it might be possible to isolate compounds similar to those from the iron trimethylphosphine cocondensation—$Fe(PMe_3)_3H(CH_2PMe_2)$—in which an initial coordinatively unsaturated zerovalent product fulfills the noble gas configuration by oxidative addition of C–H bonds. A recent report from Green's laboratory indicates that $Mo(PMe_3)_6$ can be prepared and that, in fact, it is in a reversible equilibrium with $Mo(PMe_3)_4H(CH_2PMe_2)$ and $Mo(PMe_3)_2H_2(CH_2PMe_2)_2$.

Having prepared the binary phosphite and arene complexes, we decided to attempt the ternary synthesis of $Cr(arene)(P(OMe)_3)_3$ complexes. We expected this synthesis to require a separation of the desired product from the binary products, $Cr(arene)_2$ and $Cr(P(OMe)_3)_6$. In fact, the ternary complex is formed in high yield and relatively free of either binary product. A simple recrystallization is sufficient to give analytically pure material. It is not surprising that the arene tris(phosphite) complex would be favored over the hexakis(phosphite) complex simply on the grounds of steric constraints. One π arene would cause less steric interaction than three phosphites. We do find it remarkable that the yield of the bis(arene) is low. The well-known preparative chemistry of these compounds is some indication of their stability, yet the mixed complex must be even more stable.

Registry No. $Cr(P(OMe)_3)_6$, 70948-62-8; $Cr(P(OEt)_3)_6$, 70948-60-6; $Cr(P(OMe)_3)_5H_2$, 70948-61-7; $Cr(P(OEt)_3)_5H_2$, 70948-59-3; $W(\eta^6\text{-tol})_2$, 52346-44-8; $Mo(\eta^6\text{-tol})_2$, 12131-22-5; $Mo(P(OMe)_3)_6$, 37478-27-6; $W(P(OMe)_3)_6$, 73411-63-9; $Cr(\eta^6\text{-tol})(P(OMe)_3)_3$, 93646-60-7; $Cr(\eta^6\text{-Mesit})(P(OMe)_3)_3$, 93646-61-8; $P(OEt)_3$, 122-52-1; $P(OMe)_3$, 121-45-9; Cr, 7440-47-3; W, 7440-33-7; Mo, 7439-98-7; $P(O)(OMe)_2$, 16038-03-2; toluene, 108-88-3; 1-hexene, 592-41-6; hexane, 110-54-3; mesitylene, 108-67-8.

Contribution from the Department of Chemistry, University of California, Santa Barbara, California 93106,
and Department of Chemical Engineering, Princeton University, Princeton, New Jersey 08544

Surface Coordination Chemistry of Platinum Studied by Thin-Layer Electrodes.[1] Adsorption, Orientation, and Mode of Binding of Aromatic and Quinonoid Compounds

MANUEL P. SORIAGA,*† ELIZABETH BINAMIRA-SORIAGA,† ARTHUR T. HUBBARD,*† J. B. BENZIGER,‡
and K.-W. PETER PANG‡

Received March 12, 1984

Extensive studies on the interaction of 54 aromatic and quinonoid compounds with smooth Pt thin-layer electrodes have yielded data that serve to establish the surface coordination chemistry of polycrystalline Pt with these compounds in aqueous solutions. Adsorption of the subject compounds occurred spontaneously and irreversibly at specific orientations which depended on their characteristic molecular structures and concentrations, C^0. These orientations have been represented in terms of modes of coordination derived from model compounds; supportive electrochemical and infrared spectroscopic data are presented. For simple *o*- and *p*-diphenols or quinones, adsorption at $C^0 \leq 0.1$ mM produced flat-oriented (π-bonded) quinone intermediates; adsorption at $C^0 \geq 1$ mM resulted in edge-oriented (di-σ-bonded) diphenolic species. When the Pt surface was purposely pretreated with π-bonded intermediates, severe reorientation retardation was observed, indicating that adsorption from concentrated solutions does not involve coordination in the flat orientation as an intermediate step. Substituents on or heteroatoms in the aromatic/quinonoid ring altered its surface coordination properties to varying degrees; analysis of the adsorption/orientation data enabled the formulation of a strength-of-chemisorption series for the various organic functional groups investigated. The effect of temperature on surface properties has been described in terms of perturbations to the preferred modes of attachment. Fluxional motion of chemisorbed 3,6-dihydroxypyridazine was indicated near 65 °C, similar to that of pyridazine itself in Pt coordination compounds.

Introduction

The study of heterogeneous catalytic reactions has always been concerned with the nature of intermediates present on the catalyst surface. One approach involves characterization of surface species prior to and after occurrence of a catalytic reaction. Elegant surface analytical techniques have proliferated[3] for this purpose, although many are limited to ultrahigh vacuum (UHV). Chemical representations of surface compounds are vital and have generally been derived from concepts in coordination and organometallic chemistry.[4]

We have recently studied the interaction of aromatic and quinonoid compounds with platinum[2] thin-layer electrodes[5] in an effort to determine adsorbed reaction intermediates and their influences on bulk electrocatalytic processes. An offshoot of this work has been the accumulation of data that serve to establish the surface coordination chemistry of platinum metal with the subject compounds in aqueous solutions. Qualitative description of such chemistry, as outlined in Table I, is the purpose of these articles. The adsorption and orientation of aromatic/quinonoid compounds are described in this paper, along with the representation of adsorbed molecule orientation in terms of modes of coordination derived from model, well-characterized molecular

---

† University of California.

‡ Princeton University.

(1) This and the succeeding article are dedicated to the memory of Professor Earl L. Muetterties, whose encouragement of this study is appreciated.

(2) (a) Soriaga, M. P.; Hubbard, A. T. *J. Am. Chem. Soc.* **1982**, *104*, 2735. (b) Soriaga, M. P.; Hubbard, A. T. *J. Am. Chem. Soc.* **1982**, *104*, 2742. (c) Soriaga, M. P.; Hubbard, A. T. *J. Am. Chem. Soc.* **1982**, *104*, 3937. (d) Soriaga, M. P.; Wilson, P. H.; Hubbard, A. T.; Benton, C. S. *J. Electroanal. Chem. Interfacial Electrochem.* **1982**, *142*, 317. (e) Chia, V. K. F.; Soriaga, M. P.; Hubbard, A. T.; Anderson, S. E. *J. Phys. Chem.* **1983**, *87*, 232. (f) Soriaga, M. P.; White, J. H.; Hubbard, A. T. *J. Phys. Chem.* **1983**, *87*, 3048. (g) Stickney, J. L.; Soriaga, M. P.; Hubbard, A. T.; Anderson, S. E. *J. Electroanal. Chem. Interfacial Electrochem.* **1981**, *125*, 73. (h) Soriaga, M. P.; Stickney, J. L.; Hubbard, A. T. *J. Electroanal. Chem. Interfacial Electrochem.* **1983**, *144*, 207. (i) Soriaga, M. P.; Stickney, J. L.; Hubbard, A. T. *J. Mol. Catal.* **1983**, *21*, 211. (j) Soriaga, M. P.; Hubbard, A. T. *J. Electroanal. Chem. Interfacial Electrochem.* **1983**, *159*, 101. (k) Soriaga, M. P.; Hubbard, A. T. *J. Phys. Chem.* **1984**, *88*, 1758. (l) Soriaga, M. P.; Hubbard, A. T. *J. Phys. Chem.* **1984**, *88*, 1089. (m) Soriaga, M. P.; Chia, V. K. F.; White, J. H.; Song, D.; Hubbard, A. T. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *162*, 143. (n) Soriaga, M. P.; Hubbard, A. T. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *167*, 79. (o) Chia, V. K. F.; Soriaga, M. P.; Hubbard, A. T. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *167*, 97. (p) Soriaga, M. P.; White, J. H.; Song, D.; Hubbard, A. T. *J. Phys. Chem.* **1984**, *88*, 2284. (q) Soriaga, M. P.; White, J. H.; Song, D.; Hubbard, A. T. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *171*, 359.

