starting styrene and that recovered after partial reaction were converted quantitatively to styrene dibromide for radioactivity determination. The radioactivity of the addition product was measured directly. All radioactivity measurements were made by liquid scintillation counting with a Beckman DPM-100 instrument and a dioxane based cocktail solution by use of the external standard ratio method. The values of $^{12}k/^{14}k$ reported above are averages (and standard deviations) of values for five different fractions of reaction ranging from 20% to 70% with the calculations being made by all four of the Tong and Yankwich equations[22,23] for each fraction of reaction. There were no trends in the $^{12}k/^{14}k$ values as the fraction of reaction varied, and as can be seen by the low standard deviations, there was good agreement among the values calculated by the four equations. We take these two facts to indicate that the starting materials were of high chemical and radiochemical purity and that the procedures used in the isotope effect experiments were accurate and properly controlled.

Acknowledgment. We are indepted to Dr. John R. I. Eubanks for preparation of the benzyl-7-^{14}C chloride and to Professor L. B. Sims for many helpful discussions. Support of this research by National Science Foudation Grant CHE-80-1-16398 is gratefully acknowledged.

Registry No. 2,4-Dinitrobenzenesulfenyl chloride, 528-76-7; styrene, 100-42-5; ^{14}C, 14762-75-5.

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(23) In two cases for the α-labeled styrene, the styrene recovered after partial reaction polymerized, so its activity could not be determined; in these two cases, only one of the four equations could be used.

Electrooxidative Catalysis Using Dispersed Alumina on Glassy Carbon Surfaces[1]

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We have long stressed the importance of cleaning and polishing carbon electrode surfaces with small particle abrasives such as alumina and of completely removing these particles from the surface via ultrasonic cleaning.[2] We have felt that the presence of such particles on surfaces led to irreproducibility and had deleterious effects on the rate of electron transfer. Recently, much to our surprise, we have found that the presence of alumina particles dispersed on glassy carbon surfaces would strongly adsorb compounds such as catechols and catalyze their oxidation. The observed catalysis makes possible the electrochemical differentiation and analysis[3,4] of the various catechols in the presence of ascorbic acid. Previously, this has been very difficult.

In a typical experiment for the catalysis of catechol, a glassy carbon electrode (Bioanalytical Systems glassy carbon mounted in Kel-F sheath or a Tokai glassy carbon GC-10 in disc form) is prepolished by using alumina (Buehler α-alumina, 1.0, 0.3, and 0.05 μm). After cleaning in an ultrasonic bath with distilled water, the electrode is lightly repolished by using 1.0-μm α-alumina and rinsed with water. The electrode is immediately immersed into the catechol-containing solution. The current–potential (*i–E*) waves resulting from successive cyclic voltammetric (CV) scans at varying scan rates using this electrode in a solution containing 5×10^{-4} M of catechol in 0.1 M phosphate buffer at pH 2.0 are shown in Figure 1A. The shape of the *i–E* waves is characteristic of the electrolysis of a strongly adsorbed electroactive species.[5] In addition to the shape, the peak potential is dramatically shifted in comparison to those obtained at a "clean" electrode (see Figure 1B). These uncatalyzed, irreversible waves were taken with a "clean" glassy carbon electrode that had been cleaned ultrasonically and not repolished with alumina. The peak potentials for the catalyzed oxidation (anodic peak potential, E_{pa}) and reduction (cathodic peak potential, E_{pc}) are shifted ca. 150 mV from the uncatalyzed ones obtained on "clean" carbon. The *i–E* waves for the adsorbed catechols persisted when the electrode was transferred to an electrolyte solution that did not contain any catechol.

