Electrochemistry of Chemisorbed Molecules.[1-4] 4. The Effect of Chirality on the Orientation and Electrochemical Oxidation of *l*- and *dl*-DOPA

Victor K. F. Chia, Manuel P. Soriaga, Arthur T. Hubbard,*

Department of Chemistry, University of California, Santa Barbara, California 93106

and Stanley E. Anderson

Department of Chemistry, Westmont College, Santa Barbara, California 93108 *(Received: June 1, 1982; In Final Form: August 16, 1982)*

The influence of chirality on the orientation and electrochemical oxidation of *l*- and *dl*-DOPA chemisorbed on Pt electrodes has been studied. Measurements were made in 1 M $HClO_4$ with thin-layer electrochemical methods. In the flat orientation, Γ (the packing density) and n_{ox} (the number of electrons for oxidative desorption of an adsorbed molecule) were the same for pure enantiomer and racemate. However, in the edge orientation, Γ for *l*-DOPA was significantly greater than for the racemic mixture. n_{ox} was found to be strongly dependent on orientation but not on the chirality of the chemisorbed monolayer; this implies that the oxidation product distribution is a function of orientation but not of optical isomerism.

Introduction

Accurate measurements of adsorbed molecule packing density by means of thin-layer electrodes demonstrated that aromatic compounds chemisorbed from aqueous solutions onto smooth platinum electrodes adopt specific orientations which depend on the adsorbate molecular structure[5] and change as a function of solute concentration,[6,7] the nature of the supporting electrolyte,[8] and the pH of the solution.[5-8] Preliminary work on the influence of orientation on the electrochemical oxidation of chemisorbed aromatics has shown that n_{ox}, *the number of electrons for oxidative desorption of an adsorbed molecule*, is sensitive to initial orientation,[9,10] suggesting that anodic oxidation of adsorbed molecules leads to product distributions which depend on orientation. This result is not unexpected since aromatic molecules are strongly chemisorbed to the platinum electrode[7,11] and, as such, they are analogous to ligands in an organometallic complex in which the alternative modes of binding are indicated by the orientational transitions.[7] In the present article we describe the effect of chirality in a pendant (surface-inactive) substituent on the orientation and anodic oxidation of chemisorbed chiral vs. racemic β-(3,4-dihydroxyphenyl)alanine (*l*- and *dl*-DOPA).

Experimental Section

Electrochemistry with thin-layer cells has been reviewed.[12] Thin-layer electrodes employed for this study have been described.[7,13] In cells of this design a thin-layer of solution is contained between a cylindrical Pt electrode and surrounding precision glass tubing. Spent liquid is removed by application of pressurized inert gas. Filling occurs due to capillary action when the pressure is released. When the thin-layer cavity is filled only once, the Pt electrode is exposed to only a single aliquot of solution containing a precise molar amount of adsorbate. If the electrode is clean, a fraction of the surfactant is adsorbed and the concentration C of adsorbate *inside* the thin-layer cavity is lower than the bulk concentration C^0:

$$VC = VC^0 - A\Gamma \tag{1}$$

where V is the volume of the thin-layer cavity, A is the geometric electrode surface area, and Γ (mol cm^{-2}) is the interfacial concentration of the adsorbed solute molecules. In the adsorbed state, DOPA is electrochemically inactive in the potential region where the unadsorbed species display electrochemical reactivity (see below); hence, the electrolytic charge required for electrolysis of *unadsorbed* solute in the thin-layer cavity after a single filling is given by Faraday's law:

$$Q_1 - Q_{1b} = nFVC = nFVC^0 - nFA\Gamma \tag{2}$$

where Q_1 denotes the electrolytic charge observed for a single filling of the thin-layer cavity, Q_{1b} the background charge measured under similar conditions except that unadsorbed solute is removed from the cell by thorough rinsing with pure supporting electrolyte, and n is the number of Faradays, F, consumed per mole of reactant. On the other hand, if the thin-layer cavity is rinsed repeatedly with the adsorbate solution, the concentration in the thin layer cavity will equal that in the bulk since no further adsorption occurs after the initial rinses; in this case, the electrolytic charge Q is given by

$$Q - Q_b = nFVC^0 \tag{3}$$

In general, Q_{1b} is equal to Q_b provided that saturation

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coverage is attained during the first filling. Subtracting eq 2 from 3 yields an expression for Γ in terms of measurable charges:

$$\Gamma = \frac{Q - Q_1}{nFA} \qquad (4)$$

In the event that $Q_{1b} \neq Q_b$, then the numerator in eq 4 is replaced by the quantity $[(Q - Q_b) - (Q_1 - Q_{1b})]$. It will be pointed out that eq 4 gives the *total* adsorbed amount regardless of the electroactivity of the adsorbed species, as discussed elsewhere.[7]

