

Homogeneous and biphasic autoxidation of tetralin catalyzed by transition metal salts and complexes

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Abstract

The biphasic autoxidation of tetralin was carried out using various Co, Ni and Mn complexes as catalysts. Cobalt-*N,N'*-dimethylethylenediamine complex, which is amphiphilic and surface-active, was found to be most effective; it could be easily recovered in a compact emulsion layer after the reaction and could be reused with no apparent loss of activity. The biphasic reaction differs from the homogeneous counterpart in that (1) little hydroperoxide product is formed, (2) there is lesser sensitivity to product inhibition and a greater degree of conversion and (3) there is an easier catalyst recovery and substrate recycle. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

In a conventional liquid-phase synthesis, an organic solvent typically takes on multiple functions that may include (1) solubilizing the reactant(s), catalyst, or intermediate product(s) of the reaction, (2) serving as a catalyst ligand and promoting the desired reaction through an electronic or steric effect at the catalyst and (3) acting as an acid or base. These functional requirements severely restrict the choice of the solvent candidates that are often toxic, hazardous or environmentally troublesome. In a biphasic synthesis, the choice of solvent candi-

dates is broadened and the chances for a benign synthesis are improved by decoupling the functional requirements of the reaction medium and separately assigning them to a combination of aqueous and organic phases. A surface-active ligand or complexing agent is used to draw the catalyst to the organic–water interface where it effects the desired synthesis reaction. Aside from an increased environmental safety, the biphasic synthesis that is based on the use of a surface-active catalyst complex also offers other significant advantages over the homogeneous synthesis: ease of catalyst recovery and separation of product and substrate, and the attainment of high reactivity, selectivity and reproducibility under mild reaction conditions [1].

It should be noted that the new biphasic synthesis technique differs from conventional

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phase-transfer and micellar techniques. The catalyst complex is designed to operate at the organic–water interface as opposed to a bulk phase in a phase transfer technique, and catalyst recovery is easier. The dispersed phase is larger than that of the micellar technique, and phase separation is often spontaneous.

In this work, the new biphasic technique has been extended to the autoxidation of tetralin with various combinations of transition metals and surface-active ligands. The tetralin autoxidation reaction is of interest because it is a key intermediary step in the commercial production of α -naphthol. For comparison with the biphasic mode of the reaction, the reaction was also studied in a homogeneous mode with dimethylformamide (DMF) as the solvent. The results, as will be shown shortly, reveal some fundamental differences between the two modes of the reaction.

2. Experimental

The experimental apparatus is shown schematically in Fig. 1. The biphasic reaction was carried out batchwise at 1 atm in a 1000 ml three-necked flask reactor using tetralin–water as the biphasic mixture, Co–DMEDA complex as the catalyst, and dodecyl sodium sulfate (DSS) as the emulsifier with vigorous mechanical stirring. The reactor was charged with 100 ml of a 1:1 (by volume) tetralin–water mixture and the desired amount of the reaction ingredients. The reactor was placed in a water bath and purged with oxygen for about 10 min and allowed to equilibrate to the set temperature, which was typically 60°C. The catalyst was then added to initiate the reaction. After the reaction was started, the oxygen uptake rate was monitored using a constant-pressure manometric unit. After completion of the reaction, the reaction

