; number of scans 20000-60000.

Me_3COOH concentration exceeds 1 M, only the increase of the concentration of complex **II** with respect to the concentrations of complexes **III**, **IV** and **V** is observed after such heating. After addition of the next portion of Me_3COOH (to make $[Me_3COOH] = 1.5$ M *) to the sample of Fig. 6b, at 293 K, the concentration of $MoO_2(acac)_2$ decreases and those of complexes **II** and **III** increases (Fig. 6c). In addition, the broad line with $\Delta\nu \approx 1300$ Hz from the new complex **VI** is observed near 60 ppm. The shape of this line is indicated in Fig. 6c with the dotted line. Further heating of the sample of Fig. 6c for 3 min at 353 K gives rise to the disappearance of complexes **II**, **III** and $MoO_2(acac)_2$ (Fig. 6d). At the same time, the intensity of the line from complex **VI** sharply increases. The lines of complexes **IV**, **V** are also observed in Fig. 6d. Note, on the basis of ^1H NMR, in the sample of Fig. 6d practically all cyclohexene has already converted into cyclohexene oxide. Heating of the sample of Fig. 6d and the addition of further portions of Me_3COOH do not change its ^{95}Mo NMR spectrum.

It is very important to note that the addition of further portions of cyclohexene (to make [cyclohexene] = 2 M *) to the sample of Fig. 6d, and its subsequent heating for 1 min at 353 K cause the decrease of the concentration of complex **VI** and the increase of the concentrations of complexes **IV** and **V** (Fig. 6e). Thus, complex **VI** reacts with cyclohexene to yield complexes **IV** and **V**. After the addition, at 293 K, of a further portion of Me_3COOH (to make $[Me_3COOH] = 2.0$ M *) to the sample of Fig. 6e, the concentration of complexes **IV** and **V** decreases, and that of complex **VI** increases again (Fig. 6f). Thus, the addition, at 293 K, of Me_3COOH converts complexes **IV** and **V** back to complex **VI**. Heating the sample of Fig. 6f during 5 min at 353 K decreases the concentration of complex **VI** and again increases the concentration of complexes **IV** and **V** (Fig. 6g).

When Me_3COOH is replaced by $PhMe_2COOH$, the formation of complexes **II**, **IV**, **V** and **VI** from $MoO_2(acac)_2$ is also observed in the ^{95}Mo NMR spectra of the catalytic system "Mo(VI) + ROOH + cyclohexene in benzene". Within the accuracy of the measurements, no difference was detected in the ^{95}Mo NMR parameters of complexes **I–VI** prepared in the reaction with Me_3COOH and $PhMe_2COOH$.

Note, that in the absence of cyclohexene, complex **III** is the main product which is formed from $MoO_2(acac)_2$ and $PhMe_2COOH$ (Fig. 2a–c). However, as the reaction of $MoO_2(acac)_2$ with $PhMe_2COOH$ proceeds, at 293 K in benzene containing 3 M cyclohexene, the line from complex **III** is not observed and only complex **II** is formed from $MoO_2(acac)_2$ (see, *e.g.*, Fig. 2d).

As was found earlier [3], the rate of epoxidation of olefins with organic hydroperoxides is not sensitive to the nature of molybdenum complex that was used as the starting material for the catalyst, and the starting complex was converted during the reaction into a 1,2-diolo molybdenum(VI) species. In agreement with this observation, we found that the same complexes **IV**, **V** and **VI** were formed when $Mo(CO)_6$ was used instead of $MoO_2(acac)_2$ as the starting material for the catalyst, with both $PhMe_2COOH$ and Me_3COOH as oxidants. From the data of ref. 3 it is natural to suppose that **IV** and **V** are different types of *trans*-cyclohexane-diolo-1,2 molybdenum(VI) complexes. To provide conclusive evidence for this assumption we attempted to obtain complexes **IV** and **V** by the ligand substitution reaction of $MoO_2(acac)_2$ with *trans*-cyclohexane-diolo-1,2.

