used in the catalyst preparation was loaned to us by the Matthey-Bishop Co., Inc.

Registry No.—Vinyl bromide, 593-60-2; (*Z*)-1-bromopropene, 590-13-6; 2-bromopropene, 557-93-7; (*Z*)-3-iodo-3-hexene, 16403-13-7; 1-bromo-2-methyl-1-propene, 3017-69-4; (*E*)-1,3-pentadiene, 2004-70-8; isoprene, 78-79-5; 1,3-butadiene, 106-99-0; 4-methyl-1,3-pentadiene, 926-56-7; 1,3-cyclohexadiene, 592-57-4; 1-methyl-1,3-cyclohexadiene, 1489-56-1; morpholine, 110-91-8; piperidine, 110-89-4; P(o-tol)$_3$, 6163-58-2; palladium acetate, 3375-31-3; 1-chloro-2,6-dimethyl-2,5-heptadiene, 68965-42-4; (*E*)-ethyl 3,7-dimethyl-3,6-octadienoate, 68965-43-5; (*Z*)-ethyl 3,7-dimethyl-3,6-octadienoate, 16750-89-3.

Supplementary Material Available: Table II, containing NMR spectra, boiling points, and molecular weights of the products prepared (2 pages). Ordering information is given on any current masthead page.

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Oxidation of Alcohols by Molybdenum and Tungsten Peroxo Complexes

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It has been demonstrated that peroxo complexes of molybdenum and tungsten oxidize secondary alcohols to ketones. The best yields have been obtained with hydrogen oxodiperoxo(pyridine-2-carboxylato)molybdate(VI) and its tungsten analogue. The latter complex proved to be a good catalyst for oxidation of secondary alcohols to ketones by hydrogen peroxide. The kinetics of the catalytic oxidation are reported, and a mechanism of the reaction is suggested.

Peroxo complexes of molybdenum and tungsten, although known for some time, have not been extensively studied as oxidants for organic substrates. So far peroxo complexes of molybdenum have been used only for stoichiometric epoxidation of olefins[1] and oxidation of cyclohexanonelithium enolate to 2-hydroxycyclohexanone.[2] Our effort has been directed toward the extension of the chemistry of peroxo complexes to other organic substrates. We have shown that, in methanol and in the presence of catalytic quantities of molybdenum and tungsten peroxo complexes stabilized by pyridinecarboxylato ligands, 2-methylcyclohexanone is oxidized to a mixture of methyl 6-hydroxyheptanoate and methyl 6-oxoheptanoate.[3] This finding suggested to us that methyl 6-oxoheptanoate may be a product of oxidation of methyl 6-hydroxyheptanoate. Therefore, a study of secondary alcohol oxidation by group 6 metal peroxo complexes has been initiated. We now wish to report the use of molybdenum and tungsten peroxo complexes as stoichiometric oxidants of secondary alcohols as well as catalysts for oxidation of secondary alcohols by H_2O_2.

Results and Discussion

Peroxo Complexes as Stoichiometric Oxidants. Four alcohols were selected as representatives of different classes of secondary alcohols. For the purpose of comparison, the reaction conditions were chosen to be analogous to those used for oxidation of cyclic ketones[3] without any attempt for optimization.

The results of secondary alcohol oxidation by different peroxo complexes of molybdenum and tungsten are summarized in Table I. The complexes containing monodentate ligands such as hexamethylphosphoric triamide (HMPA) as in $M(O)(O_2)_2(HMPA)(H_2O)$ (**1**, M = Mo; **2**, M = W)[4] or nicotinic acid as in $W(O)(O_2)(C_5H_4NCO_2H)(H_2O)$[5] (**3**) decompose to "blue metal oxides" in the course of oxidation. Therefore, no ketone or low yields of ketones are obtained. Introduction of a tridentate pyridine-2,6-dicarboxylato ligand as in $M(O)(O_2)[C_5H_3N(CO_2)_2](H_2O)$[6] (**4**, M = Mo; **5**, M = W) renders the complex completely inactive. Only complexes stabilized by the bidentate picolinato ligand such as in $H^+[M(O)(O_2)_2(C_5H_4NCO_2)]^-\cdot H_2O$ (**6**, M = Mo; **7**, M = W)[6] oxidize secondary alcohols to ketones in good yields. A 1-mol amount of complex **6** or **7** oxidizes more than 1 mol of secondary alcohol, yielding up to 1.7 mol of ketone per mol of the peroxo complex (Table I). This result suggests that both peroxo moieties in the complexes **6** and **7** are active, although the second one may react more slowly than the first one. Even though the reaction mixtures were analyzed only at the time indicated in Table I, the molybdenum complex **6** seems to react much more slowly than the corresponding tungsten complex **7**. During the oxidations a precipitate is formed. In the case of **7** the precipitate was isolated and shown, by IR and iodometric titration, to contain only metal oxo bonds and no peroxo bonds. Elemental analysis of the isolated precipitate indicated the presence of about 1 mol of picolinic acid per mol of $WO_3\cdot H_2O$, suggesting a tungsten oxo complex $W(O)_3(C_5H_4NCO_2H)(H_2O)$.

