

Multinuclear NMR-spectroscopic characterization of alkylperoxo complexes of molybdenum(VI)

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An alkylperoxo molybdenum(VI) intermediate was identified in the reaction of Bu^tOOH with the 1,2-cyclohexanediolo complex of molybdenum(VI) in CHCl₃ using ¹³C, ¹⁷O and ⁹⁵Mo NMR spectroscopy.

Molybdenum-catalysed epoxidation with organic hydroperoxides remains the basis for the industrial production of propylene oxide, as well as a convenient laboratory method for the epoxidation of alkyl olefins.^{1–5} It is generally agreed that alkylperoxo molybdenum complexes are the active species of these reactions. However, the alkylperoxo complexes of molybdenum have been neither isolated nor adequately characterised by spectroscopy. Recently, Kühn *et al.*⁶ suggested the formation of an alkylperoxo complex of molybdenum(VI) based on the detection of new IR bands in the reaction of [MoO₂Cl₂L₂] with Bu^tOOH [L₂ = 4,4'-bis(*n*-hexyl)-2,2'-bipyridine].⁶ These bands were similar to those reported for the OOBu^t moiety of the vanadium(V) alkylperoxo complex [VO(dipic)(OOBu^t)] (dipic = 2,6-pyridinecarboxylate).⁷ However, the [MoO₂Cl₂L₂]/Bu^tOOH catalytic system exhibits only a moderate activity in epoxidation of olefins.⁶ For highly active and practically attractive molybdenum-based catalytic systems, the rate of epoxidation of olefins with organic hydroperoxides is independent of the nature of the molybdenum complex used as a catalyst precursor and the starting complex was converted into molybdenum(VI) complexes with 1,2-alkanediol (the by-product of epoxidation).² Thus, in order to model molybdenum-based epoxidising systems, it is important to characterise the alkylperoxo complexes formed in the reaction of an organic hydroperoxide with 1,2-alkanediolo molybdenum(VI) species.

Our previous attempt to characterise the alkylperoxo complexes of molybdenum in the MoO₂(acac)₂/Bu^tOOH/cyclohexene system by ⁹⁵Mo NMR spectroscopy showed that the ⁹⁵Mo peaks of *in situ* formed 1,2-cyclohexanediolo molybdenum complexes broadened dramatically upon the addition of Bu^tOOH. On this basis the formation of the alkylperoxo complexes of molybdenum was proposed.⁴ To test this hypothesis and to study the structure of the alkylperoxo complexes, we examined the interaction of 1,2-cyclohexanediolo complexes of molybdenum(VI) with Bu^tOOH in CHCl₃ using ¹³C, ¹⁷O and ⁹⁵Mo NMR spectroscopy. The ¹H and ¹³C NMR spectroscopic data were reported for the *tert*-butyl peroxo complexes of titanium,^{8–10} vanadium^{11,12} and chromium.¹³ These data were used for the assignment of

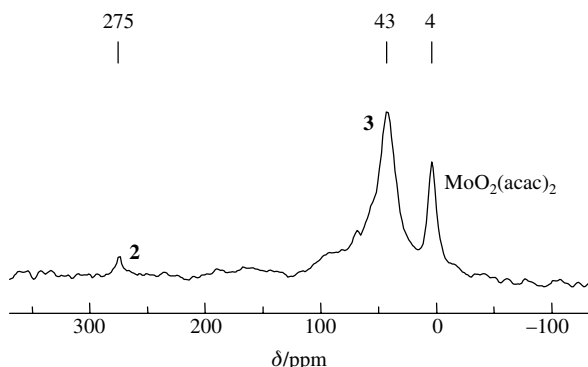


Figure 1 The ⁹⁵Mo NMR spectrum of the MoO₂(acac)₂/1 system in CHCl₃ at 20 °C, [MoO₂(acac)₂] = 0.1 mol dm⁻³, [1] = 0.2 mol dm⁻³. To facilitate further detection of the ¹⁷O NMR spectrum, this sample contained small amount of H₂¹⁷O, 0.003 ml of H₂¹⁷O (3% enrichment in ¹⁷O) per 1.5 ml of the solution.

