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Organic-Water Interfacial Synthesis of α-Tetralone Using Nickel-Tetraethylenepentamine Complex Catalysts

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Biphasic autoxidation of tetralin to α-tetralone has been carried out using surface-active ligand complexes of nickel as catalysts, tetralin as the substrate and organic phase, and dodecyl sodium sulfate as an emulsifier. The major products formed under the mild reaction conditions of 60°C and 1 atm were α-tetralone and α-tetralol, and the highest selectivity of 71% to the preferred product α-tetralone was obtained with nickel-tetraethylenepentamine complex. Depending on the ligand used, ligand to catalyst ratio of 2 : 1 or 1 : 1 was optimum accelerating the reaction rate and phase separation. The organic-water phase volume ratio around which the maximum reaction rate was obtained varied somewhat with the ligand used in the reaction, but generally 1 : 1 or 2 : 1 was adequate. The reaction order with respect to oxygen shifted from first to zero as its partial pressure increased and the reaction order with respect to nickel catalyst concentration varied from 1.7 to 1, and subsequently to 0 with further increases in the metal concentration. A kinetic model based on a free radical mechanism is proposed which yields a rate law in accord with the experimental findings.

I. INTRODUCTION

Biphasic catalytic reaction schemes in which a surface-active complexing agent or ligand is used to draw the catalyst to the organic-water interface where it effects the desired reaction can offer the following advantages over the corresponding homogeneous or heterogeneous reactions: the avoidance of the use of a toxic or environmentally-troublesome solvent, ease of catalyst recovery and substrate recycle, and the attainment of high reactivity and selectivity under mild reaction conditions (1). This interfacial technique has some similarity with phase-transfer, micellar or other biphasic techniques using a water-soluble ligand, but important and fundamental differences exist. One of the functions of the complexing agent in the interfacial technique is to draw the catalyst to the organic-water interface, and therefore, surface affinity of the complexing agent is desirable. In the phase-transfer technique, since the complexing agent would draw a reactant from one bulk phase to another (usually from aqueous to organic phase), surface affinity of the complexing agent only increases resistance to phase transfer. In addition, the interfacial technique, in comparison with the micellar technique, has much larger dispersed phase and greater capacity for holding the reactants. Coalescence of the dispersed phase occurs spontaneously on standing, making phase separation and catalyst recovery easier. The interfacial technique is also different from the biphasic reaction method using a water-soluble ligand. With a water-soluble ligand, the catalyst is dispersed in the aqueous phase where the reaction is designated to occur unless the substrate has a low aqueous solubility and cannot be drawn into the aqueous phase by the use of a reverse phase-transfer agent. Overall, interfacial synthesis technique can be viewed as an optimal hybrid of the micellar and phase-transfer techniques with respect to the interfacial area and the size of the dispersed phase. It combines a concentration-enrichment capability with a high substrate-holding capacity. This means that a high reaction rate and a high conversion capacity can be achieved simultaneously. Several studies employing the organic-water interfacial technique have been reported with promising results in carbonylation (2), oxidative coupling (3, 4), and in autoxidation (5).

In this work, organic-water interfacial technique has been applied to the autoxidation of tetralin (1,2,3,4-tetrahydronaphthalene) to α-tetralone using nickel catalysts. Dehydrogenation of α-tetralone is a commercial process for the production of α-naphthol (6, 7). Since tetralin can serve as both organic phase and substrate in the biphasic autoxidation scheme, the recovery and recycle of the unreacted tetralin is greatly facilitated, and the use of such noxious and expensive solvents as acetic acid, chlorobenzene, or N,N-dialkylamide (8) can be avoided.

II. EXPERIMENTAL

The experimental apparatus is shown schematically in Fig. 1. The reaction was carried out batchwise at 1atm in a

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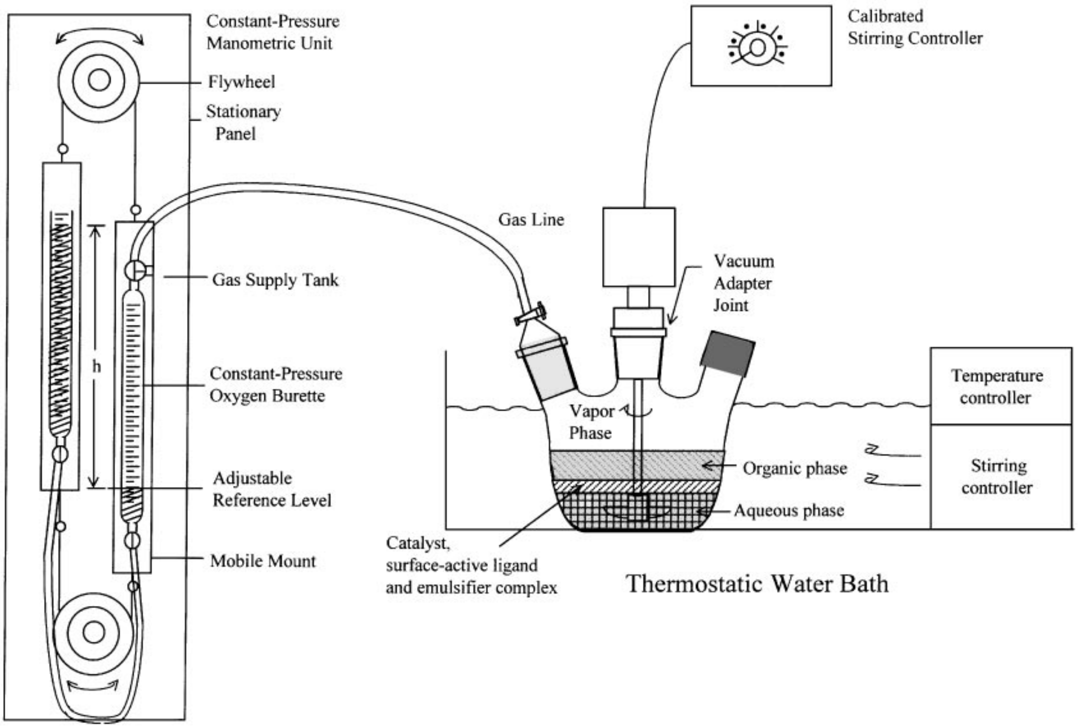


FIG. 1. The experimental scheme for biphasic synthesis.

