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Reactivity of Peroxopolyoxo Complexes. Oxidation of Thioethers, Alkenes, and Sulfoxides by Tetrahexylammonium Tetrakis(diperoxomolybdo)phosphate

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Kinetics of oxidation of thioethers, alkenes, and sulfoxides by tetrahexylammonium tetrakis(diperoxomolybdo)phosphate (TEAM) were performed in chloroform. The results obtained, compared with the corresponding data of a series of Mo(VI) peroxo complexes, rule out a nucleophilic oxygen transfer mechanism. Rather, the data point to Mo(VI) peroxopolyoxo complexes as well as simple peroxo complexes behave as electrophilic oxidants toward nucleophilic substrates such as thioethers and alkenes. A study of the countercation effects indicates that the increasing bulkiness of the cation reduces the electrophilicity of the peroxopolyoxo complex. With sulfoxides, incursion of SET processes might be a likely event.

Introduction

Oxidation processes, employing dilute hydrogen peroxide and heteropoly acids such as $H_3PM_{12}O_{40}$ (M = Mo(VI), W(VI)) or their salts, are of increasing interest in the selective synthesis of oxygenated organic compounds.

Various substrates, e.g. alkenes,[1-3] alkynes,[4,5] alcohols,[1,6] diols,[1,6,7] sulfides,[3,8] and amines,[9] were shown to be suitable candidates for such oxidation reactions.

It has been suggested that the activity of these oxidant systems is due to the formation in situ of peroxopolyoxo species, which are the real oxidizing agents.[1a] Therefore it appears relevant to isolate these peroxopolyoxo species in order to study their reactive behavior.

A few years ago Venturello et al. isolated a W(VI) peroxopolyoxo species and obtained X-ray structural information.[10] The compound is a salt, $[(C_6H_{13})_4N^+]_3\{PO_4[WO(O_2)_2]_4\}^{3-}$ (TEAW), whose structure consists of four distorted $WO(O_2)_2$ pentagonal bipyramids, joined to a tetrahedral central PO_4 group by W–O single bonds. Two more Mo(VI)[1a] and W(VI)[1b] peroxopolyoxo complexes have been isolated, but it has not been possible to obtain X-ray information on them. However, elemental analysis, iodometric titer, and IR spectroscopy point to formulas $[C_5H_5N^+(CH_2)_{15}CH_3]_3\{PO_4[MoO(O_2)_2]_4\}^{3-}$ (PCMP) and $[C_5H_5N^+(CH_2)_{15}CH_3]_3\{PO_4[WO(O_2)_2]_4\}^{3-}$ (PCWP), respectively, for Mo and W, which would indicate that these peroxo complexes belong to the same class as TEAW. Preliminary kinetic investigations[3,8] indicated that organic substrates, with reaction sites carrying lone pairs or π electrons, behave as nucleophiles toward such peroxo complexes which, therefore, are regarded as electrophilic oxidants. Indeed, this behavior would seem at variance with the fact that it is the anionic part of the oxidants which bears the transferable oxygen (for this reason these oxidants are also known as *anionic* peroxo complexes). On this basis one would expect these oxidants to be nucleophilic rather than electrophilic in character. In order to collect further information to define the reactivity of this class of oxidants, we have synthesized a novel peroxopolyoxo complex, i.e. tetrahexylammonium tetrakis(diperoxomolybdo)phosphate (TEAM), which is the analogue of TEAW. We have studied some simple oxidation reactions and compared the results with those obtained by PCMP and by other Mo(VI) simple peroxo complexes.

Table I. Oxidation of Organic Substrates with TEAM[a] in $CHCl_3$ at 40 °C

substrate (mmol)	time (h)	product	yield[b] (%)
cyclooctene (1.9)	94	cyclooctene oxide	93
phenyl methyl sulfide[c] (5.7)	0.5	phenyl methyl sulfoxide	97
phenyl methyl sulfoxide (1.7)	1.7	phenyl methyl sulfone	96
propan-1-ol (3.1)	24,[d] 48[d]	propanal	98
octan-1-ol (3.1)	21,[d], 45[d]	octanal	97
octan-2-ol (2.4)	24,[d] 48[d]	octan-2-one	100
geraniol (2.5)	7	2,3-epoxygeraniol	100

[a] In all experiments $[O]_{active}$ = 8[TEAM] = 0.32 mmol. [b] Calculated with respect to the oxidant after its complete consumption. [c] At t = 0 °C. [d] In these reactions the presence of induction time and not reproducible reaction times might indicate incursion of radical pathways.