The ^{95}Mo NMR spectrum of the sample obtained by heating $MoO_2(acac)_2$ with *trans*-cyclohexane-1,2-diol for 5 min at 353 K in benzene is presented in Fig 7a ($[MoO_2(acac)_2] = 0.1$ M, $[1,2\text{-diol}] = 0.5$ M). It is seen that, indeed, complexes **IV** and **V** are formed in this reaction. Thus, complexes **IV** and **V** are two types of 1,2-diolo molybdenum(VI) complexes. When Me_3COH (Fig. 7b) is added to a solution containing complexes **IV** and **V** in benzene, the broad line near 60 ppm appears. This line resembles the line of complex **VI**. It can be attributed to the complex formed as a result of the substitution of one of the

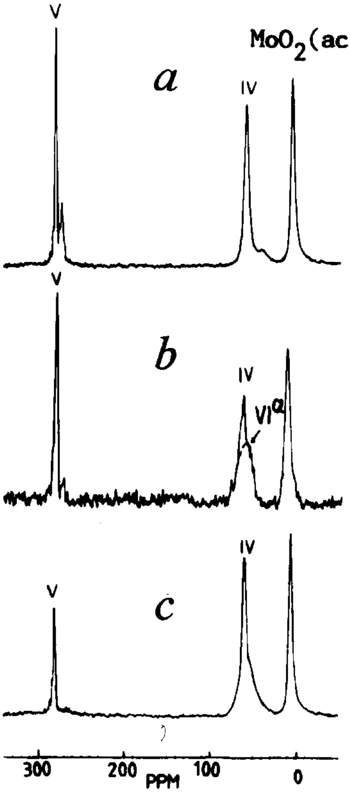


Fig. 7. ^{95}Mo NMR spectra of 1.2-diolo molybdenum(VI) species obtained by different procedures: (a) by heating 0.1 M $MoO_2(acac)_2$ + 0.5 M *trans*-cyclohexane-1,2-diol in benzene for 5 min at 353 K; (b) by addition of Me_3COH (to make $[Me_3COH] = 2$ M) to sample in (a) at 293 K; (c) by addition of a further portion of *trans*-cyclohexane-1,2-diol (to make $[1,2\text{-diol}] = 3$ M) to sample in (a) at 293 K.

1,2-diolo ligands by the Me_3CO^- ligand. After addition of an excess of *trans*-cyclohexane-1,2-diol to the solution containing complexes **IV** and **V** in benzene, the intensity of the line of complex **V** decreases and that of **IV** increases (Fig. 7c). When butane-2,3-diol is used instead of *trans*-cyclohexane-1,2-diol, complexes **IV** and **V** are also formed, but the chemical shift for complex **V** is 220 rather than 277 ppm. The chemical shift for **IV** is the same for both diols (within the accuracy of our measurements ±1 ppm).

^1H nuclear magnetic resonance

In an excess of cyclohexene it is difficult to identify ^1H NMR spectra of molybdenum(VI) complexes formed in the reaction of $MoO_2(acac)_2$ with Me_3COOH against the background of the intense lines from cyclohexene and cyclohexene oxide. However, a singlet line at 2.198 ppm is observed, and can be tentatively attributed to complex **II**. Indeed, on the basis of the ^{95}Mo NMR spectra, three minutes after the addition, at 293 K, of pure Me_3COOH (to make its concentration 1 M) to the 0.05 M $MoO_2(acac)_2$ in benzene containing 3 M cyclohexene, complexes **II**, **IV** and **V** exist in solution as predominant species. After heating the sample at 353 K for 3 min, the intensity of the ^{95}Mo line from complex **II** increases sharply. Simultaneously, the intensity of the singlet line at 2.198 ppm in the ^1H NMR spectrum also increases.

