

Heterogenized polymetallic catalysts. Part I. Catalytic air oxidation of 3,5-di-*t*-butylphenol by Cu(II) and Fe(III) complexed to a polyphenylene polymer containing β -di- and tri-ketone surface ligands

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Abstract

Catalysis preparation involves the cyclic trimerization polymerization of acetylated aromatics. The polymer is coated on a high surface area support, Celite, and cured to give insoluble high molecular weight polymer. Reaction of the remaining acetyl end groups with base and methyl acetate gave β -diketone groups on the surface of the polymer. A second reaction with base and methyl acetate places β -triketones on the surface. The β -triketones can bind two metal ions in a known geometry. The chemically modified surfaces containing β -diketone and β -triketone surface ligands were reacted with $\text{Cu}(\text{OAc})_2$ and FeCl_3 to give mono- and bi-metallic surface complexes. The oxidation of 3,5-di-*t*-butylcatechol was studied with all the surfaces. The monometallic catalysts gave only the *ortho*-quinone as product. The bimetallic catalysts absorbed about twice as much dioxygen as the monometallic catalysts and gave ring cleaved products. Both gave induction periods before dioxygen uptake began. With the bimetallic catalysts the dioxygen uptake stopped at about the ratio: 2 O_2 /1 catechol. This is twice as much dioxygen as that required for ring cleavage so H_2O_2 may be the dioxygen reduction product rather than water. The monomeric $\text{Cu}(\text{OAc})_2$ dioxygen uptake curve reached a maximum and then released gas. This could result from Cu(II) catalyzed decomposition of H_2O_2 .

Keywords: Bimetallic catalysts; Catechol derivatives; Copper(II); Dioxygen; Iron(III); Oxidation; Ring cleavage

1. Introduction

1.1. General

Many metallic heterogeneous catalysts on supports appear to have crystallites which are very small, containing only a few metal atoms. These

atoms can interact cooperatively to readily carry out reactions which cannot be achieved by homogeneous, mononuclear catalysts. Examples on platinum surfaces include the oxidation of methanol [1], the four-electron reduction of dioxygen at fuel cell electrodes [2], and the isomerization of alkanes [3]. These catalysts may have a further advantage. As they are surface species, they would have bare coordination sites and thus be more reactive than completely coordinated soluble catalysts. A real advance in catalysis would be the

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development of heterogeneous polymetallic catalysts of known structure which have activity similar to the above systems.

The objective of an overall research program of the author is to prepare heterogeneous catalysts by placing polynucleating ligands on polymer surfaces. These ligands will complex two metal ions in such a fashion that they can, by cooperative action, catalyze reactions which would not be catalyzed by monomeric catalysts. This paper describes the initial steps in the development of such catalysts. In these studies the polymer system will be tested for its effectiveness as a catalytic modifying layer for oxidation of catechols.

Iron and copper complexes have received considerable attention because they are the main metals found in biological dioxygen metabolism [4]. Although heme-iron systems for dioxygen bonding [5] and dioxygen activation [6] are now fairly well understood, non-heme iron systems are not. Thus the oxidative cleavage of catechol by the high-spin ferric enzymes, pyrocatechase and metapyrocatechase is one of the most interesting and widely studied biological oxygenating processes [7]. In spite of considerable effort, only three model systems give the activity of the natural enzymes [8–10]. Two give the intradiol cleavage to *cis,cis*-muconic acid [8,9] while the other gives both types of cleavage, thus more closely duplicating the pyrocatechase activity [10].

