

Biphasic Autoxidation of Tetralin Catalyzed by Surface-Active Transition Metal Complexes[†]

Wha Seung Ahn,[‡] Yaping Zhong, Cameron F. Abrams, and P. K. Lim*

Department of Chemical Engineering, North Carolina State University, Raleigh, North Carolina 27695-7905

Phillip A. Brown

Mallinckrodt Chemical, Inc., Raleigh, North Carolina 27619

Received: September 6, 1996[⊗]

Biphasic autoxidation of tetralin has been carried out using surface-active tetramethylethylenediamine complexes of manganese, chromium, and nickel as catalysts, tetralin as the substrate and organic phase, and dodecyl sodium sulfate as emulsifier. Advantages of the biphasic reaction over the homogeneous and heterogeneous counterparts include avoidance of the use of a troublesome solvent, ease of catalyst recovery and substrate recycle, and attainment of high reactivity, selectivity, and reproducibility under mild reaction conditions ($T \sim 60\text{ }^\circ\text{C}$, $P \sim 1\text{ atm}$). The main reaction products are α -tetralone and α -tetralol. The selectivity for the former decreases from 95% with the chromium complex to 90% with the nickel complex and 60% with the manganese complex, and the activity varies in a reverse order. The biphasic reaction stops at a bulk tetralin conversion of 35% due to the buildup of inhibitive, higher oxidation products. Similar product inhibition has been reported in one-liquid-phase systems. The biphasic scheme, however, permits a more convenient recovery and recycle of the catalyst and unreacted substrate. The reaction order with respect to oxygen decreases from 1.0 to 0 above an oxygen pressure of 0.15 atm. The reaction order with respect to catalyst decreases from 2.0 or 1.4 to 1.0 and then 0 with increasing metal concentration. Manganese switches role from catalyst to inhibitor above a threshold metal concentration, as indicated by a lengthening of the induction period of the reaction. A generalized reaction mechanism is proposed which yields model results in good agreement with the experimental findings.

Introduction

Recent studies from our laboratory^{1–5} have demonstrated the feasibility and advantages of chemical synthesis at organic–water (hereafter O–W) interface using surface-active catalyst complexes. Compared to conventional liquid-phase synthesis, biphasic synthesis based on surface-active catalyst complexes offers the following advantages: (1) circumvention of a solubility incompatibility between reactants or between a reactant and catalyst, (2) avoidance of the use of a toxic or environmentally troublesome organic solvent that may otherwise be needed, (3) ease of catalyst recovery in a compact form unencumbered by the solubilities of reactants and products in either aqueous or organic phase, (4) attainment of high reactivity, selectivity, and reproducibility under mild reaction conditions, (5) ease of processing and control, (6) avoidance of an adverse gelling effect on a polymerization reaction, (7) a low-pressure requirement for a dissolved gas reaction (see later), and (8) possibility of regio- and enantioselectivity control due to the directional influence of the interface on molecular orientations.

In this report, we present our findings on extending the biphasic technique to the autoxidation of tetralin (or 1,2,3,4-tetrahydronaphthalene). The latter reaction is a key intermediary step in the commercial production of α -naphthol.^{6,7} Numerous studies of the reaction^{6–28} have been carried out, either in a solvent^{6–15,17–21,23–28} or in undiluted tetralin.^{15,16,22,25} To our knowledge, this is the first study in which the reaction has been carried out in a biphasic mode. Aside from its novelty, the

biphasic reaction offers the following specific advantages over the homogeneous and heterogeneous counterparts: (i) avoidance of the use of a noxious, troublesome, or expensive solvent, such as acetic acid, chlorobenzene, or *N,N*-dialkylamide, (ii) easier catalyst recovery and substrate recycle than the homogeneous reaction, and (iii) a higher rate, selectivity, and reproducibility than the heterogeneous reaction. Because the conversion of tetralin is ultimately limited by the formation of inhibitive side products,^{8,20,22} recycle of unreacted tetralin is an important consideration. The fact that tetralin can serve as the organic phase, in addition to being the substrate, greatly facilitates the recovery and recycle of the unreacted tetralin. Moreover, as will be shown in this report, the biphasic reaction differs in some significant ways from the corresponding reactions in a solvent or undiluted tetralin.

Experimental Section

The apparatus and procedure for the biphasic autoxidation reaction were similar to that used in the studies of other biphasic reactions.^{2–5} Specifically, the reaction was carried out batchwise at 1 atm in a 250-mL Morton flask reactor using tetralin–water as the biphasic mixture, a transition metal complex of a surface-active ligand as the catalyst, and dodecyl sodium sulfate (DSS) as the emulsifier.

A representative run was performed as follows: The reactor was charged with 75 mL of a 1:1 (by vol) tetralin–water mixture and the desired amount of DSS and surface-active ligand. The reactor was placed in a water bath, purged with oxygen for about 10 min, and then allowed to equilibrate to the set temperature, which was typically 60 °C. The reaction was initiated by catalyst addition with the help of a needle-stemmed spoon that could be raised or lowered through a septum joint on a side

[†] Accepted for presentation at the 1996 Annual AIChE Convention in Chicago, IL.

* To whom correspondence should be addressed.

[‡] On sabbatical leave from Inha University, Incheon, Korea.

[⊗] Abstract published in *Advance ACS Abstracts*, January 1, 1997.

neck of the reactor. A measured amount of the desired transition metal salt was placed on the spoon in a suspended position initially and then lowered into the reaction mixture following the temperature equilibration.