0020-1669/85/1324-0065$01.50/0

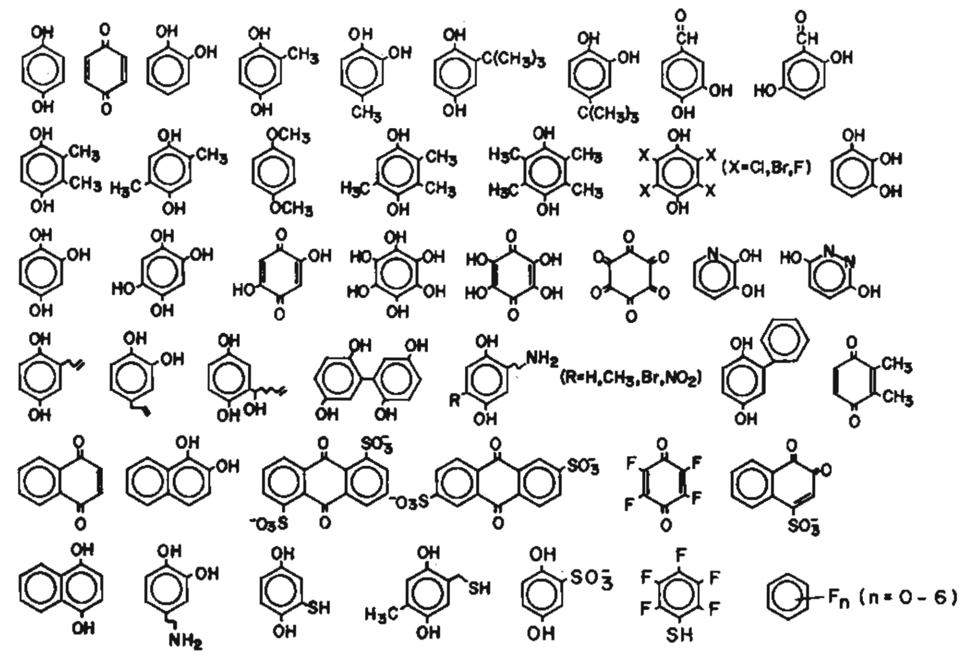


Figure 1. Compounds studied.

Table I. Coordination Chemistry of Pt: Surface and Molecular Compounds

surface studies by thin-layer electrodes	analogous studies on molecular complexes
adsorption	synthesis
adsorbed molecule orientation	mode of coordination
competitive adsorption with halides	ligand substitution
exchange between adsorbed and unadsorbed species	ligand exchange
reactivity of adsorbed intermediates	reactivity of coordinated ligands
electrocatalysis	homogeneous catalysis

complexes; supportive electrochemical and infrared spectroscopic evidences are also presented. Reactions of the intermediates adsorbed in specific orientational states are described in the succeeding paper.

The compounds employed in our studies are shown in Figure 1. These (of which hydroquinone and benzoquinone are the prototypes) were chosen because they interact strongly with Pt, display comparatively uncomplicated electrochemical reactivity, and represent a range of structures and chemical properties.

Experimental Section

Thin-Layer Cell. Figure 2 illustrates the thin-layer electrode[5] employed in our studies. Analyte solution of thickness $t \approx 0.025$ cm is contained between the Pt electrode (surface area, $A \approx 1$ cm^2) and surrounding glass tubing; the volume V of solution in this cavity is $\sim$4 μL. Spent liquid is removed through pinholes at the bottom of the cell by application of pressurized pure inert gas; filling occurs by capillary action. Thin-layer cells are suitable for surface chemical studies due to (i) the absence of diffusional mass transport to and from the cell, which, combined with (ii) extremely small cell volumes, helps to minimize surface contamination and enables (iii) isolation (for subsequent characterization) of species generated from surface reactions, and (iv) large A/V ratios, which ensure magnification of surface processes relative to those in solution.

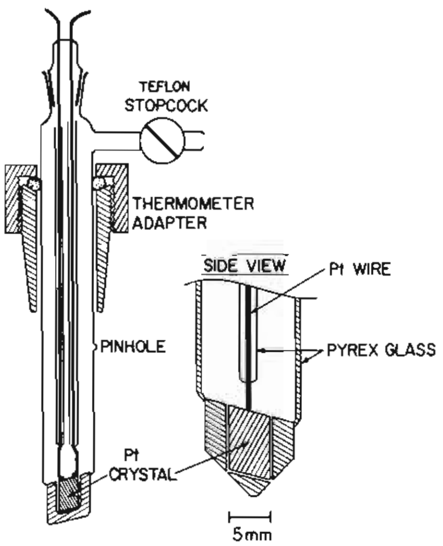


Figure 2. Thin-layer electrode. The design shown is for a Pt(111) single crystal. Typical parameters are as follows: volume, $V = 4$ μL; electrode surface area, $A = 1$ cm^2; thickness of solution, $t = 0.025$ cm.

Measurement of Adsorbed Amounts. Measurement of *absolute* surface concentrations is based upon (electrochemical) detection of the disappearance of sample from the solution phase upon contact with the Pt surface;[2a] for example, detection of *unadsorbed* hydroquinone takes advantage of its reversible quinone $\rightleftarrows$ diphenol redox couple.

When the thin-layer electrochemical cell is filled *once* with surfactant solution, the Pt electrode is exposed to a single aliquot of solution containing a precise molar amount of adsorbate. Adsorption lowers the concentration, C, of the unadsorbed aromatic *inside* the thin-layer cavity relative to the bulk concentration C^0

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

where Γ (in mol cm^{-2}) is the surface concentration of the adsorbed aromatic. The single-filling electrolytic charge ($Q_1 - Q_{1b}$, where Q_{1b} is the background charge) required for reversible (quinone/diphenol) electrolysis of unadsorbed material is, from Faraday's law, equal to the

---

(3) Somorjai, G. A. "Chemistry in Two Dimensions: Solids"; Cornell University Press: Ithaca, NY, 1981. Tsai, M.-C.; Muetterties, E. L. *J. Am. Chem. Soc.* **1982**, *104*, 2534. Lee, L.-H., Ed. "Characterization of Metal and Polymer Surfaces"; Academic Press: New York, 1977; Vols. 1 and 2. Czanderna, A. W., Ed. "Methods of Surface Analysis"; Elsevier: Amsterdam, 1975.

(4) Ugo, R. *Catal. Rev.—Sci. Eng.* **1975**, *11*, 225. Muetterties, E. L.; Bleeke, J. R.; Wucherer, E. J.; Albright, T. A. *Chem. Rev.* **1982**, *82*, 499. Basset, J. M.; Choplin, A. *J. Mol. Catal.* **1983**, *21*, 95. Deeba, M.; Gates, B. C. *J. Catal.* **1981**, *67*, 303.

(5) Hubbard, A. T. *CRC Crit. Rev. Anal. Chem.* **1973**, *3*, 201. Lai, C. N.; Hubbard, A. T. *Inorg. Chem.* **1972**, *11*, 2081.

(6) Stickney, J. L.; Rosasco, S. D.; Song, D.; Soriaga, M. P.; Hubbard, A. T. *Surf. Sci.* **1983**, *130*, 326. Hubbard, A. T. *Acc. Chem. Res.* **1980**, *13*, 177. Hubbard, A. T. *J. Vac. Sci. Technol.* **1980**, *17*, 48. Ishikawa, R. M.; Katekaru, J. Y.; Hubbard, A. T. *J. Electroanal. Chem. Interfacial Electrochem.* **1970**, *86*, 271.

charge due to the unadsorbed reactant ($nFVC$) plus any charge due to the adsorbed material ($n_aFA\Gamma$)

$$Q_1 - Q_{1b} = nFVC + n_aFA\Gamma \qquad (2)$$

where the n values refer to the number of faradays F consumed per mole of dissolved (n) and adsorbed (n_a) reactant. If the adsorbed material reacts *identically* with the unadsorbed reactant, $Q_1 - Q_{1b}$ will equal $nFVC^0$, the charge expected from the bulk concentration; otherwise, the two values will differ. The exact relationship is obtained by substitution of eq 1 into eq 2:

$$Q_1 - Q_{1b} = nFVC^0 + (n - n_a)FA\Gamma \qquad (3)$$

When the thin-layer cavity is rinsed repeatedly with the adsorbate solution, the concentration in the cavity will equal that in the bulk since no further adsorption occurs after the initial rinses; in this case, the measured electrolytic charge $Q - Q_b$ is given by the bulk value plus any charge due to the adsorbed species:

$$Q - Q_b = nFVC^0 + n_aFA\Gamma \qquad (4)$$

Subtraction of eq 3 from eq 4 yields an expression for Γ in terms of measurable charges:

$$\Gamma = \frac{(Q - Q_b) - (Q_1 - Q_{1b})}{nFA} \qquad (5)$$

It must be noted that n_a does not appear in eq 5; that is, the present method of Γ measurement is independent of the electrochemical behavior of the adsorbed intermediates. As discussed in detail elsewhere, slight modifications in the procedures (and eq 5) are necessary for very dilute analyte concentrations.[2c,d] At regions where Γ is extremely sensitive to concentration, the term $(Q - Q_b) - (Q_2 - Q_{2b})$, Q_2 being the charge after two rinses, is added to the numerator of eq 5.[2n]

Direct chemisorption of the electroactive center alters the reactivity of the surface species relative to that of the unadsorbed material.[2j] In such cases, the kinetics of adsorption may be studied by noting the changes in Q_1 with respect to the time allowed for adsorption

$$\Gamma(t) = \frac{(Q - Q_b) - [Q_1(t) - Q_{1b}(t)]}{nFA} \qquad (6)$$

where t is adsorption time, and the Q values are measured at potentials where only unadsorbed species react.