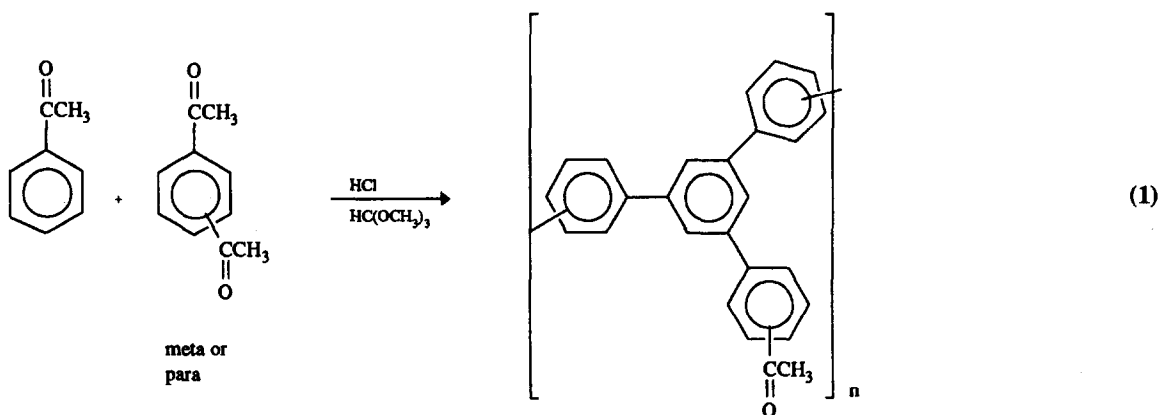
Considerable effort has also been put into studies of model compounds for dioxygen binding or

dioxygen-activating copper proteins [11]. An example of the former is hemocyanins, found in molluscs and arthropods, while an example of the latter is the tyrosinase monooxygenases which catalyze the orthohydroxylation of phenols [12]. All of these copper model systems are bimetallic.

There has also been considerable study of the use of simple copper complexes, which are also usually bimetallic, for the oxidation of 3,5-di-*t*-butylcatechol (DTBC) to 3,5-di-*t*-butylquinone (DTBQ) [13–16]. Some copper [17,18] and iron [19] homogeneous catalysts cause the ring cleavage of catechols. Several of the systems studied have been polymeric since catalyst removal is facilitated [20–22].

1.2. Catalyst system

One ligand which strongly binds a large variety of metal species is the β -diketone group. A closely related binucleating ligand is the β -triketone group which is capable of holding two metal species in a known geometry [23] which could be suitable for joint catalysis in certain organic transformations. The strategy for attaching these ligands to a surface involves the preparation of polyphenylene polymers by the aromatization polymerization shown in Eq. 1 (Scheme 1). Acetophenone and *m*- or *p*-diacetyl benzene have been the most extensively used monomers. The *p*-diacetyl benzene polymer (PDAB) were used for the present studies. These polymers are extremely



Scheme 1.

2.3. Preparation of catalytic surfaces

The polymerization uses the procedure of Teplyakov and coworkers [24]. The acetyl containing monomers are dissolved in benzene containing triethyl- or trimethyl-orthoformate at room temperature. HCl gas is passed through the solution for 5–45 min depending on the monomers and rate of HCl flow. The flow is discontinued before any precipitate appeared. N₂ is then passed through the solution. The catalysts are prepared by coating the polymer on a solid support followed by curing. For the air oxidation catalysts the prepolymer solution was evaporated in a rotary evaporator in the presence of a calculated amount of celite to give a thin coating on this support. To obtain a high molecular weight surface coating, the prepolymer treated Celite is then sprayed with a fine mist of a saturated solution of *p*-toluenesulfonic acid in benzene, and heated in a vacuum oven at 150°C. Films prepared on Celite as described above were also used for characterization.

For the electrochemical characterization studies, the procedure for electrode coating involved spin coating using a photoresist spinner from Headway Research, Inc. Variation of film thicknesses can be held to 10% [29]. Film thicknesses from 50 Å to 1 μ can be prepared depending on prepolymer concentration and the spin rate [30]. It was found that very thin films (ca 50 Å) had to be employed or no response was obtained. The coating was cured onto the electrode surface by the procedure described above. The cured coating was subjected to a series of cyclic voltammetric cycles to see if it adheres under the conditions of the experimental procedure.

The chemical modification was carried out by procedures analogous to those used for preparing β-di- and tri-ketones with non-polymeric species. The base used initially was KNH₂ in liquid NH₃ [31]. NaH was next used [32] but a more recent development has been the use of LiN(*i*-Pr)₂ formed from LiCH₃ and HN(*i*-Pr)₂ in diglyme solvent [33]. All three procedures have been used to put β-di- and tri-ketone ligands on the polymer

coated surfaces. For most of the present studies the LiN(*i*-Pr)₂ procedure was used. The metal ion coating was carried out by exposing the chemically modified surface to a solution of the metal salt of known concentration. For the Celite coated catalyst, after stirring the mixture for an hour, the solids were removed by filtration, and the filtrate analyzed for metal ion content. The amount of metal ion taken up by the surface could then be readily calculated from the known initial concentration of the solution. For the electrochemical experiments the metal ion uptake was followed by cyclic voltammetry.