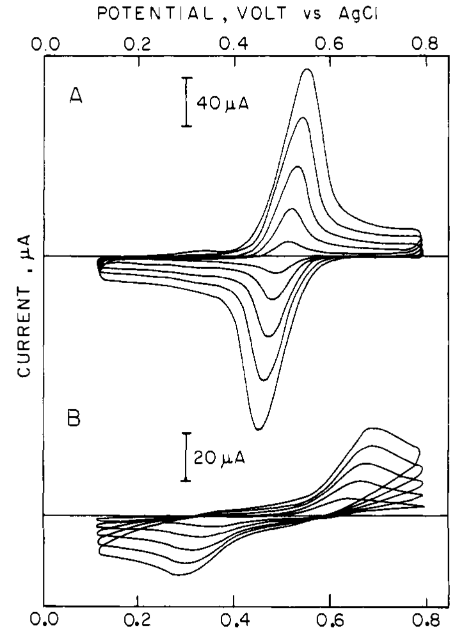

Figure 1. Cyclic voltammograms of alumina dispersed (A) and "clean" glassy carbon (B) electrodes for 5×10^{-4} M catechol in 0.1 M phosphate buffer at pH 2.0: scan rates 0.400, 0.256, 0.144, 0.064, and 0.016 V/s; geometric surface area of carbon, 0.071 cm^2.

Examinations of the clean and the alumina-repolished carbon by scanning electron microscopy (SEM) clearly show the absence and the presence of dispersed alumina particles on the carbon surface. The α-alumina particles are ca. 1 μm in diameter and are dispersed as single and clustered particles. The estimated surface covered by alumina for a typical repolished electrode was ca. 30%. X-ray photoelectron and scanning Auger spectroscopy also confirmed the presence of alumina on the surface.

To study the extent of catechol adsorption caused by the presence of alumina, we recorded CV scans for various concentrations of catechol. At low concentrations such as 5×10^{-5} M, the anodic and cathodic *i–E* waves were symmetric, and for a freshly immersed electrode, the peak currents would continue to grow with successive cycles until a maximum value was attained. The peak separation between E_{pa} and E_{pc} was 10–12 mV at a scan rate of 100 mV/s and the full width at half-height of either wave was ca. 60 mV. The maximum *i–E* wave was assumed to correspond to that for a saturation coverage of catechol on the alumina surface. The peak current for this maximum, $i_{p,max}$, varied linearly with scan rate as expected for an electrode reaction of a strongly adsorbed redox species.[5] If the concentration of catechol in the solution increased while the scan rate was kept constant, the shape of the *i–E* wave became more characteristic of a reversible, diffusion-controlled redox reaction. Thus, at intermediate values of concentration such as 0.5 to 1.0×10^{-3} M, the *i–E* wave is a result of the convolution of the two currents due to the adsorbed and the diffusing catechol.

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(1) The financial support of this work by the National Science Foundation is gratefully acknowledged.

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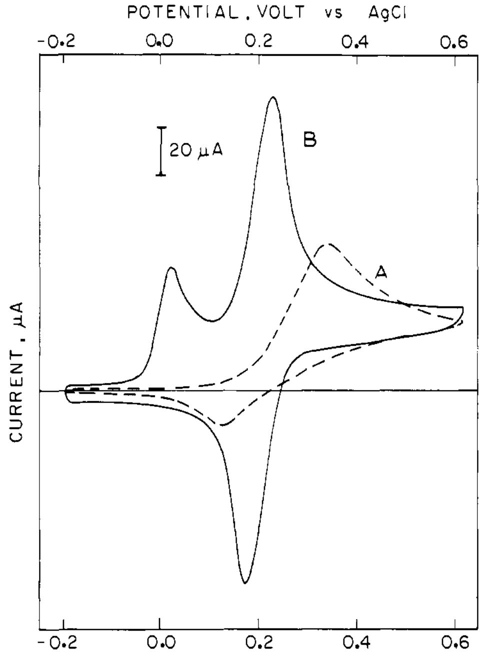

Figure 2. Cyclic voltammograms for oxidation of a mixture containing 1.0 mM catechol and 1.0 mM ascorbic acid in phosphate buffer at pH 7.0 without (---) and with (—) alumina dispersed on carbon surface: scan rate 0.1 V/s; geometric area of glassy carbon electrode, 0.071 cm^2.