Electrode and Electrolyte Solutions. The analyte and reference solutions contained 1M perchlorate in pyrolytically triply distilled water.[7] Aqueous perchlorate is unreactive and weakly coordinating; it is totally and irreversibly displaced from the surface by strongly surface-active compounds such as those used in this study.[2a,m]

Smooth polycrystalline Pt electrodes were employed; the preparation of these electrodes, which consist of 55% Pt(111) and 45% Pt(100) planes,[6] has been described.[2a,6] Between experimental trials, the electrodes were cleaned by electrochemical oxidation in 1 M $HClO_4$ at 1.2 V (Ag/AgCl (1 M Cl^-) reference) and reduction at −0.2 V. For studies at neutral pH, the solutions were buffered with NaH_2PO_4 and NaOH;[2a] phosphate behaves identically with perchlorate.[2m] Solutions were deaerated with oxygen-free high-purity nitrogen.

Thin-layer linear-potential sweep voltammetry and potential-step coulometry were done with use of a conventional multipurpose electronic circuit based on operational amplifiers, as described previously.[5]

Determination of Adsorbed Molecule Orientation. The average area occupied by an adsorbed molecule, σ (Å^2), is related to the inverse of Γ

$$\sigma = 10^{16}/N_A\Gamma \qquad (7)$$

where N_A is Avogadro's number. Adsorbed molecule orientations were determined with use of the traditional method[8] of comparing measured σ values with those calculated for various possible orientations;[1a,d] covalent and van der Waals radii tabulated by Pauling[9] were used to calculate σ. Sample calculations[2d] and a tabulation of σ_{calcd} values[2a] have been given.

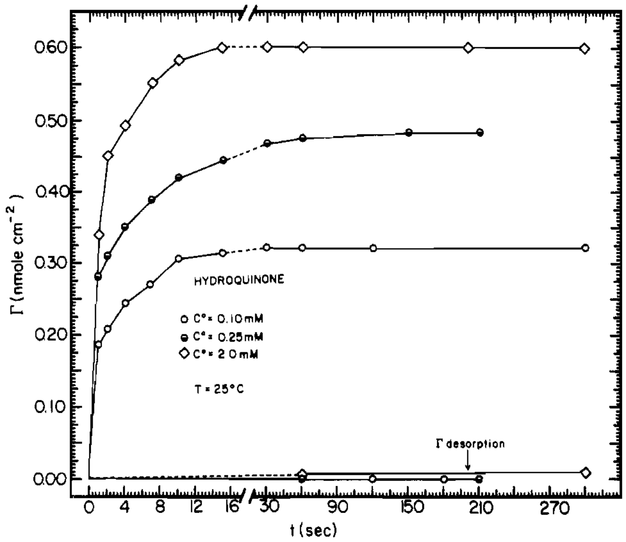


Figure 3. Hydroquinone adsorption (Γ) on and desorption (Γ_{des}) from smooth polycrystalline Pt as a function of time (t) at selected concentrations. The solutions contained 1 M $HClO_4$: $V = 3.62\ \mu L$; $A = 1.16$ cm^2. The average standard deviations were as follows: t ±0.5 s; Γ ±3% below 1 mM, Γ ±6% at higher concentrations. The solid lines interconnect the data points and do not represent any theoretical curve.

Surface Infrared Reflection-Adsorption Spectroscopy. Image dipole effects on metallic surfaces restrict infrared activity of adsorbed molecule vibrations to those with dipole moments oscillating *perpendicularly* to the metal surface.[11] Hence, the relative intensities of certain vibrations in the surface state relative to those in the free state provide a direct diagnosis of adsorbed molecule orientation. For single molecular layers at self-supported metal substrates, reflectivity measurements of p-polarized radiation at near-grazing incidence are essential;[11] changes in substrate reflectivity due to adsorbate absorption give rise to reflection–absorption spectra.

The infrared reflection–absorption spectra for hydroquinone and benzoquinone on smooth[6] polycrystalline Pt foil ($A = 1.44$ cm^2) were obtained with a combined infrared spectroscopy–electrochemistry apparatus described elsewhere.[12] Adsorption was carried out by immersion of the clean Pt foil in analyte solution of given concentration followed by rinsing with pure solvent; electrodes were dried prior to spectroscopic measurements by purging with pure nitrogen.

Results

Figure 3 shows the kinetics of hydroquinone (HQ) adsorption on and the desorption from smooth polycrystalline Pt at selected concentrations. The following may be noted: (i) The initial rate of adsorption is extremely high; regardless of concentration $\Gamma(t)/\Gamma_{max}$ reached about 60% after only 1 s. This immediate and spontaneous interaction suggests a large free energy and low activation energy of surface coordination. (ii) Adsorption is virtually complete in 15 s; the nonlinearity of $\Gamma(t)$ at 1 s $< t <$ 15 s reflects the coverage dependence of the adsorption rate. (iii) The *limiting* Γ is dependent on the concentration of aromatic in solution. (iv) Adsorption is irreversible. In pure supporting electrolyte, no desorption was observed from the low-coverage layers (0.1 and 0.25 mM); less than 5% was desorbed from the high-coverage layer (2 mM) even after 10 min. Figure 3 is typical of the subject compounds.

The effect of concentration on Γ can be seen more clearly in Figure 4, which shows adsorption isotherms (25 °C) for representative compounds.[2c,d] Molecular area calculations have shown that, except for tetrafluorohydroquinone (TFHQ) at low con-

---

(7) Conway, B. E.; Angerstein-Kozlowska, H.; Sharp, W. B. A.; Criddle, E. E. *Anal. Chem.* **1973**, *45*, 1331.

(8) Langmuir, I. *Proc. R. Soc. London, Ser. A* **1939**, *170*, 1. Adam, N. K. "Physics and Chemistry of Surfaces"; Oxford University Press: London, 1941.

(9) Pauling, L. C. "The Nature of the Chemical Bond"; Cornell University Press: Ithaca, NY, 1960.

(10) "Sadtler Standard Infrared Spectra"; Sadtler Research Laboratories: Philadelphia, 1973. "CRC Atlas of Spectral Data and Physical Constants for Organic Compounds" Chemical Rubber Publishing Co.: Cleveland, OH, 1975.

(11) Greenler, R. G. *CRC Crit. Rev. Solid State Sci.* **1974**, *4*, 415. Pearce, H. A.; Sheppard, N. *Surf. Sci.* **1976**, *59*, 205.

(12) Pang, K.-W. P.; Benzinger, J. B.; Soriaga, M. P.; Hubbard, A. T. *J. Phys. Chem.* **1984**, *88*, 4583. Pang, K.-W. P. Ph.D. Dissertation, Princeton University, 1984.

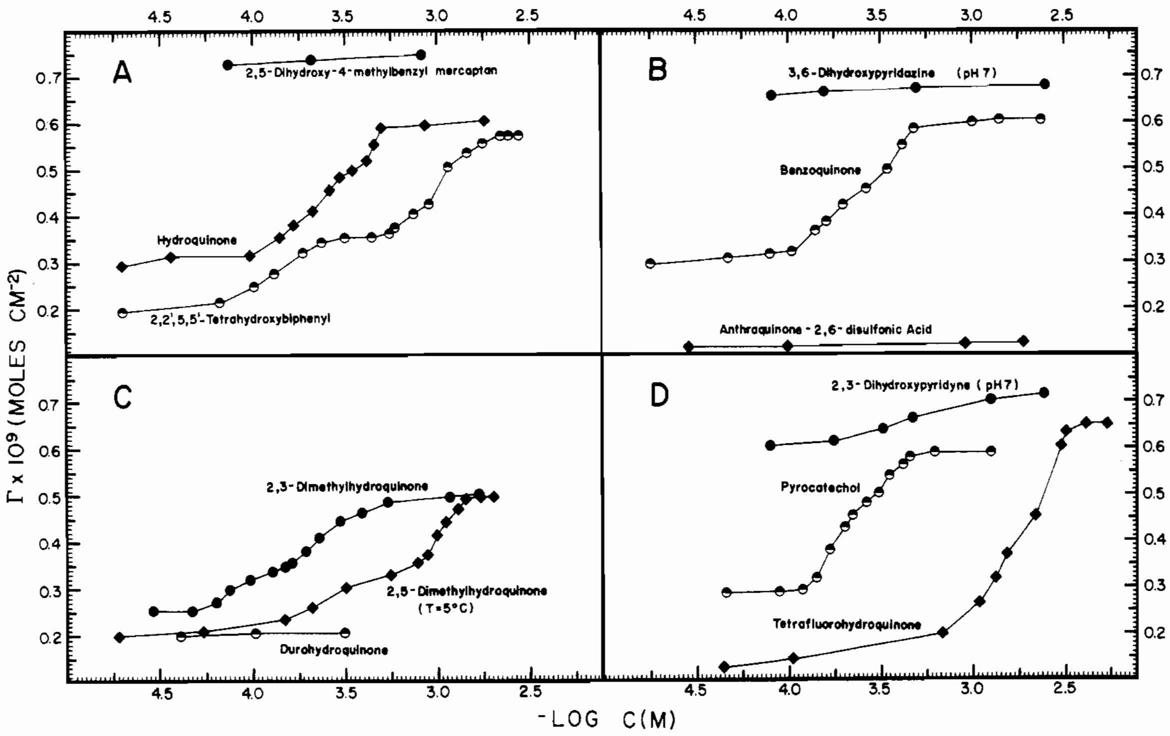


Figure 4. Packing density (Γ) as a function of adsorbate concentration (C^0) at which adsorption was carried out for representative compounds. Experimental conditions were as in Figure 3. The solid lines simply connect the data points and do not assume any theoretical equation.