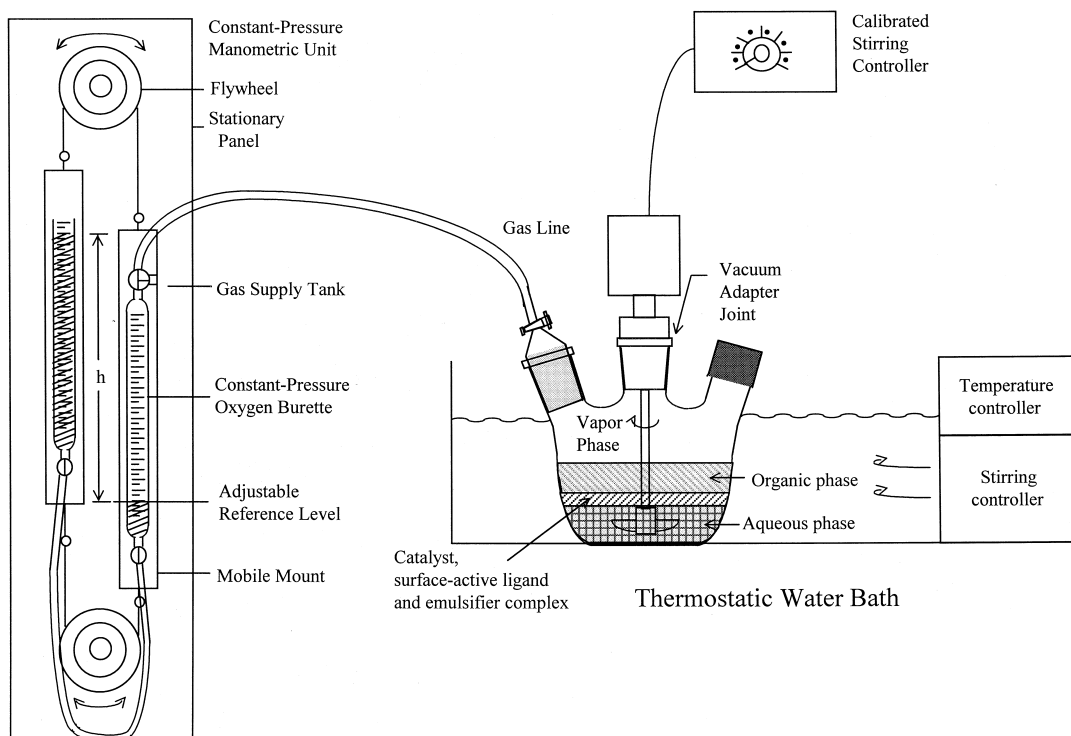


Fig. 1. The experimental scheme for autoxidation of tetralin.

mixture was emptied into a separatory funnel where, upon standing overnight, it separated into an aqueous phase, an organic phase, and a compact interfacial emulsion layer that was loaded with the catalyst complex. A similar procedure was used in carrying out the homogeneous reaction, except that no emulsifier was used and the biphasic reaction medium was replaced by DMF. In either case, the reaction products were identified and quantified using a SHIMADZU GC-14A gas chromatograph equipped with a CBP-20 capillary column.

3. Results and discussion

The standard reaction conditions upon which the parametric variations were made are represented in Table 1. Ligand–catalyst ratio is expected to influence the reaction rates at the organic–water interface via two factors; a greater ability to position the catalyst at the organic–water interface and a lower accessibility of the reactants to the catalyst's coordination sites at increasingly higher ligand–catalyst ratios. In our previous study [2], it was established that the ligand–catalyst ratio of 2:1 corresponded to an optimum balance between these competing factors, and the ratio was adopted in this work. The organic–water (O–W) volume ratio was fixed to 1:1, since the interfacial area

would be largest and the maximum reaction rate was attained at this phase ratio. The stirring and emulsifier effects can be ascribed to a greater dispersion action and a faster mass transport. Anionic emulsifier is effective in biphasic reaction due to its ability to stabilize the positively charged catalyst complex at the interface. The use of an anionic emulsifier, DSS, increased the reaction rate by more than 300% by bringing about a greater dispersion action which produces a finer emulsion that can provide a larger interfacial area and a shorter diffusion path length for the reactants and catalyst complex. The use of a mechanical stirrer also increased the reaction rate. However, beyond 1200 rpm, the reaction rate was essentially independent of the stirring speed, and 1500 rpm was chosen as a base run condition. Further details on the effect of reaction parameters and kinetics in tetralin autoxidation can be found in our earlier studies [2,3].

