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Some Features of Epoxidation of Cyclohexene Catalyzed by Oxoperoxometallates under Phase-Transfer Conditions

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The epoxidation of cyclohexene with hydrogen peroxide was investigated in the biphasic water–chlorobenzene system. It was observed that the autoxidation of cyclohexene to 2-cyclohexenylhydroperoxide is inhibited by the presence of the aqueous phase, but the inhibition caused by water is largely eliminated by the application of a phase-transfer catalyst (PTC). It was found that the yield of epoxide increased nearly linearly with increasing concentration of the molybdenum(VI) catalyst. A pH of 3–4 was found to be optimal for epoxide formation; the epoxide yield decreased with increase of the H^+ ion concentration mainly due to the H^+ ion-catalyzed hydrolysis of the epoxide formed. A PTC excess inhibits the epoxidation. In the case of molybdenum(VI), arsenate ion proved to be a more active promoter than phosphate ions by a factor of 1.6 when $[Mo] \geq [PTC]$; however, the sequence of promoter activity was reversed when the PTC was applied in a 10-fold excess. Tungsten(VI) is about 3 times more active catalyst than molybdenum(VI). However, for tungsten(VI) the activity sequence was $PO_4^{3-} > AsO_4^{3-}$. The view is advanced that the enormous differences between the reactivities of the investigated oxoperoxometallate complexes and their heteropoly derivatives are connected with differences in the dissymmetry of the η^2 diperoxo-ligands in these complexes, which otherwise have similar structures. © 1991 Academic Press, Inc.

INTRODUCTION

In the past decade, several interesting reports have been made of the successful applications of hydrogen peroxide for the epoxidation of olefins with oxometallates as catalysts under phase-transfer conditions (*1–5*). The problem was attacked mostly from the aspect of synthetic chemistry, and the regio- and enantioselective potentialities of this technique were emphasized. However, little is known about the experimental conditions which give the optimal yield of the epoxidation, or about the active species involved in the catalysis. Further, the puzzling question remains open as to why the reactivities of various oxoperoxometallate complexes toward a common organic reactant (substrate) can be so variable, even though the structures of these complexes are very similar. This paper presents experimental results and considerations on some features of the biphasic epoxidation of cyclohexene by hydrogen peroxide.

EXPERIMENTAL

C.p. reagents were applied without any purification. The solvent chlorobenzene was purified by the method usual for liquid-phase oxidation reactions (*6*). Epoxidation was carried out in a thermostatted glass reaction vessel of about 35 cm^3, fitted with a reflux condenser cooled with water at 10°C. The aqueous phase (5.0 cm^3) contained the catalyst, hydrogen peroxide, and acid, while the organic phase (10.0 cm^3) contained the PTC and cyclohexene. The two phases were applied as a reaction mixture, which was intensively stirred with a magnetic stirrer. When the O_2 uptake was also measured, the reaction mixture was previously saturated with dioxygen at room temperature, then warmed up and the reflux condenser was connected to a thermostatted gas burette.

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When the reaction was finished, the reaction mixture was cooled down quickly and the phases were separated by centrifugation. The aqueous phase was filtered on an ordinary quantitative paper, and the organic phase on a Whatman 1PS silicone-treated phase separator. In the aqueous phase, the residual hydrogen peroxide was determined by iodometry. The 1,2-cyclohexanediol content was similarly estimated in the aqueous phase with a modified periodate procedure (*7*). The O_{act} content (cyclohexenyl hydroperoxide formed during the autoxidation of substrate + the inorganic peroxide species transferred) of the organic phase was determined by means of the arsenious acid method (*8*). Cyclohexene oxide (7-oxabicyclo[4.1.0]heptane, or in short the epoxide) was analyzed by gas chromatography on a 2-m-long, 4-mm-i.d. column filled with Chromosorb W coated with 10% Carbowax 20M. Carrier gas: N_2 30 $cm^3\ min^{-1}$; detector: FID.

