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Long Optical Path Length Thin-Layer Spectroelectrochemistry. Catalytic Oxidation of Hydroquinones by Oxygen at Platinum

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A clean, open-circuited Pt electrode, in the presence of dissolved oxygen, catalyzes the oxidation of hydroquinones in 1 M H_2SO_4. The oxidation rate is independent of hydroquinone, but dependent upon O_2 concentration. If iodine is preadsorbed onto the Pt surface, the catalysis is inhibited, although reversible electron transfer to electrolyze the dissolved hydroquinone is not.

There has been much interest in the catalytic oxidation of hydroquinones by molecular O_2 using metal salts, metal oxides, and supported metals as catalysts.1) However, the kinetic and mechanistic information regarding this oxidation in an aqueous solution has not been previously quantitated. In order to understand this catalytic oxidation process, a study was conducted using a long optical path length thin-layer cell (LOPTLC) which, with its high optical sensitivity, large electrode area-to-solution volume ratio, and short electrolysis time, provided unprecendented opportunities to investigate various homogeneous and heterogeneous chemical processes.2) We report herein the rates and mechanism for the oxidation of hydroquinones in the presence of dissolved oxygen catalyzed by an open-circuited Pt electrode.

The catalytic oxidation experiments were performed with a Kel-F LOPTLC at T = 30 ± 2 °C. The UV-VIS spectrophotometer, the potentiostat and the auxiliary, reference, and working electrodes were the same as reported previously.2c) The pretreatment of the Pt working electrode and determinations of electrode area (0.405 cm^2), LOPTLC volume (V = 8.34 μl), and optical path length (b = 1.05 cm) have also been described.2c) To control the O_2 concentration, the LOPTLC was sealed into the spectrophotometric cell chamber and the solution filling apparatus was placed inside a glove bag. Both were then saturated with either N_2, air, or O_2 (in later discussions they will be referred to as the N_2-, air-, or O_2-sat'd case). Three high purity grade hydroquinones, 1,4-dihydroxynaphthalene (DNH, Aldrich), 1,2,4-trihydroxybenzene (triol, Aldrich), and 1,4-dihydroxybenzene (H_2Q, Matheson), and potassium iodide (Mallinckrodt) were used as received. The supporting electrolyte was 1 M (1 M = 1 mol dm^{-3}) H_2SO_4 (ultrapure, GFS) prepared with NANOpure water (Sybron Barnstead). A typical A-t (absorbance vs. time) experimental procedure for the catalytic oxidation is as follows:

1) A Pt electrode was electrochemically cleaned in 1 M H_2SO_4 by potential cycling as reported earlier.[2c)] The last cycling was terminated at a resting potential, 0.25 V for triol and H_2Q, but 0.15 V for DHN. (All potentials in the text were referred to sat'd Ag/AgCl.)
2) The circuit was open-circuited and the LOPTL cell was evacuated.
3) The cell was filled with a hydroquinone solution and the resting potential was re-applied immediately after the filling. The absorbance at the maximum absorbance wavelength (λ_{max}) was monitored with time.
4) After the absorbance reached a steady-state value at the resting potential, the circuit was opened and absorbance was continuously monitored with time.

The evidence for catalytic oxidation of hydroquinones by O_2 at Pt is shown in Fig. 1A, using triol as an example. The A-t curves were obtained after the third filling of triol in the air-sat'd case. The wavelength of 288 nm, λ_{max} for triol, was used to monitor the absorbance. As one can see from Fig. 1A, the A-t curve decreases linearly with time after open circuit (marked as O.C.) and finally approaches a steady-state value. The same experiment was repeated with a teflon plate replacing the Pt, and the A-t curves remained unchanged (for 30 min) with the solution triol unoxidized as confirmed by absorbance spectra. The difference in the A-t responses with and without Pt clearly demonstrates that Pt catalyzes the oxidation of hydroquinones by O_2. It should be pointed out that the source of O_2 is the O_2 diffusion through the Kel-F cell body, not the O_2 originally present in the filling solution, because it had been evacuated before filling and any trace of O_2 in this solution had been further reduced at $E = 0.25$ V. The permeability of O_2 through the Kel-F has been reported,[3)] and also indicated by our electrochemical result that a steady-state O_2 reduction current at $E = 0.25$ V was observed. The possibility of observing the oxidation of hydroquinones by O_2 diffusing through the Kel-F cell body at Pt takes advantage of this LOPTLC because of its large surface area-to-volume ratio.

The catalytic oxidation products of DHN, triol, and H_2Q have been spectrally identified as their corresponding quinone forms, as shown in Fig. 1B for triol. Spectra 1, 2, and 3 in Fig. 1B were taken at 0.25 V, O.C., and 0.50 V during the A-t experiment intervals marked 1, 2, and 3, respectively (Fig. 1A). Since the formal reversible potential ($E^{o'}$) of triol in 1 M H_2SO_4 is 0.40 V, spectrum 3, taken at 0.50 V (the same spectrum can also be obtained at 0.50 V before the open circuit), is the spectrum for the oxidized form of triol, 2-hydroxyquinone. The fact that spectra 2 and 3 are identical indicates that the final open-circuit oxidation product is 2-hydroxyquinone.