Results and Discussion

TEAM was prepared by a synthetic procedure similar to that used by Venturello for the preparation of the analogous W compound.[10] Iodometric titer allows an evaluation of an active oxygen content as expected for the presence of eight peroxidic bridges in the molecule.

The IR spectrum of TEAM shows two bands[10] at 540 and 590 cm^{-1} assigned respectively to the symmetric and antisymmetric vibration modes of $\overline{\text{Mo–O–O}}$, an absorption at 865 and 875 cm^{-1} assigned to the stretching frequency of the O–O bond,[11a] a band at 965 cm^{-1} assigned to the Mo=O symmetric vibration, and a band at 1075 cm^{-1} due

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Table II. Rate Constants for the Stoichiometric Oxidation of p-$XC_6H_4SCH_3$ to p-$XC_6H_4SOCH_3$ and for the Epoxidation of Alkenes with Mo(VI) Peroxo Complexes in $CHCl_3$

X	$10^2k_2^{TEAM}$ $(M^{-1}\ s^{-1})^a$	$10^2k_2^{PCMP}$ $(M^{-1}\ s^{-1})^b$	$10^2k_2^{MoO_5HMPT}$ $(M^{-1}\ s^{-1})^b$	$10^2k_2^{PICO}$ $(M^{-1}\ s^{-1})^c$
OCH_3	1.85			
CH_3		5.0	2.1	$(0.33)^d$
H	1.13	4.0	1.1	$0.70\ (0.24)^d$
Cl		1.8	0.65	$0.97\ (0.18)^d$
NO_2	0.25	0.16	0.10	$(0.08)^d$
alkene[e]				
1-octene		2.1	9.2	nr
trans-2-octene	0.09	4.7	14	nr
cyclohexene		4.5	37	nr
cyclooctene	0.66	6.4	68	nr

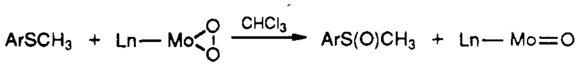
[a] This work. [b] Rate constants measured at −40 °C.[3] [c] Rate constants measured at 40 °C,[13] PICO stands for $[(C_4H_9)_4N^+][MoO(O_2)_2O_2C(O)NC_5H_4]^-$. [d] Values in DCE.[14] [e] Rate constants measured at 40 °C; PCMP and MoO_5HMPT epoxidation rate constants from ref 3.

to the asymmetric vibration of the tetrahedral P–O.[11b] As a whole, the spectrum is very similar to that reported for PCMP.[1b] Therefore it seems reasonable to conclude that TEAM is a peroxopolyoxo species belonging to the same family of aforementioned oxidants.[12]

In order to establish the synthetic scope of TEAM, thus allowing a comparison with PCMP, we have examined the oxidation reactions of some model compounds. The pertinent results are shown in Table I. It is interesting to note that TEAM is at least as versatile as PCMP. Thus, cyclooctene is quantitatively epoxidized (entry 1), sulfides and sulfoxides form sulfoxides and sulfones, respectively (entries 2 and 3), primary alcohols give the corresponding aldehydes (entries 4 and 5), and 2-octanol, a secondary alcohol, yields the corresponding ketone (entry 6). Geraniol, an allylic alcohol which in principle offers three possible sites of attack, i.e. the two double bonds and the OH functionality, produces 2,3-epoxygeraniol exclusively, in a regio- and chemoselective manner.

The oxidation chemistry indicates that PCMP and TEAM are two oxidants of the same family. The difference in the countercation, cetylpyridinium (PCMP) vs tetrahexylammonium (TEAM), has no influence on the identity of the oxidation products.

Oxidation of Thioethers. For mechanistic investigations, we selected the oxidation process of highly nucleophilic substrates such as thioethers. Kinetic studies were carried out in $CHCl_3$ under pseudo-first-order conditions, the following stoichiometry (eq 1) having been established:



$$ArSCH_3 + Ln{-}Mo(O_2) \xrightarrow{CHCl_3} ArS(O)CH_3 + Ln{-}Mo{=}O \quad (1)$$

The process follows a second-order rate law, first order with respect to each reactant. The second-order rate constants are collected in Table II. It can be observed that the oxidation rate increases with increasing the nucleophilicity of the substrate, thus establishing that TEAM behaves as the electrophilic partner in the reaction.

