Registry No. 1, 35193-70-5; 2, 79044-24-9; 3, 79044-29-4; 4, 79044-27-2; 5, 114459-67-5; 6, 79044-26-1; 7, 115510-90-2; 8, 93621-64-8; 9, 13323-81-4; 10, 98976-10-4; 11, 60686-64-8; 12, 115510-91-3; 13, 115463-56-4; 14, 115463-57-5; quinine, 130-95-0.

Metal Catalysis in Oxidation by Peroxides.[1] A ^{17}O NMR Spectroscopic Investigation of Neutral and Anionic Molybdenum Peroxo Complexes

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In connection with our interest[2] in the mechanism of metal-catalyzed oxidations[3] of various organic substrates with peroxides and, in particular, in the structure of the peroxo species involved, we have undertaken a ^{17}O NMR investigation of a series of neutral[4] and anionic[1,5] molybdenum (VI)–oxodiperoxo complexes. The broad scope of ^{17}O NMR spectroscopy as a structural probe is well known.[6] As an example, this technique has been successfully applied to the study of polyoxo anions of the early transition elements in solution[6] and quantitative correlations have been established.[6,7] In particular, a chemical shifts scale for molybdenum-bound oxygens has been constructed.[6] More recently, ^{17}O NMR investigations of oxo, peroxo, and superoxo derivatives of V, Cr, Mo, W, Fe, Ir, and Pt have been reported in the literature.[8-10]

Neutral molybdenum–peroxo complexes of the type $MoO(O_2)_2L$ (L = HMPT, DMF, Py, etc.) oxidize nucleophilic substrates such as alkenes or sulfides both in protic and aprotic solvent via an electrophilic peroxo oxygen transfer mechanism,[2,3] whereas they are rather unreactive toward alcohols.

By contrast, anionic molybdenum–peroxo complexes of the type $[MoO(O_2)_2PIC]^-Bu_4N^+$ (PIC = picolinic acid anion) or $[MoO(O_2)_2PICO]^-Bu_4N^+$ (PICO = picolinic acid *N*-oxido anion),[1] soluble in aprotic solvents owing to the presence of the lipophilic cation, readily oxidize primary and secondary alcohols to the corresponding carbonyl compounds.[1,11] At the same time, their efficiency as electrophilic oxidants is greatly reduced, though not cancelled.[12] In particular, the oxidation of very nucleophilic substrates such as sulfides is still feasible.[11,12]

Table I. ^{17}O NMR Chemical Shifts of the Oxo Resonance of Various Oxo-Diperoxo Mo(VI) Complexes

complex	δ (natural)[a]	δ (enriched)	lit.[8]
$MoO(O_2)_2HMPT$	840 (DCE)	846 (DCE)[b]	863[d]
	857 (CH_3CN)	840 (DCE)[c]	
	830 (CH_2Cl_2)	855 (CH_3CN)[c]	
$MoO(O_2)_2PyO$	854 (CH_3CN)	854 (CH_3CN)[c]	
$MoO(O_2)_2Py$		865 (CH_3CN)[c]	897[d]
$[MoO(O_2)_2PIC]^-Bu_4N^+$	844 (DCE)	847 (DCE)[b]	
		849 (CH_3CN)[b]	
		847 (DCE)[c]	
$[MoO(O_2)_2PICO]^-Bu_4N^+$	834 (DCE)	833 (DCE)[b]	
		836 (CH_3CN)[b]	
		834 (DCE)[c]	
		843 (CH_3CN)[c]	
$[MoO(O_2)_2PIC]^-H_3O^+$		840 (CH_3CN)[c]	940[d]

[a] Saturated solution (0.2–0.01 M) of unlabeled peroxo complexes. Signal/noise ≥ 5. [b] Peroxo compounds prepared in H_2O–$H_2{}^{17}O$ (10% enrichment Stohler Isotope Chemicals). [c] Saturated solution of unlabeled peroxo complexes after shaking with minute amounts of $H_2{}^{17}O$. [d] Solvent not specified.

The different oxidation chemistry of neutral and anionic peroxo complexes could be accompanied by some difference in the ground-state structure being the localization of the negative charge of the anions a central point. The formation of a peracid-like, end-on complex, such as Mo–O–O$^-$, in solution is rather unlikely. Several pieces of evidence discussed in previous papers,[2,13-15] and even ^{17}O NMR investigations of the peroxo oxygens,[8,9] militate against this hypothesis. An alternative possibility, i.e. that the negative charge is mainly located on the Mo=O moiety, giving rise to oxo anions like species such as Mo–O$^-$, is, in turn, somehow questioned by the X-ray data available.[1] These, in fact, indicate that in the solid state the Mo–O bond lengths are almost the same either in neutral[16-18] or in anionic species.[1,5] Indeed the same pentagonal-bipyramid geometry is observed for all the peroxo complexes examined.[2b] On the other hand, direct information of the situation in solution is lacking. Moreover the ^{17}O chemical shift might be a more sensitive measure than the bond length. Therefore we have collected the ^{17}O NMR data presented in Table I.[19]

Control experiments by ^1H or ^{13}C NMR spectroscopy have confirmed[1,2,11] that under the experimental conditions adopted the ligands remain coordinated to the metal center.