Adsorption occurred from aqueous[14] electrolyte (1 M $HClO_4$) at constant potential, 0.20 V (*N* AgCl reference). The average area, σ, occupied by an adsorbed molecule was found from the inverse of the interfacial concentration: $\sigma = 10^{16}/6.023 \times 10^{23}\Gamma$. The predominant adsorbate orientation was determined by comparing observed σ with values calculated, for various possible orientations, on the basis of covalent and van der Waals distances tabulated by Pauling.[15] Calculation of σ has been discussed elsewhere.[5,7]

Determination of n_{ox} required precise measurement of Γ and of Q_{ox}, the electrolytic charge to oxidize *and* desorb the surface-attached material. Values of Q_{ox} were determined as follows: (i) the clean Pt thin-layer electrode was exposed for 180 s to a surfactant solution for which Γ had been measured, (ii) excess dissolved material was then removed by rinsing with pure supporting electrolyte; and (iii) the (uncorrected) electrolytic charge Q'_{ox} for oxidation was determined at a potential just below that for oxygen evolution (nominally, 1.18 V in 1 M $HClO_4$). The background charge $Q_{ox,b}$ was determined by a procedure identical except for omission of the adsorbed material. Q'_{ox} and $Q_{ox,b}$ were evaluated where the charge–time curves became parallel, indicating complete oxidation of the organic material. Values of n_{ox} were extracted from the data by using Faraday's law in the form of eq 5. This procedure

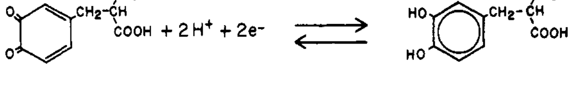
$$Q_{ox} \equiv Q'_{ox} - Q_{ox,b} = n_{ox}FA\Gamma \qquad (5)$$

is applicable only to adsorbed compounds which do not desorb rapidly during rinsing, a condition satisfied by aromatic compounds on Pt electrodes.[5-10]

l- and *dl*-DOPA were obtained from Sigma Chemical Co. (St. Louis, MO) and used without further purification. Solutions were deaerated with high-purity oxygen-free nitrogen.

Results and Discussion

Figure 1 shows thin-layer current–potential curves for unadsorbed and adsorbed *dl*-DOPA. The dashed curve in Figure 1A corresponds to the reversible two-electron oxidation–reduction of *dl*-DOPA, after only one filling of the TLE cavity, according to 6. The solid curve was

 (6)

$$O_2C_6H_3CH_2CH(NH_3^+)COOH + 2H^+ + 2e^- \rightleftharpoons (HO)_2C_6H_3CH_2CH(NH_3^+)COOH \qquad (6)$$

obtained after multiple fillings (in which case the surface had been presaturated with aromatic). The amount of reversibly electroactive material present after one filling was relatively small because, like other 1,2-diphenols, adsorbed DOPA is bound through the pyrocatechol moiety and does not display reversible electroactivity.[5] The difference between the dashed and solid curves (obtained by potential-step coulometry at 0.52 ± 0.10 V) is a measure of the amount of aromatic taken up by the Pt surface, eq 4.