Peroxo Complex 7 as Catalyst. Regeneration of peroxo complexes by the reaction of oxo complexes with hydrogen peroxide is very fast.[5] Therefore, it became apparent that secondary alcohols should be oxidized by hydrogen peroxide in the presence of catalytic quantities of peroxo complexes **6** or **7**. The data summarized in Table II indeed demonstrate that the complex **7** is an active catalyst. The molybdenum analogue **6**, which is a slow oxidant of secondary alcohols (Table I), was found to be very inefficient. The catalytic oxidation is not limited to secondary alcohols. Primary alcohols can be oxidized as well, though at a lower rate.[7]

Kinetics of the Catalytic Oxidation. In order to gain a better understanding of the reaction mechanism, the oxidation of cyclohexanol was followed by iodometric titration. At the end of every run the amount of cyclohexanone formed was analyzed[8] by GC and shown to correspond to the amount of consumed hydrogen peroxide. Therefore, oxidation of methanol is negligible and it does not contribute to the consumption of hydrogen peroxide. In the kinetic runs the ratio of cy-

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Table I. Stoichiometric Oxidation of Secondary Alcohols by Molybdenum and Tungsten Peroxo Complexes in Methanol at 50 °C

alcohol, mmol	peroxo complex (mmol)	time, h	mmol of ketone/mmol of metal
	2-octanol		
0.505	$H^+[W(O)(O_2)_2(C_5H_4NCO_2)]^- \cdot H_2O$ (**7**) (0.256)	18[a]	1.32
0.473	$H^+[Mo(O)(O_2)_2(C_5H_4NCO_2)]^- \cdot H_2O$ (**6**) (0.266)	29	1.34
0.525	$Mo(O)(O_2)_2(HMPA)(H_2O)$[b] (**1**) (0.251)	40	0.36[c]
0.529	$W(O)(O_2)_2(HMPA)(H_2O)$[b] (**2**) (0.294)	18[a]	0.36[c]
0.500	$W(O)(O_2)_2(C_5H_4NCO_2H)(H_2O)$[d] (**3**) (0.252)	45	0[c]
	cyclohexanol		
0.495	$H^+[W(O)(O_2)_2(C_5H_4NCO_2)]^- \cdot H_2O$ (**7**) (0.249)	23[a]	1.15
0.562	$H^+[Mo(O)(O_2)_2(C_5H_4NCO_2)]^- \cdot H_2O$ (**6**) (0.287)	29	0.783
0.568	$W(O)(O_2)[C_5H_3N(CO_2)_2](H_2O)_2$ (**5**) (0.219)	65	0
0.587	$Mo(O)(O_2)[C_5H_3N(CO_2)_2](H_2O)$ (**4**) (0.291)	92	0
	1-phenylethanol		
0.51	$H^+[Mo(O)(O_2)_2(C_5H_4NCO_2)]^- \cdot H_2O$ (**6**) (0.227)	40	1.86
0.53	$[H^+W(O)(O_2)_2(C_5H_4NCO_2)]^- \cdot H_2O$ (**7**) (0.257)	17	1.46
0.50	$W(O)(O_2)[C_5H_3N(CO_2)_2](H_2O)_2$ (**5**) (0.252)	22	0
	methyl 6-hydroxyheptanoate		
0.513	$H^+[W(O)(O_2)_2(C_5H_4NCO_2)]^- \cdot H_2O$ (**7**) (0.252)	23[a]	1.52
0.542	$H^+[Mo(O)(O_2)_2(C_5H_4NCO_2)]^- \cdot H_2O$ (**6**) (0.251)	63	1.19
0.586	$Mo(O)(O_2)[C_5H_3N(CO_2)_2](H_2O)$ (**4**) (0.291)	92	0
	mixture of cyclopentanol and cycloheptanol		
5.69 ($C_5H_{10}O$)	$H^+[W(O)(O_2)_2(C_5H_4NCO_2)]^- \cdot H_2O$ (**7**) (4.37)	21[a]	0.41[e]
5.87 ($C_7H_{14}O$)			1.25[e]

[a] The reaction mixture was not analyzed until the time indicated. [b] HMPA stands for hexamethylphosphoric triamide. [c] The peroxo complexes were decomposed into "blue metal oxides". [d] $C_5H_4NCO_2H$ represents nicotinic acid. [e] 1.66 mmol of the ketones was produced for 1 mol of the complex.