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(19) Incidentally, these results appear to be somehow in contrast with previous data,[8] which indicated a significant variation of the ^{17}O chemical shift of the Mo=O group with the nature of the ligand. Such a discrepancy could be rationalized if the literature data[8] refer to protic solvent where solvolysis of the ligands and acid–base equilibria of the complexes may occur.

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The data of Table I indicate that the chemical shifts of the oxo oxygens are almost unaffected by the nature of the peroxo compounds, either neutral or anionic, the basicity of the coordinated ligands, and the nature of the associated cation, either H_3O^+ or Bu_4N^+. Moreover there is a very little effect by varying the nature of the solvent, e.g. from DCE to CH_3CN.

The chemical shifts reported in Table I fit the correlation, established in 1979 by Miller and Wentworth,[7] between ^{17}O chemical shifts of oxygen bound to Mo and Mo–O bond length, respectively. In fact for all the complexes analyzed, either neutral or anionic, the ^{17}O oxo resonance falls in the range 830–860 ppm in agreement with the 1.6-Å bond length as it is measured in the solid state.[1,5,16] Therefore, we can be quite confident that the negative charge of the anionic compounds investigated should not be localized on the oxo oxygen. As discussed above, it is also unlikely that the charge is on the peroxo oxygen. Consequently, we are left with the suggestion that the negative charge has to be located on the ligand.

Recently we have shown[19] that, in aqueous solution at pH 3, $[MoO_5 \cdot nH_2O]$ is in equilibrium with its monoanion which can be extracted into a chlorinated solvent by a phase transfer agent such as a tetraalkylammonium salt.[20] The oxo resonance of the peroxo molybdenum anion extracted with this procedure is found at 791 ppm. Therefore in this case, where no bidentate ligands are present and, hence, the negative charge has to be localized on the peroxo molybdenum ion, the oxo resonance is markedly shifted upfield (56 ppm) with respect to the average of the other signals reported in Table I. This could either mean that the M=O bond is longer[7] or that the complex has a different spatial arrangement.

The significance of this result is confirmed by the following control experiment. After extraction from an aqueous solution at pH 1.2, with the neutral lipophilic ligand hexaethylphosphoric triamide,[21] of the neutral peroxo species, an oxo resonance of 837 ppm has been measured, i.e. the same value found for $MoO(O_2)_2HMPT$, first entry of the Table I.

As far as the oxidation chemistry is concerned, it is worthy of notice that the extracted anionic peroxo complexes, where no bidentate ligands are present, behave differently from the anionic picolinate and picolinate *N*-oxido analogues.[20] In fact the latter are much more efficient than the former in the oxidation of primary alcohols to aldehydes.[1,20]

A correlation between the localization of the negative charge, as indicated by the spectroscopic evidence reported here, and the oxidative behavior might be envisaged. This could be useful in the understanding of the mechanism of alcohol oxidations currently under investigation.

Experimental Section

The ^{17}O NMR spectra were obtained with a Bruker WP 200 SY multinuclear spectrometer operating at 27.1 MHz for ^{17}O. No field/frequency locking system was used, and the spectra were obtained at about 30 °C. Chemical shifts were measured relative to acetone as external reference. The acetone chemical shift (+572 ppm from water) was previously determined in a separate experiment.

A sweep width of 62.5 kHz was used; the number of scans accumulated varied from 2×10^4 to 10^6 depending on the concentration and on the enrichment of the sample. The data were acquired as 4K data points in the time domain and transformed as 2K. No relaxation delay was used and, before FT, about 40 points were zeroed and exponential multiplication (LB 50Hz) was performed. It was estimated that the limit error for the chemical shifts reported in Table I is ±5 ppm.

Commercially available solvents were purified according to standard procedures.

All peroxo complexes were synthesized and purified by known literature methods.[1,4,5] The peroxidic oxygen content was always ≥98%.

The extraction of the peroxo complexes both neutral or anionic from the aqueous phase into the organic one was carried out via procedures described elsewhere.[14,20]

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Registry No. $MoO(O_2)_2HMPT$, 25377-12-2; $MoO(O_2)_2PyO$, 115406-87-6; $MoO(O_2)_2Py$, 67228-13-1; $[MoO(O_2)_2PIC]^-Bu_4N^+$, 105177-38-6; $[MoO(O_2)_2PICO]^-Bu_4N^+$, 105194-63-6; $[MoO(O_2)_2PIC]^-H_3O^+$, 72074-55-6.

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Direct Perfluoroalkylation Including Trifluoromethylation of Aromatics with Perfluoro Carboxylic Acids Mediated by Xenon Difluoride

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It is now recognized that the regioselective replacement of hydrogen in an aromatic or heterocyclic system by a perfluoroalkyl group may have profound influence on the physical and biological properties of such molecules.[2] As a result, considerable effort has been devoted to the introduction of perfluoroalkyl units in such systems, as exemplified by the reactions of the reactive perfluoroalkyl cationic or radical species.[3] However, these processes often required careful preparation of the reactive intermediates[4] and were not available to conduct both perfluoroalkylation ($\geq C_2$) and trifluoromethylation.

We now describe a facile and general perfluoroalkylation procedure of electron-poor aromatic and heterocyclic systems by a common (both perfluoroalkylation ($\geq C_2$) and trifluoromethylation) and simple one-pot procedure.

Our method is based on the observation of several groups which reported that the commercially available reagent xenon difluoride[5] reacts with trifluoroacetic acid

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