Under biphasic conditions, α -tetralone and α -tetralol were the major products irrespective of the catalyst and ligand used to promote the reaction according to the stoichiometry as follows:

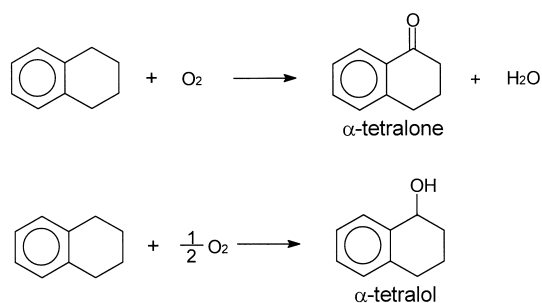


Table 1
Standard reaction conditions for the biphasic autoxidation of tetralin

Kinetic parameter	Specification
Total pressure	760 mmHg
O ₂ partial pressure	605 mmHg
Temperature	60°C
Stirrer speed	1500 rpm
Organic phase volume	50 ml
Aqueous phase volume	50 ml
Emulsifier and amount	DSS (Dodecyl Sodium Sulfate), 0.004 M
Catalyst and amount	CoBr ₂ , 0.02 M
Ligand and amount	DMEDA ^a , 0.04 M

^a N,N'-Dimethylethylenediamine.

α -Tetralyl hydroperoxide which has been reported as a major product in homogeneous systems [4,5] was found to be negligible, and the higher oxidation products, i.e., α -naphthol, 1,2-dihydronaphthalene were formed only in trace amounts in extended runs.

In the presence of a suitable surface-active catalyst complex, such as cobalt–dimethylethyl-

enediamine (DMEDA) complex, the reaction took off after a brief induction period which typically lasted less than 5 min. A gradual change of color in the reaction mixture was observed as the reaction progressed. The reaction mixture was opaque and white initially but gradually took on a distinctive brown color that was characteristic of a build up of α -tetralone. The reaction stopped at a tetralin conversion of about 35% in biphasic mode due to the build up of higher oxidation products that suppressed the propagation chain of the reaction [3]. Similar product inhibition has been reported in one-liquid phase systems [6–8]. Presumably, these phenolic products inhibited the reaction by scavenging free-radical chain carriers.

The screening results on potential catalysts are presented in Table 2. Among the transition metals tried, cobalt showed the best performance overall with the highest α -tetralone selectivity. Since α -tetralone can be more easily and directly converted to α -naphthol than α -tetralol, high α -tetralone selectivity is commercially desirable. Manganese was found to be as active as cobalt, but it gave a lower α -tetralone selectivity. Nickel was comparable to cobalt in α -tetralone selectivity, but its activity was significantly lower. Consequently, cobalt was chosen as a standard catalyst for subsequent studies.

The results of the ligand screening are summarized in Table 3. They show that amino ligands were more effective than substituted phosphine and phosphites, and that *N,N'*-dimethylethylenediamine (DMEDA) was most ef-

fective among the amino ligands. After 3 h reaction, tetralin conversion was 24.2% with α -tetralone selectivity of 68%. The results may be rationalized in terms of the relative ‘hardness’ of the ligands in Pearson’s sense [9], steric effect, and difference in surface activity. Presumably, amino ligands are ‘harder’ than substituted phosphine and phosphites in Pearson’s sense and are better able to stabilize the catalyst in a higher valence transition state that favors an oxidation reaction. In addition to being softer, the results that phosphine and phosphite ligands were less effective could be due to their easier oxidation. The differences in activity of the various amino ligands may be ascribed to steric effect and a difference in surface activity. Thus, the ineffectiveness of *N,N,N',N'*-tetraethylethylenediamine (TEEDA) and *N,N*-dibenzylethylenediamine (DBZEDA) may reflect steric crowding around nitrogen that limits the substrate’s accessibility to the catalyst. The lower activity of tetraethylenepentamine (TEPA) relative to DMEDA could be due to TEPA being more hydrophilic and less surface-active than DMEDA.

It should be noted that the phase separation of the biphasic reaction mixture was facilitated by the presence of a ligand, such as DMEDA, that has an amphiphilic character. With DMEDA in the reaction mixture, spontaneous phase separation occurred upon standing overnight and the cobalt–DMEDA complex that could be quantitatively recovered could be reused with no apparent loss of activity. On the other hand, in the absence of any ligand, phase separation hardly occurred even after one month, and catalyst recovery was difficult, if not impossible.