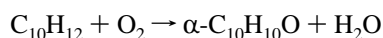
The reaction was followed by monitoring the oxygen uptake with the help of a constant-pressure manometric unit.²⁻⁵ The reaction mixture was analyzed using high-performance liquid chromatography, gas chromatography, and mass spectroscopy. The analytical equipment, all made by Perkin Elmer, included a Series 4 liquid chromatograph equipped with a continuous wavelength detector and a reversed-phase column, a Sigma 2000 gas chromatograph equipped with a Hewlett-Packard 19001A-C51 packed column, and an AutoSystem gas chromatograph equipped with a Hewlett-Packard 1 capillary column and operated in conjunction with a Q-Mass 910 mass spectrometer. The latter was supported by a 54 000-compound mass spectral library. Evidence of free radicals' involvement in the reaction was sought using a Bruker ER-200 ESR spectrometer. Reagent-grade chemicals were acquired from Aldrich and Fisher Scientific and used without further purification or treatment.

To demonstrate the feasibility of substrate recycling, unreacted tetralin was separated from the autoxidation reaction products by means of a 15-plate, vacuum-jacketed Oldershaw distillation column (available from Aldrich) operated at 4 mmHg.

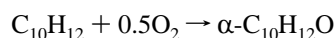
Results and Discussion

(A) General Characteristics of the Biphasic Autoxidation Reaction. (1) *Reaction Products and Product Inhibition.* The biphasic autoxidation reaction proceeded very slowly in the absence of a surface-active catalyst complex. In the presence of a suitable surface-active catalyst complex, such as a tetramethylethylenediamine complex of manganese, chromium, or nickel (see section B), the reaction took off after an induction period, as evident in Figure 1 which shows a representative oxygen uptake profile of a reaction run. The reaction conditions for Figure 1 are presented in Table 1, and they correspond to the base runs upon which parametric variations would be introduced subsequently for the manganese- and chromium-catalyzed reactions.

Following the induction period, the reaction proceeded at a steady rate for about 15 h before slowing progressively to a halt after 18 h. During the steady-rate phase, the biphasic reaction produced α -tetralone as the main reaction product according to the stoichiometry:



Depending on the catalyst complex used to promote the reaction, varying amounts of α -tetralol were also formed as side product according to the stoichiometry:



Under biphasic conditions, α -tetralone and α -tetralol were the major autoxidation products, independent of the catalyst and ligand used to promote the reaction. α -Tetralyl hydroperoxide, which has been reported as a major product in one-liquid-phase systems,^{14-17,25} was found in a very small amount and could only be detected by distilling off the bulk of the unreacted tetralin under reduced pressure. Traces of higher oxidation products were also formed in an extended reaction run, including α -naphthol, 1,4-dihydroxynaphthalene, and dihydronaphthoquinone. The small presence of tetralyl hydroperoxide in the reaction mixture suggests the decomposition of hydroperoxide which is catalyzed by metals.^{6,13-18,25-27} Evidently, the formation of hydroperoxide in the immediate vicinity of the segregated

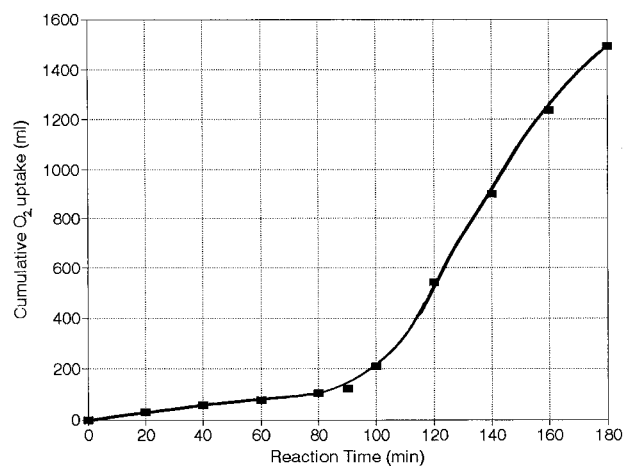


Figure 1. Representative O₂ uptake profile of tetralin autoxidation using Mn catalyst.

TABLE 1: Reaction Conditions of the Base Runs for Figures 1-9

kinetic parameter	specification
temperature	60 °C
total pressure	760 mmHg
O ₂ partial pressure	605 mmHg
stirrer speed	1800 rpm
organic phase volume	75 mL
aqueous phase volume	75 mL
emulsifier, volume	DSS (dodecyl sodium sulfate)
	0.0015 g-mol
ligand, amount	TMEN (tetramethylethylenediamine)
	0.03 g-mol
catalyst, amount	Mn(Ac) ₃ or CrCl ₃
	0.015 g-mol

metal complexes, coupled possibly with an amphiphilic character of the hydroperoxide, favors the decomposition reaction to the point that very little hydroperoxide survived the decomposition reaction.

The reaction stoppage occurred at a conversion of about 35% of the bulk tetralin phase, and it was caused by the formation of higher oxidation products that were inhibitive. Control runs with small additions of α -naphthol and 1,4-dihydroxynaphthalene confirmed the pronounced inhibiting effect of these products. It should be noted that a similar product inhibition effect has also been observed in the homogeneous reaction.^{8,20,22} Presumably, these phenolic products inhibit the reaction by scavenging free radicals.

