

COMMUNICATIONS

LETTERS

An Immobilized Fenton Catalyst¹

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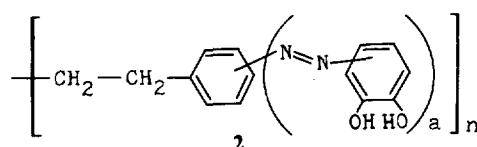
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Ferrous ion catalyzes reactions of hydrogen peroxide with various organic substances, and this reaction is called Fenton reaction.² Addition of enediols such as ascorbic acid, hydroquinone, catechol, and others enhances the rate and yield of ferric (or ferrous³) ion-catalyzed hydroxylation of aromatic compounds.⁴⁻⁶

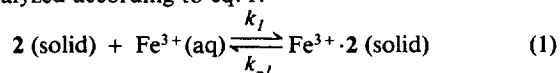
The proposed mechanism^{5,6} or the Fe(III)-catechol complex-catalyzed hydroxylation of anisole is summarized in Scheme 1. In this reaction, however, inactivation of the catalyst occurs as the reaction turns over probably due to the attack at catalytic intermediate 1 by water. In an attempt to devise iron-catechol derivatives with a much longer catalytic life, we have tried immobilization of the catalyst.

Polystyrene (M.W. 1×10^5) prepared⁷ by the benzoyl peroxide-initiated polymerization of styrene was chosen as the supporting matrix. Nitration of polystyrene and reduction of the resultant nitropolystyrene with stannous chloride producing aminopolystyrene were carried out according to the literature.⁸ Diazoniumpolystyrene was obtained by treating aminopolystyrene with sodium nitrite and hydrochloric acid

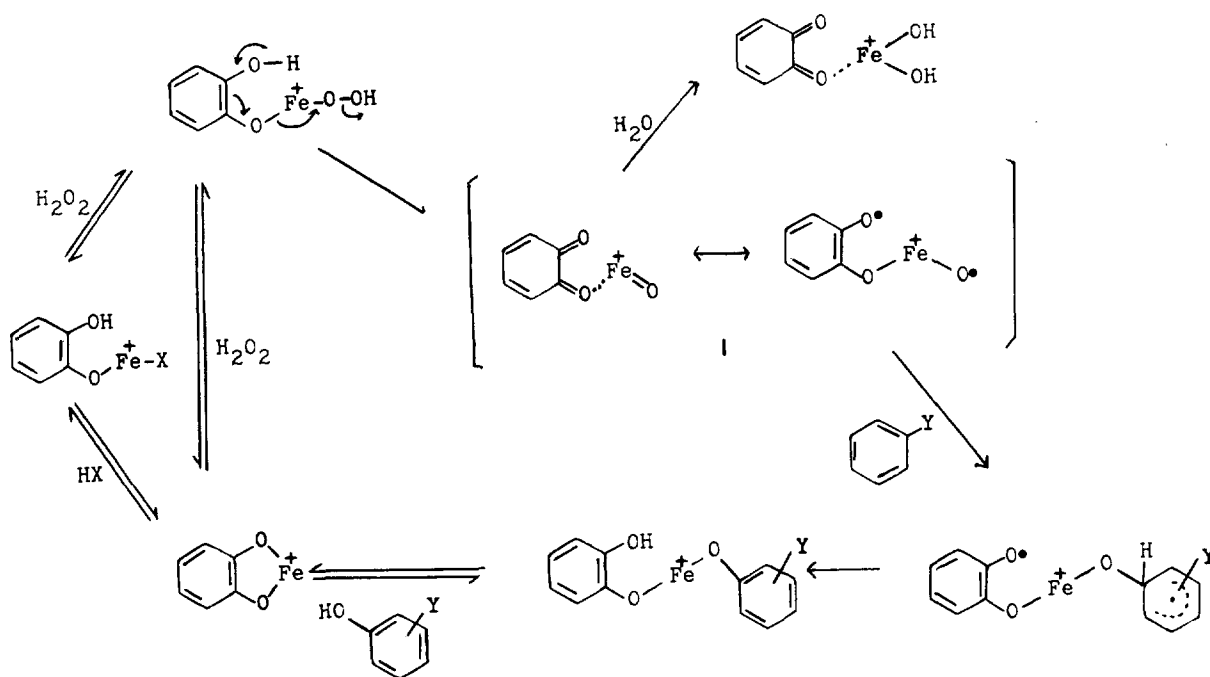
and then was coupled with catechol at pH 10 yielding non-swelling and deep purple catechol derivative of polystyrene. The catechol containing polystyrene (**2**) can be described as