Table 4 summarizes the contrasting results of tetralin autoxidation in homogeneous and biphasic modes using two different cobalt salts, CoBr_2 and $\text{Co}(\text{Ac})_2$. CoBr_2 showed a negligible catalytic activity for the homogeneous reaction with or without the presence of a ligand. However, in conjunction with TEPA or DMEDA though not by itself, CoBr_2 showed a moderate to high catalytic activity for the biphasic reac-

Table 2
Results of catalyst screening in the biphasic autoxidation of tetralin^a

Metal salt	O ₂ uptake rate (M/h)	α -Tetralone selectivity (%)
NiCl ₂	0.41	65
Mn(Ac) ₃	0.95	56
CoBr ₂	0.91	68

^aReaction conditions are the same as those specified in Table 1, except for the metal.

Table 3
Results of ligand screening in the biphasic autoxidation of tetralin

Metal	Ligand	O ₂ uptake rate (M/h)	α-Tetralone selectivity (%)	
CoBr ₂	<i>N,N'</i> -Dimethylethylenediamine (DMEDA)	0.91	68	
	<i>N,N,N',N'</i> -Tetraethylethylenediamine (TEEDA)	Negligible	–	
	<i>N,N</i> -Dibenzylethylenediamine (DBZNEDA)	Negligible	–	
	Tetraethylenepentamine (TEPA)	0.16	34	
	(4-Dimethylaminophenyl)diphenylphosphine	Negligible	–	
	Triethyl phosphite	Negligible	–	
	Tributyl phosphite	Negligible	–	
NiCl ₂	<i>N,N'</i> -Dimethylethylenediamine (DMEDA)	0.41	65	
	<i>N,N,N',N'</i> -Tetraethylethylenediamine (TEEDA)	Negligible	–	
	<i>N,N</i> -Dibenzylethylenediamine (DBZEDA)	Negligible	–	
	Tetraethylenepentamine (TEPA)	0.26	71	
	(4-Dimethylaminophenyl)diphenylphosphine	Negligible	–	
	Triethyl phosphite	Negligible	–	
	Tributyl phosphite	Negligible	–	

tion. Co(Ac)₂, on the other hand, showed a high catalytic activity for the homogeneous reaction by itself. The presence of DMEDA or TEPA suppressed the catalytic activity of Co(Ac)₂ in the homogeneous reaction. However, in the biphasic reaction, DMEDA actually had a promoting effect on the catalytic activity of Co(Ac)₂.

The precise reason for the absence of catalytic activity of CoBr₂ in the homogeneous reaction is not clear, but it is known from other studies of the homogeneous reaction [10–12] that CoBr₂ must first dissociate to cobalt monobromide before any catalytic activity can be

derived. Evidently, no dissociation occurred in DMF with or without the presence of a ligand, but dissociation occurred in the biphasic medium in the presence of DMEDA or TEPA.

The inhibiting effects of DMEDA and TEPA on Co(Ac)₂ in the homogeneous reaction may be attributed to steric hindrance. Presumably, the cobalt complex existed in the coordinatively saturated form, Co(Ac)₂L₂, where L = DMEDA or TEPA. In the biphasic medium, however, the highly water-soluble acetate ion can dissociate from the cobalt complex to make room for the substrate, thereby allowing the complex to be catalytically active. The descending order of

Table 4
Autoxidation of tetralin catalyzed by different cobalt salts in homogeneous and biphasic modes

Metal salt	Reaction mode	Ligand	O ₂ uptake rate (M/h)	Selectivity (%)	
				α-Tetralone	Peroxide
CoBr ₂	Homogeneous	None	Negligible	–	–
		TEPA	Negligible	–	–
		DMEDA	Negligible	–	–
	Biphasic	None	Negligible		
		TEPA	0.16	34	Negligible
		DMEDA	0.91	68	Negligible
Co(Ac) ₂	Homogeneous	None	0.84	63	13
		TEPA	Negligible	–	–
		DMEDA	Negligible	–	–
	Biphasic	None	0.33	60	8
		TEPA	0.12	58	Negligible
		DMEDA	0.88	61	Negligible

catalytic activity in the biphasic reaction, cobalt–DMEDA complex > cobalt–acetate complex > cobalt–TEPA complex, may be explained in terms of a parallel descending order in the surface activity of the complexes.