The catalytic oxidation rate, dC/dt, is, of course, dependent upon the molecular structure. The rates for DHN, triol, and H_2Q have been calculated from the A-t curves such as the one shown in Fig. 1A, and are listed in Table 1 along with their oxidation products and $E^{o'}$s. From Table 1, we can see that the order of oxidation rates is opposite to their $E^{o'}$ order. The catalytic oxidation rate for triol has also been studied as a function of both O_2 and triol concentrations. The experimental results for the oxidation rate

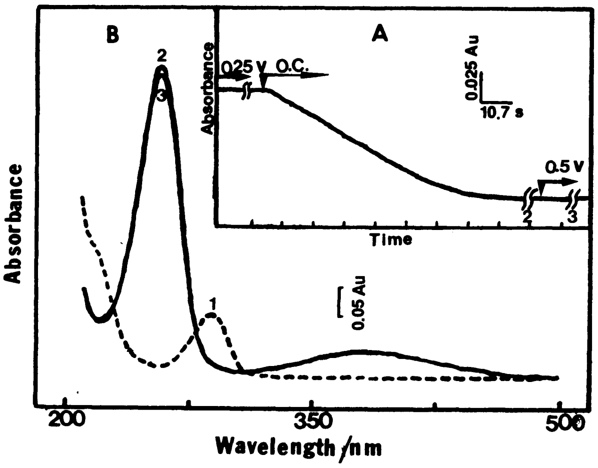
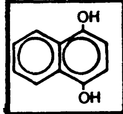
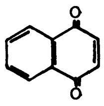
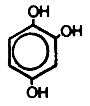
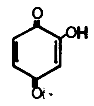
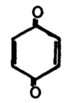


Fig. 1. A) Typical A-t response (λ = 288 nm) and B) A-λ spectra before and after catalytic oxidation of 0.34 x 10^{-4} M triol. See text for details.

Table 1. Catalytic oxidation rates for DHN, triol, and H_2Q in air-sat'd cases. All concentrations used were between 0.3 x 10^{-4} and 1.0 x 10^{-4} M.

Compound	Product	E°'/V	Rate/Ms^{-1} [a]
		0.27	4.90×10^{-7}
		0.40	4.29×10^{-7}
		0.50	2.93×10^{-7}

[a] Avg. dev. = 6.5% for 5 trials each.

dependence on O_2 concentration are shown in Fig. 2. The experimental condition for obtaining curves a, b, and c are the same except that the O_2 concentrations are different. As the slopes from curves a, b, and c show, the catalytic oxidation rate decreases as O_2 concentration decreases, and no oxidation can be observed in the N_2-sat'd case. It should be pointed out that the catalytic oxidation rate is not proportional to the O_2 partial pressure outside of the LOPTLC because the rate calculated from curve a is only twice as large as that from curve b, while O_2 partial pressure is almost five times larger in the case of curve a than in the case of curve b (O_2 % in air is about 20.9%). This experimental observation rules out the possibility of oxidation rate being controlled by O_2 diffusion through the cell body. If the assumption is made that the O_2 solubility in this experimental condition follows Henry's law, it can be concluded that the oxidation rate is approximately proportional to the square root of O_2 concentration in the solution. This may imply that the O_2 is

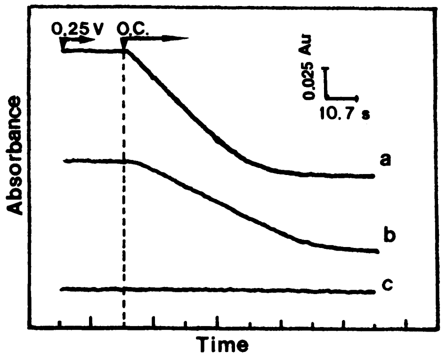


Fig. 2. Dependence of catalytic oxidation rate on O_2 concentration, where a, b, and c are A-t curves obtained under O_2-, air-, and N_2-sat'd conditions, respectively. Triol concentrations are (a) 0.4 x 10^{-4} M, (b) 0.3 x 10^{-4} M and (c) 0.8 x 10^{-4} M. The absorbance (at λ = 288 nm) was offset on the absorbance scale for traces a, b, and c. The circuit was open-circuited at the same time in all three cases (dotted line).

dissociatively adsorbed on a Pt surface which is not covered by adsorbed hydroquinone molecules. Unlike the O_2 concentration, the initial triol filling concentration has essentially no effect on the oxidation rate, consistent with the linear A-t response in the open-circuited oxidation process. This is probably due to the fact that the adsorptive coverage of triol at Pt is independent of triol concentration in the concentration range studied ($\leq 10^{-4}$ M).

Catalytic oxidation has also been studied as a function of the Pt surface state, when the usual open-circuited oxidative A-t experiment for triol in the O_2-sat'd case was carried out with a Pt-I electrode (Pt with a monolayer of preadsorbed iodine).[2c,4] No catalytic oxidation was observed, as indicated by a steady-state A-t respones curve like curve c in Fig. 2. This clearly demonstrates that preadsorbed iodine can totally inhibit the catalytic oxidation, although it does not inhibit the electron transfer to electrolyze the solution triol molecules near its $E^{o'}$. However, if the same A-t experiment is performed for the hydroquinones in the N_2-sat'd case with a PtO electrode (Pt with a monolayer of adsorbed oxygen obtained by oxidizing clean Pt in 1 M H_2SO_4 at E = 1.4 V for 23 min), the hydroquinones can be oxidized to their quinone forms by reacting with the adsorbed oxygen. One important point that should be mentioned here is that our experimental results have shown that hydroquinones do not irreversibly adsorb on a PtO electrode.

The preceding experimental results clearly illustrate that the open-circuited catalytic oxidation is a surface reaction with the slowest step being the reaction of hydroquinone molecules with adsorbed oxygen atoms. However, thus far we are not absolutely certain which form of hydroquinone molecule is involved in the above slowest step, irreversibly adsorbed hydroquinone or solution hydroquinone which is interacting with the surface by van der Waals forces. They could be distinguished by preadsorbing labeled hydroquinones on a clean Pt electrode, carrying out an oxidation experiment with unlabeled hydroquinones, and finally identifying the oxidation products.

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