1000 ml three-necked flask reactor using tetralin-water as the biphasic mixture, a nickel complex of a surface-active ligand as the catalyst, and dodecyl sodium sulfate (DSS) as the emulsifier with vigorous mechanical stirring. The use of a mechanical stirrer and an anionic emulsifier (DSS) increased the dispersion lifetime and interfacial area of the biphasic reaction mixture and had a significant effect on the reaction rate.

A representative run was performed as follows: The reactor was charged with 100 ml of a 1 : 1 (by volume) tetralin-water mixture and the desired amount of DSS, surface-active ligand, and nickel chloride. The reactor was placed in a water bath and purged with oxygen for about 10 min and then allowed to equilibrate to the set temperature, which was typically 60°C. After the reaction was initiated by starting the mechanical stirrer, the oxygen uptake was monitored using a constant-pressure manometric unit.

After completion of the reaction, the reaction mixture was emptied into a separating funnel. Upon standing overnight, the organic and aqueous phase was separated out with an emulsion layer formed between the organic and aqueous phase. The emulsion layer had a bubbly appearance that was indicative of surface affinity. The reaction products were analyzed using a SHIMADZU GC-14A gas chromatograph equipped with a CBP-20 capillary column. The separation conditions and the gas-chromatogram of the calibration mixture are shown in Fig. 2.

III. RESULTS AND DISCUSSION

A. *General Characteristics*

Figure 3 shows a set of representative oxygen uptake profiles of reaction runs with different ligands. The reaction conditions for Fig. 3 are summarized in Table 1, and they correspond to the base runs upon which parametric variations would be made subsequently for ligand screening and detailed kinetic studies. The use of a mechanical stirrer and an emulsifier significantly increased the reaction rate. However, beyond 1200 rpm, the reaction rate was essentially independent of the stirring speed, and 1500 rpm was chosen

TABLE 1

Base Reaction Conditions for Tetralin Autoxidation

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 & amount	DSS (dodecyl sodium sulfate), 0.004 M
Catalyst & amount	$NiCl_2xH_2O$, 0.02 M
Ligand & amount	TEPA (Tetraethylenepentamine), 0.04 M

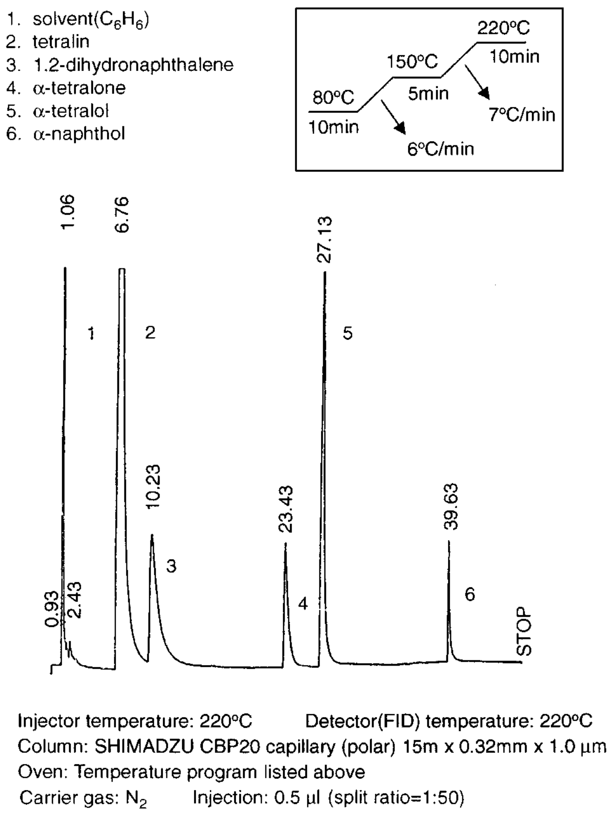


FIG. 2. Gas chromatogram of the calibration mixture for the autoxidation of tetralin.

as a base run condition. With a suitable surface-active catalyst complex, such as tetraethylenepentamine complex of nickel, the reaction took off after an induction period. Irrespective of the ligand used, α-tetralone and α-tetralol were the major reaction products, and α-tetralyl hydroperoxide which has been reported as a major product in homogeneous systems (6, 7) was found to be negligible. It seems that the formation of hydroperoxide in the immediate vicinity of the segregated nickel complexes coupled with its amphiphilic character led to decomposition (5). The higher oxidation products, i.e. α-naphthol, 1,2-dihydronaphthalene were formed only in a trace amount in an extended run. As the reaction progresses, a gradual change of color in the mixture was observed. Initially, the reaction mixture was opaque and white, but as the reaction time elapses, a distinctive brown color of α-tetralone developed.

When the tetralin conversion level reached around 23%, the organic phase underwent a phase inversion. The phase inversion is due to α-tetralone and α-tetralol having a higher density (namely, 1.099 and 1.090 g/ml, respectively) than tetralin (0.973 g/ml). The formation of higher density products caused the organic phase to settle below the aqueous phase. The reaction stopped at a tetralin conversion of 35% due to the build up of higher oxidation products that suppress the propagation chain of the reaction (5). Similar product inhibition has been reported in one-solvent systems (9). Presumably, these phenolic products inhibit the reaction by scavenging the free radicals involved in the autoxidation.