Table II. Oxidation of Secondary Alcohols by Hydrogen Peroxide Catalyzed by Complex 7 at 65 °C[a]

alcohol	mmol[b]	H_2O_2, mmol[c]	time,[d] h	conversion,[e] %	catalyst turnover
cyclohexanol	1.82	1.80	4.25	50	17.2
1-phenylethanol	1.79	1.94	1.5	48	14.1
2-octanol	1.81	1.83	18	70	21.1
methyl 6-hydroxyheptanoate	1.77	1.81	4.5	53	15.3
cyclobutanol	3.81	1.83	8	61.4	9.3
mixture of cyclopentanol and cycloheptanol	7.44 7.46	15.3	1.5	19.0 42.6	16.6

[a] No attempt has been made to optimize the reaction conditions. [b] The ratio of alcohol/catalyst is ~30:1. [c] The amount of H_2O_2 at the end of the reaction has not been analyzed. [d] Not analyzed sooner than after the time indicated. [e] The yields of the ketones based on the alcohols consumed were about 90%.

clohexanol/hydrogen peroxide/complex **7** was about 100:10:1. Under these conditions the reaction was found to follow pseudo-zero-order kinetics. The linear relationship between the concentration of hydrogen peroxide and time, dictated by the pseudo-zero-order kinetics, is obeyed until the concentration of hydrogen peroxide reaches that of the peroxo complex. The pseudo-zero-order rate constants k_0 were found to be a linear function of the catalyst concentration (Table III). The rate constants k_0 divided by the catalyst concentration gave the pseudo-first-order rate constants k_1 (Table III), which were shown to be a linear function of cyclohexanol concentration. The rate constants k_1 corrected for cyclohexanol concentration yielded the second-order rate constants k_2, which are practically independent of the hydrogen peroxide concentration (Table III). The catalytic oxidation of secondary alcohols can therefore be described by second-order kinetics (eq 1), first order in catalyst and first order in cyclohexanol, suggesting that the rate-determining step involves interaction of the peroxo complex with the secondary alcohol.

Table III. Dependence of the Rate of Cyclohexanol Oxidation on Concentrations of the Alcohol, Complex 7, and Hydrogen Peroxide at 65 °C

$C_6H_{11}OH$, mol/kg	complex 7, mol/kg 10^3	H_2O_2, mol/kg	$k_0 \cdot 10^2$ mol/kg·h	k_1, h^{-1}	k_2, kg/mol·h
0.595	5.15	0.12	2.0	3.9	6.5
1.12	2.96	0.11	2.1	7.1	6.3
1.00	9.37	0.10	6.0	6.4	6.4
1.00	19.3	0.11	12.1	6.3	6.3
2.74	4.04	0.09	7.5	18.7	6.8
2.60	7.80	0.27	13.6	17.4	6.7
2.60	7.60	0.53	13.6	17.8	6.8

$$-d[H_2O_2]/dt = k_0 = k_1[\text{cat}] = k_2[\text{cat}][\text{alcohol}] \qquad (1)$$

Oxidation of secondary alcohols by oxides of Cr(VI) or V(V) proceeds via formation of esters between alcohols and metal

Table IV. Second-Order Rate Constants k_2 for Different Substrates[a]

alcohol	k_2, kg/mol·h
cyclohexanol	6.0
cyclohexanol and 2,6-di-*tert*-butyl-4-methylphenol (0.1 mol kg^{-1})	5.9
cyclohexanol-*1-d*	2.9
ethoxycyclohexane	0.76
2-octanol	4.0
methyl 6-hydroxyheptanoate	3.5
1-phenylethanol	7.0
1-phenylethanol-*1-d*	3.1

[a] Unless stated otherwise, the rate constants were measured at 65 °C and concentrations were as follows: alcohol, ~1 mol/kg; H_2O_2, ~0.1 mol/kg; and complex 7, 0.01 mol/kg.