2.4. Metal ion analysis

The iron was analyzed by visible spectroscopy as the Fe(SCN)₆³⁻ ion which, in strong acid solution, has a strong absorption at 447 nm [34] (a). Standard solutions for preparing calibration curves were prepared by dissolving 0.2825 g iron powder (5.0 mmol) in 1:1 HNO₃:H₂O solution which was diluted to 500 ml with distilled water to give a 0.01 M solution. A 5 ml aliquot of this solution was diluted to 50 ml to give a solution for which [Fe(III)] = 1 × 10⁻³ M. A series of six solutions varying in concentration from 2 × 10⁻⁵ M to 4.8 × 10⁻⁴ M were prepared by adding various aliquots of this last solution to 20 ml of 0.5 M HNO₃ and 1.0 ml of 1 M SCN⁻ solution followed by dilution to 25 ml with 0.5 M HNO₃. The absorption of these six solutions was measured and a calibration curve prepared. As expected, a linear relationship between [Fe(III)] and absorbance was found.

The iron(III) ion uptake was measured using 0.01 M solutions of FeCl₃. To 20 ml of this solution was added 0.25 g of polymer coated Celite containing 0.075 mmol of potential ligand binding sites. This is the number of binding sites potentially present if all of the methyl benzoate groups had reacted to form β-di- or tri-ketone ligands. Of course a triketone provides two binding sites while a diketone provides only one. The mixture was stirred for 2–4 h in a 25 ml volumetric flask in a closed system at room temperature under N₂. Then

the mixture was filtered and 10 ml of the filtrate was transferred into a 100 ml volumetric flask to which 3.5 ml of conc. HNO_3 was added. The resulting solution was heated in air on a steam bath for 30 min or until the solution became colorless indicating all the Fe(II) had been oxidized to Fe(III). This treatment was carried out for solutions in contact with unmodified coated Celite, polymer modified to give diketone and polymer coated Celite modified to give triketone. This last treatment was also performed on the original stock solution which was not in contact with polymer coated Celite. The solutions were now made up to 100 ml with distilled water to give solutions of approximately 10^{-4} M Fe(III). A 2.5 ml aliquot of this solution was added to 20 ml 0.5 M HNO_3 followed by addition of 1 ml of 1 M SCN^- solution. Finally they were diluted to 25 ml with 0.5 M HNO_3 and the intensity of the absorbance measured. From the intensity [Fe(III)] was calculated.

The Cu(II) was coated on the polymer by procedures analogous to those for Fe(III). Analysis of the solutions before and after treatment with the catalyst was carried out by adding KI and titrating the I_3^- released with thiosulfate [34] (b).

2.5. Oxidation procedure

To provide good gas liquid mixing, the reactions were run in creased flasks at 25°C at a constant dioxygen pressure of one atmosphere. The progress of the oxidations were followed by dioxygen uptake measured by gas burets thermostated at the reaction temperature. The reaction flask was a 250 ml two-necked cone-shaped flask with the sides indented at four places to increase stirring efficiency. The apparatus is similar to that previously described [35]. In a typical run the flask containing 50 ml of reaction mixture was placed in a constant temperature bath and connected to the gas buret. The system was then evacuated for 10 m on the vacuum line with the stirrer running. The stirring was then stopped and the system pressured to 1.0 atm with dioxygen. The mercury in the gas buret and the leveling bulb were then equalized and a reading taken. The stirrer was then

turned on to start the run. The pressure was kept constant by continuously leveling the mercury in the gas buret and the bulb. Readings were taken immediately after the levels were equalized.