B. Ligand Screening

The screening result on potential ligands to nickel for the tetralin autoxidation is presented in Table 2. Because α-tetralone can be more easily and directly converted to α-naphthol than α-tetralol, a high α-tetralone selectivity is commercially desirable, and in this regard, tetraethyenepentamine (TEPA) was the most effective among the ligands tested; the selectivity of α-tetralone was 71% with nickel-TEPA complex. Furthermore, when the ligand to catalyst ratio was changed from 2 : 1 to 1 : 1, its steady state oxygen uptake rate increased from 0.263 to 0.36 M/h. It was reported that long-chain primary amines were less effective as complexing agents owing to their low aqueous solubility which cause metal to fall out of the aqueous solutions as metal hydroxide (10). It appears that this problem is not serious in the case of TEPA which has additional three secondary amine groups. The reaction using N,N′-dimethylethylenediamine (DMEDA), although its oxygen uptake rate was nearly 1.5 times faster than that with TEPA, led to lower α-tetralone selectivity of 65% followed

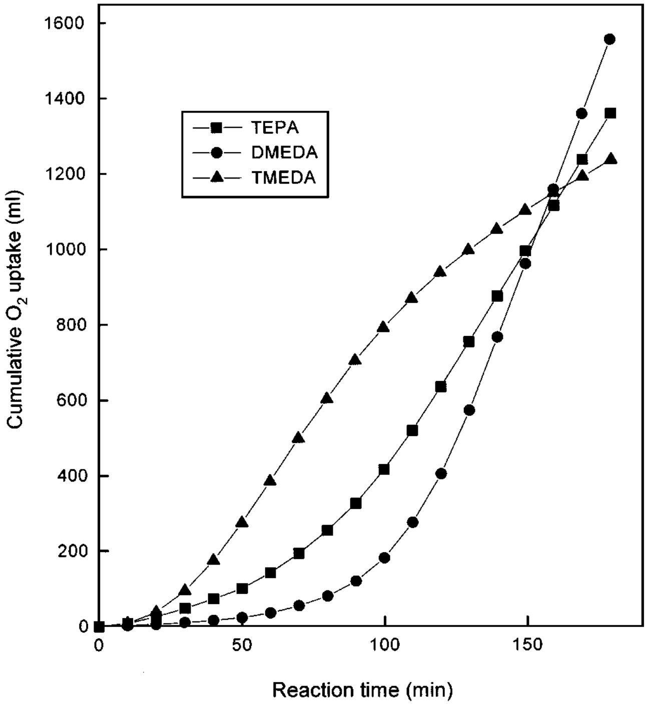


FIG. 3. Cumulative O_2 uptake profile of autoxidation of tetralin using a Nickel catalyst with different ligands. TEPA, Tetraethylenepentamine; DMEDA, N,N′-dimethylethylenediamine; TMEDA, N,N,N′,N′-tetramethylethylenediamine.

TABLE 2

Results of Ligand Screening in the Biphasic Autoxidation of Tetralin[a]

Ligand	O_2 Uptake rate, M/h	α-Tetralone selectivity, %	Induction period (min)
Ethylenediamine	Negligible	—	—
N,N′-Dimethylethylenediamine (DMEDA)	0.4104	65	90
N,N,N′,N′-Tetramethylethylenediamine (TMEDA)	0.246	62	30
N,N-Dibutylethylenediamine (DBEDA)	0.018	33.3	—
N,N,N′,N′-Tetraethylethylenediamine (TEEDA)	Negligible	—	—
N,N-Dibenzylethylenediamine (DBZNEDA)	Negligible	—	—
N,N,N′,N′-Tetraethyldiethylenetriamine	0.008	22.7	—
Tetraethylenepentamine (TEPA)	0.263[b]	71	30
Diethylenetriaminepentaacetic acid	Negligible	—	—
EDTA	Negligible	—	—
4-(Dimethylamino)phenyldiphenylphosphine	Negligible	—	—
Triethyl phosphite	Negligible	—	—
2,2,6,6-Tetramethyl-3,5-heptanedione	Negligible	—	—

[a] Reaction conditions are the same as those specified in Table 1, except for the ligand.

[b] 0.36 M/h at ligand-catalyst ratio of 1 : 1.

by N,N,N′,N′-tetramethylethylenediamine (TMEDA) with oxygen uptake rate of 0.246 M/h and α-tetralone selectivity of 62%. Primary and secondary amines can undergo oxidation to imines via elimination of hydrogen from the α-carbon and for this reason tetramethylethylenediamine is often used in place of ethylenediamine with metals which are oxidizing agents (11).

It is interesting to note that among the potential bidentate ligands tested (entries 2 to 6), the oxygen uptake rate varies substantially depending on the substituent groups; depending on the bulkiness of the substituent groups attached to N, the oxygen uptake rate varied in the order of DMEDA > TMEDA > DBEDA > TEEDA = DBZNEDA (see Table 2). Essentially, the primary effect of the ligands used on the reaction is chemical in nature, but they can also exert an influence on the reaction rates by affecting the interfacial area due to their surface-activity.

C. Detailed Kinetic Results

(1) Rate dependence on the catalyst concentration and oxygen partial pressure. The variation of the steady state oxygen uptake rate with respect to catalyst concentration is shown in Fig. 4. Regardless of the ligand used, the induction period was almost independent of nickel concentration. The induction periods of the reactions with both nickel-TEPA complex and nickel-TMEDA were approximately thirty minutes. In the case of DMEDA, though the induction period was longer, about ninety minutes, the steady-state oxygen uptake rate immediately following the induction period was faster (see Fig. 3) than with TEPA.

The reaction order with respect to nickel catalyst concentration varied from 1.7 to 1, and subsequently to 0 with further increases in the metal concentration. Corresponding reaction in one-liquid-phase systems is reported to show a limiting catalyst order of 0.5 or 1.0 (12). A variable reaction order with respect to catalyst concentration with a limiting value greater than unity is unusual, and this may be a unique feature of the biphasic autoxidation reactions.

The effect of oxygen partial pressure on the biphasic autoxidation reaction is presented in Fig. 5. In contrast to one-liquid-phase systems in which rate dependence on oxygen partial pressure was mostly first order over a much wider pressure range (12, 13), in the biphasic reaction the reaction order with respect to oxygen partial pressure shifted from first to zero order above an oxygen partial pressure of about 0.15 atm. The zero order rate dependence on the dissolved gas concentration under atmospheric conditions seems to be the feature of biphasic reactions (2, 4, 5). The segregation of surface-active catalyst complex and its ability to absorb the gaseous reactant may create a localized high concentration of the dissolved gas around the organic-water