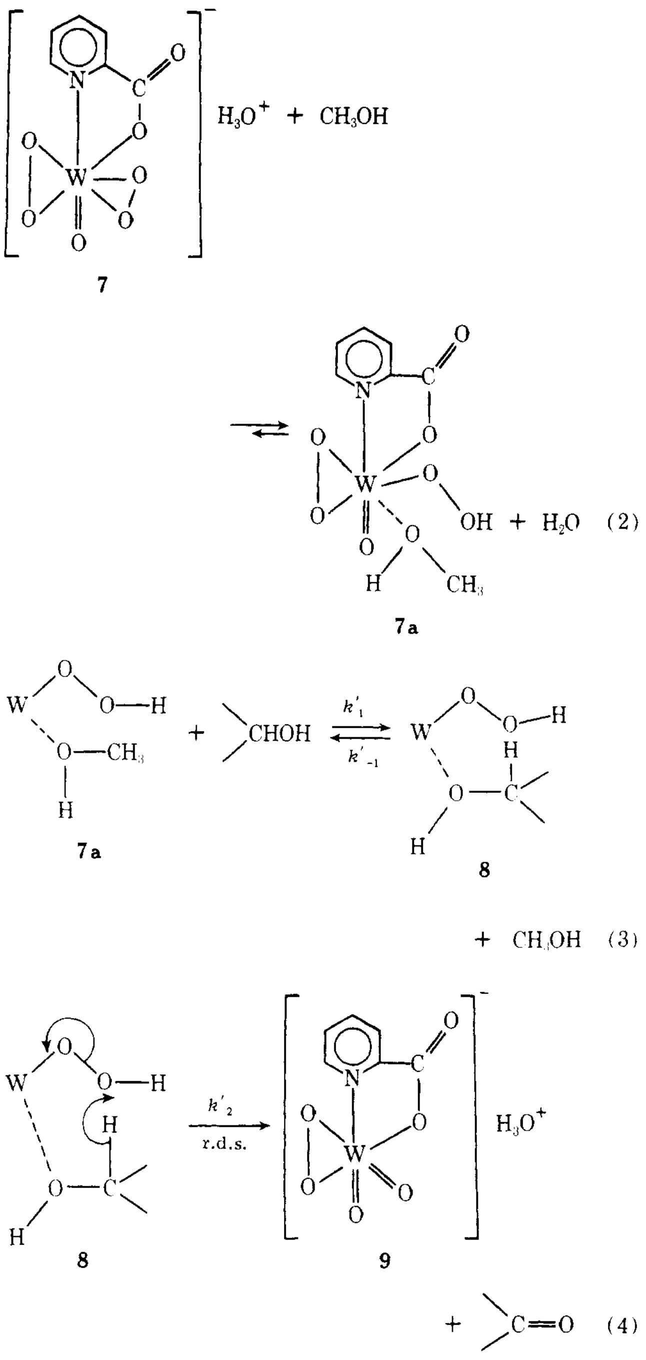
oxides. As a result, oxidation of secondary alcohols by oxides of Cr(VI) or V(V) is about 10^4 faster than the oxidation of the corresponding methyl ethers.[9] In our system, ethyl cyclohexyl ether is oxidized only seven times more slowly than cyclohexanol (Table IV), suggesting that ester formation between alcohol and peroxo complex 7 probably does not play an important role. Instead, the alcohol or the ether may only form complexes with the metal center.

The isotope effect of 2.07 for cyclohexanol and 2.24 for 1-phenylethanol (Table IV) strongly suggests that the C–H bond is broken in the rate-determining step.

One- vs. Two-Electron Oxidation. Several tests can be devised in order to decide if the alcohol oxidation involves a one- or two-electron transfer in the rate-determining step. Thus, interaction of cyclobutanol with two-electron oxidants leads predominantly to cyclobutanone, while a one-electron oxidant cleaves the four-membered ring to derivatives of butyraldehyde.[9b] Oxidation of cyclobutanol by hydrogen peroxide catalyzed by complex 7 leads to cyclobutanone. No open-chain products were detected (Table II). Cella and coworkers[10] demonstrated that reactions of an equimolar mixture of cyclopentanol and cycloheptanol with a deficiency of oxidant can give rise to different product distributions depending on the oxidation process involved. Oxidation by insufficient amounts of *m*-chloroperbenzoic acid leads predominantly to cycloheptanone in a nonradical, mineral acid catalyzed oxidation. On the contrary, cyclopentanone is the prevailing product in a nitroxide-catalyzed process which is believed to be of a radical nature. In our case, reaction of an equal molar mixture of cyclopentanol and cycloheptanol, either with stoichiometric quantities of 7 (Table I) or with hydrogen peroxide in the presence of catalytic quantities of 7 (Table II), yields predominantly cycloheptanone with cyclopentanone as a minor product. Finally, the rate of alcohol oxidation is not affected by radical scavengers (e.g., 2,6-di-*tert*-butyl-4-methylphenol) even if the scavenger is present at a concentration ten times higher than the concentration of the catalyst and equimolar with the concentration of hydrogen peroxide (Table IV). All of the above findings are in agreement with a two-electron transfer in the rate-determining step rather than a radical process.