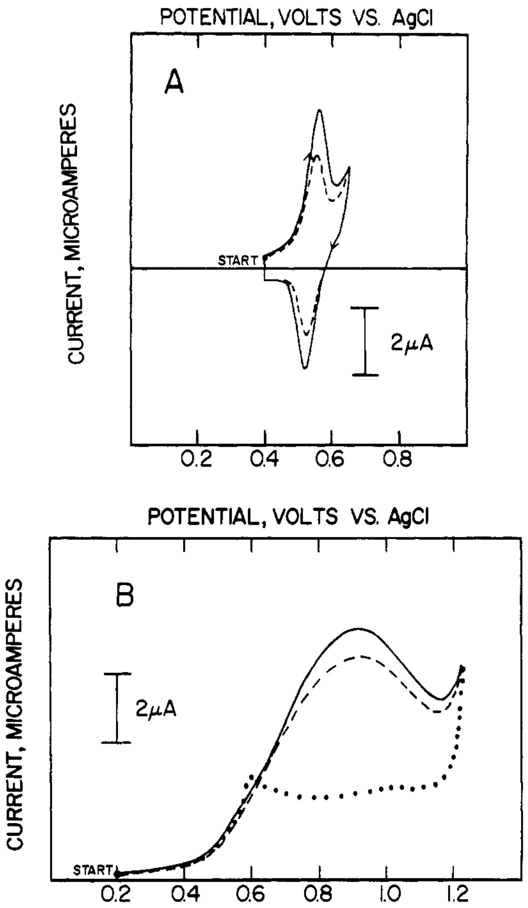


Figure 1. Thin-layer current–potential curves for *dl*-DOPA at a polycrystalline platinum electrode. A. Unadsorbed species: The solution contained initially 10^{-4} M reactant and 1 M $HClO_4$: (----) first filling; (—) presaturated surface. B. Chemisorbed material only: (—) adsorbed from 2 mM DOPA solution (η^2 orientation); (----) from 0.1 mM solution (η^6 orientation); (····) clean surface. Thin-layer volume, $V = 4.08$ μL; platinum electrode area, $A = 1.18 \pm 0.02$ cm^2; rate of potential sweep, $r = 2.00$ mV sec^{-1}; solution temperature, $T = 296 \pm 1$ K.

Figure 1B compares the current–potential curves for anodic oxidation of *dl*-DOPA, adsorbed from 0.1 mM solution (dashed curve) and from 2 mM solution (solid curve), in the absence of unadsorbed *dl*-DOPA. It is evident that adsorption from 2 mM solution results in a moderate increase of anodic (oxidative) charge over that from 0.1 mM concentration. Q'_{ox} was given by the area under the peak at 0.93 V while $Q_{ox,b}$ was obtained from the corresponding area under the curve for the clean electrode (dotted curve).

Γ, Q_{ox}, and n_{ox} were determined at various concentrations between 0.02 and 3 mM. The results are plotted in Figure 2. Four important features may be noted from Figure 2: (i) *l*- and *dl*-DOPA undergo a transition to higher packing density as the concentration is increased from 0.12 to 1.0 mM; (ii) above 1 mM, *l*-DOPA achieves a higher packing density (0.468 ± 0.014 nmol cm^{-2}) than racemic (0.407 ± 0.014); (iii) transitions in n_{ox} occur at the concentrations where changes in Γ take place; and, (iv) *l*- and *dl*-DOPA yield n_{ox} values identical within experimental error even at concentrations where differences in the Γ values were observed.

Previous studies have demonstrated that transitions in Γ result from reorientation of adsorbed aromatics from flat (η^6) to edgewise (η^2) orientations.[6,7] DOPA and the

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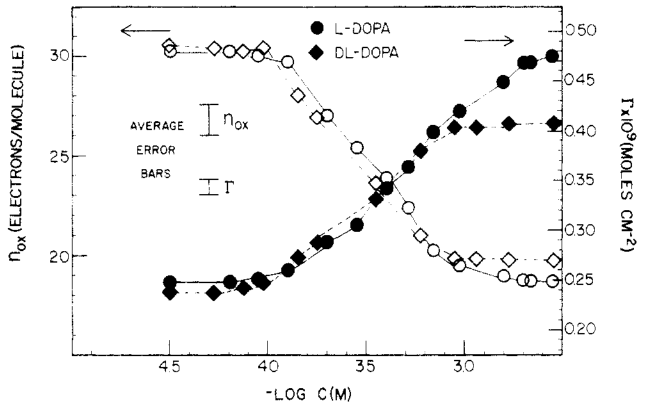

Figure 2. Number of electrons for oxidative desorption (n_{ox}) and packing density (Γ) vs. the solute concentration at which adsorption was carried out: (○) Γ(*l*-DOPA); (●) n_{ox}(*l*-DOPA); (◇) Γ(*dl*-DOPA); (◆) n_{ox}(*dl*-DOPA). The lines interconnect the experimental points and do not assume any theoretical curve.

analogous compound dopamine [2-(2-aminoethyl)pyrocatechol][6,7] display somewhat less abrupt transitions than pyrocatechol derivatives not containing amine substituents.[6,7] This difference probably results from the fact that the amine group is protonated in acidic media giving the adsorbed molecules a positive charge which causes repulsion between neighboring adsorbed molecules.[6]

The data in Figure 2 show that chirality of the pendant alanine moiety has no detectable influence on Γ or n_{ox} values for the *flat orientation.* This indicates that in the η^6 orientation the amino acid moiety does not influence the packing density. That the side chain is folded away from the surface in the η^6 orientation was noted previously for various hydroquinone and pyrocatechol derivatives.[5,6] Insofar as packing density is concerned, the alanine moiety resembles a methyl group [σ_{expt}(flat; DOPA) = 66.0 Å^2; σ_{calcd}(flat; 4-methylpyrocatechol) = 62.3[5]].