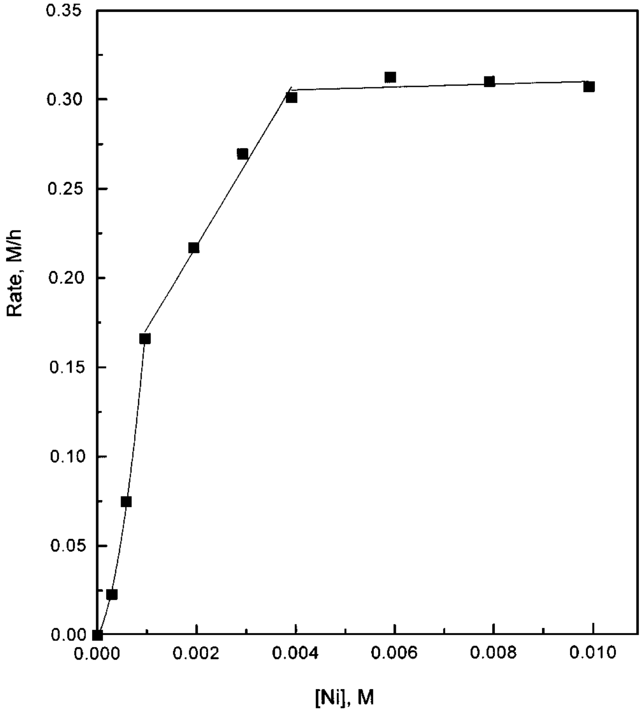


FIG. 4. Rate dependence on [Ni] concentration. Ligand: TEPA.

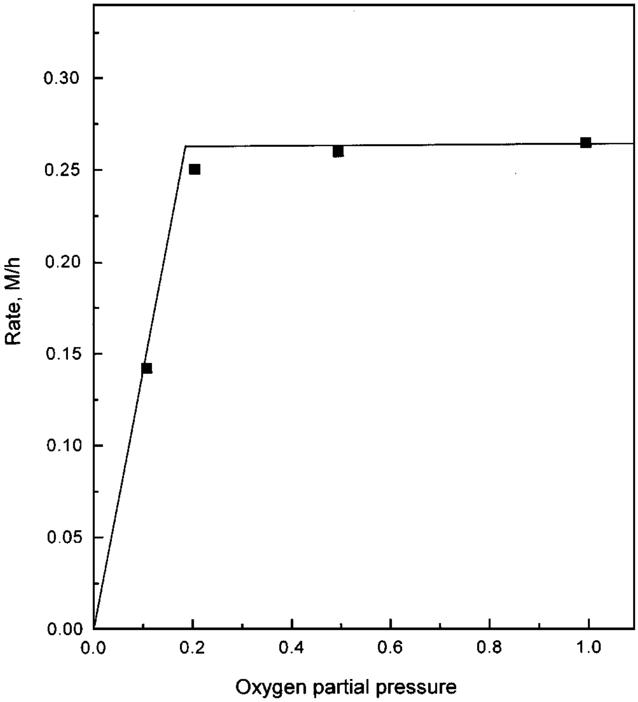


FIG. 5. Rate dependence on oxygen partial pressure. Ligand: TEPA.

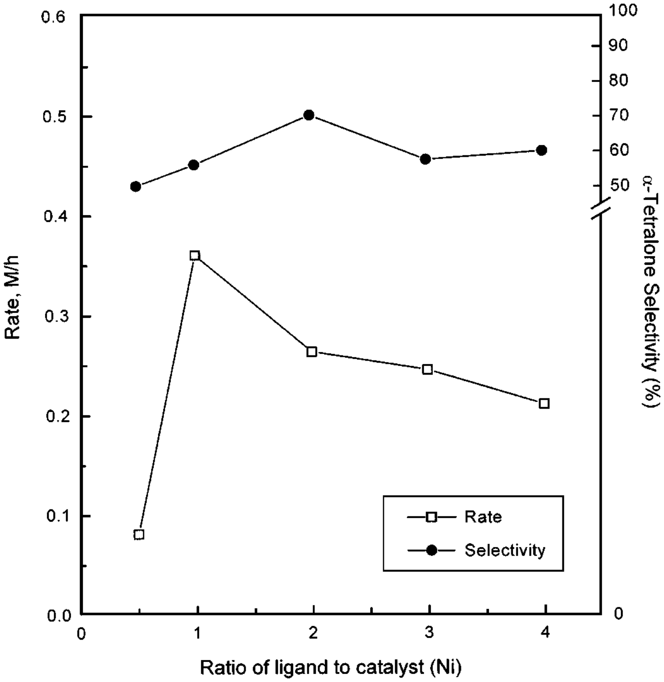


FIG. 6. The dependence of rate and α-tetralone selectivity on the ligand to catalyst ratio. Ligand: TEPA.

interface, where the reaction occurs. As a consequence, it appears that the pressure requirement of dissolved gaseous reactants may be substantially reduced in the biphasic reaction mode.

(2) The effects of ligand-catalyst ratio. The effect of ligand-catalyst ratio on the reaction rate and α-tetralone selectivity is shown in Figs. 6 and 7 for TEPA and DMEDA, respectively. A dramatic effect of ligand to catalyst ratio on the reaction rate is clearly shown and, whilst α-tetralone selectivity was a little higher around 2 : 1 ligand-catalyst ratio regardless of the ligand used, the fastest rate was found to be around 1 : 1 and 2 : 1 with TEPA and DMEDA, respectively. Ligand-catalyst ratio is expected to influence the reaction at the organic-water interface via two competing 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. Presumably, the 1 : 1 (TEPA) or 2 : 1 (DMEDA) corresponded to an optimum balance between these two competing factors. It can be speculated that, for a given coordination number of Nickel(II) complexes formed, a close to half the amount of the bidentate DMEDA would be needed to form a complex with the potentially pentadentate TEPA. The ligand-catalyst ratio also has shown effects on the phase separation.