The yield of epoxidation is characterized in terms of the turnover number, TN, which is defined as

$$TN = \text{epoxide(mmol)}/\text{catalyst(mmol)} \times \text{PTC(mmol)} \times \text{time(h)}$$

The inclusion of the PTC concentration in the expression for TN is explained by the fact that the yield of epoxide is influenced by this concentration (vide infra).

RESULTS

Oxidation of cyclohexene was investigated under the experimental conditions applied in the epoxidation experiments (Table 1). In the absence of aqueous phase and PTC catalyst, cyclohexene is considerably oxidized after a time-lag (which is the time elapsed until the first portion (0.02 cm^3) of O_2 absorption) of 16 min in the dark. When the reactor was irradiated with a high-pressure Hg lamp the time-lag was shortened and the O_{act} content was increased. In the presence of the aqueous phase, either in the dark or in diffuse daylight, no O_2 uptake was observed during the 120-min observation time. On irradiation, slow oxidation set in. When cyclohexenyl hydroperoxide was removed just before the experiment, the oxidation set in similarly, but after a longer time-lag. When methyltricapryl ammonium chloride, i.e., Aliquat 336 (ALCl), was applied as PTC in the organic phase, in the absence of the aqueous phase, the O_2 absorption started immediately and the uptake of 20 cm^3 O_2 (= 0.81 mmol O_2 at 28°C, the temperature of the gas burette, and atmospheric pressure) occurred in 28 min in the dark. The irradiation did not cause any observable change in the oxidation, but the decomposition of cyclohexenyl hydroperoxide was promoted. The presence of ALCl did not entirely eliminate the inhibitory effect of water, and the O_2 absorbed did not yield hydroperoxide alone, but other oxidized species (-ol and -one) were formed, except epoxide. The time-lag of oxidation was lengthened and the rate of oxidation was decreased by the introduction of molybdenum(VI) into the aqueous phase, but the formation of the epoxide could also be observed. When both molybdenum(VI) and excess hydrogen peroxide were applied, epoxide and hydroperoxide were formed in greater amounts and some slow decomposition of hydrogen peroxide was observed in the aqueous phase.

The epoxide yield depended on the pH of the aqueous phase (Table 2). The decrease in the epoxide yield with increase of the H^+ ion concentration was mainly connected with the acid-catalyzed hydrolysis of the epoxide into 1,2-dihydroxycyclohexane (in short, the diol); this can be seen in Table 3.

The data in Table 4 show how the epoxide yield depended on the catalyst concentration when the concentration ratio $[Mo]/[H_2O_2]$ was kept constant. The epoxide yield and TN increased with increase of the catalyst concentration, but TN started to decrease when the catalyst concentration became commensurable with that of ALCl.

The catalytic effect of molybdenum(VI) was enhanced by the addition of heteropoly acid-forming ions to the reaction mixture.

TABLE 1

O_2 Oxidation of Cyclohexene in the Biphasic System Water–Chlorobenzene at 343 K

5 cm^3 Aqueous phase	10 cm^3 Organic phase	Reaction			O_2 uptake (mmol)	$O_{act\ org.}$ (mmol)	Epoxide (mmol)
		Mode	Time-lag (min)	Time[a]			
−	ch	d	16	120	0.633	0.571	0.00
−	ch	i	10	120	0.796	0.679	0.00
+	ch	d	120	120	0.000	0.000	0.00
+	ch	sc	120	120	0.000	0.010	0.00
+	ch	i	16	120	0.344	0.239	0.00
+	*ch	i	40	120	0.135	0.063	0.00
−	ch,AL	d	0	28	0.804	0.817	0.00
−	ch,AL	i	0	31	0.799	0.445	0.00
+	ch,AL	d	2	120	0.565	0.321	0.00
+	*ch,AL	d	3	120	0.639	0.442	0.00
+	ch,AL	i	9	120	0.676	0.367	0.00
+[b]	ch,AL	d	14	120	0.407	0.267	0.15
+[b]	ch,AL	i	10	120	0.495	0.353	0.18
+[c]	ch,AL	d	—	120	0.000	0.687	0.74
+[c]	ch,AL	sc	—	120	0.015	0.734	0.75
+[c]	ch,AL	i	—	120	0.130	0.905	0.75

Note. (+) present; (−) absent. (ch) 19.7 mmol cyclohexene containing 0.147 mmol cyclohexenyl hydroperoxide; (*ch) 19.6 mmol cyclohexene free of cyclohexenyl hydroperoxide; (d) dark reaction; (i) irradiated with a high pressure Hg lamp (type HBO 500 W) from a distance of 15 cm; (sc) reaction in scattered daylight.