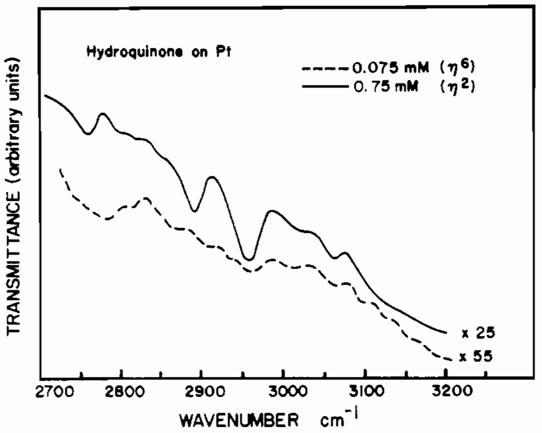


Figure 5. Reflection-absorption infrared spectra for hydroquinone adsorbed at 0.075 mM (---) and 0.75 mM (—). The surface area of smooth Pt foil was 1.44 cm^2.

Table II. Postulated Orientations for Representative Compounds[2c,d]

compd	σ_{exptl}, Å^2	orien-tation	σ_{calcd}, Å^2
hydroquinone (HQ)	52.7	η^6	53.8
	27.9	2,3-η^2	28.6
benzoquinone (BQ)	52.7	η^6	52.5
	27.7	2,3-η^2	27.9
pyrocatechol (CAT)	56.1	η^6	54.0
	28.2	3,4-η^2	26.9
2,3-dimethylhydroquinone	66.0	η^6	67.8
(2,3-DMHQ)	33.3	5,6-η^2	33.6
2,5-dimethylhydroquinone	74.4	η^6	72.1
(2,5-DMHQ)	33.6	2,3-η^2	33.6
durohydroquinone (DHQ)	83.1	η^6	83.3
tetrafluorohydroquinone (TFHQ)	25.5	O-η^1	24.7
2,3-dihydroxypyridine (DHPy), pH 7	23.6	N-η^1	23.2
3,6-dihydroxypyridazine (DHPdz), pH 0 or 7	24.7	N-η^1	24.7
2,5-dihydroxy-4-methylbenzyl mercaptan (DHBM)	22.5	S-η^1	22.0
2,2',5,5'-tetrahydroxybiphenyl (THB)	84.1	η^{12}	85.1
	47.1	η^4	39.8
	29.0	5,6-η^2	28.6
anthraquinone-2,6-disulfonic acid (2,6-AQDS)	123.9	flat	126.3

centrations, the Γ plateaus in Figure 4 correspond precisely to specific, nonrandom adsorbed molecule orientations.[2c,d] For example, Γ for HQ below 0.1 mm corresponds to a layer of flat (η^6)-adsorbed species (σ_{exptl} = 52.7 Å^2; σ_{calcd} = 53.8 Å^2), while Γ above 1.0 mM corresponds to completely vertical 2,3-η^2-adsorbed molecules (σ_{exptl} = 27.9 Å^2; σ_{calcd} = 28.6 Å^2). Decomposition upon adsorption is contraindicated not only in view of the excellent correlation between σ_{calcd} and σ_{exptl}[2c,d] but also because of *starting material* being displaced from the surface by more strongly coordinating species such as iodide.[2b,p] Orientation assignments for representative compounds[2c,d] are tabulated in Table II.

Infrared spectra for chemisorbed HQ are shown in Figure 5. The dashed curve is for the layer formed at 0.075 mM while the solid curve is for species adsorbed at 0.75 mM. The IR spectrum for *bulk* HQ[10] shows three broad peaks between 2500 and 3000 cm^{-1} characteristic of phenolic compounds in the condensed phase and a sharp peak at 3030 cm^{-1} due to the aromatic C–H stretch. The absence of these peaks for 0.075 mM HQ is indicative of η^6-orientation in view of the surface dipole selection rule.[11] The emergence of the four peaks for 0.75 mM HQ is consistent with a vertical orientation: in this orientation, the in-plane C–H and O–H vibrations are no longer parallel to the surface and, hence, are IR active.

The IR spectra for adsorbed benzoquinone (BQ) are identical with those for HQ.[12] This indicates that (i) the nature of the adsorbed species is independent of the oxidation state (HQ or BQ) of the starting material and (ii) in the η^2 orientation adsorbed BQ exists as a diphenolic intermediate.

The effect of temperature on the chemisorption of aromatics on Pt[2f] is illustrated in Figure 6 for HQ and 1,4-naphthohydroquinone (NHQ) and in Table III for the thiophenol (DHT), pyridine (DHPy), and pyridazine (DHPdz) derivatives. Increase in temperature appeared to enhance adsorption of HQ and NHQ in the flat orientation but severely suppressed adsorption in the

Table III. Adsorption Data for η^1-Oriented Diphenols at Various Temperatures[a]

compd	C^0, mM	T, °C	Γ, nmol cm^{-2}	postulated orientation[2c,d]
2,5-dihydroxythiophenol (DHT), pH 0	0.75	5	0.571	S-η^1
	0.75	25	0.569	S-η^1
	0.75	45	0.569	S-η^1
	0.75	65	0.564	S-η^1
2,3-dihydroxypyridine (DHPy), pH 7	1.0	5	0.702	N-η^1
	1.0	25	0.702	N-η^1
	1.0	45	0.698	N-η^1
	1.0	65	0.690	N-η^1
3,6-dihydroxypyridazine (DHPdz), pH 0	1.0	5	0.667	N-η^1
	1.0	25	0.660	N-η^1
	1.0	45	0.639	N-η^1
	1.0	65	0.588	$\mathrm{N}_{1\text{-}\eta^1} \rightleftarrows \mathrm{N}_{2\text{-}\eta^1}$ (fluxional)

[a] Experimental conditions were as in Figure 6.

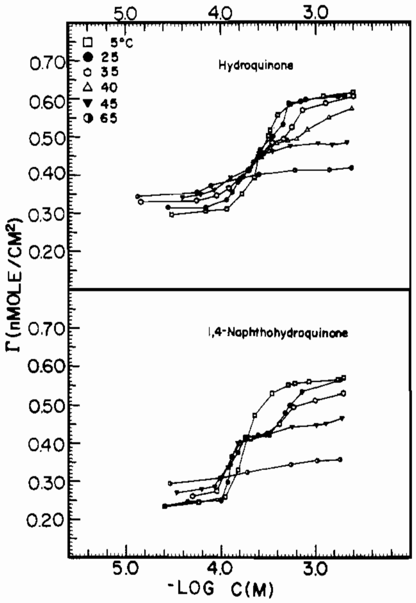


Figure 6. Γ vs. log C^0 curves for hydroquinone and 1,4-naphthohydroquinone at selected temperatures. The solid lines connect the experimental points and do not represent any theoretical curve. The relative average standard deviations in Γ were as follows: ±3% at $C^0 < 1$ m*M*, $T < 50$ °C; ±6% at $C^0 > 1$ mM, $T < 50$ °C; ±7% at $C^0 < 1$ mM, $T > 50$ °C; ±8% at $C^0 > 1$ mM, $T > 50$ °C. Other experimental conditions were as in Figure 3.