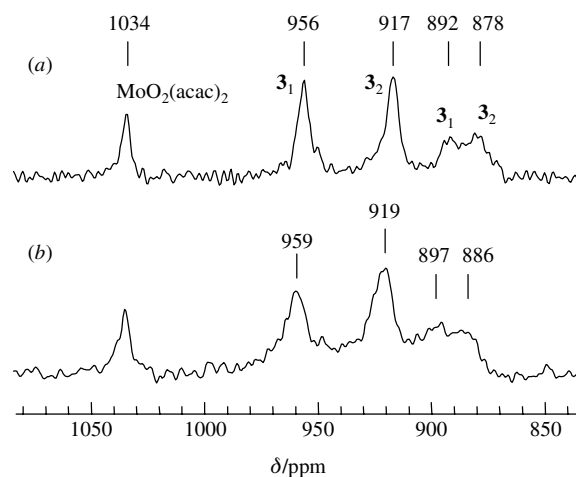


Figure 2 The ¹⁷O NMR spectra of (a) the MoO₂(acac)₂/1 system in CHCl₃ at 20 °C, [MoO₂(acac)₂] = 0.1 mol dm⁻³, [1] = 0.2 mol dm⁻³ and (b) sample *a* 30 min after the addition of Bu^tOOH ([Bu^tOOH] = 2 mol dm⁻³). This sample contained 0.003 ml of H₂¹⁷O (3% enrichment in ¹⁷O) in 1.5 ml of solution.

resonance peaks of a coordinated alkylperoxo moiety in the molybdenum-based system.

The 1,2-cyclohexanediolo complexes of molybdenum were prepared *in situ* by the addition of *trans*-1,2-cyclohexanediol **1** to a 0.1 M MoO₂(acac)₂ solution in chloroform at room temperature (Hacac = acetylacetonate).[†] It was found that as the 1/MoO₂(acac)₂ ratio increased from 1 to 3, the ¹³C NMR peaks of MoO₂(acac)₂ decreased and those of uncoordinated Hacac increased (CHCl₃, 20 °C). Thus, **1** replaces the acetylacetonate ligands of MoO₂(acac)₂ to form molybdenum(VI) complexes with *trans*-1,2-cyclohexanediol. The fraction of these complexes in solution is 85% at 1/Mo = 3 according to the integration of the ¹³C peaks of MoO₂(acac)₂ and Hacac.

The ⁹⁵Mo NMR spectrum of 1/MoO₂(acac)₂ in CHCl₃ {1/Mo = 2, [MoO₂(acac)₂] = 0.1 M} displays the peak of MoO₂(acac)₂

[†] General experimental details. The ¹³C, ¹⁷O and ⁹⁵Mo NMR spectra were recorded at 100.64, 54.043 and 26.08 MHz, respectively, using a pulsed FT-NMR technique on a Bruker MSL-400 NMR spectrometer. The ¹³C spectra were also measured on a Bruker DPX-250 NMR instrument at 62.87 MHz. To increase the sensitivity, a high-power probehead was used for ¹⁷O and ⁹⁵Mo NMR measurements. Operating conditions: sweep width, 20 (¹³C), 80 (¹⁷O) or 50 kHz (⁹⁵Mo); spectrum accumulation frequency, 0.2 (¹³C), 100 (¹⁷O) or 40 Hz (⁹⁵Mo). Number of scans: 200–1000 (¹³C), 200000 (¹⁷O), 50000 (⁹⁵Mo). 90° at 16 μs (⁹⁵Mo and ¹⁷O), 45° pulse at 10 μs (¹³C). The chemical shifts are given in ppm with positive values in the downfield direction with respect to external reference H₂O (¹⁷O), 2 M Na₂MoO₄ in D₂O (⁹⁵Mo) and with respect to internal reference TMS (¹³C). To facilitate the detection of the ¹⁷O resonances of Mo=O groups of molybdenum complexes, ¹⁷O enrichment was used. Normally, 0.003 ml of H₂¹⁷O (3% enrichment in ¹⁷O) was added to 1.5 ml of a solution of 1/MoO₂(acac)₂ in chloroform before the addition of Bu^tOOH and the recording of ¹⁷O NMR spectra. The exchange of the Mo=O oxygen atoms with those of H₂¹⁷O gave rise to their enrichment in the ¹⁷O isotope.