Therefore the kinetic data presented here do not disqualify the hypothesis that thioethers are oxidized to sulfoxides by TEAM through a simple bimolecular process, which presumably involves an external nucleophilic attack of the thioether on the peroxidic oxygen (electrophilic oxygen transfer[15]).

By way of comparison, Table II reports the second-order rate constants relative to the oxidation of thioethers by some Mo(VI) peroxo complexes. PICO and MoO_5HMPT differ from PCMP and TEAM because they are simple peroxo complexes with only two peroxidic bridges and because PICO is an "anionic complex" bearing one negative charge, whereas MoO_5HMPT is a neutral complex. As can be noted from Table II, a reactive behavior toward sulfides similar to that of TEAM had been observed for MoO_5HMPT (which is known to behave as an electrophilic oxidant[3,15,16]), as well as for PCMP and PICO. If allowance is made for a statistical correction,[17] dividing by 4 the rate constants of peroxopolyoxo complexes, we obtain the reactivity sequence $MoO_5HMPT > PCMP > TEAM \gg PICO$. The higher reactivity of neutral oxidant relative to that of "anionic" reagents seems to match with the suggested electrophilic oxygen transfer mechanism.[15] Within the "anionic" peroxo complex series, the low reactivity of PICO might be due to the lower electrophilicity of its peroxidic oxygens (one negative charge/two peroxidic bridges in comparison with three negative charges/eight peroxidic bridges). The quite lower reactivity displayed by TEAM in comparison to PCMP seems ascribable to the countercation effects in the frame of the suggested electrophilic oxygen transfer mechanism. It has been, in fact, reported[18] that for quaternary ammonium salts the interionic distance between the cation and the counteranion depends on their relative bulkiness. Particularly when the ions are quite bulky the interionic distance is larger. In such a case the ions are considered as trigonal pyramids instead of hard spheres.[18] The larger interionic distance is responsible for a higher dissociation constant, due to the lower interionic interaction. In our case the larger bulkiness of tetrahexylammonium with respect to cetylpyridinium might be responsible of a higher interionic distance in TEAM than in PCMP. Therefore the part of the molecule bearing the oxygen in TEAM does have a higher anionic character, due to the reduced interionic interaction, and therefore probably for Couloumbic reasons, it is less prone to undergo a nucleophilic attack. Also the data related to the epoxidation process of some model alkenes which are, even if weaker than thioethers, still nucleophilic substrates, are in agreement with the electrophilic oxygen transfer mechanism.

In fact, as reported in Table II, the more nucleophilic olefin appears to be also the more reactive olefin. Furthermore, we again observe the same reactivity sequence $MoO_5HMPT > PCMP > TEAM \gg PICO$[19] as in the case of sulfide oxidation; also the much higher nucleophilicity of thioethers with respect to alkenes seems to be reflected in their much larger reactivity toward these oxidants.

On the other hand since we are dealing with "anionic" peroxopolyoxo complexes it might be reasonable to suppose that, under suitable conditions, these oxidants may behave as nucleophiles. Therefore we examined the oxi-

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[12] TEAM was also subjected to X-ray diffraction analysis. It was possible to solve the crystal structure, which appears very similar to that of TEAW, as expected. However, unfortunately the molybdato groups are highly disordered, and all our results, at the moment, are not good enough for a crystallografic publication. Furthermore, determination of a molecular weight is in agreement with the expected formula.

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[17] To take in account the eight peroxidic bridges of PCMP and TEAM vs the two bridges of MoO_5HMPT and PICO, respectively.

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[19] PICO undergoes no epoxidation reaction.

Table III. Rate Constants for Stoichiometric Oxidations of p-$XC_6H_4SOCH_3$ to p-$XC_6H_4SO_2CH_3$ by TEAM in $CHCl_3$ at 40 °C[a]

X	M	10^3k_{obs} (s^{-1})	$10^2k_{obs}/[S]_o$ ($M^{-1}\ s^{-1}$)	10^2k_2 ($M^{-1}\ s^{-1}$)
	0.070	1.12	1.60	
OCH_3	0.120	1.93	1.60	1.60
	0.210	3.41	1.60	
	0.030	0.536	1.79	
CH_3	0.076	1.33	1.75	1.76
	0.165	2.86	1.73	
	0.069	1.26	1.83	
H	0.117	2.16	1.85	1.86
	0.200	3.81	1.91	
	0.027	0.682	2.53	
Cl	0.036	0.915	2.54	2.54
	0.070	1.89	2.55	
	0.017	0.793	4.66	
NO_2	0.033	1.30	3.94	4.34
	0.089	3.94	4.43	

[a] Experimental conditions as in Table II.