^{17}O nuclear magnetic resonance

As in the case when pure benzene was used as the solvent, the ^{17}O NMR chemical shifts of Me_3COOH change when $MoO_2(acac)_2$ reacts with Me_3COOH in benzene:cyclohexene mixtures at 293–353 K. The scale and direction of these changes are similar to those observed in pure benzene. No signals that can be attributed to complexes **II**, **IV**, **V** and **VI** are detected.

Electron paramagnetic resonance

As in the case when pure benzene was used as the solvent, during the reaction of $MoO_2(acac)_2$ with Me_3COOH in benzene containing cyclohexene, the EPR signal of the $Me_3COO^\cdot$ free radical (concentration 10^{-5} M) is observed. The intensity of this signal is consistent with the intensity of the signal of complex **VI** in the ^{95}Mo NMR spectra.

Discussion

Characterization of molybdenum complexes formed in the reaction of $MoO_2(acac)_2$ with ROOH ($R=Me_3C$, $PhMe_2C$) in benzene

*Complex **I** ($MoO_2(OOR)_2$)*

Complex **I** is formed when Me_3COOH is added to a solution of $MoO_2(acac)_2$ in benzene. The increase in the concentration of complex **I** is accompanied by a decrease in the concentration of $MoO_2(acac)_2$ and an increase in the concentration of free acetylacetone. Complex **I** exhibits only one singlet line in ^{1}H NMR spectra and contains no acetylacetonato ligands (see Fig. 3).

We assume that complex **I** is the alkylperoxo complex $MoO_2(OOR)_2$ which is formed in the ligand substitution reaction

$$MoO_2(acac)_2 + 2Me_3COOH \rightarrow MoO_2(OOCMe_3)_2 + 2Hacac \qquad (1)$$

The singlet line in the ^{1}H NMR spectrum of complex **I** is attributable to the CH_3 groups of the Me_3COO^- ligands. The conclusion that **I** is an alkylperoxo complex is supported by the following facts: (i) complex **I** reacts with cyclohexene to yield an alkoxo complex **II** (see below); (ii) the concentration of complex **I** is consistent with the concentration of $Me_3COO^{\cdot}$ radical, presumably, because of the reductive elimination–oxidative addition equilibrium of the type

$$Mo^{VI}O_2(OOR)_2 \rightleftharpoons Mo^{V}O_2(OOR) + RO_2^{\cdot} \qquad (2)$$

Such an equilibrium is also typical for recently studied alkylperoxo complexes of cobalt and vanadium [14,15].

Complex II ($MoO_2(OR)_2$)

In pure benzene the weak signal of complex **II** is observed only at small concentrations of Me_3COOH ($[Me_3COOH] = [MoO_2(acac)_2]$) (Fig. 1a). When the initial concentration of Me_3COOH rises, only the signal of complex **I** is observed (Fig. 1b–d). A similar result was observed in our previous work [15] for alkylperoxo and alkoxo complexes of vanadium formed in the reaction of $VO(acac)_2$ with Me_3COOH or $PhMe_2COOH$. Alkoxo complexes $VO(acac)_2OR$ were also observed only at small initial concentrations of ROOH ($[ROOH] \approx [VO(acac)_2]$). With the increase of the initial concentration of ROOH, the OR^- ligands were substituted for OOR^- ligands, and only the alkylperoxo complexes $VO(acac)_2OOR$ were observed.

After adding, at 293 K, cyclohexene to the solutions containing complexes **I** and **II**, the concentration of complex **II** increases sharply with respect to that of complex **I**. At high cyclohexene concentrations (exceeding 3 M), complex **I** is not detected at all. It is natural to suppose that alkylperoxo complex **I** transforms into alkoxo complex **II** by a reaction with cyclohexene

$$MoO_2(OOR)_2 + 2C_6H_{10} \rightarrow MoO_2(OR)_2 + 2C_6H_{10}O \qquad (3)$$

The singlet line in the ^{1}H NMR spectrum of complex **II** can be attributed to the CH_3 protons of Me_3CO^- groups.