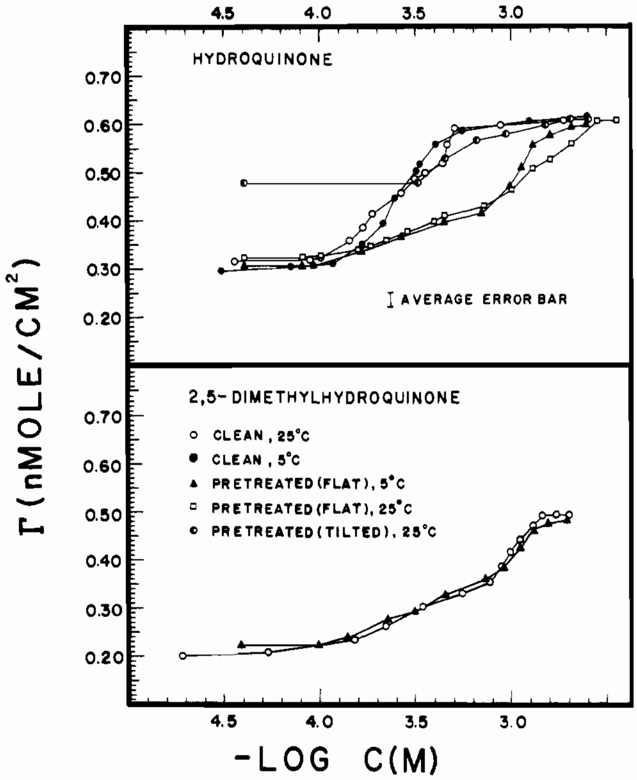


Figure 7. Adsorption data on clean and pretreated surfaces, expressed as *total* Γ vs. log C^0. The solid lines interconnect data points and do not represent any theoretical isotherm. Experimental conditions were as in Figure 3.

edge orientation; the latter effect was quasi-reversible, and the former was irreversible. In terms of cooperative phenomena, the results depicted in Figure 6 have been ascribed to increased packing efficiency in the flat orientation (aided by enhanced mobilities) and decreased packing efficiency in the edge state (due to large-amplitude librational motions).[2f] DHT and DHPy were virtually impervious to temperature variations. In contrast, the packing density of DHPdz decreased at 65 °C, a result rationalized in terms of fluxional motion of the adsorbed molecule.[2f]

The adsorption of aromatic compounds on Pt electrodes pretreated with a layer of flat-oriented intermediates has been studied as a function of concentration.[21] The results of HQ and 2,5-dimethylhydroquinone (DMHQ) are shown in Figure 7. The same edge orientations formed on the untreated surface were obtained on the pretreated surface, but the profile or *total* Γ vs. log *C* for HQ revealed that complete formation of the edge structure was severely retarded when the electrode was pretreated with a full monolayer of flat-oriented species; the same retardation was observed even when the electrode was pretreated with less than half a monolayer.[21] When the electrode was precoated with a layer of aromatic molecules in transition between flat and vertical orientation, the adsorption profile was remarkably similar to those for clean electrodes. The adsorption isotherm of 2,5-DMHQ (which on clean surfaces already displays retarded reorientation due to the edge-blocking effect of the methyl groups)[2c,d] was unaffected by surface pretreatment. Collectively, these results suggest the following:[21] (i) adsorption of unhindered aromatics such as HQ at concentrations above 1 mM on clean Pt leads primarily to direct attachment of edge-oriented species; (ii) for such compounds, complete reorientation from flat to vertical structures requires greater activation energies relative to direct adsorption in the vertical orientation; (iii) adsorption of hindered molecules such as 2,5-DMHQ in the edge orientation involves formation of flat-oriented species as an intermediate step; (iv) adsorption of aromatic molecules at high concentrations on a surface sparsely populated with flat-oriented intermediates involves completion of the flat-oriented layer prior to formation of edge-bonded species; (v) in the transition region, tilted molecules (rather than a mixture of rigidly flat- and edge-oriented species) are present on the surface.

Discussion

The irreversibility of aromatic/quinonoid adsorption at Pt surfaces indicates strong organometallic bonding. The orientational transitions suggest alternative modes of coordination.

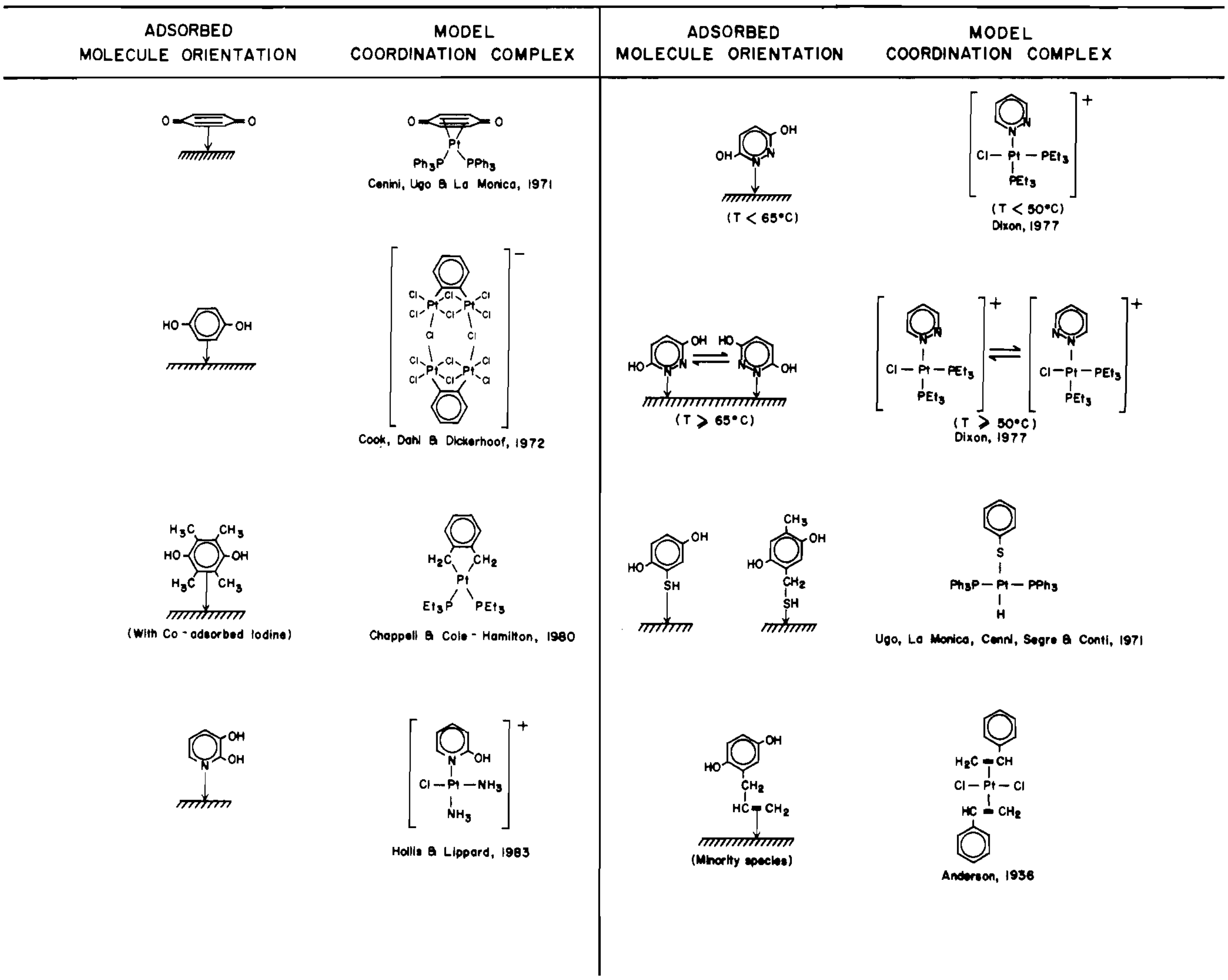


Figure 8. Chemical bonding representations, based on well-characterized molecular species,[14] of the postulated adsorbed molecule orientations.

Representations of the orientations in terms of ligand coordination in model compounds are shown in Figure 8.[13,14] *Estimates* of the strengths of adsorption may be obtained by fitting the Γ vs. log C curves to theoretical isotherms.[15] *Reversible* adsorption from solution is usually described by the Flory–Huggins isotherm[15]

$$\beta C = \frac{\theta}{m(1-\theta)^m} \exp(-\alpha\theta) \qquad (8)$$

where θ is the fraction of saturation coverage, m the ratio of the number of adsorption sites occupied by an adsorbate molecule to that occupied by a solvent molecule, β the adsorption coefficient ($\Delta G^\circ_{\mathrm{ads}}(\theta = 0) = -RT \ln \beta$), α the intermolecular interaction parameter, and C the adsorbate concentration. For $m = 1$, eq 8 reduces to the Frumkin isotherm, which simplifies to the Langmuir isotherm when $\alpha = 0$.[15] The data for HQ in Figure 6 show that adsorption on *clean* electrodes leads to two distinct (uncoupled) adsorption isotherms: η^6 orientations below ~0.12 mM and η^2 structures above ~0.12 mM. Hence, the free energy of adsorption for η^6- and η^2-HQ may be *approximated* by application of eq 8 to the experimental isotherms at the respective concentration regions. If $\alpha(\eta^6)$ was neglected and $m(\eta^6)$ was preset to $\sigma_{\eta^6\text{-HQ}}/\sigma_{\mathrm{H_2O}} \approx 5$, $\Delta G^\circ_{\mathrm{ads}}(\eta^6\text{-HQ})$ was found to be ~-20 ± 5 kcal/mol. For the edge orientation $m(\eta^2) \approx \sigma_{\eta^2\text{-HQ}}/\sigma_{\mathrm{H_2O}} \approx 3$, $\Delta G^\circ_{\mathrm{ads}}(\eta^2\text{-HQ},\theta = 0) \approx 15 \pm 4$ kcal/mol and $\alpha(\eta^2\text{–HQ}) \simeq 10 \pm 3$ kcal/mol; the latter indicates appreciable intermolecular attractions, which phenomenologically may be viewed as a major driving force for the orientational transitions. It is known that the aryl–Pt bond energy is ~60 kcal/mol.[16]

The approximate nature of the values of these adsorption parameters cannot be overemphasized; the use of eq 8 and related isotherms is complicated by the fact that while the theoretical expressions are derived under conditions of thermodynamic equilibrium, no such equilibrium exists for *irreversible* adsorption of the subject compounds on Pt. An added complication is that coordination may be accompanied by spontaneous surface chemical reactions. A well-known example is the *quantitative* oxidation of HI to adsorbed neutral I atoms (and H_2 gas) upon contact with bare Pt.[17] Evidence exists[2d,5,n] which suggests that HQ undergoes dehydrogenation/oxidation processes upon adsorption on Pt. If adsorption redox processes generate species (such as H_2 gas) that are detectable electrochemically, it is possible to measure the

---

(13) Shustorovich, E.; Baetzold, R. C.; Muetterties, E. L. *J. Phys. Chem.* **1983**, *87*, 1100.