A mechanism for the alcohol oxidation which is consistent with our observations is summarized in Scheme I.[11] The structure of complex 7 is based on a comparison of the spectral properties of complex 7 with the spectral properties of an analogous molybdenum complex whose structure was determined by X-ray diffraction of a single crystal.[6] In protic, polar media such as methanol, the complex 7 is in equilibrium with species 7a. The existence of the equilibrium 2 (Scheme I) cannot be readily demonstrated by spectral methods. However, the conductivity measurements[6] of the complex 7 dissolved in methanol show that at 25 °C more than 50% of complex 7 is in nonionic form 7a. Similar conclusions can be drawn from the alkalimetric titration of a solution of complex 7 in methanol.[6] The equilibrium 2 is required for the opening of a coordination site to which either solvent or secondary alcohol (substrate) can be bound. Based on our qualitative observations, it can be assumed that at the reaction temperature of 65 °C the equilibrium 2 (Scheme I) lies predominantly or exclusively on the side of complex 7a. In agreement with the fact that the pseudo-zero-order kinetics are fulfilled until the concentration of hydrogen peroxide reaches that of the peroxo complex employed as catalyst, the equilibrium 5 should lie predominantly to the right. This has been further confirmed by a reaction of an oxo complex with H_2O_2.[5] For derivation of the kinetic equation, it is then necessary to

Scheme I



$$9 + H_2O_2 + CH_3OH \rightleftharpoons 7a + 2H_2O \qquad (5)$$

consider only steps 3 and 4 in Scheme I. The stoichiometry of the reaction leads to eq 6. Combination of eq 1 and 6 together with application of the steady-state approximation for the species[11] 8 (Scheme I) leads to eq 7 and 8.

$$-\mathrm{d}[\mathrm{H_2O_2}]/\mathrm{d}t = \mathrm{d}[\text{ketone}]/\mathrm{d}t = k_2'C \qquad (6)$$

$$k_2'[\mathbf{8}] = [k_2'k_1'/(k_{-1}' + k_2')][\mathbf{7a}][\text{alcohol}] = k_2[\mathbf{7a}][\text{alcohol}] \qquad (7)$$

$$k_2 = k_2'k_1'/(k_{-1}' + k_2') \qquad (8)$$

The relative values of k_{-1}' and k_2' will then determine the magnitude of the isotope effect. It is therefore believed that the observed isotope effect, which is relatively low, reflects a weak ability of the secondary alcohol to compete with methanol for the coordination site (eq 3).[12] A similar explanation may be offered for relatively small differences in the reaction rate constants k_2 of different alcohols (Table IV). The observed lack of catalytic activity in the case of molybdenum peroxo complex **6**, the analogue of the tungsten catalyst **7**, may be explained by the fact that the equilibrium 2 (Scheme I) for the molybdenum complex **6** lies, at least at room temperature, predominantly or exclusively on the left side, i.e., on the side of the species analogous to **7**, as shown by conductivity measurements and alkalimetric titrations.[6] Cyclohexanol may then be prevented from entering into the coordination sphere of Mo(VI), and no oxidation of cyclohexanol can be expected.

Experimental Section

Materials. Ethyl cyclohexyl ether was prepared from ethyl phenyl ether (50 g) by hydrogenation over Raney nickel at 180 °C and a hydrogen pressure of 800 psi. Based on GC and NMR spectra, the product (48 g), bp 148.5–149.5 °C, did not contain any starting material: NMR δ 3–3.6 (3 H, quartet and multiplet), 1–2 (13 H, triplet and multiplet).