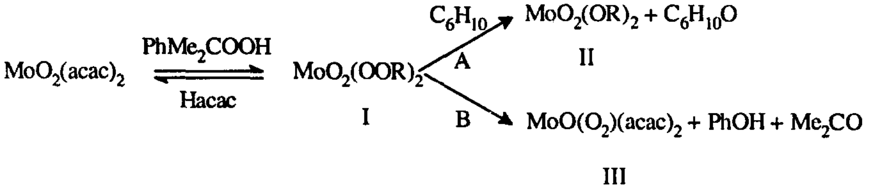
Complex III ($MoO(O_2)(acac)_2$)

Complex **III** can be obtained by reaction of $MoO_2(acac)_2$ with H_2O_2. On the basis of the ^{1}H and ^{17}O NMR spectra (Fig. 4B-c and Fig. 5b), this complex contains a M=O group and two acetylacetonato ligands. It is most probable that complex **III** is a monoperoxo complex, $MoO(O_2)(acac)_2$. The absence of the signal of the peroxo group in the ^{17}O NMR spectrum of $MoO(O_2)(acac)_2$ (Fig. 5b) may be caused by the great width of this signal. Note, that all the signals of peroxo groups in peroxo complexes of molybdenum(VI) registered so far were broader than 2000 Hz and observed only for compounds enriched with the ^{17}O isotope [16]. Our attempts to isolate complex **III** from the $MoO_2(acac)_2 + H_2O_2$ system were unsuccessful. The solid compound remaining after solvent removal under vacuum, contained admixtures of acetylacetone peroxide which exploded upon being handled. Remember that complex **III** is the main product of the reaction between $MoO_2(acac)_2$ and $PhMe_2COOH$, whereas in the reaction between $MoO_2(acac)_2$ and Me_3COOH, the alkylperoxo complex **I** is predominantly formed.

Molybdenum complexes are known to catalyze mainly the heterolytic decomposition of $PhMe_2COOH$ into phenol and acetone, whereas for Me_3COOH homolytic decomposition into Me_3COH is the main pathway [3]. In accord with this, we have observed with ^1H NMR that for the reaction of $PhMe_2COOH$ with $MoO_2(acac)_2$, $PhMe_2COH$ is predominantly formed only in the initial stage; at later stages, phenol and acetone become the main products, and $PhMe_2COH$ formed initially is converted into α-methyl styrene.

The tendency to heterolytic or homolytic decomposition of a hydroperoxide with molybdenum(VI) is probably connected with its ability to form mainly peroxo or alkylperoxo complexes. However, further studies are needed to clarify this issue.

At first glance, it may look unusual that according to our results and the literature data [3], there is no pronounced difference between cumene and *tert*-butyl hydroperoxides in the epoxidation of cyclohexene catalyzed by molybdenum complexes, despite the fact that those two hydroperoxides are decomposed along different pathways in the presence of Mo(VI) complexes. However, this controversy can be explained by the following simple scheme:



(4)

In the absence of cyclohexene the reaction proceeds mainly by route B, which leads to the heterolytic decomposition of $PhMe_2COOH$. The addition of cyclohexene makes route A predominant. In agreement with scheme (4), unreactive olefins such as allyl chloride, cannot suppress route B by making alternative route A more efficient. As a result, heterolytic decomposition of $PhMe_2COOH$, and not epoxidation, is observed for allyl chloride [3]. By contrast, Me_3COOH, for which route B is not favored, does epoxidize allyl chloride under these conditions [3].