2.6. Product identification

Since the triketone-Fe(III) catalysts gave the most complicated reaction mixtures, the product distribution was determined in this system. The reaction was terminated when the moles of dioxygen taken up was equal to the moles of DTBC originally present. The solid from the greenish brown reaction mixture was removed by filtration and the filtrate evaporated at room temperature to give an oily residue. If the residue is allowed to dry completely it tends to form insoluble polymeric species. The ^1H NMR spectra displayed several *t*-butyl and methoxy groups indicating a number of products. The oxidation products were dissolved in petroleum ether and chromatographed on silica gel (Aldrich, 70–230 mesh, 60 \AA) using a column 10 cm in length and 1 cm in diameter. Using increasing portions of ether to increase the polarity, four fractions were collected. The first fraction contained two products, **5** and **6**, which were readily identified as 3,5-di-*t*-butyl-1,2-benzoquinone ² and *cis,cis*-dimethyl 2,4-di-*t*-butyl muconate ³, respectively, from comparison of their spectra with those published [36,37]. The second fraction contained **5** and 3,5-di-*t*-butyl-5-(methylcarboxymethyl)-2-furanone, **7** ⁴, which was a condensation product from the half hydrolysis of **5**. It was also identified by comparison with published spectra [31,32]. The third fraction contained **7** and a product, **8**, which was present to a very small amount in the original reaction mixture

² **5**: ^1H NMR (CDCl_3), δ 1.19 (s, 9H), 1.23 (s, 9H), 6.45 (d, $J=2.4$ Hz, 1H), 6.85 (d, $J=2.4$ Hz, 1H) FT-IR $\nu(\text{CO})$, 1650 cm^{-1} .

³ **6**: ^1H NMR (CDCl_3), δ 1.10 (s, 9H), 1.20 (s, 9H), 3.60 (s, 3H), 3.65 (s, 3H), 5.75 (d, $J=1.5$ Hz, 1H), 6.25 (d, $J=1.5$ Hz, 1H); FTIR $\nu(\text{CO})$, 1680 cm^{-1} .

⁴ **7**: ^1H NMR (CDCl_3), δ 0.98 (s, 9H), 1.23 (s, 9H), 2.81 (d, $J=14.3$ Hz, 1H), 2.95 (d, $J=14.3$ Hz, 1H), 3.61 (s, 3H), 6.94 (s, 1H); FTIR $\nu(\text{CO})$, $1748, 1720 \text{ cm}^{-1}$.

and had one of the *t*-butyl groups removed. As **8**⁵ could not be obtained pure, no further attempt at positive identification was made. The fourth fraction contained only *t*-butyl alcohol.

The products from the runs with monometallic catalysts **2**, M = Cu or Fe, were readily identified as **5** from its ¹H NMR spectra.

2.7. Electrochemical studies

These studies used cylindrical glassy carbon electrodes cut from carbon rods (Atomergic Chemicals Corp.) and fashioned into electrodes using the procedure of Anson [38]. A standard three electrode cyclic voltammetric cell was employed.

3. Results and discussion

3.1. Polymer characterization

Spectral and electrochemical studies were employed to confirm that the chemical changes shown in Eqs. 2 and 3 (Scheme 2) are actually accomplished.

The prepolymers were coated onto a high surface area celite and cured. The coatings were then reacted with base and methyl acetate to give diketone groups, **1**, (Eq. 2). A portion of the initially modified polymer coated celite was reacted with base and methyl acetate a second time to give triketone surface groups, **3** (Eq. 3). The surface modifications, resulting from the chemical treatment, was monitored by FT-IR using Nujol mulls. The polymer coated but unmodified Celite surface displayed bands at 1676 cm⁻¹, and 1640 cm⁻¹, similar to the ketone bands in the monomers. After the initial chemical treatment, bands were present at 1688, 1630, and 1604 cm⁻¹. The first is a ketone band while the other two are enol bands [38]. After the second chemical treatment modification, the spectra showed further qualitative change. A

broad band centered at 1644 cm⁻¹ consisting of several bands, including ones at 1675 and 1600 cm⁻¹, appeared. A triketone ligand would be expected to have three bands in this region [38]. These studies were hampered by the presence of bands due to the Celite substrate.

These polymer characterization studies leave no doubt that the desired chemical modification and metal ion uptake has occurred. The changes in the infrared spectra were exactly those expected for the first chemical modification to produce diketone, **2**, in Eq. 2 and for the second modification to produce triketone, **4**, in Eq. 3.