(14) (a) Cennini, S.; Ugo, R.; La Monica, G. *J. Chem. Soc. A* **1971**, 416. (b) Cook, P. M.; Dahl, L. F.; Dickerhoof, D. W. *J. Am. Chem. Soc.* **1972**, *94*, 5511. (c) Chappell, S. D.; Cole-Hamilton, D. J. *J. Chem. Soc., Chem. Commun.* **1980**, 238. (d) Hollis, L. S.; Lippard, S. J. *Inorg. Chem.* **1983**, *22*, 2708. (e) Dixon, K. R. *Inorg. Chem.* **1977**, *16*, 2618. (f) Ugo, R.; La Monica, G.; Cenini, S.; Segre, A.; Contri, F. *J. Chem. Soc. A* **1971**, 522. See also: Nyholm, R. S.; Skinner, J. F.; Stiddard, M. H. B. *J. Chem. Soc. A* **1968**, 38. (g) Anderson, J. S. *J. Chem. Soc.* **1936**, 1042.

(15) Parsons, R. *J. Electroanal. Chem.* **1964**, *8*, 93. Gurevich, Y. Y.; Kharkats, Y. I. *J. Electroanal. Chem. Interfacial Electrochem.* **1978**, *86*, 245. Adamson, A. W. "Physical Chemistry of Surfaces"; Wiley: New York, 1976.

(16) Ashcroft, S. J.; Mortimer, C. T. *J. Chem. Soc. A* **1967**, 930.

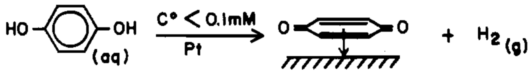
(17) Garwood, G. A.; Hubbard, A. T. *Surf. Sci.* **1980**, *92*, 617. Lane, R. F.; Hubbard, A. T. *J. Phys. Chem.* **1975**, *79*, 808.

electrolytic charge (Q_{ad}) upon adsorption. From Q_{ad}, the number of electrons (n_{ad}) transferred upon surface coordination (referenced to that for HI) are determined from Faraday's law; for example

$$n_{ad}(\mathrm{HQ}) \equiv \frac{n'_{ad}(\mathrm{HQ})}{n'_{ad}(\mathrm{HI})} = \frac{Q_{ad}(\mathrm{HQ})/[AF\Gamma(\mathrm{HQ})]}{Q_{ad}(\mathrm{HI})/[AF\Gamma(\mathrm{HI})]}$$

Oxidation n_{ad} values were obtained for HQ and pyrocatechol (CAT): $n_{ad}(\eta^6\text{-HQ}) = 2.0 \pm 0.2$; $n_{ad}(\eta^2\text{-HQ}) = 1.5 \pm 0.2$; $n_{ad}(\eta^6\text{-CAT}) = 2.1 \pm 0.2$; $n_{ad}(\eta^2\text{-CAT}) = 1.6 \pm 0.2$. Experiments with BQ itself indicated no appreciable adsorption redox processes (a negative result, however, does not preclude intramolecular redox rearrangements which are not detectable electrochemically).

By analogy with the oxidative adsorption of HI to form adsorbed I atoms,[17] adsorption of HQ *from dilute solutions* is probably accompanied by spontaneous oxidation to give η^6 surface-coordinated BQ molecules and hydrogen gas:



(9)

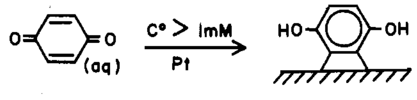
Electrochemical oxidation of the H_2 byproduct makes possible the measurement of Q_{ad}. This adsorption reaction implies that $E°$ for the BQ/HQ redox couple *in the η^6-adsorbed state* is shifted to less positive potentials relative to that in solution and explains why the adsorbed intermediate reacts differently from the unadsorbed material; changes in ligand reactivity upon coordination are discussed in greater detail in the succeeding paper. The shift in $E°$ upon surface attachment is a measure of the ratio of the (full coverage) formation constants (K_f) for adsorbed BQ and HQ:

$$RT \ln \frac{K_f(\eta^6\text{-BQ})}{K_f(\eta^6\text{-HQ})} = nF\Delta E° = nF[E° - E°(\eta^6)] \quad (10)$$

Equation 10, which is derived from the thermodynamic cycle of BQ/HQ adsorption and interconversion, assumes that the same reversible two-electron redox occurs in the adsorbed state as it does in the dissolved state. In 1 M H^+, $E° = 0.46$ V (vs. AgCl)[2a,18] but the search for $E°(\eta^6)$ was complicated by hydrogenation processes below 0.0 V. The rapid shift in equilibrium or "rest" potential from ~0.40 to ~0.0 V upon HQ adsorption[2d] suggested $\Delta E° \approx 400$ mV. However, conclusions concerning the nature of the electrode reactions were not possible. It may simply be mentioned that, for $n = 1$, a $\Delta E°$ value of 400 mV would correspond to $K_f(\eta^6\text{-BQ})/K_f(\eta^6\text{-HQ}) \approx 10^{28}$.

The preference of Pt metal, a good electron donor,[13] for quinonoid over benzenoid ligands is almost certainly related to the excellent π-acceptor properties of quinones.[14a,18] The same preference is exhibited by zerovalent Pt complexes such as $Pt(PPh_3)_3$, which is inert toward benzene but reactive toward BQ, forming a stable $Pt(PPh_3)_2BQ$ complex; also, when the latter is reacted with gaseous HCl in benzene solution, *HQ*, not BQ, is liberated.[14a] The same behavior is shown by $Fe(CO)_3DQ$ (DQ = duroquinone), which releases durohydroquinone (DHQ) upon acidification.[19] The measured σ for HQ adsorbed at $C° \geq 1$ mM correlates with a completely vertical 2,3-η^2 orientation; hence, metal–olefin π-bonding is precluded since such a type of coordination would give σ_{exptl} identical with $\sigma(\eta^6\text{-HQ})$. Rehybridization of two adjacent carbons, such as in the zerovalent Pt complex with $C_6(CF_3)_6$,[20] is likewise negated because tilted (nearly flat) orientations would have been indicated. Dehydrogenation at and surface attachment through the 2,3-carbons remain the most logical bonding representation. A suitable model for this type of interaction is provided by *o*-phenylene-bridged binuclear complexes[14b] such as shown in Figure 8. Double dehydrogenation is indicated by $n_{ad}(\eta^2\text{-HQ}) \approx 2$. The IR spectrum of η^2-HQ is also consistent with 2,3-di-σ-bonding: the relative intensity of the C–H (3030 cm^{-1}) peak is much higher in bulk than in η^2-HQ, which suggests a lesser number of C–H bonds in the latter. The bridging model in the edge orientation may help explain why Γ transitions observed at atomically smooth surfaces are suppressed at roughened surfaces.[21]

The identity of the IR spectra for η^2-HQ and η^2-BQ[12] and the absence of electrochemically detectable redox processes during BQ adsorption provide evidence that adsorption of BQ *from concentrated solutions* actually yields di-σ-bonded HQ; the reaction may involve Pt-catalyzed H atom transfers:



(11)

Aromatic C–H activation by transition metals has been reported to involve η^2-arene precoordination.[22] By analogy, it is possible for the dehydrogenation reaction to proceed via an $\eta^2(\pi)$-quinone preadsorption state. No redox is detected because the hydrogens produced from double dehydrogenation are consumed by the (adsorbed) quinone-to-diphenol reduction.