Attempts to use ESR spectroscopy to detect free-radical intermediates brought inconclusive results. No free radicals could be detected above the detection limit of the spectrometer (10⁻⁵ M). However, there was a possibility of radical intermediates being tied to the catalyst complexes. Intensity variations in the metal signal were observed, along with some line broadening. Unfortunately, these changes could not be definitively assigned to any specific metal-bound radicals. More work is needed to resolve the issue.

(2) *Phase Separation and Inversion.* The biphasic reaction mixture was opaque and white while being stirred vigorously, but when the stirring was stopped, it phase-separated upon standing into organic and aqueous phases and an interfacial emulsion layer. The time needed for the phase separation varied from several hours at the start of the reaction to just a few minutes after the induction period, and it decreased with increasing catalyst concentration and tetralin conversion. The catalyst complex could be quantitatively recovered from the emulsion layer and reused with no apparent loss of activity (see section C).

TABLE 2: Results of Catalyst Screening in the Biphasic Autoxidation of Tetralin^a

metal salt	O ₂ uptake rate, mol/(h·L)	α-tetralone selectivity (%)
CoBr ₂	0.0245	not determined
FeCl ₃	0.0082	not determined
CuSO ₄	0.0136	not determined
Mn(Ac) ₃	0.255	60
NiCl ₂	0.206	70
CrCl ₃	0.125	95

^a Reaction conditions are the same as that specified in Table 1, except for the metal salt.

TABLE 3: Results of Ligand Screening in the Biphasic Autoxidation of Tetralin^a

ligand	O ₂ uptake rate, mol/(h·L)	
	Mn-catalyzed reaction	Cr-catalyzed reaction
TMEN ^b	0.255	0.125
triethyl phosphite	0.003	0.003
TMHD ^c	0.036	0.018

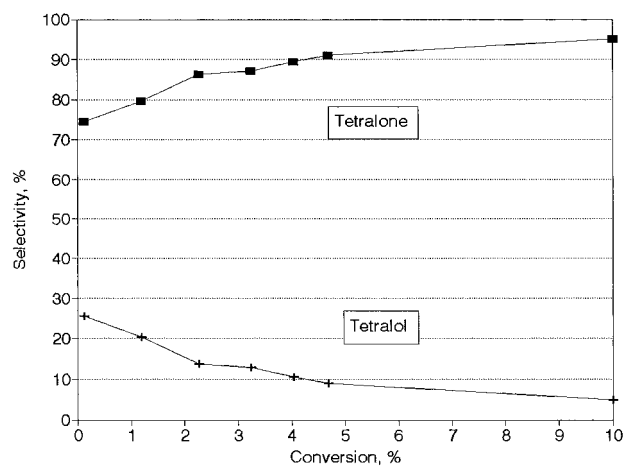
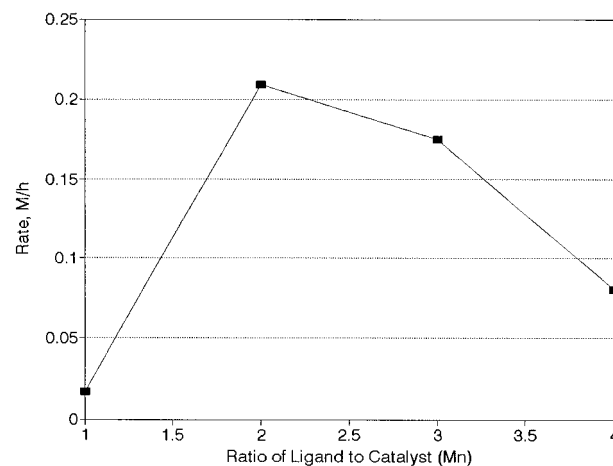
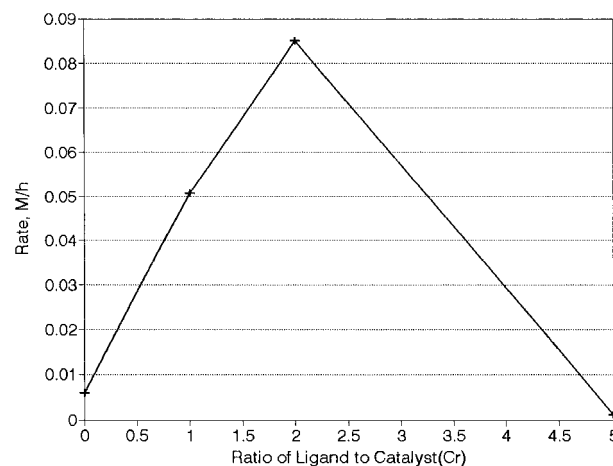
^a Reaction conditions are the same as that specified in Table 1, except for the ligand. ^b Tetramethylethylenediamine. ^c 2,2,6,6-Tetramethyl-3,5-heptanedione.

The tetralin phase underwent a phase inversion when the tetralin conversion reached about 23%, i.e., above this conversion level, the organic phase became denser than water and settled below the aqueous phase. The phase inversion resulted from α-tetralone and α-tetralol having a higher density (namely, 1.099 and 1.090 g/mL, respectively) than tetralin, which has a density of 0.973 g/mL.