As the ferric complex of a catechol derivative is the catalytically active species, binding of ferric ion to **2** was studied. After an aqueous solution of ferric ion at 25 °C and pH 4.2 (0.02 M chloroacetate buffer) was equilibrated with added **2**, the concentration of ferric ion in the aqueous layer was measured and the amount of the bound ferric ion was calculated. The data obtained with various amounts of added **2** were analyzed according to eq. 1.



Treatment of the data according to the Langmuir isotherm



Scheme 1.

gave the value of $K (=k_1/k_{-1})$ as $3.0 \times 10^4 M^{-1}$. Thus, **2** forms a quite stable Fe(III) complex. A *p*-cresol derivative of polystyrene which is identical to **2** except that *p*-cresol is substituted for catechol forms a much weaker Fe(III) complex.¹⁰ In view of the structural differences between the azo derivatives of *p*-cresol and catechol, this suggests that **2** forms a chelate complex using the two catechol oxygens as the donor atoms. Therefore, treatment of **2** with ferric ion produces the catalytically correct Fe(III)-catechol complex. Analysis with the Langmuir isotherm also revealed that 1 mole of ferric ion can be bound to 970 g of **2**.

We have also examined the catalytic activity of $Fe^{3+} \cdot 2$ in aromatic hydroxylation. Hamilton and the coworkers have reported that the ferric ion ($4 \times 10^{-5} M$)-catalyzed hydroxylation of anisole ($0.01 M$) with hydrogen peroxide ($1.8 \times 10^{-3} M$) at 25°C and pH 4.3 proceeded with a half-life of about 15 min in the presence of catechol ($1.5 \times 10^{-4} M$).⁴ With this amount of catechol, the rate was near its maximum, presumably due to the full complexation of ferric ion. Yield of methoxyphenols produced in this reaction was 55% based on the amount of added hydrogen peroxide.⁵ The distribution of *o*, *m*, and *p*-methoxyphenols was 64:3:33.

We have conducted the reaction under the identical conditions except that catechol was substituted with the polystyrene-supported catechol. Under the experimental conditions, about 40% of the added ferric ion was bound on the polymer. The heterogeneous reaction with the polymer proceeded with a half-life of approximately 2-3 hr when the reaction mixture was stirred with a laboratory magnetic stirring bar. The rate is only a few-fold slower than the homogeneous reaction considering that ferric ion is only partially bound by the catechol moiety in the heterogeneous reaction. The distribution of the isomers of the produced methoxyphenols in the polymer-catalyzed reaction was essentially identical to that in the homogeneous reaction. This indicates that the reaction occurs

through the same mechanism as the homogeneous reaction.⁵ The yield of methoxyphenols based on the added hydrogen peroxide was about 95%, substantially greater than the reactions catalyzed by catechol or other enediols.⁵ The increased yield obtained with $Fe^{3+} \cdot 2$ may be attributed to the hydrophobic environment of the polymer which enhances the attack by anisole at **1** compared with that by water. Further studies on the characterization of the polymers and the kinetic analysis of the polymer-catalyzed aromatic hydroxylation are in progress.

References

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Photodecomposition of Thianthrene Cation Radical Perchlorate in Acetonitrile. A New Method for the Preparation of Cyanomethylthianthrene

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(Received June 12, 1980)*

There have been many reports about the reactions of thianthrene cation radical perchlorate with nucleophiles in dry acetonitrile.¹ Kinetics of some of these reactions has been studied by means of an absorption spectroscopy^{2,3} and an electrochemical technique.⁴ In these cases was used dry acetonitrile as a solvent. However, it has been believed that thianthrene

cation radical perchlorate is not permanently stable in dry acetonitrile in view of the formation of 5-thianthreniumyl-thianthrene perchlorate from the stirred solution of thianthrene cation radical perchlorate in acetonitrile at room temperature for a long time depending on the amount of the cation radical.⁵