Chemical modification was also confirmed by preliminary electrochemical studies with (CH₃CO₂)₂Ru(Py)₂ (Py = pyridine), a species that has been used previously in surface absorption studies [39]. The cyclic voltammograms of untreated electrodes in aqueous CF₃CO₂H/CF₃CO₂Na (pH = 3) showed small oxidation–reduction waves resulting from an electroactive impurity in the carbon. Uncoated electrodes in the same aqueous solvent containing (CH₃CO₂)₂Ru(Py)₂ (5–10 mmol) gave reversible waves (*E*_p = 62 mV) at *E*_{1/2} = +700 mV (SSCE). When taken from this solution and put in an aqueous solvent not containing Ru(II), the waves disappeared indicating the Ru(II) was not absorbed.

After coating and curing, the graphite disks were subjected to the chemical modification to give surface diketone groups, **1**. In the absence of Ru(II) these polymers gave CV's identical to bare electrodes. The modified electrodes were then immersed in a 1% aqueous solution of (CH₃CO₂)₂Ru(Py)₂ for an hour, removed, washed with distilled water, and dried. The electrodes were then placed in an aqueous solution containing CF₃CO₂Na/CF₃CO₂H and the CV's run. Anodic and cathodic waves were detected at a potential which was 50 mV more positive than the solution (CH₂CO₂)₂Ru(Py)₂ species. Polymer-coated graphite-disk electrodes without chemical modification did not exhibit ruthenium electroactivity when treated in a similar fashion.

⁵ **8**: ¹H NMR (CDCl₃), δ 1.02 (s, 9H), 3.85 (s, 3H), 5.86 (d, *J* = 10 Hz, 1H), 6.52 (d, *J* = 10 Hz, 1H); FTIR ν(CO), 1680, 1620 cm⁻¹.

These electrochemical studies indicate that the diketone surface ligands are capable of absorbing metal ions from solution. Thus $(\text{CH}_3\text{CO}_2)_2\text{Ru}(\text{Py})_2$ was only absorbed by the electrode surface that had been chemically modified to give **2**. Furthermore the absorbed species gave waves at a different potential than the solution species.

3.2. Metal ion uptake

The number of active sites was quantified by metal ion uptake studies.

The metal ion uptake for polymer coated but unmodified celite, as well as singly modified and doubly modified samples were measured for the metal species. Results are given in Table 1. In both cases, for the same polymer sample, the metal ion uptake increased in the order: unmodified < singly modified < doubly modified.

The metal ion uptake shown in Table 1 provided further evidence for chemical modification. The unmodified surfaces displayed some metal ion uptake because of physical absorption but the surfaces chemically modified to give β -diketone surface ligand species, **2**, always gave appreciably more metal ion uptake. The most convincing result is the fact that the diketone containing surfaces, when chemically modified a second time to produce β -triketone surface ligands, displayed about twice the metal ion uptake of the diketone containing polymers. This is exactly the result expected if most of the diketone ligands are converted to triketone ligands.

3.3. Comparison of mono- and bi-molecular catalytic species

The main purpose of these studies to determine if the bimetallic catalysts have special types of reactivity not found for the monometallic catalysts. These special reactivities could express themselves in the oxygen uptake curves and nature of the oxidation products.

3.3.1. Dioxygen uptake studies

All reactions were catalytic in the metal species with turnovers reaching 200 for the triketone surfaces for the first catalytic cycle. Addition of more DTBC to spent reaction mixtures gave renewed dioxygen uptake with no inhibition period. Thus these heterogeneous systems appear to be efficient catalysts. Although the total dioxygen uptake followed the expected order: unmodified < diketone < triketone, the shapes of the oxygen uptake curves varied for the Cu(II) and Fe(III) surfaces. With copper(II) acetate catalysts, shown in Figs. 1, 2, 22 and 1, the unmodified and diketone surfaces reached a maximum of dioxygen absorption, then decreased with further reaction. The triketone surface continued to take up dioxygen during the entire course of the run with the rate of uptake gradually decreasing as O_2/DTBC molar ratios of about 2 were reached. The FeCl_3 uptake curves were quite different from those for the copper system. A typical plot is shown in Fig. 2. The reactions did display some autocatalytic behavior but the monometallic uptake curves did not reach a maximum and then decrease as for the Cu(II) surfaces. A homogeneous solution of FeCl_3 containing about the same amount of FeCl_3 as is on the catalyst surface gave

Table 1
Metal ion uptake by polymer coated Celite surfaces^a

Metal salt	Unmodified surface uptake (mmol/g)	Diketone surface uptake (mmol/g)	Triketone surface uptake (mmol/g)
$\text{Cu}(\text{OAc})_2$	0.038	0.076	0.16
FeCl_3	0.016	0.036	0.063

^a Average of three determinations. Surface coverage expressed as mmol per gram polymer-coated Celite. The acetophenone-*para*-diacetylbenzene polymer (PDAB) was used for these studies.