(3) The effects of organic-water (O-W) volume ratio and emulsifier. Interfacial reactions are strongly dependent on the interfacial area and should therefore be sensitive to parameters such as organic-water volume ratio and the degree of emulsification. Because organic liquids generally have higher solubilities for gases than water, the existence of an organic phase can significantly increase the

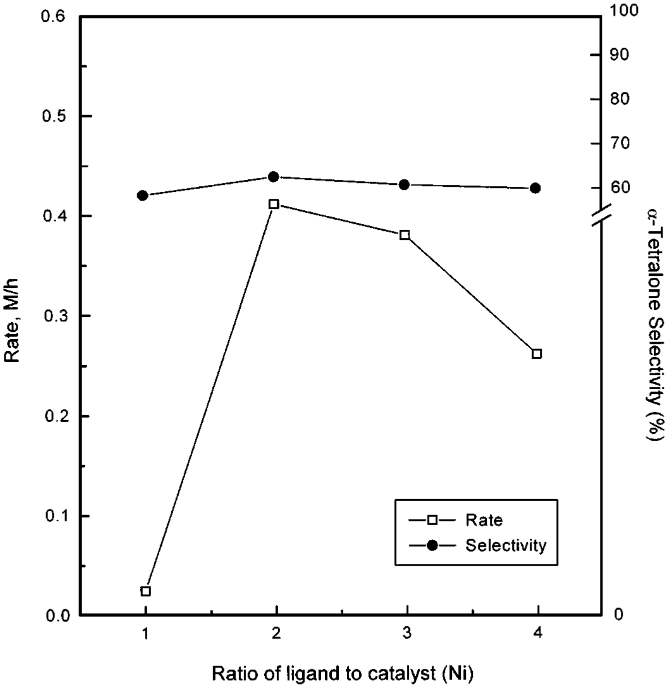


FIG. 7. The dependence of rate and α-tetralone selectivity on the ligand to catalyst ratio. Ligand: DMEDA.

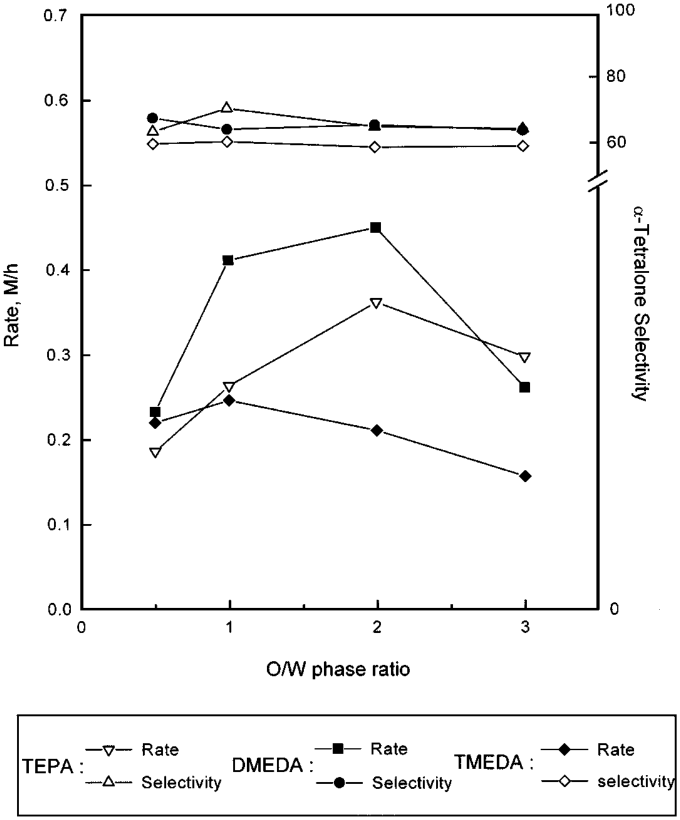


FIG. 8. The dependence of rate and α-tetralone selectivity on the organic-water (O-W) phase volume ratio. [Ligand]/[Ni] = 2 : 1.

solubility of a gaseous reactant and lead to faster reaction rate. A greater dispersion shapes a finer emulsion that can hold more reactants in the active region and provide a larger interfacial area and a shorter diffusion path length for the reactants and catalyst complex (1). In order to rigorously examine the biphasic reaction, it would be beneficial to have quantitative data on the interfacial area and concentration of the reacting species. Unfortunately, such data are not available at present. An attempt to obtain a measure of emulsion size distribution of the diluted reaction mixture using light scattering is in progress.

The effect of organic-water (O-W) volume ratio on the reaction rate and α-tetralone selectivity is shown in Fig. 8. The organic-water (O-W) volume ratio around which the maximum reaction rate was attained varied from 1 : 1 with TMEDA to 2 : 1 with TEPA and DMEDA. α-Tetralone selectivity, however, was almost independent of the O-W ratio.

The result of emulsifier screening is shown in Table 3. The reaction with an anionic surfactant (DSS or DBS) showed much higher reaction rate than without it, whilst cationic (cetyltrimethylammonium bromide), neutral (nonylphenol ethoxylates), or amphoteric(lauryl sulfobetaine) surfactant types all resulted in a significant rate reduction. It appears that the anionic surfactant stabilized the positively charged catalyst complex at the interface and enhanced the reaction rates. Among the anionic surfactants, dodecylbenzenesulfonic acid (DBS), which forms a more stable emulsion (14), yielded a little higher reaction rate than DSS. However, its stable emulsion also made the separation time of the biphasic mixture much longer than DSS.

The dependence of reaction rate and α-tetralone selectivity on the emulsifier (DSS) concentration is shown in Fig. 9. As the emulsifier (DSS) concentration increased, the reaction rate increased very sharply and then leveled off above 0.015 M. α-Tetralone selectivity showed a mild enhancement with DSS concentration, but again was almost independent above 0.015 M.