[a] Time of uptake of 0.809 mmol O_2 (20.0 cm^3 O_2 at 28°C and 1.013×10^5 Pa) if the oxidation was fast; if not, the oxidation was followed up to 120 min.

[b] Aqueous phase containing 0.1 mmol Na_2MoO_4, pH adjusted to 3 AL—0.1 mmol Aliquat 336 dissolved in the chlorobenzene.

[c] Aqueous phase containing 0.1 mmol Na_2MoO_4 + 5.0 mmol H_2O_2, pH adjusted to 3.

TABLE 2

Epoxidation of Cyclohexene as a Function of pH and Temperature in Biphasic System

Temperature (K)	Aqueous phase			Organic phase		TN
	pH	$[H_2O_2]_o$ (mmol)	$[H_2O_2]_{end}$ (mmol)	O_{act} (mmol)	Epoxide (mmol)	
343	1.03	5.626	2.687	0.075	0.092	4.6
343	2.00	5.576	2.091	0.678	0.211	10.6
343	3.00	5.328	2.909	0.726	0.568	28.4
343	4.00	5.177	3.010	0.721	0.756	37.8
343	4.98	5.449	3.105	0.741	0.593	29.6
323	3.00	5.303	4.545	0.427	0.406	20.3
333	3.00	5.334	4.071	0.575	0.483	24.2
343	3.00	5.328	2.909	0.726	0.568	28.4
353	3.00	5.366	1.856	0.875	0.721	36.1

Note. Conditions: 5.00 cm^3 aqueous phase containing 0.1 mmol Na_2MoO_4 + H_2O_2 + sulphuric acid; 10.00 cm^3 organic phase containing 0.1 mmol ALCl; and 19.7 mmol cyclohexene dissolved in chlorobenzene; reaction time 120 min.

TABLE 3

Hydrolysis of Cyclohexene Oxide as a Function of pH and Temperature in Biphasic System

Temperature (K)	Aqueous phase				Organic phase		
	pH	$[H_2O_2]_o$ (mmol)	$[H_2O_2]_{end}$ (mmol)	Diol (mmol)	Diol (mmol)	O_{act} (mmol)	Epoxide (mmol)
343	1.02	5.566	5.056	1.187	0.297	0.111	0.000
343	2.02	5.398	2.192	1.082	0.271	0.131	0.000
343	2.50	5.348	3.181	0.690	0.172	0.136	0.624
343	3.00	5.512	3.254	0.291	0.073	0.148	1.078
343	4.00	5.310	3.320	0.061	0.016	0.151	1.423
343	5.00	5.621	3.472	0.021	0.005	0.158	1.257
323	3.00	5.107	4.866	0.266	0.066	0.138	1.103
333	3.00	5.348	4.549	0.269	0.068	0.176	1.156
343	3.00	5.512	3.254	0.291	0.073	0.148	1.078
353	3.00	5.601	1.744	0.323	0.081	0.156	0.871

Note. Conditions: 5.00 cm^3 aqueous phase containing 0.1 mmol Na_2MoO_4 + 5 mmol H_2O_2 + sulphuric acid; 10.0 cm^3 organic phase containing 0.1 mmol ALCl + 1.50 mmol cyclohexene oxide dissolved in chlorobenzene; reaction time 120 min.