The extent of oxidation of the adsorbed species (reflected in the magnitude of n_{ox}) is determined primarily by the number of carbon atoms directly bound to the surface;[9,10] accordingly, chirality of the pendant substituent would be expected to have little or no bearing on the electrochemical oxidation of η^6-oriented DOPA molecules. Since the observed n_{ox} (30.2 ± 1.0) is larger than expected for oxidation of the ring alone to CO_2 (n_{ox} expected = 23), the alanine moiety apparently undergoes some degree of oxidation, likewise independent of optical isomerism. The products have not been identified. It may be noted that n_{ox} for η^6 dopamine is 28.6 ± 1.0,[10] which is not too different from that for the subject compound. This suggests that the pendant substituent is oxidized to only a limited extent.

At high concentrations, dopamine is thought to chemisorb in the 5,6-η^2 orientation, with the (protonated) ethylamine group folded away from the surface (σ_{expt} = 34.8; σ_{calcd} = 36.4).[6,7] This assignment is consistent with the earlier hypotheses that (i) *o*- and *p*-diphenols are adsorbed on Pt in the quinone form, and, (ii) quinones favor an edge orientation which places a relatively unhindered quinone double bond toward the Pt surface. By analogy, the DOPA molecule probably adopts the 5,6-η^2 orientation. Although the 3,4-edge contains a quinone double bond, the 3,4-η^2 orientation would result in considerable steric hindrance and would block the protonation of the amine nitrogen.

The higher η^2-packing density for *l*-DOPA than for *dl*-DOPA indicates that the amino acid side chain influences the edgewise packing density of the catechol moiety. Evidently the pure enantiomer packs more efficiently than the racemic mixture. This finding is in agreement with studies of *l*-, *d*-, and *dl*-tryptophan on well-defined Cu surfaces under ultrahigh-vacuum conditions, in which the layer formed by pure enantiomer was ordered, in contrast to that of the racemic mixture.[16] Similar differences in packing characteristics were noted in enantiomeric and racemic *N*-α-methylbenzylstearamide at air–liquid interfaces: the force required to pack racemic molecules, at a given molecular area, is consistently higher than for pure enantiomers.[17]

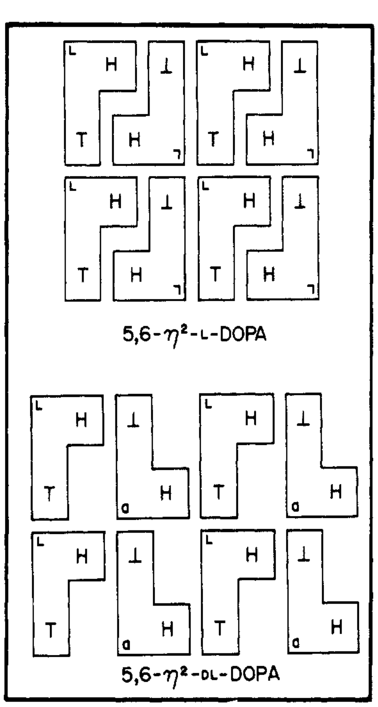

Figure 3. Schematic representation of the packing of *l*- and *dl*-DOPA adsorbed in the 5,6-η^2 orientation: H, head; T, tail.

The postulated 5,6-η^2 orientation of adsorbed DOPA leads to a rather simple explanation for the efficient packing of *l*-DOPA under the present conditions: Since the edge orientation of DOPA has nonuniform thickness, an interlocking head-to-tail arrangement such as that for edge-bonded *tert*-butyl aromatic derivatives[6] is necessary for maximum packing. A head-to-tail packing may also be dictated by the positive charges in order to minimize electrostatic repulsion. Examination of molecular models reveals that such an interlocking head-to-tail arrangement *in the 5,6-η^2 orientation* is possible only for a layer consisting of a single enantiomer, as shown in Figure 3. It could be noted that studies of enantiomeric and racemic phenylalanine *reversibly* adsorbed at mercury–aqueous solution interfaces, in surface excesses indicative of edge orientations, gave Γ(*l*) *less than* Γ(*dl*).[18] It is probably because adsorption of DOPA on Pt involves a single edge orientation that the present results differ from those for reversible adsorption.