TABLE 3

Effects of Different Emulsifiers in the Biphasic Autoxidation of Tetralin

Emulsifier	O_2 Uptake rate, M/h
Dodecyl sodium sulfate	0.263
Dodecylbenzenesulfonic acid, sodium salt	0.298
Cetyltrimethylammonium bromide	Negligible
Lauryl sulfobetaine	Negligible
Nonylphenol ethoxylates (NP + 9EO)	0.002
Without emulsifier	0.0045

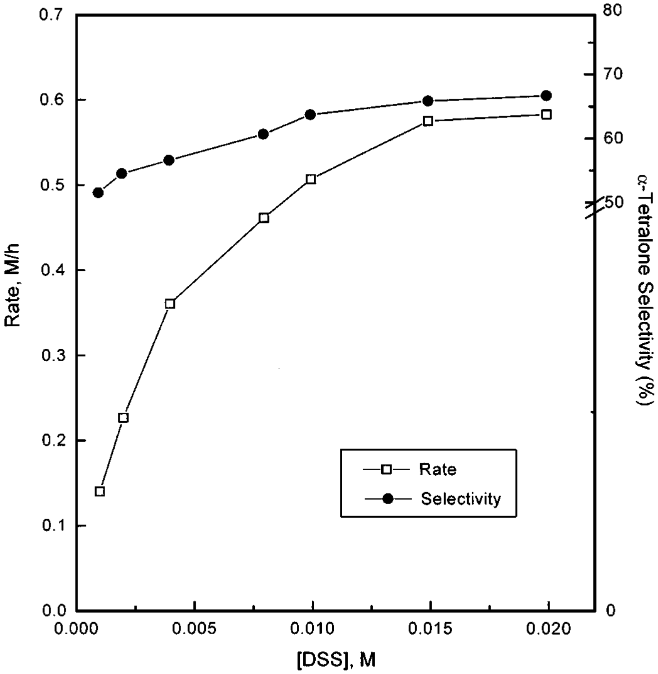


FIG. 9. The dependence of rate and α-tetralone selectivity on the emulsifier (DSS) concentration.* [Ni] = 0.02 M; [TEPA] = 0.02 M. *Other reaction conditions are same as specified in Table 1.

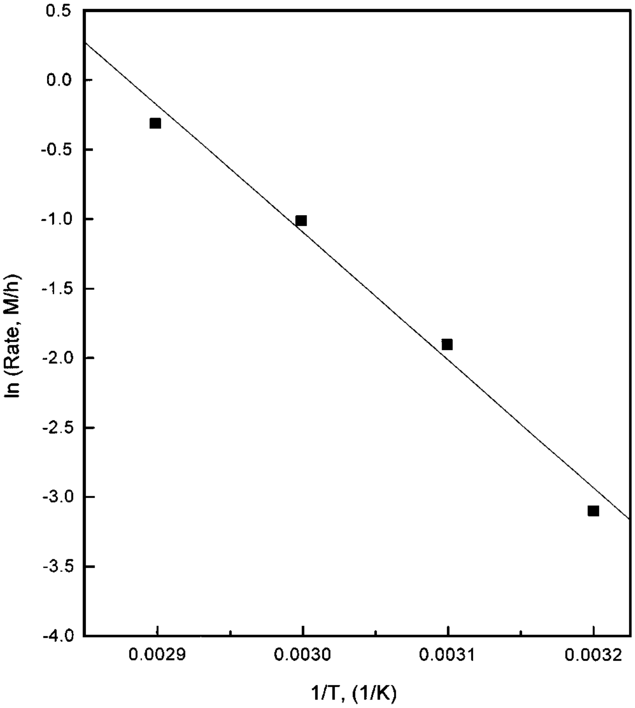


FIG. 10. The rate dependence on the reaction temperature.* [Ni] = 0.02 M; [TEPA] = 0.02 M.*Other reaction conditions are same as specified in Table 1.

(4) Rate dependence on the reaction temperature. The temperature effect on the tetralin autoxidation over 40–70°C range are presented in Fig. 10. According to this Arrhenius plot, the activation energy was estimated to be approximately 18.3 kcal/mol, which is sufficiently high to exclude the possibility of the reaction being limited by oxygen mass transfer.

D. Phase Separation and Segregation of Catalyst Complex at the O-W Interface

The ease of phase separation after the reaction was terminated was influenced by several factors: catalyst concentration, tetralin conversion, surface-activity of a ligand, ligand-catalyst ratio, type and amount of the emulsifier used in the reaction.

As catalyst concentration and tetralin conversion increased, the time needed for the phase separation decreased progressively, however, in the reaction with some ligands, N,N-dibutylethylenediamine, N,N,N′,N′-tetraethyldiethylenetriamine, diethylenetriaminepentaacetic acid and EDTA, the phase separation took more than one week or the mixture was not separated even after one month. To segregate metal complex in the interface effectively, ligands used in the biphasic reaction should be complexing agents with strong amphiphilic character to provide the driving force that pulls oil and water molecules to them. The attributes of satisfactory ligands are known as follows: 1) easy accessibility to the coordinating center, 2) chelating ability and 3) a compact umbrella-like structure (1, 10). Presumably, an umbrella-like structure increases surface affinity by making it possible for the ligand to “float” at the organic-water interface.

Among the ligands with sufficient surface-activity, the ligand-catalyst ratio was also found to affect the degree of phase separation. In the case of TEPA, within the ligand-catalyst ratio of 1 to 4, the separation time was reasonably short. At the ligand-catalyst ratio of 0.5, however, separation proceeded very slowly and, furthermore, metal was found precipitated. These phenomena were also observed in the reaction in which DMEDA was used as a ligand at the ligand-catalyst ratio below 1. If the ligand concentration is not high enough to form a complex with metal to a sufficient extent, it can be difficult to draw metals to the interface.

Depending on the emulsifier types used, the occurrence of the phase separation was different. The reaction mixture in which an anionic emulsifier was used, the phase separation occurred clear and fast. On the other hand, in the cases of cationic, amphoteric, or nonionic surfactants, the phase separation hardly occurred.

Once an emulsion layer emerged at the interface upon standing overnight after the completion of the reaction, the catalyst complex could be quantitatively recovered and it could be reused with no apparent loss of activity.