(B) Results of Catalyst and Ligand Screening. The results of a screening study on potential catalysts and ligands are presented in Tables 2 and 3. Catalysts known to promote the tetralin autoxidation reaction either homogeneously or heterogeneously—namely, manganese, nickel, and chromium—were also found to promote the biphasic autoxidation reaction, provided that they were used in conjunction with a suitable surface-active ligand or complexing agent. If the latter was absent, the biphasic reaction was slow. Other metals were less active even in the presence of a surface-active ligand. Tetramethylethylenediamine (TMEN) was most effective among the ligands tested. Triethyl phosphite, which effectively promotes an oxidative coupling reaction in conjunction with copper,^{3–5} was ineffective in promoting the biphasic autoxidation of tetralin. It appears that the autoxidation reaction requires a somewhat “harder” ligand (in Pearson’s sense) than an oxidative coupling reaction.

Manganese-TMEN complex gave the highest activity but a relatively low α-tetralone selectivity of about 60%. The latter stayed essentially constant independent of the tetralin conversion. Manganese(II)- and manganese(III)-TMEN complexes gave essentially the same results. Chromium-TMEN complex was about one-half as active as the manganese-TMEN complex, but it gave a much higher α-tetralone selectivity. The latter started out at 75% and increased to 95% beyond a tetralin conversion of 10% (see Figure 2). Nickel-TMEN complex gave intermediate activity and α-tetralone selectivity between those of the manganese- and chromium-TMEN complexes. Because α-tetralone can be more easily and directly converted to α-naphthol than α-tetralol,⁷ a high α-tetralone selectivity is commercially desired in the tetralin autoxidation reaction.

(C) Detailed Kinetic Results on the Biphasic Reaction Catalyzed by Manganese- and Chromium-Tetramethylethylenediamine Complexes. (1) *Rate Dependence on the Ligand–Catalyst Ratio.* The variation of the reaction rate with the

**Figure 2.** Selectivity vs conversion for Cr catalyst; reaction conditions as stated in Table 1.**Figure 3.** Rate dependence of the tetralin autoxidation on the ligand–catalyst (Mn) ratio; reaction conditions as stated in Table 1, [Mn] = 0.005 M.**Figure 4.** Rate dependence of the tetralin autoxidation on the ligand–catalyst (Cr) ratio; reaction conditions as stated in Table 1, [Cr] = 0.007 M.

ligand–catalyst mole ratio is shown in Figures 3 and 4 for the manganese- and chromium-catalyzed reactions, respectively. In each case, the optimal ligand–catalyst ratio was found to be around 2:1. The results may be rationalized in terms of two competing factors, namely, a greater ability to segregate the catalyst at the O–W interface at a higher ligand–catalyst ratio, on one hand, and a lower accessibility of the reactants to the catalyst’s coordination sites at the higher ligand–catalyst ratio,

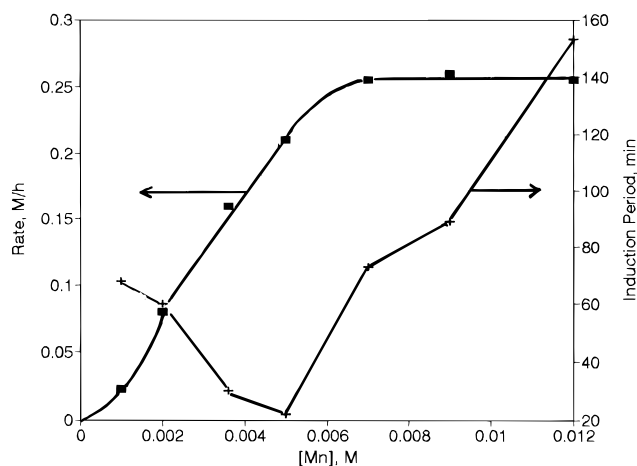


Figure 5. Rate and induction period vs Mn concentration.

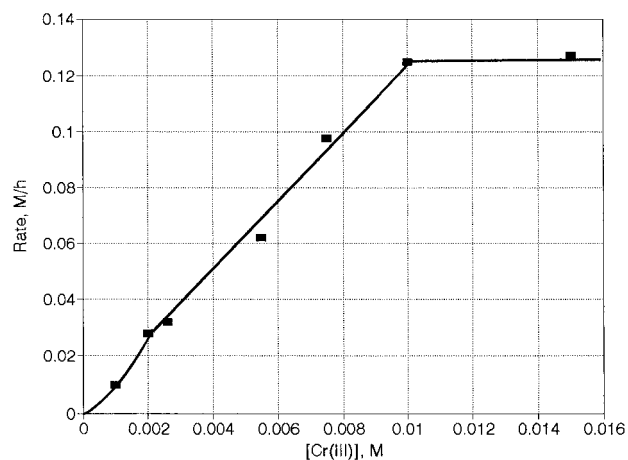


Figure 6. Rate vs Cr concentration.

on the other. Presumably, the 2:1 ratio corresponded to an optimal balance between these two competing factors.

(2) *Rate Dependence on the Catalyst Concentration and Catalyst–Inhibitor Conversion.* The variations of the rate and induction period with the catalyst concentration are shown in Figures 5 and 6, respectively, for the manganese- and chromium-catalyzed reactions. In each case, the “steady-state” rate immediately following the induction period increased with the metal concentration until a threshold metal concentration was reached, whereupon the rate leveled off with further increases in the metal concentration. The reaction order with respect to the catalyst decreased from a limiting value of 2.0 and 1.4, respectively, for the manganese- and chromium-catalyzed reactions to 1.0 and then 0 with increasing metal concentration. A variable reaction order with respect to catalyst concentration with a limiting value greater than unity is unusual and may be a unique feature of the biphasic autoxidation reactions, since the corresponding reactions in one-liquid-phase systems show a limiting catalyst order of 0.5 or 1.0.^{9,17,19,27}

The induction period for the manganese-catalyzed reaction initially decreased with increasing metal concentration, reached a minimum, and then increased with further increases in the metal concentration. The induction period for the chromium-catalyzed reaction, on the other hand, was very short and independent of chromium concentration.