As can be seen in Table 5, the epoxide yield and TN increased on increase of the heteroatom content; the optimum was found at [M] ≈ [X]. When ALCl was applied in excess over the molybdenum(VI) concentration, the epoxide was formed in considerably smaller quantity (see Table 5, E^a, and TN^a values). Arsenate proved to be a more efficient promoter than phosphate when ALCl was applied in equivalent quantity, but the activity relation was reversed when the PTC was used in a 10-fold excess with respect to the metal.

The influence of the PTC concentration on the epoxide yield is shown in Table 6. The quantity of the epoxide decreased definitely when ALCl was used in greater quantity. This behavior was also observed in cases when heteroions too were applied.

Some data are presented in Table 7 to compare the catalytic activities of molybde-

TABLE 4

Dependence of Epoxide Yield on the Concentration of Molybdenum(VI) at Constant Ratio $[MoO_4^{2-}]/[H_2O_2]$

MoO_4^{2-}	$[H_2O_2]_o$ (mmol)	$[H_2O_2]_{end}$ (mmol)	$\Delta[H_2O_2]$ (mmol)	$[Diol]_{aq}$ (mmol)	$[Diol]_{org}$ (mmol)	O_{act} (mmol)	Epoxide (mmol)	TN
0.02	1.128	0.887	0.241	0.013	0.003	0.339	0.088	11.0
0.04	2.180	1.457	0.723	0.064	0.016	0.493	0.205	12.8
0.06	3.244	1.850	1.394	0.113	0.028	0.583	0.345	14.4
0.08	4.372	2.002	2.370	0.179	0.045	0.641	0.533	16.6
0.10	5.378	2.610	2.768	0.249	0.062	0.794	0.728	18.2
0.20	10.847	4.537	6.310	0.462	0.115	1.154	1.347	16.8

Note. Conditions: 5.00 cm^3 aqueous phase containing Na_2MoO_4 + H_2O_2, pH adjusted to 3; 10.00 cm^3 organic phase containing 19.7 mmol cyclohexene + 0.2 mmol ALCl dissolved in chlorobenzene; in the dark, at 343 K, reaction time 120 min.

TABLE 5

Dependence of Epoxide Yield on the Metal/Heteroatom Ratio

$\frac{\text{Mo}}{X}$	X								$\frac{E_\text{P}}{E_\text{As}}$	$\frac{E^a_\text{P}}{E^a_\text{As}}$
	As				P					
	E (mmol)	TN	E^a (mmol)	TN^a	E (mmol)	TN	E^a (mmol)	TN^a		
24.0	1.44	72.0			0.85	42.5			0.59	
12.0	1.80	90.0			1.31	65.5			0.73	
6.0	2.20	110.0			1.52	76.0			0.69	
3.0	2.43	121.5	0.62	3.1	1.64	82.0	0.73	3.6	0.67	1.17
1.0	3.28	164.0	0.70	3.5	2.06	103.0	0.77	3.8	0.63	1.10
0.5	3.43	171.5	0.73	3.6	2.06	103.0	0.71	3.5	0.60	0.97
0.2	3.19	159.5	0.66	3.3	1.73	86.5	1.03	5.1	0.54	1.56

Note. Conditions: 5.00 cm^3 aqueous phase containing 0.1 mmol Na_2MoO_4 + X(= PO_4^{3-} or AsO_4^{3-}) in increasing quantities + 5.0 mmol H_2O_2, pH adjusted to 3; 10.00 cm^3 organic phase containing 19.7 mmol cyclohexene + 0.1 mmol ALCl dissolved in chlorobenzene; 343 K, reaction time 120 min.

[a] When 1.0 mmol ALCl was used in the organic phase.

num(VI) and tungsten(VI) both in the absence and in the presence of heteroions. Tungsten(VI) was about 3 times more active than molybdenum(VI) in the absence of heteroatoms. This tendency remained, but with a lower factor (1.2–1.6), in the presence of phosphate. When arsenate was applied as heteroacid component, molybdenum(VI) proved to be 1.2–1.4 times more active than tungsten(VI).