It is perhaps significant that although $\Gamma_{\eta^2}(l)$ is greater than $\Gamma_{\eta^2}(dl)$, the n_{ox} value for the *l* and *dl* species are nearly the same [$n_{ox}(\eta^2; l)$ = 18.7 ± 0.7; $n_{ox}(\eta^2; dl)$ = 19.7 ± 0.8]. This indicates that anodic oxidation of the diphenol anchor, regardless of orientation, is not a sensitive function of the optical isomerism of its pendant substituent. In addition, the n_{ox} value for 5,6-η^2-dopamine[10] (19.2 ± 0.8)

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is the same as for the subject compounds, supporting the suggestion that dopamine and DOPA adopt the same 5,6-η^2 orientation. The decrease in n_ox on going from flat to edgewise orientation implies that the product distribution from electrochemical oxidation is dependent on initial orientation, in agreement with previous results.[9,10]

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Registry No. *l*-DOPA, 59-92-7; *dl*-DOPA, 63-84-3; Pt, 7440-06-4; $HClO_4$, 7601-90-3.

Cooling Rate Dependence of the Ice I Nucleation Temperature in Aqueous LiCl Solutions

D. R. MacFarlane,† **R. K. Kadiyala, and C. A. Angell***

Department of Chemistry, Purdue University, West Lafayette, Indiana 47907 *(Received: April 12, 1982; In Final Form: September 29, 1982)*

The cooling rate dependence of the homogeneous nucleation temperature, T_h, has been determined for several compositions in the system $LiCl/H_2O$. This cooling rate dependence was found to be small except at concentrations close to the edge of the glass-forming range. An explanation of the often observed termination of the T_h curve at $\sim T_\mathrm{g} + 22$ K is developed. Little prospect is found of improving the vitrification range of cryoprotectant solutions by the imposition of high quench rates.

The homogeneous nucleation temperature, T_h, for crystallization of simple liquids is a much-discussed quantity in the theory of phase changes, but it is difficult to determine with confidence due to the difficulty of excluding heterogeneous impurities. In the interesting and much-studied case of water, and its aqueous solutions, an important advance was made by Rasmussen and McKenzie[1] who developed a stable "water-in-oil" emulsion, using sorbitan tristearate as surfactant, with which repeated supercoolings to temperatures within 3 K of the lowest recorded (cloud chamber droplet) nucleation temperature could be obtained. Although not strictly true, it is convenient for the purpose of exploring the effect of experimental variables (such as pressure, composition, and, in the present instance, cooling rate) on the nucleation probability to regard the emulsion crystallization temperatures as "homogeneous nucleation temperatures".

In pure water T_h is found[2] to lie within a few degrees of the temperature at which the thermodynamic properties are thought to diverge. T_h has also been studied as a function of pressure in H_2O[3,4] where it is depressed with increasing pressure up to 2 kbar as the hydrogen-bonded structure becomes increasingly distorted relative to the structure at atmospheric pressure. In dilute aqueous solutions, T_h has been studied as a function of concentration[1,5] and pressure[6] and appears to behave as a colligative property of the solution presumably because the nucleation rate $I(T)$, on which T_h depends, is dependent, among other quantities, on the liquidus temperature of the solution.

At higher concentrations and pressures (up to 2 kbar) T_h rapidly approaches T_g, the glass transition temperature, and eventually becomes unobservable when the nucleation and growth rates become too small to produce significant crystallization during cooling. The liquid then continues to follow the liquid free energy surface down in temperature until the structural relaxation time becomes too long for internal equilibration to be obtained and the structure is arrested at T_g. So long as T_h, observed at lower and lower cooling rates, remains above T_g, the glass obtained by rapid quenching can in principle relax, given sufficient time, toward both internal (liquid) and external (crystalline) equilibrium and is hence termed doubly unstable.[7] This behavior is illustrated by $LiCl/H_2O$ solutions which show a doubly unstable region around 8–10 mol % LiCl.

A recent study[8] has shown that isothermal measurements made below T_g can be analyzed in a way which yields T_h for compositions where it lies below T_g. This extrapolation to sub-T_g temperatures is important[9] in assessing proposed resolutions of Kauzmann's paradox.[10]

Other studies of T_h as a function of concentration and pressure in aqueous solutions of organic glass formers such as dimethyl sulfoxide and propylene glycol have been useful in cryobiological applications[11,12] where the first disappearance of T_h with increasing composition or pressure indicates the lowest, and hence least toxic, vitrifiable concentration which can be used for the low temperature preservation of certain organs. One recent study[13] has shown that the imposition of moderate, nonlethal, pressures can extend the glass-forming range to compositions

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