Reduction of cyclohexanone (18 g, 0.184 mol) by $\mathrm{LiAlD_4}$ (3.69 g, 0.086 mol) in ether afforded cyclohexanol-*1-d* (16.2 g, 0.162 mol), bp 159–160 °C, containing 0.2% of cyclohexanone (GC analysis): NMR δ 4.2 (1 H, s), 1–2 (10 H, m); no CHOH was found by NMR; mass spectrum, *m/e* 101 ($\mathrm{C_6H_{11}DO}$) more than 99%.

All other alcohols and all ketones were purchased from Aldrich and used without further purification. The synthesis and characterization of the peroxo complexes **3–7** are reported in a separate paper.[6] The peroxo complexes **1** and **2** were prepared by known procedures[4] and characterized by elemental analysis and IR spectra.

Oxidation Procedures and Product Analysis. All stoichiometric oxidations of secondary alcohols by peroxo complexes were carried out in the same manner. Oxidation of 2-octanol is chosen as an example. The peroxo complex **7** (0.1036 g, 0.256 mmol) was dissolved in a mixture of 2-octanol (0.0658 g, 0.505 mmol), an internal standard (trichloroethylene, 0.662 g, 0.506 mmol), and perdeuteriomethanol (0.6 g). The mixture was transferred into an NMR tube, degassed on a vacuum line, and sealed. The tube was then heated in a constant temperature bath at 50 °C. The reaction was monitored by NMR, following the decrease of the -CH(OH)- protons and the increase of the $\mathrm{CH_3C({=}O)}$– protons relative to the internal standard. At the end of the run, the tube was opened and the contents were analyzed by GC, employing a 4-ft column filled with 5% of Carbowax on Chromosorb W in the temperature range from 80 to 180 °C. The results for all alcohols studied are summarized in Table I.

A precipitate was gradually formed during the course of the run. When the tube was opened, the precipitate was filtered off, washed with water and methanol, and dried under vacuum at ambient temperature: IR (Nujol mull) 880 and 970 $\mathrm{cm^{-1}}$ (W=O), no peroxo bridge. Anal. Calcd for $\mathrm{C_6H_7NO_6W}$: C, 19.32; H, 1.89; N, 3.76; W, 49.29; no peroxidic $\mathrm{O_2}$. Found: C, 19.91; H, 1.74; N, 3.36; W, 47.7; no peroxidic $\mathrm{O_2}$. The sample was contaminated by a small amount of methanol.

A typical procedure for the catalytic oxidation is again exemplified with 2-octanol. In a small vial, 2-octanol (0.2363 g, 1.81 mmol) was mixed with 0.2 g of perdeuteriomethanol and a solution of 90% aqueous hydrogen peroxide in perdeuteriomethanol (0.2463 g) containing 0.253 g of hydrogen peroxide per gram of the solution. Trichloroethylene (0.2306 g, 1.75 mmol) was dissolved in the above mixture. The clear solution was degassed, sealed in an NMR tube, and subsequently heated at 80 °C. The reaction was monitored by NMR and analyzed by GC at the end of every run.

Kinetic Measurements. The rates of oxidation of secondary alcohols were measured by iodometric titration of hydrogen peroxide in aliquots removed from the reaction mixture at appropriate intervals. The pseudo-zero-order rate constants were calculated from the slope of the plots of hydrogen peroxide concentration vs. time. In order to assure a good precision, the aliquots withdrawn from the reaction mixture were weighed. Therefore, the concentration is given in molalities (mol/kg) rather than the conventional molarities.

Registry No.—**1,** 36671-04-2; **2,** 23273-35-0; **3,** 68854-27-3; **4,** 55173-45-0; **5,** 55174-46-1; **6,** 67584-06-9; **7,** 67584-05-8; 2-octanol, 123-96-6; cyclobutanol, 2919-23-5; cyclopentanol, 96-41-3; cyclohexanol, 108-93-0; cyclohexanol-*1-d*, 21273-02-9; cycloheptanol, 502-41-0; 1-phenylethanol, 98-85-1; 1-phenylethanol-*1-d*, 3101-96-0; 2,6-di-*tert*-butyl-4-methylphenol, 128-37-0; ethoxycyclohexane, 932-92-3; methyl 6-hydroxyheptanoate, 2517-46-6.

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(7) Oxidation of primary alcohols leads to a mixture of products which was not fully characterized.

(8) Part of the cyclohexanone appeared on GC as 1-methoxycyclohexene, which can be formed in the GC from cyclohexanone. This has been demonstrated when a mixture of cyclohexanone and a small amount of the complex was dissolved in a tenfold excess of methanol and injected into the GC. If most of the methanol is evaporated before injection, only cyclohexanone is found.

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