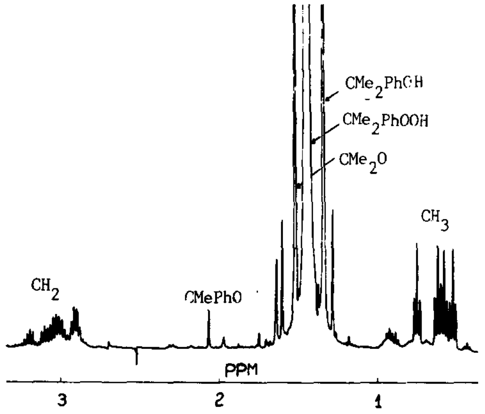
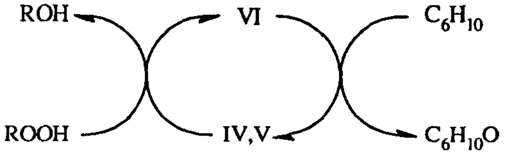


Fig. 8. ^1H NMR spectrum of 0.01 M dioxobis(diethyldithiocarbamato)molybdenum (VI) in benzene-d_6 5 min after the addition of $PhMe_2COOH$ (to make $[PhMe_2COOH]=0.1$ M) at 293 K.

Note that the formation of a monoperoxo complex is also observed in the reaction of $PhMe_2COOH$ or H_2O_2 with dioxobis(diethyldithiocarbamato)molybdenum(VI) ($MoO_2(DTCM)_2$). This monoperoxo complex which is similar to complex **III**, shows a line at −82 ppm, $\Delta\nu_{1/2}=120$ Hz in the ^{95}Mo NMR spectrum (compare with the line at −112 ppm for complex **III**) and the lines from four non-equivalent ethyl groups of two diethyldithiocarbamato ligands in the ^1H NMR spectrum (see Fig. 8). The initial complex MoO (DTCM) shows a line with $\delta=176$ ppm, $\Delta\nu_{1/2}=500$ Hz in the ^{95}Mo NMR spectrum and according to ^1H NMR all ethyl groups of this complex are equivalent.

Characterization of molybdenum complexes formed in reactions of $MoO_2(acac)_2$ and $Mo(CO)_6$ with ROOH ($R=Me_3C$, Me_2PhC) in benzene containing cyclohexene

Under the real conditions of the epoxidation reactions (*i.e.* with the large excess of organic hydroperoxide and cyclohexene, $T=353$ K), complexes **I**, **II** and **III** exist only in the initial stage of the reaction between $MoO_2(acac)_2$ and ROOH ($R=Me_3C$, $PhMe_2C$). Then, the new complexes **IV**, **V** and **VI** are formed and operate in the catalytic cycle:



(5)

The same complexes, **IV**, **V** and **VI**, are also formed when $Mo(CO)_6$ is used instead of $MoO_2(acac)_2$ as the starting material for catalyst. Thus the composition of complexes **IV**, **V** and **VI** is independent of the nature of the initial molybdenum complexes.

Complexes IV and V (MoO_2(1,2-diolo)$_2$)

On the basis of the ^{95}Mo NMR data, complexes **IV** and **V** are two different types of diolo molybdenum(VI) complexes. Indeed, the lines of complexes **IV** and **V** are observed in the ^{95}Mo NMR spectrum, when MoO_2(acac)$_2$ reacts with *trans*-cyclohexane-1,2-diol in benzene (Fig 7a).

Complex **IV** has a larger number of 1,2-diolo ligands per molybdenum atom, than complex **V**. Indeed, in accordance with this assumption, the concentration of complex **IV** increases with respect to that of **V**, when the excess of *trans*-cyclohexane-1,2-diol is added to the solution containing complexes **IV** and **V** in benzene. From the chemistry of its preparation from MoO_2(acac)$_2$ by the ligand substitution reaction, for complex **IV** we tentatively suggest the composition MoO_2(1,2-diolo)$_2$. However, further studies are needed to clarify the precise composition of complexes **IV** and **V**.