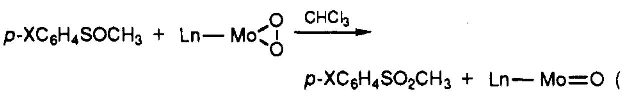
Table IV. Second-Order Rate Constants for the Stoichiometric Oxidation of p-$XC_6H_4SOCH_3$ to p-$XC_6H_4SO_2CH_3$

X	$10^2k_2^{TEAM}$ ($M^{-1}\ s^{-1}$)[a]	$10^2k_2^{PCMP}$ ($M^{-1}\ s^{-1}$)[b]	$10^2k_2^{PICO}$ ($M^{-1}\ s^{-1}$)[c]
OCH_3	1.6	2.9	
CH_3	1.8	2.1	0.088 (0.081)[d]
H	1.9	2.1	0.082 (0.074)[d]
Cl	2.5	2.4	0.13 (0.091)[d]
NO_2	4.3	2.2	(0.083)[d]

[a] This work. [b] At 20 °C, ref 8. [c] At 40 °C, ref 13. [d] At 40 °C in DCE, ref 14.

dation process of sulfoxides to sulfones, because such substrates are able to be oxidized by both nucleophilic oxidants (organic peracids anions)[20] and electrophilic oxidants (organic peracids),[21] the former process being faster than the latter.

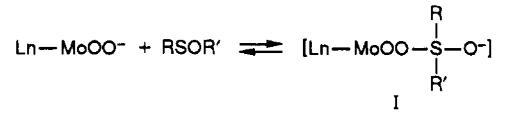
Oxidation of Sulfoxides. The oxidation of sulfoxides by TEAM was performed in $CHCl_3$ at 40 °C after having established the quantitative formation of the products (eq 2)



(2)

X = OCH_3, CH_3, H, Cl, NO_2

Even in this case the process follows a second-order kinetic law; the pertinent rate constants are shown in Table III. It can be noted that the reactivity pattern is different from that observed for sulfides. In particular, in the series of substituted phenyl methyl sulfoxides, the reaction rates show little dependence on the nature of the substituent. In passing from p-OCH_3 to p-NO_2 a less than 3-fold reaction rate decrease is observed. A very similar pattern, as shown in Table IV for comparison, has already been reported for PCMP and PICO. In such cases there is no appreciable rate dependence on the identity of the sulfoxide reactant. To offer a rationale for this reactivity behavior, which seems to be quite general within the series of anionic peroxo complexes, we suggest that these oxidants exhibit a nucleophilic character in sulfoxide oxidation. According to the classical scheme of nucleophilic oxidations by peroxides, a negatively charged oxygen of the peroxo complex attacks the SO functionality, leading to the formation of a peroxide intermediate:



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$$\mathrm{I} \rightarrow RSO_2R' + Ln{-}Mo{=}O$$

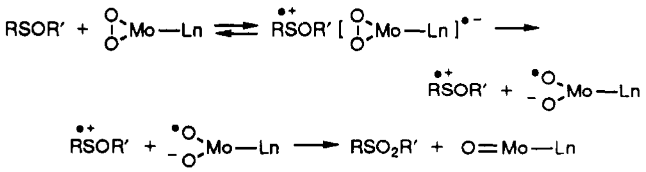
The mechanistic scheme would therefore be similar to that reported for the oxidation of sulfoxides by organic peracid anions.[21] Under this hypothesis, the electronic demands of the substituents in the two steps being opposite, their eventual balance could lead to the observed small substituent effects if the rates of each step were comparable.