The electrical charge, Q, was evaluated as a function of scan rate for differing concentrations of solution catechol to study the adsorption and to verify the catalysis. The anodic and cathodic charges (Q_a and Q_c) were plotted as a function of the inverse of the square root of the scan rate for a glassy carbon electrode with and without alumina. The "clean" electrode exhibited the usual current dependence characteristic of the electrolysis of a diffusing species with the extrapolated intercept on the charge axis at zero (background corrected).[6] On the other hand, the intercept for the alumina-dispersed electrode is nonzero. This intercept value of Q is assumed to correspond to the saturation coverage of catechol on alumina as evidenced by the common intercept for all three concentrations. In addition, the close correspondence of the slopes for Q_a and Q_c for the glassy carbon electrodes with and without alumina indicates that the diffusing catechol is indeed being electrolyzed in the potential range where the adsorbed catechol is being electrolyzed. The saturation coverage of catechol adsorbed on the surface depended on the amount of alumina dispersed. The extent of catalysis was also dependent on the amount adsorbed. At low alumina coverages, high concentrations of solution catechol, and high scan rates, the uncatalyzed wave due to electrolysis on the bare carbon becomes evident and is superimposed on the wings of the adsorbed/catalyzed wave.

An interesting bioanalytical problem is the in vivo identification and quantitation of various catechols such as dopamine and epinepherine in the presence of ascorbic acid in the neural system.[3,4] The irreversible oxidation of these substances at most electrodes produces ill-defined i–E waves without any clear separation between individual components. For example, trace A in Figure 2 is a typical i–E wave at a bare glassy carbon electrode in a solution containing 1.0 mM catechol and 1.0 mM ascorbic acid in 0.1 M phosphate buffer at pH 7.0. The irreversible ascorbic acid wave merges with the catechol wave. Trace B is the repeat of the same experiment using an α-alumina-modified glassy carbon electrode. The i–E wave for ascorbic acid with a peak potential of +0.025 V is well separated from that of catechol (E_{pa} = +0.23V). The ascorbic acid wave also is catalyzed by adsorption on alumina and appears at a potential of ca. 200 mV less than that of the uncatalyzed wave on bare carbon. We have also been able to easily distinguish three separate waves for the oxidation of a mixture containing 1,2-dihydroxybenzene, 1,4-dihydroxybenzene, and ascorbic acid at pH 7.0 at the alumina-modified electrode. The applicability of this electrode for the catalysis of other oxidizable compounds and for the quantitative analysis of mixtures is currently under study.

Although alumina itself is a nonconductor, the adsorbed species are apparently electroactive, similar to the case of catechols that have been "anchored" to graphitic surfaces via large aromatic side chains[7] or incorporated into polymeric matrices.[8,9] Electrocatalysis using immobilized redox mediators[10] such as the catechols can be understood in terms of an *ec* catalytic regeneration mechanism where the mediator acts as an effective "bridge" for electron transfer from the electrode to the isolation species.[11] In the case of alumina, it appears that any oxidative process involving the loss of a proton in the electron-transfer process can be catalyzed. Tentatively, we believe that the alumina is "base" catalyzing the oxidation. The variation in acid–base properties of alumina in effecting chromatographic separations is well-known, and correlation of these properties with their applicability to electrochemical adsorption/catalysis is in progress.[12]

Registry No. Al_2O_3, 1344-28-1; carbon, 7440-44-0; 1,4-hydroquinone, 123-31-9; ascorbic acid, 50-81-7; catechol, 120-80-9.

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(12) Contributions of R. J. H. Chan and D. Karweik to this work are hereby acknowledged.

Molecular Structure and Charge Transfer Excitation of Electron Donor–Acceptor Complexes. Ion Pairs from Arenes and Mercury(II)

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We report the isolation and crystal structure of an unusual electron donor–acceptor (EDA) complex, in which the irradiation of the charge-transfer (CT) absorption band induces electron transfer and ion-pair formation. Although numerous types of donor–acceptor complexes are known, the direct relationship between the structure (established by X-ray crystallography) and the CT excitation (performed in solution) has been difficult to achieve.[1,2] For this study, we chose the intermolecular interaction of aromatic compounds with mercuric complexes since new charge–transfer bands are observed immediately upon mixing.[3]

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