DISCUSSION

It has long been known that polar molecules such as water, alcohols, and amines, which are able to form H bonds with peroxo-

TABLE 6

Dependence of Epoxide Yield on the Concentration of ALCl

ALCl (mmol)	X						E_P/E_As
	None		P		As		
	E (mmol)	TN	E (mmol)	TN	E (mmol)	TN	
0.10	0.70	35	1.78	89.0	2.59	189.5	0.69
0.30	0.60	10	0.85	14.0	1.08	18.0	0.79
0.60	0.67	5.6	0.90	7.5	0.77	6.4	1.17
1.00	0.53	2.6	0.65	3.3	0.62	3.1	1.05

Note. Conditions: 5.00 cm^3 aqueous phase containing 0.1 mmol Na_2MoO_4 + 0.0333 mmol X(= PO_4^{3-} or AsO_4^{3-}) + 5.0 mmol H_2O_2, pH adjusted to 3; 10.00 cm^3 organic phase containing 19.7 mmol cyclohexene and AlCl in increasing quantities dissolved in chlorobenzene; 343 K, reaction time 120 min.

TABLE 7

Comparison of Catalytic Efficiencies of Molybdenum(VI) and Tungsten(VI)

MoO_4^{2-} (mmol)	WO_4^{2-} (mmol)	*X* (mmol)	*X*						E_p/E_{As}
			None		*P*		As		
			E (mmol)	TN	*E* (mmol)	TN	*E* (mmol)	TN	
0.10	—	—	0.61	30	—	—	—	—	—
0.10	—	0.0333	—	—	1.64	82	2.43	121	0.67
0.10	—	0.10	—	—	2.06	103	3.28	164	0.63
—	0.10	—	1.58	79	—	—	—	—	—
—	0.10	0.0333	—	—	2.62	131	2.04	102	1.28
—	0.10	0.10	—	—	2.50	125	2.37	118	1.05

Note. Conditions: 5.00 cm^3 aqueous phase containing Na_2MoO_4 + $X(= PO_4^{3-}$ or $AsO_4^{3-})$ + 5.00 mmol H_2O_2, pH adjusted to 3; 10.00 cm^3 organic phase containing 19.7 mmol cyclohexene + 0.1 mmol ALCl dissolved in chlorobenzene; 343 K, reaction time 120 min.

radicals, inhibit the autoxidation of hydrocarbons. This includes cyclohexene, but in the presence of ALCl, a definite acceleration was observed: in the dark, a fairly fast oxidation took place, almost without any time-lag. It is assumed that ALCl participates in the activation of cyclohexenyl hydroperoxide (*9–11*).

Molybdenum(VI) promoted the formation of the epoxide to a small extent when only cyclohexenyl hydroperoxide (formed by O_2 uptake) was present at O-atom source under phase-transfer conditions. The formation of a molybdenum(VI) hydroperoxo-complex can be detected by spectrophotometry in the organic phase. The epoxide yield is so small, however, that epoxide production cannot be based on molybdenum(VI)-catalyzed O_2 oxidation of alkene under phase-transfer conditions.

In the presence of excess hydrogen peroxide, the epoxide yield was found to be directly proportional to the molybdenum(VI) concentration of the aqueous phase when the ALCl concentration was sufficient for transfer of the metal catalyst. When the catalyst concentration became commensurable with that of ALCl, the epoxide yield and TN both decreased.

The pH of the aqueous phase proved to be an important factor for the epoxidation. At pH ≤ 2, the epoxide formed was hydrolyzed almost quantitatively to the diol, as the H^+ ion-catalyzed hydrolysis rate is many orders of magnitude higher than the rate in neutral aqueous medium. On the other hand, the increased H^+ ion concentration results in a decrease in the epoxide yield because the active species, the oxodiperoxometallates, are protolytes which undergo protonation:

$$MO(OO)_2(OH)^- + H^+ \rightleftharpoons MO(OO)_2 \cdot H_2O$$

The decadic logarithms of the protonation constants were 1.88 and 0.99 for molybdenum(VI) (*13*) and tungsten(VI) (14), respectively. Since a cationic PTC was applied at pH $\leq \log K_{prot}$ in these experiments, only part of the metal catalyst could be extracted; the hydrophilic protonated peroxo-species does not dissolve in a nonpolar solvent. At pH ≥ 5, the decrease in the epoxide yield is connected with the increasing rate of decomposition of hydrogen peroxide in the aqueous phase. Formation of the very unstable tetraperoxomolybdate can be observed via its reddish-brown color.