However some additional findings are at odds with such a mechanistic hypothesis. Firstly, several pieces of evidence, particularly ^{17}O NMR[22] measurements, militate against the occurrence in solution of peracid-like, end-on complexes such as Mo-O-O⁻. A second alternative, namely that the negative charge is located mainly on the Mo=O moiety, is brought into question by both available X-ray data and ^{17}O NMR data.[22]

On the other hand, efforts to find examples of nucleophilic behavior by these peroxo complexes failed. In fact it was observed that both MoO_5HMPT and PICO do not react with olefins bearing electron-withdrawing groups which usually react with nucleophilic oxidants. Even in the literature there is no report of nucleophilic behavior for these oxidants. The only claimed example of nucleophilic reactivity, i.e. Baeyer–Villiger ketone oxidation by H_2O_2 catalyzed by Mo(VI) peroxo complexes,[23] has been shown recently[24] to be indeed an oxidation carried on by H_2O_2, in which the metal plays only the role of a Lewis acid catalyst. Also, competitive experiments, performed recently in our laboratory to assess the electronic nature of such oxidants, gave indication of their electrophilic character.[16]

Therefore all pieces of collected information seem to give no support to the hypothesis of a nucleophilic attack by the oxidant on the sulfoxide moiety. Even the reactivity sequence, PCMP > TEAM > PICO, observed also in the oxidation of sulfoxides is hardly reconcilable with the nucleophilic mechanism.

Therefore, as far as sulfoxides are concerned, the overall picture is less conclusive than in the case of sulfides and alkenes. However, a possible rationale of sulfoxide behavior might be based on the involvement of a single-electron transfer (SET) from the sulfoxide to the peroxo complex, which would generate a radical anion of the oxidant:



Taking in account that the reduction potential of TEAM was estimated to be $E_{1/2} = -1.8$ V (DMF)[16d] and that a

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value of $E_{ox} = 1.97$[25] was reported for the process C_6H_5S-$OCH_3 \overset{-e}{\rightleftharpoons} C_6H_5S^{\cdot+}OCH_3$, the possibility of occurrence of SET processes between the sulfoxides and TEAM might be reasonable. In such a case the oxidant behaves as an electrophile (acceptor) in the SET step and as a nucleophile in the collapse step. Suitable balance between these two behaviors might be responsible for the experimental observations.

Indeed an increasing number of peroxide reactions, believed to occur via ionic paths, have been shown to undergo SET processes.[26] Recently the occurrence of SET mechanisms has been pointed out in the oxidation reactions of alkenes[27] and sulfides[28] by V(V) peroxo complex, in the oxidation of amines by MoO_5HMPT[29] and PCWP,[9] and in the oxidation of thianthrene 5-oxide with Mo(VI) and W(VI) peroxo complexes.[16d]

Conclusion

The results presented here disqualify the possibility of a nucleophilic oxygen transfer mechanism from Mo(VI) peroxopolyoxo complexes. Rather, they indicate that Mo(VI) peroxopolyoxo complexes as well as simple peroxo complexes behave as electrophilic oxidants toward nucleophilic substrates as thioethers and alkenes. A study of the countercation effects shows that the increasing bulkiness of the cation reduces the electrophilicity of the peroxopolyoxo complex. With substrates, as sulfoxides, which are suitable probes for testing a nucleophilic behavior of such oxidants, incursion of SET processes might be a likely event, although more mechanistic work is warranted.

Experimental Section

Materials. Chloroform (Carlo Erba, RPE) was distilled over P_4O_{10}. 4-Methoxy-, 4-methyl-, and 4-chlorophenyl methyl sulfides were prepared by methylation of the commercially available thiols;[30,13] 4-nitrophenyl methyl sulfide was obtained in the same way from the corresponding thiol, prepared according to reported procedure.[3] Thioanisole was a commercially available product (Aldrich). Sulfoxides were prepared from the corresponding sulfides by oxidation with acidic hydrogen peroxide in ethanol and purification by column chromatography[31] (silica gel, petroleum ether–diethyl ether).

Alkenes and alcohols are commercially available (Aldrich). Samples of each were distilled before use. Epoxides were prepared from the parent olefins by oxidation with *m*-chloroperbenzoic acid in CH_2Cl_2.[32] Sulfones were obtained from the corresponding sulfides by oxidation with 2 equivs of *m*-chloroperbenzoic acid in CH_2Cl_2 and purified by column chromatography[33] (silica gel, petroleum ether–diethyl ether).

Tetrakis(diperoxomolybdo)phosphate, $[(C_6H_{13})N^+]_3\{PO_4[MoO(O_2)_2]_4\}^{3-}$, was prepared by dissolving 1.56 g (4 mmol) of tetrahexylammonium chloride in 40 mL of benzene (sol A); then an aqueous solution of H_2MoO_4 was prepared by dissolving 2.4 g (10 mmol) of $Na_2MoO_4{\cdot}2H_2O$ in 4 mL of water containing 0.53 mL of 98% H_2SO_4 (10 mmol) (sol B).