Two possible causes for the leveling of the rate beyond a threshold metal concentration are (1) a biphasic solubility limit on the active catalyst species and (2) a catalyst–inhibitor conversion. The former could be a contributing, but not the

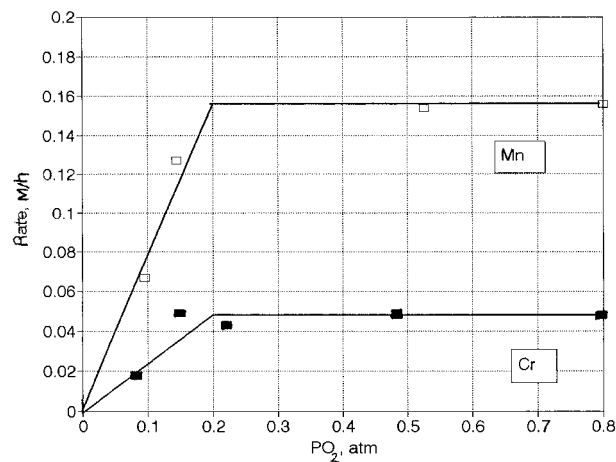


Figure 7. Rate vs O₂ partial pressure; [Cr] = 0.004 M, [Mn] = 0.004 M.

sole factor since it could not account for the lengthening of the induction period of the manganese-catalyzed reaction at high metal concentrations. Manganese is known to undergo a concentration-dependent role reversal from catalyst to inhibitor in both the homogeneous and heterogeneous modes of tetralin autoxidation reaction.^{17,27} It is also known to undergo a pH-dependent catalyst–inhibitor conversion in the autoxidation of aqueous sulfur dioxide and hydrazine.^{29,30} Other transition metals are also known to show a similar phenomenon in other autoxidation reactions.^{31,32}

(3) *Rate Dependence on the Oxygen Partial Pressure.* The rate dependence of the biphasic autoxidation reaction on the oxygen partial pressure is shown in Figure 7. The data indicate that the reaction order with respect to oxygen decreased from first to zeroth order above an oxygen pressure of about 0.15 atm. It is surprising that the rate dependence on oxygen was confined to such a narrow and low-pressure range since other studies of the same reaction in one-liquid-phase systems^{9,10,19,21} have reported a positive rate dependence (mostly first order) over a much wider—if not the entire—pressure range.

The zeroth-order rate dependence on oxygen under atmospheric conditions follows an emerging pattern shown by other biphasic reactions, namely, carbonylation and oxidative coupling reactions which show a similar zeroth-order rate dependence on the dissolved gas reactants.^{2,3} The empirical finding suggests that the segregation of a surface-active catalyst complex, coupled with the latter’s ability to absorb the gaseous reactant, may create a localized high concentration of the dissolved gas around the O–W interface, where the reaction occurs. The postulated phenomenon has to be tested by additional studies, but if confirmed, it carries an intriguing implication, namely, that the pressure requirement of a dissolved gas reaction—such as autoxidation, carbonylation, hydrogenation, or hydroformylation—may be reduced substantially by running the reaction in a biphasic mode with the help of a surface-active catalyst.

(4) *Rate Dependence on the O–W Phase Ratio and Emulsifier.* The dependence of the rate and tetralone selectivity of the chromium-catalyzed reaction on the O–W phase ratio is presented in Figure 8. Both the rate and tetralone selectivity attained maximum values at an O–W phase ratio of around 1:1 (by vol). The results may be rationalized in terms of the dispersion of the two phases and the interfacial area associated with it. Both may be expected to be maximized at a phase ratio of around 1:1.

Consistent with the dispersion effect, the use of an anionic surfactant, DSS, increased the reaction rate by more than 300%

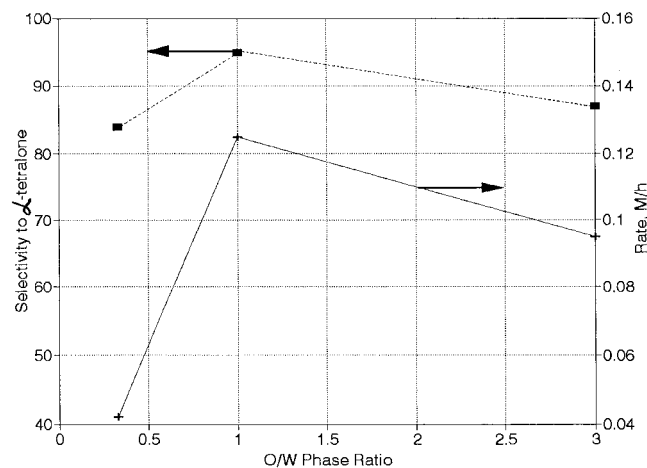


Figure 8. Rate and α -tetralone selectivity dependence on the organic–water phase ratio for Cr catalyst.

TABLE 4: Effects of Different Emulsifiers in the Biphasic Autoxidation of Tetralin^a

emulsifier	O ₂ uptake rate, mol/(h·L)	
	Mn-catalyzed reaction	Cr-catalyzed reaction
dodecyl sodium sulfate	0.255	0.125
poly(oxyethylenedodecanol)	0.0183	
cetyltrimethylammonium bromide		0.002
without emulsifier	0.075	

^a Reaction conditions are the same as that specified in Table 1, except for the emulsifier.