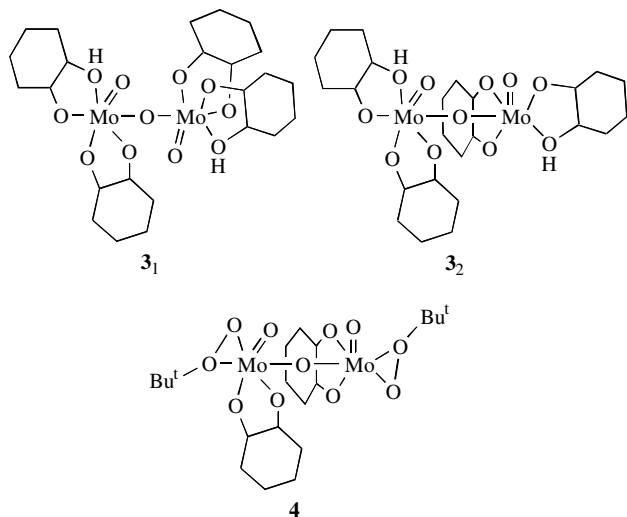


Figure 3 The structures of complexes **3** and **4**.

at 4 ppm ($\Delta\nu_{1/2} = 200$ Hz), a weak resonance at 275 ppm ($\Delta\nu_{1/2} = 130$ Hz) and an intense resonance at 43 ppm ($\Delta\nu_{1/2} = 500$ Hz) (Figure 1). The latter two resonances were assigned to various types of the 1,2-cyclohexanediolo complexes of molybdenum(VI). These species are denoted as complexes **2** and **3**. The concentration of **2** is very small, and the ratio $[2]/[3]$ in Figure 1 is 1/30. In the ^{17}O NMR spectrum of **3** [Figure 2(a)], two peaks at δ 956 (2O) and 917 (2O) from Mo=O oxygen atoms and two peaks at 892 (O) and 878 (O) from Mo–O–Mo oxygen atoms are observed. The relative intensities of the peaks are shown in parentheses. Note that difference in the chemical shifts of terminal and bridging oxygen atoms in **3** (40–65 ppm) is close to that (75 ppm) observed for Ti=O (903 ppm) and Ti–O–Ti (828 ppm) oxygen atoms in the complexes $\text{TiO}(\text{acac})_2$ and $[\text{Ti}(\text{acac})_2]_2\text{O}(\text{O}_2)$.¹⁴ The ^{95}Mo and ^{17}O NMR spectra [Figures 1 and 2(a)] show that **3** exists in solution in the form of two isomers **3**₁ and **3**₂ exhibiting a common ^{95}Mo peak at 42 ppm and various ^{17}O NMR patterns. The concentrations of these isomers are close. Isomer **3**₁ has ^{17}O resonances at δ 956 and 892 ppm from the O=Mo–O–Mo=O moiety; isomer **3**₂ has two peaks at δ 917 and 878 ppm [Figure 2(a)]. The widths of the NMR resonances of quadrupolar nuclei increase with molecular size.¹⁵ The ^{95}Mo NMR peak of **3** in Figure 1 is twice as broad as that of the mononuclear complex $\text{MoO}_2(\text{acac})_2$. Most probably, **3**₁ and **3**₂ are μ -oxo dinuclear species with the structures shown in Figure 3. Complex **2** exhibits a relatively sharp ^{95}Mo NMR peak (Figure 1). Probably, **2** is the mononuclear complex $\text{MoO}_2(1,2\text{-cyclohexanediolo})_2$. Note that ^{95}Mo peaks of **2** and **3** can be detected in the $\text{Mo}(\text{CO})_6/\text{Bu}^t\text{OOH}/\text{cyclohexene}$ system in benzene.⁴ This allows us to exclude the incorporation of acac ligands into their composition. The above results show that the reaction of $\text{MoO}_2(\text{acac})_2$ with **1** ($[\text{1}]/[\text{Mo}] = 2$) in CHCl_3 at room temperature gives rise mainly to the formation of dinuclear μ -oxo bridged complex **3** (Figure 3).