From the temperature dependence of the

overall rate of epoxidation, a value of 17.8 kJ mol^{-1} was obtained for the apparent enthalpy of activation and an unusually large negative value of -290.4 J K^{-1} mol^{-1} for the activation entropy. This may indicate that the rate-determining step involves an interaction with an unfavorable entropy change and this is in harmony with the widely accepted Sharpless mechanism of epoxidation (vide infra).

Application of heteropoly acid-forming ions such as arsenate and phosphate enhances the rate of epoxidation considerably; the promoter effect is maximum when [M] $\approx$ [X]. It was found earlier (*12*) that, in the presence of a large excess of hydrogen peroxide, $PMo_{12}O_{40}^{3-}$ and $AsMo_{12}O_{40}^{3-}$ resulted in a rate increase under phase-transfer conditions, in spite of the fact that phosphate and arsenate could be detected only in traces in the organic phase. Phosphate and arsenate are rather hydrophilic ions, and their heteropolyoxometallate complexes are less stable in water than in organic solvents. They should be applied in greater quantity in the aqueous phase in order to ensure a sufficient concentration in the organic phase for the catalytically active oxoperoxoheteropolymetallate complex to build up in greater quantity (*8*). Further, the heteroion concentration of the nonpolar phase can be influenced by the concentration of the PTC, too. At lower and higher ALCl concentrations, adducts with compositions XM_{5-6} and X_2M_{5-6}, respectively, exist in the organic phase (*8*); the catalytic activities of these species are different. It can be assumed that in the former case a central XO_4, and in the latter an X_2O_7 core, is coordinated by the appropriate number of $MO(OO)_2(OH)^-$ ligands, molybdenum(VI) and tungsten(VI) being present in their monomeric oxodiperoxo-form despite the acidic medium. In the oxodiperoxometallate unit, the metal (Cr, Mo, and W) is 7-coordinated and has a pentagonal bipyramidal structure. The equatorial plane is occupied by the two bidentate peroxo ligands and one hydroxy group (or H_2O at higher acidity); in the axial positions there is an O ligand with considerable double-bond character, and a loosely bonded H_2O ligand. This pentagonal bipyramidal structure is not perfectly symmetrical: the central metal ion is displaced 30–40 pm out of the equatorial plane toward the double-bonded O atom. The H_2O ligands can readily be replaced by O^{2-} ligands from the XO_4 or X_2O_7 cores, when heteropoly species are formed (*3*, *8*).

It is known that the O atom of the epoxide arises exclusively from the peroxo-oxygens of the complexes $MO(OO)_2L_2$ (where L is H_2O or other monodentate ligand) (*15*); two explanations are widely accepted for the mechanism of the epoxidation. Mimoun *et al.* (*16*) proposed the formation of a five-membered dioxometallocycle as active intermediate, whereas Sharpless *et al.*(*15*) suggested the reaction of the alkene with one of the peroxooxygens. These mechanisms were recently analyzed by Jörgensen and Hoffmann (*17*) from a frontier orbital point of view. They concluded that in the cases of molybdenum(VI) and tungsten(VI) the most probable mechanism is that of Sharpless *et al.*, according to which the first step is the formation of an alkene-transition metal complex. The next step is the slipping of the alkene into a perpendicular or parallel position relative to the metal peroxo-plane, giving a three-membered transition state and then leading to a concerted reaction of the alkene with this peroxooxygen.