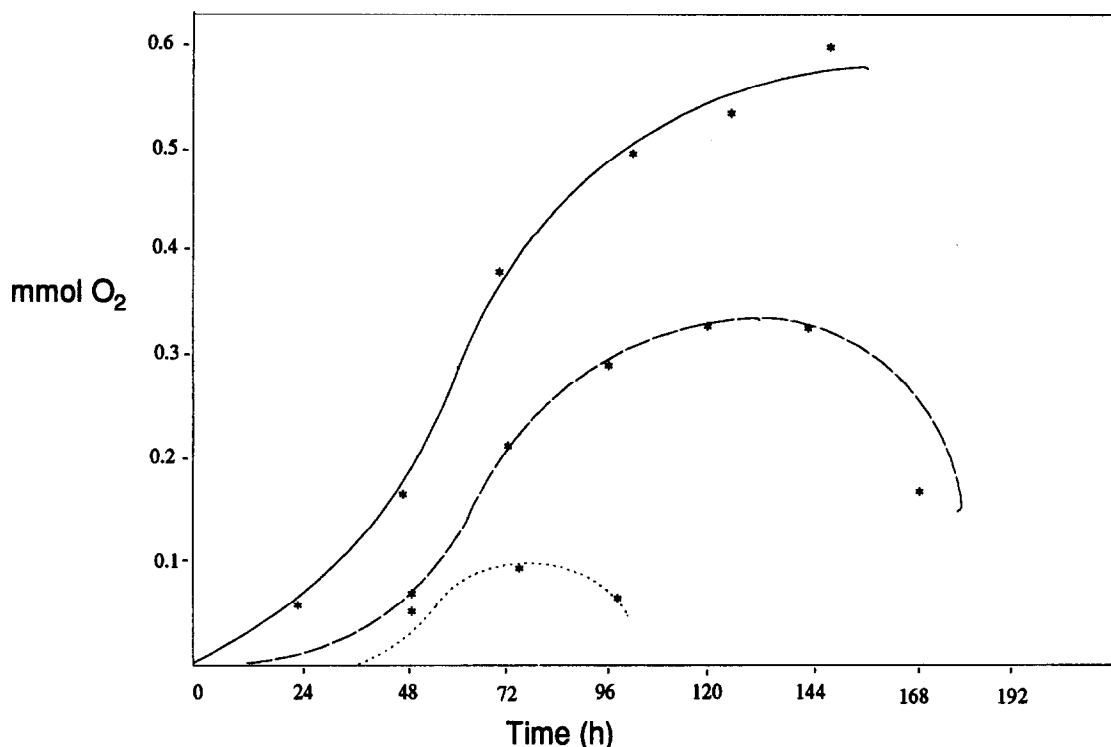


Fig. 1. Oxidation of DTBC by PDAB polymer supported $\text{Cu}(\text{OAc})_2$ in methanol. Reaction mixture contains 0.5 g polymer coated Celite and 0.25 mmol DTBC in 25 ml methanol: (.....) unmodified polymer, $\text{Cu}(\text{II}) = 1.9 \times 10^{-2}$ mmol; (- - -) diketone polymer, $\text{Cu}(\text{II}) = 3.8 \times 10^{-2}$ mmol; (—) triketone polymer, $\text{Cu}(\text{II}) = 7.8 \times 10^{-2}$ mmol.

no dioxygen uptake. As with Fig. 1, the uptake curve levels off at O_2/DTBC ratios of about 2. The induction periods can be completely removed by increasing the amount of catalyst or increasing the catechol concentration.