E. Proposed Reaction Mechanism

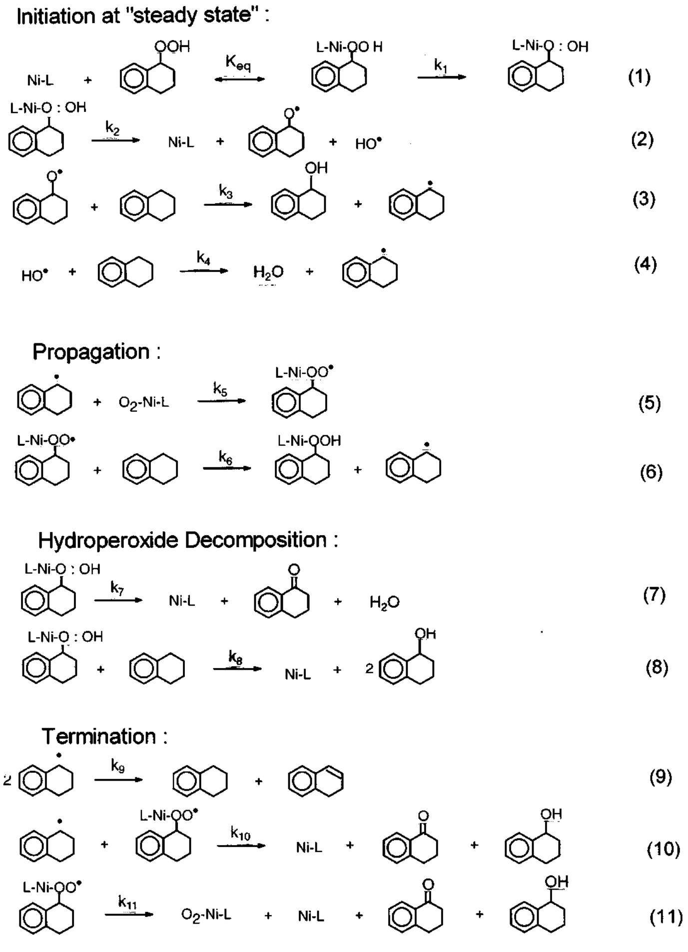
A generalized kinetic model based upon a chain reaction sequence for the biphasic autoxidation of tetralin catalyzed by nickel-TEPA complex is proposed in Scheme 1.

In order to explain the observed product distribution, tetralyl hydroperoxide 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 and α-tetralol.

In accord with other biphasic reactions that also show a weak dependence on dissolved gas reactants (3, 4), the involvement of an oxygenated metal complex is proposed in the propagation step (Step 5) to account for the weak dependence of the biphasic autoxidation reaction on oxygen pressure.

In order to explain the shift to zero-order dependence on the catalyst at a high metal concentration, metal species are presumed to participate in chain termination reactions (Steps 10 and 11).

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. 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.



SCHEME 1. A postulated reaction mechanism.

Assuming the reaction is pseudo-homogeneous and applying the steady-state approximations on the reactive intermediates, the proposed mechanism in Scheme 1 leads to appropriate rate expression as follows:

The rate of oxygen consumption is

$$\begin{aligned}-\frac{d[\mathrm{O_2}]}{dt} &= k_5[\mathrm{R\cdot}][\mathrm{TEPA}\cdots\mathrm{Ni}\cdots(\mathrm{O_2})]\\ &= k_6[\mathrm{TEPA}\cdots\mathrm{Ni}\cdots(\mathrm{RO_2\cdot})][\mathrm{RH}] \qquad [1]\end{aligned}$$

where [RH] represents tetralin concentration.

The initiation rate is equal to the termination rate, therefore

$$\begin{aligned}&2k_2[\mathrm{TEPA}\cdots\mathrm{Ni}\cdots(\mathrm{RO\cdot})(\mathrm{HO\cdot})]\\ &\quad = 2k_9[\mathrm{R\cdot}]^2 + 2k_{10}[\mathrm{R\cdot}][\mathrm{TEPA}\cdots\mathrm{Ni}\cdots(\mathrm{RO_2\cdot})]\\ &\qquad + 2k_{11}[\mathrm{TEPA}\cdots\mathrm{Ni}\cdots(\mathrm{RO_2\cdot})]^2 \qquad [2]\end{aligned}$$

The concentration of TEPA-Ni-tetralyl hydroperoxy radical complex and tetralyl hydroperoxide are nearly zero, so

$$\begin{aligned}&\frac{d[\mathrm{TEPA}\cdots\mathrm{Ni}\cdots(\mathrm{RO\cdot})(\mathrm{HO\cdot})]}{dt}\\ &\quad = k_1[\mathrm{TEPA}\cdots\mathrm{Ni}\cdots(\mathrm{ROOH})]\\ &\qquad - k_2[\mathrm{TEPA}\cdots\mathrm{Ni}\cdots(\mathrm{RO\cdot})(\mathrm{HO\cdot})]\\ &\qquad - k_7[\mathrm{TEPA}\cdots\mathrm{Ni}\cdots(\mathrm{RO\cdot})(\mathrm{HO\cdot})]\\ &\qquad - k_8[\mathrm{TEPA}\cdots\mathrm{Ni}\cdots(\mathrm{RO\cdot})(\mathrm{HO\cdot})][\mathrm{RH}] = 0\\ &\therefore [\mathrm{TEPA}\cdots\mathrm{Ni}\cdots(\mathrm{RO\cdot})(\mathrm{HO\cdot})](k_2 + k_7 + k_8[\mathrm{RH}])\\ &\quad = k_1[\mathrm{TEPA}\cdots\mathrm{Ni}\cdots(\mathrm{ROOH})] \qquad [3]\end{aligned}$$

$$\begin{aligned}\frac{d[\mathrm{ROOH}]}{dt} &= -k_1[\mathrm{TEPA}\cdots\mathrm{Ni}\cdots(\mathrm{ROOH})]\\ &\quad + k_6[\mathrm{TEPA}\cdots\mathrm{Ni}\cdots(\mathrm{RO_2\cdot})][\mathrm{RH}] = 0 \qquad [4]\end{aligned}$$

From combination of [1], [3]

$$\begin{aligned}&k_6[\mathrm{TEPA}\cdots\mathrm{Ni}\cdots(\mathrm{RO_2\cdot})][\mathrm{RH}]\\ &\quad = k_5[R\cdot][\mathrm{TEPA}\cdots\mathrm{Ni}\cdots(\mathrm{O_2})]\\ &\quad = k_1[\mathrm{TEPA}\cdots\mathrm{Ni}\cdots(\mathrm{ROOH})] \qquad [5]\end{aligned}$$