Complex VI (MoO_2(1,2-diolo)(OOR))

Complex **VI** reacts with cyclohexene to yield the complexes **IV** and **V**. The new portion of ROOH converts complexes **IV** and **V** back into complex **VI** (see Figs. 6d and 6f and the catalytic cycle in scheme (5)). It is natural to suppose that complex **VI** is an alkylperoxo complex, *i.e.* it contains the ROO^- group as a ligand. This is in agreement with the observation of the EPR signal of $Me_3COO^{\cdot}$ free radical, the concentration of which is consistent with the concentration of complex **VI**. When complex **VI** is formed from complexes **IV** and **V**, one of the ligands in complexes **IV** and **V** is probably substituted by the ROO^- ligand. The substitution of both 1,2-diolo ligands would have given rise to complex **I**, which was not observed. Thus, presumably, complex **VI** has the composition MoO_2(1,2-diolo)(OOR) and is the main candidate for the role of active particle of epoxidation.

When the alkylperoxo complex MoO_2(1,2-diolo)OOR reacts with cyclohexene, the alkoxo complex MoO_2(1,2-diolo)OR must be formed. But then again, the OR^- ligand in this complex may, perhaps, be substituted for a (1,2-diolo) one. Note that ^{95}Mo NMR chemical shift of MoO_2(1,2-diolo)OR seems to be close to that of MoO_2(1,2-diolo)OOR. Indeed, after adding ROH to a benzene solution containing complexes **IV** and **V**, we observed a broad line near 60 ppm (Fig. 7b). This line is quite similar to that observed when ROOH is added to a solution of **IV** and **V** (Fig. 6f). That is perhaps why the line from MoO_2(1,2-diolo)OR cannot be distinguished in the spectra of Fig. 6.

Let us compare the compositions and reactivities of the complexes formed in the epoxidizing catalytic systems MoO_2(acac)$_2$+ROOH and VO(acac)$_2$+ROOH. On the basis of our previous work [15], the same complexes LVO(OOR), LVO(OR) and VO(OR)$_3$ are formed in solutions of VO(acac)$_2$+ROOH in benzene and in a mixture of benzene with cyclohexene. The nature of the ligand L is still not established, though it has been shown to be an inorganic, rather than an organic anion [15]. In contrast to this, in the catalytic system MoO_2(acac)$_2$+ROOH, three new complexes **IV**, **V** and **VI** are formed when adding cyclohexene to benzene. However, the most essential difference is the following. The supposed key intermediate in the vanadium system (complex LVO(OOR)) is unstable with respect to side reactions. It rapidly converts into $VO(OR)_3$ at 293 K in benzene even in the absence of the oxidized substrate (cyclohexene). In contrast to this, the supposed active particle of epoxidation with the molybdenum system *i.e.* complex **VI** (presumably, MoO_2(1,2-diolo)(OOR)), is stable in benzene for at least 5–10 min even at 353 K (Fig. 6d), but rapidly reacts with cyclohexene (Fig. 6c). The stability of complex **VI** to side reactions may be one of the reasons for its high efficiency, and in particular, for its high selectivity, in the epoxidation of simple olefins.

Conclusions

Using ^{95}Mo, ^{1}H and ^{17}O NMR data, we have for the first time detected spectroscopically and characterized *in situ* the key intermediates of the Halcon process. In the initial step of cyclohexene epoxidation by the $MoO_2(acac)_2$+ROOH ($R=PhMe_2C$, Me_3C) system, three types of Mo(VI) complexes (**I**, **II** and **III**) exist in solution. They are characterized as: **I**, the alkylperoxo complex $MoO_2(OOR)_2$; **II**, the alkoxo complex $MoO_2(OR)_2$; and **III**, the monoperoxo complex $MoO(O_2)(acac)_2$.

During the reaction complexes **I–III** gradually disappear and three new complexes **IV**, **V** and **VI** appear, and drive the catalytic cycle of cyclohexene epoxidation. Complex **VI** reacts with cyclohexene to give the epoxide and complexes **IV** and **V**, whereas the hydroperoxides convert complexes **IV** and **V** back to complex **VI**. Complex **VI** serves as the active particle of epoxidation and, presumably, has the composition: MoO_2(1,2-diolo)(OOR). Complexes **IV** and **V** are two different types of 1,2-diolo molybdenum(VI) species.

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