

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

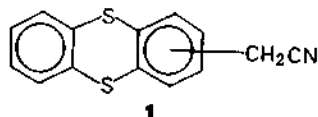
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There have been many reports about the reactions of thianthrene cation radical perchlorate with nucleophiles in dry acetonitrile.¹ Kinetics of some of these reactions has been studied by means of an absorption spectroscopy^{2,3} and an electrochemical 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

Thianthrene cation radical perchlorate has absorption maxima at 276, 290, and 546 m μ in acetonitrile. However, little has been known about the photostability of the thianthrene cation radical. In order to examine the photostability of the cation radical, the solution of the cation radical in dry acetonitrile was irradiated with a Hanovia 450-W mercury-vapor lamp. The progress of the photoreaction was monitored by the change of the color of the cation radical. From the photolysate was obtained a compound which was believed to be cyanomethylthianthrene (1).



The position of a cyanomethyl group attached to the thianthrene ring has not been established. However, the presence of cyano group indicates that the solvent, acetonitrile, may participate during the photolysis somehow. The study of the mechanism of the formation of 1 and the identification of other products are being sought.

Preparation and separation of 1 have been achieved as follows: Thianthrene cation radical perchlorate⁶ (3.744 g, 0.0119 mol) and a stirring magnet were placed in a reaction vessel constructed of borosilicate glass with one angle joint connected to the nitrogen tank, one vertical joint equipped with a condenser with a drying tube, and one thread side arm joint to accommodate a thermometer. The center mouth was accommodated by a double-walled quartz immersion well with inlet and outlet tubes for cooling. Distilled water used for the coolant was cooled to 5°C by a circulator.

Thianthrene cation radical perchlorate was dissolved in 300 ml dry acetonitrile (dried with P₂O₅, followed by the distillation twice and kept over 4 Å molecular sieve) and the solution was vigorously stirred for 10 min. Nitrogen gas dried by bubbling through conc. H₂SO₄ was introduced to wash out the air. The solution was irradiated with a Hanovia 450-W mercury-vapor lamp until the purple color of the solution had completely disappeared. As the reaction time proceeds the purple color slowly disappeared and some solid looking grey was formed. It took 5 hr to get the reaction complete and the solution became pale brown. After the solvent was removed on a rotary evaporator, the residue was chromatographed on

the silica gel (Merck Art. 7734, 70-325 ASTM mesh, 0.05-0.2 mm, 4.5x12.5 cm) column, elution with hexane (3f) gave 1.267 g (0.00586 mol) of thianthrene. Elution with a mixture of hexane and ether (9:1 v/v, 1f) gave no residue. Consequent elution with a mixture of hexane and ether (4:1 v/v, 1f) gave 0.286 g of residue, which was developed on silica gel (Merck Art. 7749, Kiesel Gel 60 PF₂₅₄ Gipsaltig) plate to give one spot with a tail. The residue was washed with a large volume of hexane. Hexane soluble material, after the solvent was evaporated to dryness, was recrystallized from ethanol. A pale violet, plate-type crystal (0.084 g) was obtained. Decolorization, followed by recrystallization of the crystal from methanol gave 0.060 g of a white solid, melted at 111.5 to 113.0°C. $\lambda_{\text{max}}^{\text{MeOH}}$ 256, 242, and 212 nm;⁷ IR (KBr) 2240 (CN)cm⁻¹.

¹H NMR (CDCl₃) 3.97 (s, 2H, methylene) and 7.33 (m, 7H, aromatic); MS *m/e* 255 (M⁺). These spectroscopic data coincide with structure of 1.

Elution with a series of the solvents such as benzene (1f), chloroform (0.3f), ether (1.8f), ethyl acetate (0.1f), acetone (1f), and ethanol (0.3f) gave 0.220, 0.025, 0.336, 0.580, 1.516, and 0.142 g of residues, respectively. Characterization of each residue has been troublesome because of primarily difficulty of finding a proper solvent for recrystallization. Further study on this matter is in progress.

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