If all this holds true for the very similar structures of the oxodiperoxometallate complexes and the mechanism of epoxidation, the question remains to be answered as to why the rate of epoxidation of cyclohexene is so different when different oxodiperoxometallates as well as their heteropoly derivatives are applied. In our opinion, the different epoxidation activities of the oxodiperoxometallates and their derivatives arise from the fact that the bidentate peroxoligands are bonded dissymmetrically. As a consequence of this bond dissymmetry, one of the peroxo-O-atoms is somewhat electrophilic, while the other is nucleophilic,

TABLE 8

Dissymmetry of O–O Bonds in η^2 Oxoperoxometallate Complexes

Compound	Distances (pm)					
	$M–O_{peroxo}$		$M–O_{ax.}$	O–O	M equat. plane	Ref.
$K_2[O(MoO(OO)_2(H_2O)]_2 \cdot 2H_2O$	197.4 198.0	195.3 195.9	166.4	152.5 145.5	38.0 39.0	*18*
$K_2[MoO(OO)_2(ox)]$	193 195	194 196	168	144 147	35	*19*
$CrO(OO)_2(py)$	179.4 182.5		157.6	140.7	51	*20*
$K_2[WO(OO)_2(ox)]$	192.8 196.5	194.1 196.8	171.6	149.6 151.0	35.8	*21*
$K_2[O\{WO(OO)_2 \cdot H_2O\}_2] \cdot 2H_2O$	193 196	196 200	166	150 154	35	*22*
$[Zn(H_3N)_4][Mo(OO)_4]$	Mean	193 200	—	155	—	*23*
$K_4[Mo_2O_2(OO)_4(tartrato)] \cdot 4H_2O$	Mean	193.8 197.3	168.5	148.1	—	*24*
$K_2[MoO(OO)_2(glyc)] \cdot 2H_2O$	192.8 196.1	192.6 197.0	168.6	147.2 146.9	—	*25*
$MoO(OO)_2(bipy)$	191.2 195.3	190.9 194.8	168.2	145.9 146.5	38.2	*26*
$K_2[MoO(OO)_2(citrato)] \cdot 1/2H_2O_2 \cdot 3H_2O$	Mean	192.6 197.5	165.5	148.2	—	*27*
$CrO(OO)_2 \cdot (phen)$	180 187		156	140	27	*28*
$Q_3[PO_4\{WO(OO)_2\}_4]$ Q = tetrahexylammonium	192 188 203 197	184 185 188 195	164	151 143 156 163	—	*29*
$CrO(OO)_2(bipy)$	Mean	178 192	157.0	140.0	31	*30*

thereby facilitating the interaction with the nucleophilic substrate. To support this idea, the corresponding data on some peroxo-derivatives of transition metals are compiled in Table 8. These indicate that the differences between the $M–O_{peroxo}$ bond lengths for given bidentate peroxo-ligands may vary from a value of 0.6 to 14 pm, i.e., the electrophilicity of the O atoms in the O–O bonds may differ in the different peroxo-derivatives. Further, the nonequivalence of the $M–O_{peroxo}$ bonds is usually accompanied by lengthening of the O–O bond. It must be admitted that the bond distances determined in crystals do not necessarily remain the same after dissolution, but it is assumed that the deformation of the structure of these complexes will be negligible when they are transferred into the nonpolar and non- or hardly solvating organic solvent with the aid of the PTC. If dissymmetry of the O–O bonds really does exist in solution too, discrete ^{17}O NMR signals are to be expected. For the oxodiperoxochromium(VI) complex two well-separated signals were observed (*32*), while the analogous molybdenum(VI) compound gave only one broader signal (*31–32*) and the Vaska-type iridium and platinum complexes did not show any ^{17}O NMR activity. The nuclear quadrupolar resonance study, however, proved the presence of two nonequivalent O atoms in the iridium complex (*31*). In spite of the difficulties in the detection of nonequivalent peroxidic O atoms, we persist in our view that the dissymmetry is retained after dissolution and is responsible for the different reactivity. Further anionic and neutral peroxocomplexes are now under investigation to obtain direct evidence to support the advanced assumption.

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