These dioxygen uptake curves provide a graphic demonstration of the differences between the surfaces. In both cases, the bimetallic dioxygen uptake passes the point where the O_2/DTBC mole ratio is 1 and reach an O_2/DTBC molar ratio of about 2. On the other hand, the monometallic diketone uptake curves did not pass far beyond the ratio: $\text{O}_2/\text{DTBC} = 1$. These results indicate a higher degree of oxidation for the bimetallic than for the monometallic catalyst.

3.3.2. Product distributions

The products of the oxidation depended solely on the type of catalytic surface. As shown in Eq. 4 (Scheme 3), with both $\text{Cu}(\text{II})$ and $\text{Fe}(\text{III})$ the β -diketone surfaces gave only 1,2-benzoquinone.

The triketone catalytic surfaces also gave ring cleaved products. The detailed distribution with the FeCl_3 treated surface, at the point where the molar uptake of dioxygen to DTBC was equal, is shown in Eq. 5 (Scheme 4). Although the 1,2-benzoquinone, **5**, is present, the additional products **6**, **7**, and **8** were formed. While the product distribution given in Eq. 5 is at the point where $\text{O}_2/\text{DTBC} = 1$, the dioxygen uptake curves in Figs. 34 and 1 and Fig. 2 leveled off at O_2/DTBC molar ratios of about 2. Thus, product distributions for the final reaction mixtures in these systems must have contained a much higher ratio of **6** + **7** + **8** to benzoquinone, **5**.

The oxidation of the quinone, **5**, by the bimetallic catalyst, **4** ($\text{M} = \text{Fe}(\text{III})$ or $\text{Cu}(\text{II})$), also gave **6** and **7** with larger amounts of **8**. The monometallic catalyst, **2**, was completely unreactive for the oxidation of **5**.

The product distribution studies clearly answer the question as to the two types of oxidation found

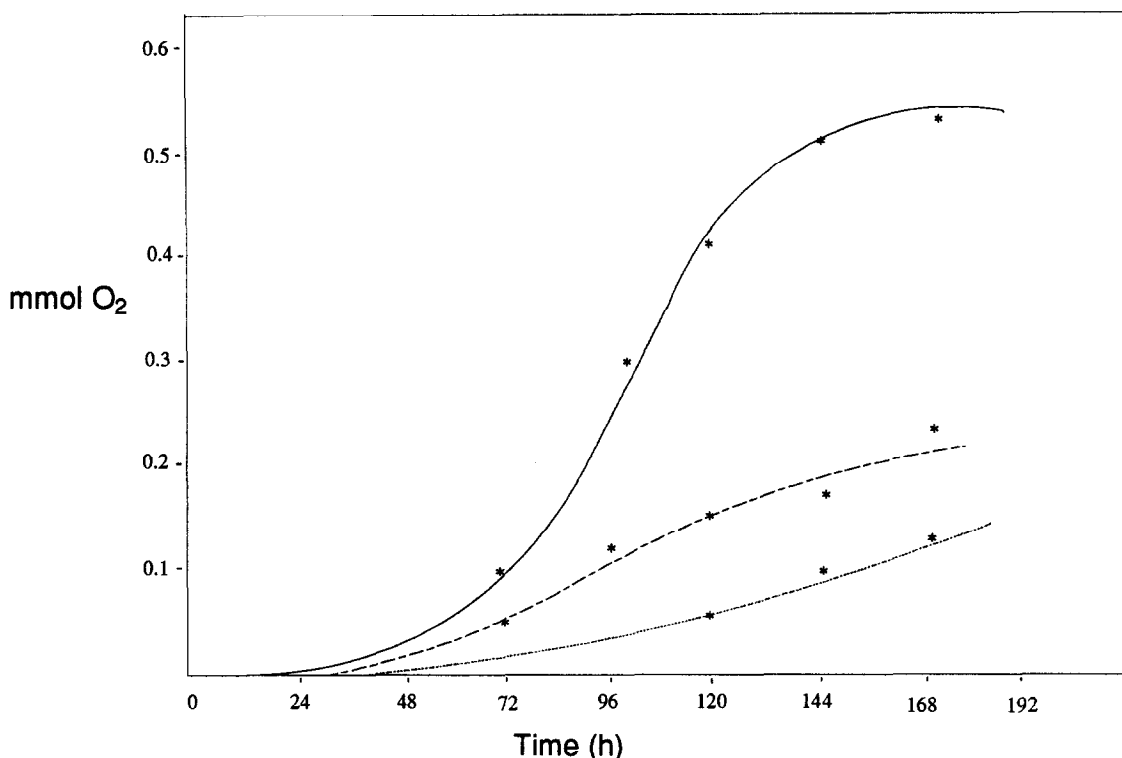
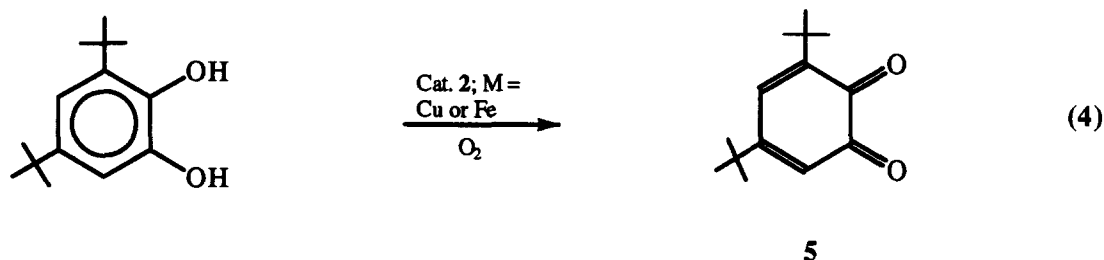
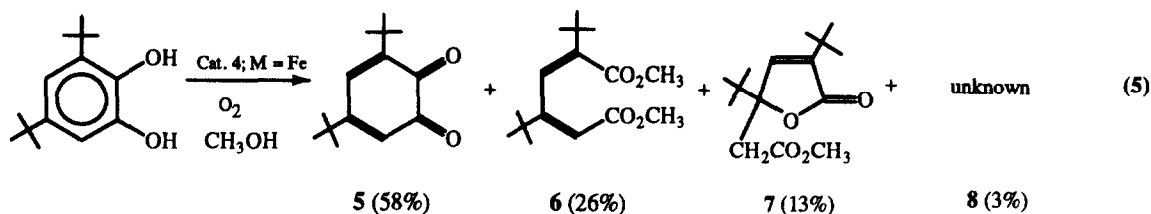