In contrast to $\eta^6(\pi)$-attachment, di-σ-bonding renders surface coordination of HQ more stable than that of BQ; that is $E°(\eta^2) > E°$ and $K_f(\eta^2\text{-HQ}) \gg K_f(\eta^2\text{-BQ})$ ($E°(\eta^2)$ determinations were complicated by *irreversible* oxidation[2g,h] of adsorbed material above 0.70 V). Retention of the aromatic (diphenolic) functionality in di-σ-attachment, but not in η^6-coordination, correlates with the fact that while σ-bonded aryl–Pt compounds abound, no η^6-(π)-bonded arene–Pt complexes have been isolated and characterized;[23] the kinetic stability of aryl–Pt complexes is well-known.[23]

Mechanistic differences between HQ/BQ adsorption at $C° \leq 0.1$ mM (eq 9) and that at $C° \geq 1$ mM (eq 11) is evidenced by the data in Figure 7, which show that complete formation of η^2-HQ is severely retarded when the Pt surface is purposely pretreated with a layer of η^6-HQ. This retardation occurs because η^2-surface coordination apparently involves double dehydrogenation, but dehydrogenation does not proceed as readily on precoated surfaces as it does on clean Pt.[3] It is possible for η^2-HQ adsorption to occur directly by dehydrogenation of the HQ ring, but such a mechanism would not account for the observation that η^2-adsorption of *o*- and *p*-diphenols is invariably through an *unhindered edge which contains a quinone double bond*;[2b] in view of the latter, it appears that an $\eta^2(\pi)$-quinone precoordination step is involved. In 2,5-DMHQ, the (quinone) edges are hindered by a CH_3 group, and adsorption at all concentrations proceeds by formation of η^6-oriented species as an intermediate step. The bonding in 2,3-η^2-2,5-DMHQ is difficult to model; some Pt–CH_3 interaction might be expected because of the close proximity of a methyl group to the surface. Pt–alkane interactions, however, are weak as evidenced by the fact that saturated hydrocarbons are not chemisorbed on Pt under ambient conditions.[2g] Also, η^2-adsorption of the 2,3-DMHQ isomer appears to be facilitated considerably by placement of the two CH_3 groups along only one edge (Figure 4); that the *non-methylated* (5,6) edge is closest to the surface is further indicated by the fact that durohydroquinone, with both quinone edges blocked by two CH_3 groups, does not show any

---

[18] Fieser, L. F.; Fieser, M. "Organic Chemistry"; D. C. Heath: Boston, 1956; Chapter 30. Chambers, J. Q. In "The Chemistry of Quinonoid Compounds"; Patai, S., Ed.; Wiley: New York, 1974; Vol. 1, Chapter 14.

[19] Foster, R.; Foreman, M. I. In "The Chemistry of Quinonoid Compounds"; Patai, S., Ed.; Wiley: New York, 1974; Vol. 1, Chapter 6.

[20] Browning, J.; Green, M.; Spencer, J.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1974**, 97.

[21] White, J. H.; Soriaga, M. P.; Hubbard, A. T. *J. Electroanal. Chem. Interfacial Electrochem.*, in press.

[22] Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1982**, *104*, 4240. Sweet, R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 305. Parshall, G. W. *Catalysis (London)* **1977**, *1*, 335. Muetterties, E. L.; Bleeke, J. R. *Acc. Chem. Res.* **1979**, *12*, 325.

[23] Hartley, F. R. "The Chemistry of Platinum and Palladium"; Applied Science Publishers: London, 1973.

tendency toward reorientation. The differences in the adsorption/orientation characteristics of these and other alkyl-substituted diphenols[2c,d,f] may also be used to argue against preferential η^1 (C–Pt or O–Pt) bonding in the vertical orientation. For example, if η^1 C–Pt bonding occurred, HQ and the various methylated derivatives would have displayed essentially identical adsorption isotherms; O–Pt attachment would have allowed DHQ reorientation. O–Pt bonding is further contraindicated by the observation that the adsorbabilities of cyclic alcohols and ketones decreased in the series HQ ≫ 1,4-cyclohexanediol > 1,4-cyclohexanedione ≫ cyclohexane.[2a]

The measured σ for CAT (Table II) indicates that this compound adopts two orientations: η^6 below 0.1 mM (π-bonding through the quinone ring) and 3,4-η^2 above 2 mM (di-σ-bonding through an edge that contains a double bond in the *o*-quinone form). This result is quite unexpected because, in transition-metal complexes, *o*-diphenols or σ-quinones are invariably chelated through both oxygens;[24] in particular, coordination of *o*-quinone to $Pt(PPh_3)_3$ is in the *catecholate* form, with concomitant oxidation of the zerovalent Pt to Pt(II).[14a] The difference in mode of CAT binding at Pt surfaces and in transition-metal complexes arises probably because stable catecholate coordination involves not only double deprotonation of CAT but also the existence of positively charged Pt, requirements that may not be readily fulfilled on metal surfaces in acid media; direct interaction of Pt with –OH is possible, but as already mentioned, it is considerably weaker than that of Pt with the aromatic/quinonoid ring.[2a]

The description of the effect of temperature[2f] on the oriented adsorption of simple diphenols in terms of classical cooperative-adsorption phenomena[25] may be extended to include metal–adsorbate bonding considerations. For example, by analogy with molecular species,[23] the stability of di-σ-bonded HQ probably includes a large kinetic component. Hence, an increase in temperature would be expected to facilitate η^2-HQ desorption. On the other hand, the stability of η^6-EQ is mainly thermodynamic, and no dramatic desorption would be expected from a moderate increase in temperature; but, because of enhanced adsorbate mobilities, an increase in temperature may in fact lead to better η^6-packing efficiency. These expectations are borne out by the data shown in Figure 6. Since $\Gamma(\eta^2)$ does not tend to zero but approaches the value for $\Gamma(\eta^6)$, it is possible to envisage the η^6 and η^2 orientational states in terms of two potential-energy wells with depths decreasing as $\eta^6 > \eta^2$ and separated by an energy barrier. Apparently, at $T > 65$ °C, the di-σ-attached species acquire sufficient energy to overcome the activation barrier and spill over into the thermodynamically more stable η^6-adsorbed state. The activated complex is probably characterized by librational motions of exceedingly large amplitudes. The barrier for the reverse ($\eta^6 \rightarrow \eta^2$) reaction is reflected by the retardation effects when the surface is pretreated with η^6-coordinated intermediates (Figure 7). Construction of the double-potential well is not trivial since it must account for the fact that exposure of *clean* Pt surfaces to *concentrated* HQ solution allows direct η^2-adsorption without apparent regard for the η^6-potential well; this high-concentration effect is phenomenologically attributed to intermolecular attractions ($\alpha(\eta^2) > 0$).

Modification of the diphenolic/quinonoid ring such as by insertion of heteroatoms or addition of surface-active or electronegative substituents alters its surface coordination properties to varying degrees.[2a,d] For example, in neutral solutions, pyridine-type compounds are preferentially attached through the nitrogen heteroatom. Thiophenol derivatives are invariably bound through the –SH group and are characterized by reversible electroactivity of the *pendant* HQ moiety.[2c,d] Fluorination of the phenyl ring has been shown to decrease its adsorbability.[2g] Thus, the unique behavior of TFHQ is attributable to surface attachment through an –OH group; the comparative weakness of the metal–OH bond is reflected by lower than saturation coverages below 3 mM. Experiments with tetrafluorobenzoquinone (TFBQ) showed even lower coverages,[2a] which, by analogy with cyclohexanediol and cyclohexanedione,[2a] indicated coordination through the quinone oxygens. This is one instance in which the packing density of a quinone is different from that of the corresponding diphenol. Coordination of tetrachlorobenzoquinone (TCBQ) to $Pt(PPh_3)_3$ involves abstraction of a Cl atom with subsequent metal–organic group binding through the dechlorinated carbon and Cl attachment to the metal center.[14a] Studies with TCBQ were not possible here because of its poor solubility, but results with the fluorinated analogues do not suggest halide abstraction. Halide elimination may occur with the heavier halides, as was noted for ethyl iodide;[2g] in the latter case, however, iodine atoms were the predominant adsorbed species.