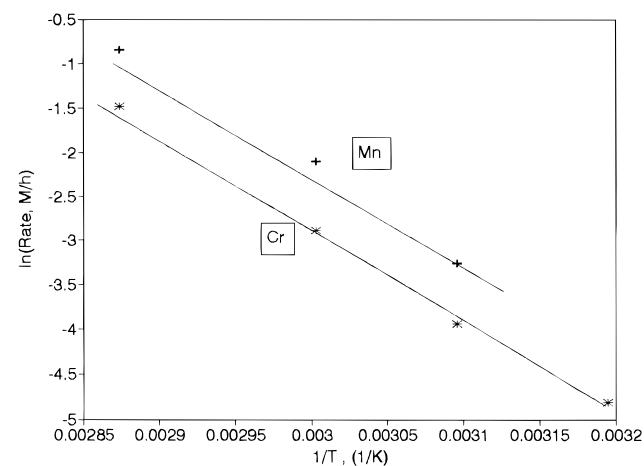


Figure 9. Rate dependence of the tetralin autoxidation on the reaction temperature.

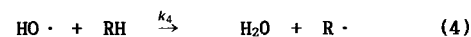
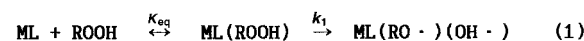
(see Table 4). The use of a nonionic surfactant, poly(oxyethylenedodecanol), or a cationic surfactant, cetyltrimethylammonium bromide, on the other hand, resulted in a significant rate reduction. It appears that the anionic surfactant stabilized the positively charged catalyst complex at the interface, whereas the cationic surfactant had the opposite effect.

(5) *Rate Dependence on the Reaction Temperature.* The temperature effect on the manganese- and chromium-catalyzed reactions is shown in Figure 9. Over the temperature range 40–75 °C, both reactions have an apparent activity energy of 20.5 kcal/mol, which is sufficiently high to rule out the possibility of the biphasic autoxidation reaction being limited by oxygen mass transfer.

(6) *Recovery and Recycling of Catalyst Complex and Unreacted Tetralin.* A controlled run was made to test the feasibility of recovering and recycling the catalyst complex and the

SCHEME 1: Postulated Reaction Mechanism for the Autoxidation of Tetralin

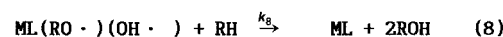
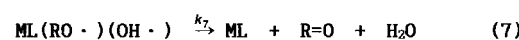
Initiation at "Steady State" :



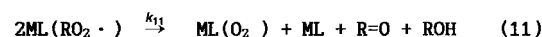
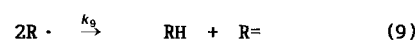
Propagation :



Hydroperoxide Decomposition :



Termination :



unreacted tetralin. The catalyst complex was recovered as a compact emulsion/suspension layer at the O–W interface after the reaction mixture from a preceding run was allowed to phase-separate overnight in a separating funnel. The interfacial layer was isolated by siphoning off the top organic phase and then draining off the bottom aqueous phase. It was then washed three times with *p*-xylene to remove the inhibitive oxidation products.

Unreacted tetralin was recovered by distilling the organic phase that had been collected from several preceding runs. Distillation was carried out at 4 mmHg in a 15-plate, vacuum-jacketed Olderhaw column. Make-up aqueous phase and distilled tetralin were added in appropriate amounts to the interfacial emulsion layer to give the same total volume and O–W phase ratio as that of a regular run. No make-up dodecyl sodium sulfate was added nor any additional catalyst or ligand. The results of the recycle run show that the rate was 75% of the rate of the virgin run and that the product selectivity was essentially the same. The small reduction in rate might be due to an incomplete recovery of the emulsifier, ligand, and catalyst. The results demonstrate the feasibility of recovering and recycling the catalyst complex and the unreacted tetralin in the biphasic scheme. A similar recovery and recycle of unreacted tetralin would be difficult in an organic–solvent system in which the unreacted tetralin would have to be separated as a minor component from the solvent.

(D) **A Proposed Reaction Mechanism.** In Scheme 1, a generalized kinetic model for the biphasic autoxidation of tetralin (RH) catalyzed by the manganese- or chromium-TMEN complexes (ML) is presented. Consistent with the sensitivity of the reaction to free-radical scavengers, the proposed scheme consists of a chain reaction sequence. However, to account for the observed product distribution, tetralyl hydroperoxide (ROOH) is presumed to undergo decomposition reactions after it is

formed in the propagation chain. The catalyst's selectivity toward the hydroperoxide decomposition reactions is presumed to determine relative distribution of α -tetralone (R=O) and α -tetralol (ROH).

In accord with other biphasic reactions that also show a weak dependence on dissolved gas reactants^{2,3} and consistent with the known existence of oxygenated manganese and chromium complexes,^{33,34} the involvement of an oxygenated metal complex is proposed in the propagation chain (step 5) to explain the weak dependence of the biphasic autoxidation reaction on oxygen pressure. As will be shown shortly, the same postulated involvement of the oxygenated metal complex could also explain the rate dependence on the catalyst.