Fig. 2. Oxidation of DTBC by PDAB polymer supported FeCl_3 in methanol. Reaction mixture contains 0.5 g polymer coated Celite and 0.25 mmol DTBC in 25 ml methanol. (.....) unmodified polymer, $\text{Fe(III)} = 0.6 \times 10^{-2}$ mmol; (----) diketone polymer, $\text{Fe(III)} = 1.8 \times 10^{-2}$ mmol; (—) triketone polymer, $\text{Fe(II)} = 3.8 \times 10^{-2}$ mmol.



Scheme 3.



Scheme 4.

with the mono- and bi-metallic surfaces. Thus, as shown in Eq. 4 (Scheme 3), the monometallic catalysts give only 3,5-di-*t*-butyl-1,2-benzoquinone (DTBQ) while the bimetallic catalysts gave DTBQ plus ring-cleaved products, **6** and **7**. The

only explanation for these results is that the bimetallic catalyst has a reaction route for oxidizing DTBQ, which the monometallic catalyst does not. As shown in Eq. 6 (Scheme 5), the most likely mechanism for this route is complexation of each

Another Cu(II) catalyzed catechol oxidation which has received considerable attention is the oxidation of DTBC with copper(II) chloride and methoxide catalysts. [17,18,36]. In this system the copper(II) is a strong enough oxidant to cause ring-cleavage. It has been postulated that both the initial oxidation as well the subsequent ring-cleavage require dicopper(II) species with one Cu(II) coordinated to each of the DTBC or DTBQ reactants to give oxidation. However, in homogeneous solution definitive evidence for such dicopper species cannot be obtained. The present studies confirm that, in fact, a dicopper(II) oxidant is required for ring cleavage.

3.6. Conclusion

These initial results indicate bimetallic heterogeneous catalysts can give special reactivity patterns with DTBC as substrate. Future papers will describe improved heterogeneous systems and the study of other organic oxidations.

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