The ^{13}C NMR spectrum of **1** (CHCl_3 , 20 °C) displays peaks at δ 75.4 (2C, CH_2OH), 33.1 (2C, CH_2), 24.6 (2C, CH_2) ppm. The ^{13}C NMR spectrum of **3** shows broadened peaks near 33 and 24.5 ppm due to 1,2-cyclohexanediolo ligands. After the addition of Bu^tOOH to the solution of $\text{MoO}_2(\text{acac})_2$ and **1** in CHCl_3 at room temperature ($[\text{1}]/[\text{MoO}_2(\text{acac})_2] = 2$, $[\text{Bu}^t\text{OOH}]/[\text{1}] = 10$), the ^{13}C NMR peaks of the coordinated OOBu^t moiety of alkylperoxo complex **4** appeared. The resonance at 26.0 ppm and two resonances at 83.3 and 82.9 ppm can be assigned to primary and quaternary carbon atoms of the coordinated alkylperoxo moiety of **4**, respectively (Figure 4). Uncoordinated Bu^tOOH exhibits corresponding peaks at 25.4 and 80.2 ppm in our particular sample. The chemical shifts of peaks at 83.3 and 82.9 ppm are close to that for η^2 -(*tert*-butylperoxy)titanatrane dimer (83.93 ppm in CD_2Cl_2).⁸ Thus, the η^2 -coordination of OOBu^t ligands is most probable for complex **4**. The peaks of **4** disappear when Bu^tOOH decomposes to Bu^tOH . Two peaks at

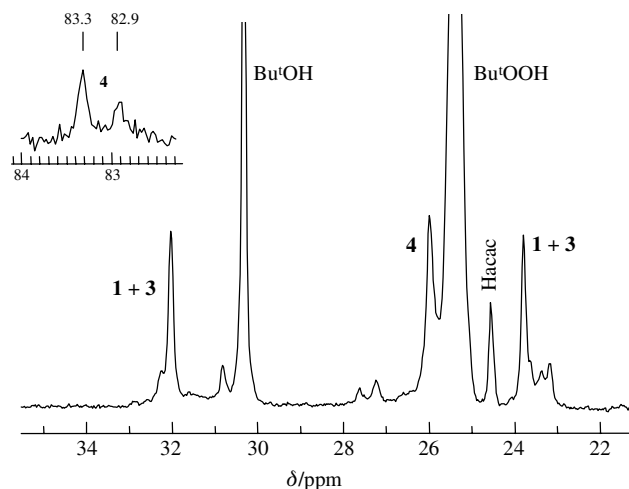


Figure 4 The ^{13}C NMR spectrum of the $\text{MoO}_2(\text{acac})_2/\text{1}$ system in CHCl_3 15 min after the addition of Bu^tOOH at 20 °C. The ^{13}C NMR spectrum was recorded at –10 °C, $[\text{MoO}_2(\text{acac})_2] = 0.1 \text{ mol dm}^{-3}$, $[\text{1}] = 0.2 \text{ mol dm}^{-3}$, $[\text{Bu}^t\text{OOH}] = 2 \text{ mol dm}^{-3}$.

83.3 and 82.9 ppm for **4**, probably, reflect the existence of two isomers for starting complex **3**. The concentration of **4** reached 70% of the starting molybdenum complex.

The ^{17}O NMR data evidence that the $\text{O}=\text{Mo}-\text{O}-\text{Mo}=\text{O}$ fragment remains intact upon the formation of alkylperoxo complex **4**. The addition of Bu^tOOH ($[\text{Bu}^t\text{OOH}] = 2 \text{ mol dm}^{-3}$) to the sample shown in Figure 2(a) gave rise to a slight (about 2 ppm) increase of chemical shifts of $\text{M}=\text{O}$ oxygen atoms, and a more pronounced (by 5–8 ppm) increase of the chemical shifts of $\text{Mo}-\text{O}-\text{Mo}$ oxygen atoms [Figure 2(b)], whereas peak intensities remained unchanged. Thus, the formation of **4** occurs via the replacement of 1,2-cyclohexanediolo ligands in **3** by OOBu^t . A comparison of the intensities of the corresponding ^{13}C NMR peaks shows that **4** incorporates one OOBu^t and one 1,2-cyclohexanediolo ligand per molybdenum. The structure proposed for **4** is shown in Figure 3. Thus, the key intermediate of the practically attractive molybdenum-based catalytic system $\text{MoO}_2(\text{acac})_2/\text{olefin}/\text{Bu}^t\text{OOH}$ is a dinuclear μ -oxo bridged alkylperoxo complex of molybdenum(VI). This complex contains one *in situ* formed 1,2-alkanediolo ligand and one η^2 -coordinated alkylperoxo group per molybdenum atom.

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