To 7 mL of 35% H_2O_2 was added 0.62 mL of 85% H_3PO_4 (2.5 mmol) followed by sol B, under vigorous stirring at room temperature, and then, drop by drop sol A was added. The reaction mixture was stirred an additional 20 min and then cooled with an ice bath. The yellow precipitate obtained, after filtration, was washed with small amounts of water, benzene, and diethyl ether and then dried; yield 2.2 g. Recrystallization from CH_2Cl_2/Et_2O at −25 °C gave yellow crystals (mp 149 °C). Elemental analysis (C, 46.5%; H, 8.71%; N, 2.18%, and Mo, 20.1%, respectively) is in agreement with the calculated values (C, 46.4%; H, 8.44%; N, 2.25%; and Mo, 20.6%) referred to the formula $[(C_6H_{13})_4N^+]_3\{PO_4[MoO(O_2)_2]_4\}^{3-}$. The molecular weight was performed following Rast's camphor method,[34] using cyclopentadecanone as the reference compound. The agreement between the observed value (1942) and the calculated value (1863) is within 4%.

Kinetics. All kinetic runs were carried out under a nitrogen atmosphere. In a typical run, 5 mL of $CHCl_3$ containing 0.04 mmol of peroxo complex were added to a $CHCl_3$ solution (20 mL) containing 3 mmol of substrate in a glass reactor maintained at the appropriate temperature. Aliquots of the reaction mixture were withdrawn at various time intervals, and the disappearance of the oxidant was followed by iodometric titration, under pseudo-first-order conditions, employing a 10–100 times excess of substrate over the oxidant. Blank experiments indicated that the decomposition of the oxidant is a negligible process in the time scale of the oxidation reactions. The reactions followed pseudo-first-order kinetics for 2 half-lives; pseudo-first-order rate constants, obtained as slopes from conventional plots of $\ln [O]_{act}$ vs time, were evaluated by using a linear least-squares computer program and were reproducible within ±5%.

For the study of the stoichiometry of the oxidation reactions an appropriate internal GC standard was added in the reaction mixture and the amount of the products formed determined by GLC.

Instrumentation. Gas-chromatographic analyses of the reaction mixtures were carried out on a Perkin-Elmer 8420 gas chromatograph equipped with a flame ionization detector and program capability; a 25-m SE-30 capillary column was used for product determinations.

GC–MS analyses of reaction mixtures were obtained using a Hewlett-Packard Model 5890 gas chromatograph (using an HP-1 dimethylpolysiloxane 25-m capillary column), equipped with a Hewlett-Packard MS computerized system Model 5971A.

The identities of the products in the reaction mixture were confirmed by isolation of sulfoxides and sulfones which showed ^1H NMR and mass spectra identical with those of authentic samples.

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Registry No. TEAM, 130664-12-9; PCMP, 130214-99-2; MoO_5HMPT, 25377-12-2; PICO, 105194-63-6; MeSPh, 100-68-5; MeSOPh, 1193-82-4; PrOH, 71-23-8; $C_8H_{17}OH$, 111-87-5; $C_6H_{13}CH(OH)CH_3$, 123-96-6; $MeSO_2Ph$, 3112-85-4; EtCHO, 123-38-6; $C_7H_{15}CHO$, 124-13-0; $C_6H_{13}COCH_3$, 111-13-7; *p*-$MeOC_6H_4SOCH_3$, 3517-99-5; *p*-$MeC_6H_4SOCH_3$, 934-72-5; *p*-$ClC_6H_4SOCH_3$, 934-73-6; *p*-$NO_2C_6H_4SOCH_3$, 940-12-5; *p*-$MeOC_6H_4SO_2CH_3$, 3517-90-6; *p*-$MeC_6H_4SO_2CH_3$, 3185-99-7; *p*-$ClC_6H_4SO_2CH_3$, 98-57-7; *p*-$NO_2C_6H_4SO_2CH_3$, 2976-30-9; cyclooctene, 931-88-4; (*E*)-geraniol, 106-24-1; cyclooctene oxide, 286-62-4; 2,3-epoxygeraniol, 50727-94-1; 1-octene, 111-66-0; (*E*)-2-octene, 13389-42-9; cyclohexene, 110-83-8.

Supplementary Material Available: Table of rate constants (1 page). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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