To explain the shift to zeroth-order dependence on the catalyst at a high metal concentration and to account for the lengthening of the induction period in the manganese-catalyzed reaction, metal species are presumed to participate in chain termination reactions (steps 10 and 11). In conjunction with step 5 and the proposed initiation sequence, steps 10 and 11 may be shown to give rise to first- and zeroth-order rate dependence, respectively, on the metal concentration. Step 9, which may be shown to give a second-order rate dependence on catalyst, is supported by the detection of 1,2-dihydronaphthalene (R=) as a side product in the reaction mixture.^{22,28}

The initiation sequence is presumed to be established during the induction period during which hydroperoxide and other reaction intermediates are built up to some "steady-state" concentrations. The chain carrier, tetralyl radical (R^{*}), is presumed to derive from the decomposition of tetralyl hydroperoxide. The latter reaction would produce geminate radicals in a solvent cage, and most of the radicals would react with each other or with tetralin to form α -tetralone and α -tetralol (steps 7 and 8), but some might break out of the solvent cage to produce the tetralyl radical.

The above reaction steps presumably occur at or near the O-W interface. In order to rigorously model the biphasic reaction, it would be necessary to have quantitative data on the interfacial area and interfacial concentrations of the reacting species. Such data, unfortunately, are not available presently, and it is necessary to simplify the model. On account of the vigorous and rapid mechanical stirring used in this study, the reaction mixture could be treated as a uniform emulsion for simplicity. With the dispersion and mass transfer effects being averaged out by the rapid mixing process, the reaction effectively becomes a pseudohomogeneous reaction.

Assuming the reaction is pseudohomogeneous and applying the usual steady-state approximations on the reactive intermediates, the proposed mechanism in Scheme 1 may be shown to lead to the following model rate expression:

$$-\frac{1}{V} \frac{dN_{O_2}}{dt} = \frac{k_2 k_5^2 [ML(O_2)]^2}{(k_2 + k_7 + k_8[RH]) \left\{ k_9 + \frac{k_5}{k_6} k_{10} \frac{[ML(O_2)]}{[RH]} + k_{11} \left(\frac{k_5 [ML(O_2)]}{k_6 [RH]} \right)^2 \right\}} \quad (I)$$

At an oxygen pressure above 0.15 atm, the majority metal complex may be assumed to exist mainly in the oxygenated form, i.e., $[ML(O_2)] \sim [ML]_T$, where $[ML]_T$ represents the total concentration of the transition metal-ligand complex, and eq I reduces to the following limiting forms for different catalyst concentration ranges:

$$-\frac{1}{V} \frac{dN_{O_2}}{dt} \approx \frac{k_2 k_5^2 [ML]_T^2}{(k_2 + k_7 + k_8[RH]) k_9} \propto [ML]_T^2 \text{ at low } [ML]_T \quad (I-1)$$

$$-\frac{1}{V} \frac{dN_{O_2}}{dt} \approx \frac{k_2 k_5 k_6 [ML]_T [RH]}{(k_2 + k_7 + k_8[RH]) k_{10}} \propto [ML]_T^1 \text{ at intermediate } [ML]_T \quad (I-2)$$

$$-\frac{1}{V} \frac{dN_{O_2}}{dt} \approx \frac{k_2 k_6^2 [RH]^2}{(k_2 + k_7 + k_8[RH]) k_{11}} \propto [ML]_T^0 \text{ at high } [ML]_T \quad (I-3)$$

Thus, above an oxygen pressure of 0.15 atm, the model predicts second-, first-, and zeroth-order rate dependence on the catalyst at low-, intermediate, and high-catalyst concentration ranges, respectively. The model results are in accord with the experimental finding on the manganese-catalyzed reaction. They are also in accordance with the experimental findings on the chromium-catalyzed reaction if it is assumed that in the low-catalyst concentration range in which rate data are available, step 10 makes a comparable contribution to step 9 toward chain termination. With this assumption, the model would predict, for the low-catalyst concentration range, a limiting catalyst order of about 1.5, which is in good agreement with the experimental value of 1.4. For the intermediate and high-chromium concentrations, the model and experimental results are in agreement on the first- and zeroth-order rate dependence on the catalyst.

At a low-oxygen pressure (<0.15 atm), the metal complex may be assumed to exist predominantly in a nonoxygenated form, i.e., $[ML(O_2)] = K[ML]P_{O_2} \approx K[ML]_T P_{O_2}$, where K is the stability constant of the oxygenated complex. Equation I then reduces to the following limiting form for the intermediate catalyst concentration range for which rate data are available:

$$-\frac{1}{V} \frac{dN_{O_2}}{dt} \approx \frac{k_2 k_5 k_6 K [ML]_T P_{O_2} [RH]}{(k_2 + k_7 + k_8[RH]) k_{10}} \propto [ML]_T P_{O_2} \quad (I-4)$$

Thus, at a low-oxygen pressure and an intermediate catalyst concentration, the model predicts a first-order rate dependence each on oxygen and on catalyst, which agrees with the experimental results.

Conclusion

Biphasic autoxidation of tetralin has been carried out using surface-active tetramethylethylenediamine complexes of manganese, chromium, and nickel as catalysts, tetralin as the substrate and organic phase, and dodecyl sodium sulfate as emulsifier. The biphasic reaction was found to offer significant advantages over the homogeneous and heterogeneous counterparts, including avoidance of the use of a troublesome solvent, ease of catalyst recovery and substrate recycle, and attainment of high reactivity, selectivity, and reproducibility under mild reaction conditions. The main reaction products were α -tetralone and α -tetralol. The selectivity for the former decreased from 95% with the chromium complex to 90% with the nickel complex and 60% with the manganese complex, and the activity varied in a reverse order. The biphasic reaction was inhibited by higher oxidation products that are radical scavengers.