Division of [2] by [3] gives

$$\frac{k_2}{(k_2 + k_7 + k_8[\mathrm{RH}])} = \frac{k_9 + k_{10}\frac{k_5}{k_6}\frac{[\mathrm{TEPA}\cdots\mathrm{Ni}\cdots(\mathrm{O_2})]}{[\mathrm{RH}]} + k_{11}\left(\frac{k_5}{k_6}\frac{[\mathrm{TEPA}\cdots\mathrm{Ni}\cdots(\mathrm{O_2})]}{[\mathrm{RH}]}\right)^2[\mathrm{R\cdot}]}{k_5[\mathrm{TEPA}\cdots\mathrm{Ni}\cdots(\mathrm{O_2})]}$$

$$\therefore [\mathrm{R\cdot}] = \frac{k_2k_5[\mathrm{TEPA}\cdots\mathrm{Ni}\cdots(\mathrm{O_2})]}{(k_2 + k_7 + k_8[\mathrm{RH}])\left\{k_9 + k_{10}\frac{k_5}{k_6}\frac{[\mathrm{TEPA}\cdots\mathrm{Ni}\cdots(\mathrm{O_2})]}{[\mathrm{RH}]} + k_{11}\left(\frac{k_5}{k_6}\frac{[\mathrm{TEPA}\cdots\mathrm{Ni}\cdots(\mathrm{O_2})]}{[\mathrm{RH}]}\right)^2\right\}} \qquad [6]$$

From combination of [1], [6], the following model rate expression is derived:

$$\therefore -\frac{d[\mathrm{O_2}]}{dt} = \frac{k_2k_5^2[\mathrm{TEPA}\cdots\mathrm{Ni}\cdots(\mathrm{O_2})]^2}{(k_2 + k_7 + k_8[\mathrm{RH}])\left\{k_9 + k_{10}\frac{k_5}{k_6}\frac{[\mathrm{TEPA}\cdots\mathrm{Ni}\cdots(\mathrm{O_2})]}{[\mathrm{RH}]} + k_{11}\left(\frac{k_5}{k_6}\frac{[\mathrm{TEPA}\cdots\mathrm{Ni}\cdots(\mathrm{O_2})]}{[\mathrm{RH}]}\right)^2\right\}} \qquad [7]$$

At an oxygen pressure above 0.15 atm, the majority of the metal complex may be assumed to exist mainly in the oxygenated form, i.e., $[\mathrm{Ni}\cdots\mathrm{TEPA}\cdots(\mathrm{O_2})] \doteqdot [\mathrm{Ni}\cdots\mathrm{TEPA}]_\mathrm{T}$, and Eq. [7] reduces to the following limiting forms for different catalyst concentration ranges:

$$-\frac{d[\mathrm{O_2}]}{dt} \approx \frac{k_2k_5^2[\mathrm{TEPA}\cdots\mathrm{Ni}\cdots(\mathrm{O_2})]_T^2}{(k_2 + k_7 + k_8[\mathrm{RH}])k_9} \propto [\mathrm{TEPA}\cdots\mathrm{Ni}]_T^2$$

$$\text{at low } [\mathrm{TEPA}\cdots\mathrm{Ni}]_T \qquad [7\text{-}1]$$

$$-\frac{d[\mathrm{O}_2]}{dt} \approx \frac{k_2k_5k_6[\mathrm{TEPA}\cdots\mathrm{Ni}\cdots(\mathrm{O}_2)]_T[\mathrm{RH}]}{(k_2+k_7+k_8[\mathrm{RH}])k_{10}} \propto [\mathrm{TEPA}\cdots\mathrm{Ni}]_T^1 \quad \text{at intermediate } [\mathrm{TEPA}\cdots\mathrm{Ni}]_T \qquad [7\text{-}2]$$

$$-\frac{d[\mathrm{O}_2]}{dt} \approx \frac{k_2k_6^2[\mathrm{RH}]^2}{(k_2+k_7+k_8[\mathrm{RH}])k_{11}} \propto [\mathrm{TEPA}\cdots\mathrm{Ni}]_T^0 \quad \text{at high } [\mathrm{TEPA}\cdots\mathrm{Ni}]_T \qquad [7\text{-}3]$$

Thus, above an oxygen pressure of 0.15 atm, the model predicts second-, first- and zero-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 nickel-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 1.7.

At a low oxygen pressure (<0.15 atm), the metal complex may be assumed to exist predominately in a nonoxygenated form, i.e., $[\mathrm{Ni}\cdots\mathrm{TEPA}\cdots(\mathrm{O}_2)] = K[\mathrm{Ni}\cdots\mathrm{TEPA}]P_{\mathrm{O}2} \fallingdotseq K[\mathrm{Ni}\cdots\mathrm{TEPA}]_T P_{\mathrm{O}2}$, where K is the stability constant of the oxygenated complex. Equation [7] then reduces to the following limiting form for the intermediate catalyst concentration range for which rate data are available:

$$\therefore -\frac{d[\mathrm{O}_2]}{dt} \approx \frac{k_2k_5k_6K[\mathrm{TEPA}\cdots\mathrm{Ni}]_T P_{\mathrm{O}_2}[\mathrm{RH}]}{(k_2+k_7+k_8[\mathrm{RH}])k_{10}} \propto [\mathrm{TEPA}\cdots\mathrm{Ni}]_T P_{\mathrm{O}_2} \qquad [7\text{-}4]$$

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

IV. CONCLUSION

A biphasic reaction technique was applied in the commercially useful autoxidation of tetralin using a surface-active ligand complex of nickel as catalyst, tetralin as the substrate and organic phase, and dodecyl sodium sulfate as emulsifier. The organic-water interfacial reaction scheme can provide several advantages such as avoidance of using troublesome solvent, ease of catalyst recovery and substrate recycle. The main products were α-tetralone and α-tetralol independent of ligands used. The α-tetralone selectivity was 71% with a tetraethylenepentamine complex of nickel. The reaction order with respect to oxygen shifted from first to zero order as its partial pressure increased and the reaction order with nickel catalyst concentration varied from 1.7 to 1, and subsequently to 0 with further increases in the metal concentration.

Depending on the ligand used in the reaction, an optimum ligand-catalyst ratio of either 2 : 1 or 1 : 1 was obtained and the ligand-catalyst ratio also had some effect on the ease of phase separation after reaction was stopped. The organic-water phase ratio around which the maximum reaction rate was attained varied with regard to ligand used between 2 : 1 or 1 : 1.

A generalized reaction mechanism is proposed which yields model results in good agreement with the experimental findings.

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