It is also noteworthy that the hydroperoxide species that was formed in substantial amount in homogeneous reaction was formed negligibly in the biphasic reaction. It appears that the hydroperoxide may have some amphiphilic character and may be preferentially decomposed by the catalyst complex segregated at the organic–aqueous interface.

It should be noted that both the homogeneous and biphasic reactions catalyzed by $\text{Co}(\text{Ac})_2$ and the DMEDA complex derived from it showed evidence of product inhibition in the form of an eventual stoppage of oxygen uptake. The reaction stoppage was caused by a build up of potent radical inhibitors [3]. However, the product inhibition effect was less pronounced in the biphasic reaction than in the homogeneous reaction, as evidenced in Figs. 2 and 3 by a greater cumulative uptake of oxygen and a longer extended reaction in the biphasic mode than in the homogeneous mode. It is interesting

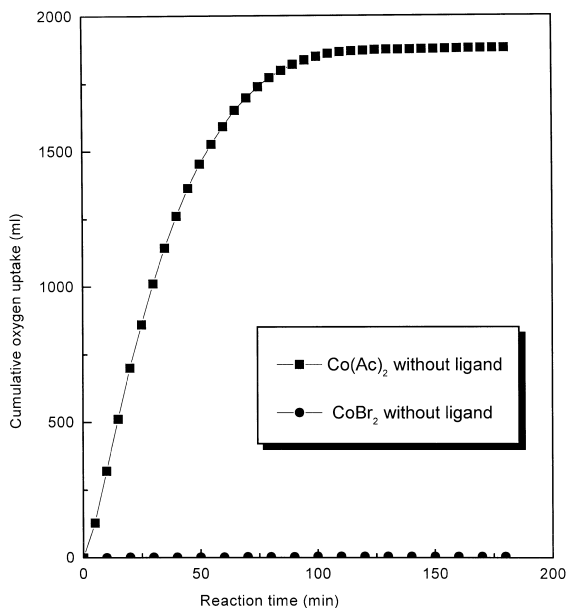


Fig. 2. Cumulative O_2 uptake profiles of autoxidation of tetralin in homogeneous mode.

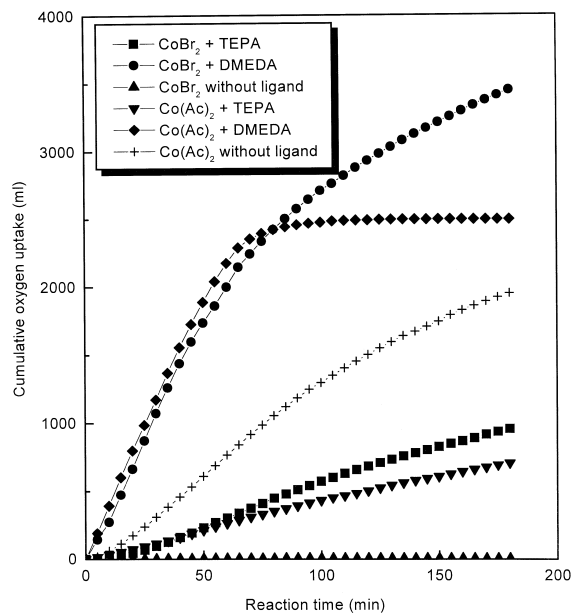


Fig. 3. Cumulative O_2 uptake profiles of autoxidation of tetralin in biphasic mode.

to note that in the biphasic reaction, the DMEDA complex derived from CoBr_2 showed much less sensitivity to product inhibition than the DMEDA complex derived from $\text{Co}(\text{Ac})_2$.

4. Conclusions

The biphasic autoxidation of tetralin is effectively catalyzed by the cobalt–DMEDA complex, which is amphiphilic and surface-active and can be easily recovered and reused with no apparent loss of activity. The biphasic reaction differs from the homogeneous counterpart in that (1) little hydroperoxide product is formed, (2) there is lesser sensitivity to product inhibition and a greater degree of conversion, and (3) there is an easier catalyst recovery and substrate recycle.

Acknowledgements

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