The reaction order with respect to oxygen decreased from 1.0 to 0 above an oxygen partial pressure of 0.15 atm. The reaction order with respect to catalyst decreased from 2.0 or 1.4 to 1.0 and then 0 with increasing metal concentration. A

generalized kinetic model has been developed which gives model results in good agreement with the experimental findings.

Acknowledgment. Financial support from the U.S. National Science Foundation (Grant No. CTS-9217443-01) is gratefully acknowledged.

References and Notes

- (1) Lim, P. K.; Zhong, Y. In *Green Chemistry-Designing Chemistry for the Environment*; Anastas, P., Williamson, T., Eds.; ACS Symposium Series 626; American Chemical Society: Washington, DC, 1996; pp 168–177.
- (2) Zhong, Y.; Godfrey, V. M.; Brown, P.; Lim, P. K. *Chem. Eng. Sci.* **1996**, *51*, 757–767.
- (3) Zhong, Y.; Abrams, C. F.; Lim, P. K. *Ind. Eng. Chem. Res.* **1995**, *34*, 1529–1535.
- (4) Dautenhahn, P. C.; Lim, P. K. *Ind. Eng. Chem. Res.* **1992**, *31*, 463–469.
- (5) Lim, P. K. Environmentally-Benign Oil-Water Interfacial Synthesis. Presented at Design for Environment, session Designing Chemical Syntheses for the Environment. Part II; ACS Symposium, Washington, DC, Aug. 22, 1994.
- (6) Mizukami, F.; Imamura, J. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1404–1412.
- (7) Mizukami, F.; Horiguchi, Y.; Tajima, M.; Imamura, J. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2689–2695.
- (8) Martan, M.; Manassen, J.; Vofsi, D. *Tetrahedron* **1970**, *26*, 3815–3827.
- (9) Guan, Y.; Zhang, Z.; Zhou, J. *Ranliao Huaxue Xuebao* **1980**, *8* (1), 62–70; *Chem. Abstr.* **1982**, *96*, 6331n.
- (10) Zhou, J.; Zhang, Z.; Yude, G. *Ranliao Huaxue Xuebao* **1980**, *8* (1), 71–78; *Chem. Abstr.* **1982**, *96*, 6332p.
- (11) Lunak, S.; Vaskova, M.; Lederer, P. *Collect. Czech. Chem. Commun.* **1990**, *55*, 1015–1021.
- (12) Hay, A. S.; Blanchard, H. S. *Can. J. Chem.* **1965**, *43*, 1306–1317.
- (13) Kamiya, Y. *Tetrahedron* **1966**, *22*, 2029–2038.
- (14) Kamiya, Y.; Beaton, S.; Lafortune, A.; Ingold, K. U. *Can. J. Chem.* **1963**, *41*, 2020–2033.
- (15) Kamiya, Y.; Beaton, S.; Lafortune, A.; Ingold, K. U. *Can. J. Chem.* **1963**, *41*, 2034–2053.
- (16) Kamiya, Y.; Ingold, K. U. *Can. J. Chem.* **1964**, *42*, 1027–1043.
- (17) Kamiya, Y.; Ingold, K. U. *Can. J. Chem.* **1964**, *42*, 2424–2433.
- (18) Woodward, A. E.; Mesrobian, R. B. *J. Am. Chem. Soc.* **1953**, *75*, 6189–6195.
- (19) George, P.; Robertson, A. *Trans. Faraday Soc.* **1946**, *42*, 217–224.
- (20) Robertson, A.; Waters, W. A. *Trans. Faraday Soc.* **1946**, *42*, 201–210.
- (21) George, P. *Proc. R. Soc. (London)* **1946**, *A185*, 337–351.
- (22) Robertson, A.; Waters, W. A. *J. Chem. Soc.* **1948**, 1574–1578.
- (23) Robertson, A.; Waters, W. A. *J. Chem. Soc.* **1948**, 1578–1585.
- (24) Robertson, A.; Waters, W. A. *J. Chem. Soc.* **1948**, 1585–1590.
- (25) Prasad, K. M.; Athappan, R.; Srivastava, R. D. *J. Catal.* **1979**, *59*, 460–464.
- (26) Fukuzumi, S. I.; Ono, Y. *J. Phys. Chem.* **1976**, *80*, 2973–2978.
- (27) Mukherjee, A.; Graydon, W. F. *J. Phys. Chem.* **1967**, *71*, 4232–4240.
- (28) Taylor, W. F. *J. Phys. Chem.* **1970**, *74*, 2250–2256.
- (29) Lim, P. K.; Hamrick, G. T. *J. Phys. Chem.* **1984**, *88*, 1133–1136.
- (30) Lim, P. K.; Fagg, B. S. *J. Phys. Chem.* **1984**, *88*, 1136–1140.
- (31) Betts, A. T.; Uri, N. *Makromol. Chem.* **1966**, *95*, 22–39.
- (32) Denisov, E. T.; Emanuel, N. M. *Russ. Chem. Rev.* **1960**, *29*, 645–662.
- (33) Matsushita, T.; Yarino, T.; Masuda, I.; Shono, T.; Shinra, K. *B. Chem. Soc. Jpn.* **1973**, *46*, 1712–1716.
- (34) Wieghardt, K. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1153–1172.