Analysis of adsorption/orientation data for the compounds shown in Figure 1 allows the formulation of the following strength-of-chemisorption series for the various functional groups investigated: –SH > hetero N > quinone/diphenol ring > C=C ≥ benzene ring > amine N (pH >7) > –OH > (>C=O) > perfluorinated ring (diphenol > quinone > benzene) > alkyl. While the pyridine derivatives were displaced by dilute aqueous iodide, the thiophenol compounds were not.[2b] Preference of Pt metal for the diphenolic/quinonoid over the benzenoid ring, similar to that of $Pt(PPh_3)_3$,[14a] was demonstrated here in studies with η^2-NHQ and η^2-phenylhydroquinone, which indicated attachment through the HQ moiety;[2c,d] perhaps C–H activation by Pt is a more facile process for quinone/diphenol then for simple arene systems. Adsorption of allylhydroquinone and allylpyrocatechol showed a greater tendency for binding through the diphenol rather than the allyl moiety,[2c,d] although it may be mentioned that, in Pt(II)–styrene complexes, styrene is coordinated solely through the ethylenic double bond.[14g] In acid solutions, the amine group is unreactive toward Pt, but studies with dopamine-type compounds in neutral solutions showed that adsorption through the aromatic/quinonoid ring is favored over the nonprotonated nitrogen.[2a–d] This mode of coordination is different from that in tetrakis(benzylamine)platinum(II)[26] and arises almost certainly from the absence of π-back-bonding with the amine nitrogen; metal-to-ligand back-donation is requisite for stable coordination to zerovalent metals.[23]

Saturated hydrocarbons such as pentane and cyclohexane do not chemisorb on Pt, even from neat solutions, at room temperature.[2g] The adsorption isotherms for DMHQ and DHA also indicate a weak affinity for alkyl substituents. However, when an electrode pretreated with DHQ was exposed to dilute HI, DHQ reorientation from η^6 to 2,3-η^2 was observed.[2b] (The ability of coadsorbed iodine to enforce adsorbed molecule reorientations from strongly to comparatively weakly bound structures has also been noted on well-defined surfaces in UHV, such as the reorientation of dimethyl sulfoxide on Pt(111) from S to O attachment.[27]) Direct alkyl–Pt interaction appears more likely than double demethylation, with the bonding probably similar to that shown in Figure 8 for a benzoplatinacyclopentene organometallic complex reported recently.[14c]

The decrease in Γ for DHPdz at 65 °C has been attributed to fluxional motion afforded by the presence of two *equivalent* nitrogens; in terms of space-filling models, the fluxional molecule resembles a rigid 1,2-η^2-oriented species ($\sigma_{exptl} = 28.2$ Å^2; $\sigma_{calcd} = 28.6$ Å^2).[2f] The fluxionality of pyridazine itself has been ob-

---

(24) Pierpont, C. G.; Buchanan, R. M. *Coord. Chem. Rev.* **1981**, *18*, 45.

(25) Langmuir, I. *J. Chem. Phys.* **1933**, *1*, 756. Hedge, D. G. *J. Colloid Interface Sci.* **1957**, *12*, 417. Mittelman, R.; Palmer, R. C. *Trans. Faraday Soc.* **1942**, *38*, 506. Smith, T. *J. Colloid Interface Sci.* **1967**, *23*, 27.

(26) Mellor, J. W. "A Comprehensive Treatise on Inorganic and Theoretical Chemistry"; Longmans, Green and Co.: London, 1937; Vol. XVI.

(27) Katekaru, J. Y.; Garwood, G. A.; Hershberger, J. F.; Hubbard, A. T. *Surf. Sci.* **1982**, *121*, 396.

served above 50 °C in the molecular complex *cis*-$[PtCl(PEt_3)_2(Pdz)][BF_4]$.[14e] The present result is quite remarkable: (i) It is evident that fluxionality of coordinated ligands transpires not only in molecular species but also in surface compounds. (ii) It illustrates a unique case in which a dynamic (fluxional) process is detected by a static (packing density) measurement; this is possible because the fluxional motion occurs at the expense of *close-packing* efficiency, and the decrease in efficiency is readily apparent from measurements of Γ.

Acknowledgment is made to the donors of the Petroleum Research fund, administered by the American Chemical Society, and to the Air Force Office of Scientific Research for support of this research.

Registry No. HQ, 123-31-9; BQ, 106-51-4; CAT, 120-80-9; 2,3-DMHQ, 608-43-5; 2,5-DMHQ, 615-90-7; DHQ, 527-18-4; TFHQ, 527-21-9; DHPy, 16867-04-2; DHPdz, 123-33-1; DHBM, 81753-11-9; THB, 4371-32-8; 2,6-AQDS, 84-50-4; DHT, 2889-61-4; NHQ, 571-60-8; Pt, 7440-06-4.

Contribution from the Department of Chemistry,
University of California, Santa Barbara, California 93106

Surface Coordination Chemistry of Platinum Studied by Thin-Layer Electrodes.[1] Surface Chemical Reactivity of Aromatic and Quinonoid Compounds Adsorbed in Specific Orientational States

MANUEL P. SORIAGA,* JAMES H. WHITE, DIAN SONG, VICTOR K. F. CHIA, PETER O. ARRHENIUS, and ARTHUR T. HUBBARD*

Received March 12, 1984

The surface chemical reactivity of aromatic and quinonoid compounds chemisorbed at smooth polycrystalline Pt surfaces in specific coordination or orientational states has been investigated, primarily by thin-layer electrochemical and gas chromatographic techniques. Five reactions were studied as functions of mode of coordination, temperature, and surface (electrode) potential: (i) reversible electrochemical reactivity in adsorbed and free states; (ii) electrocatalytic oxidation of compounds exhibiting multiple orientational states; (iii) electrocatalytic hydrogenation of hydroquinone and S-attached thiophenol derivatives; (iv) exchange reactions between adsorbates; (v) substitution reactions between halides and aromatics. Reversible electroactivity in the adsorbed state was vastly different from that in the free state when the electroactive center was directly coordinated to the surface. The extent of catalytic oxidation or hydrogenation proved to be a sensitive function of initial orientation. Ring carbons close to the Pt surface underwent more drastic oxidation/hydrogenation than those further away. Hydrodesulfurization efficiency was influenced by the nature of the substituent directly linked to the –SH anchor. Ring hydrogenation that accompanied desulfurization was energetically favorable, but kinetically hindered. Ligand exchange/coadsorption reactions were functions of initial adsorbate orientation and concentration of species in solution. Appreciable exchange was noted only between molecules in η^2-oriented layers and concentrated solutions. The influence of halides in ligand/coadsorption reactions decreased in the order $I^- \gg Br^- > Cl^- \gg F^-$. Simple aromatics were displayed virtually quantitatively by I^-. Alkyl substituents on the aromatic/quinonoid ring rendered it less labile, but its flat-adsorbed states underwent reorientation upon coadsorption of iodine.

Introduction

Studies described in the preceding article[1] have demonstrated spontaneous and irreversible adsorption of a variety of aromatic and quinonoid compounds at smooth polycrystalline Pt surfaces in specific orientational (coordination) states. The nature of these states has hitherto not been recognized because they emerge under conditions[2] neglected by previous investigations. For example, earlier studies of benzene adsorption at well-defined Pt single crystals in ultrahigh vacuum (UHV) employed sample pressures near 10^{-6} torr, at which only $\eta^6(\pi)$-bonded intermediates are to be expected.[3] The partial pressure corresponding to concentrations at which flat-to-vertical orientational transitions were observed for species adsorbed from aqueous solutions is about 20 torr.[21] Prolonged and/or comparatively higher sample dosages were reported to induce reorientation of benzene adsorbed on Pt(111) and Pt(100).[4]

In the present article, surface chemical reactivities of selected diphenolic and quinonoid compounds[2] are described. Five reactions have been investigated with respect to mode of attachment, temperature, and electrode potential: (i) reversible electrochemical reactivity of the adsorbed state compared with that of the free state; (ii) electrocatalytic oxidation of compounds exhibiting multiple orientational states; (iii) electrocatalytic hydrogenation of hydroquinone and S-attached thiophenol derivatives; (iv) exchange reactions between nonidentical aromatic adsorbates; (v) substitution reactions between aromatics and halides. A few other studies of reactions of simple aromatics adsorbed on atomically flat or stepped Pt surfaces have been reported[6] but only under conditions where mainly flat-adsorbed intermediates are present.[2]

Experimental Section

Experiments were based primarily on thin-layer voltammetry and coulometry.[5] Thin-layer electrodes (TLE) employed in this work have been described, and their performance in surface chemical studies has been described.[1] The aqueous solutions contained molar perchloric or sulfuric acid supporting electrolyte. Product identification utilized gas chromatographic techniques.

Electrochemical Reactivity of Adsorbed Intermediates. The subject compounds display reversible two-electron quinone/diphenol reactivity

---

(1) Soriaga, M. P.; Binamira-Soriaga, E.; Hubbard, A. T.; Benziger, J. B.; Pang, K.-W. P. *Inorg. Chem.*, preceding paper in this issue.

(2) For parts a–q see ref 2 of the preceding paper in this issue.

(3) Fischer, T. E.; Kelemen, S. R.; Bonzel, H. P. *Surf. Sci.* **1977**, *64*, 157. Richardson, N. V.; Palmer, N. R. *Surf. Sci.* **1982**, *114*, L1. Netzer, F. P.; Matthew, J. A. D. *Solid State Commun.* **1979**, *29*, 209. Lehwald, S.; Ibach, H.; Demuth, J. E. *Surf. Sci.* **1978**, *78*, 577. Gavezzotti, A.; Simonetta, M. *Surf. Sci.* **1982**, *116*, L207.

(4) Gland, J. L.; Somorjai, G. A. *Adv. Colloid Interface Sci.* **1976**, *5*, 205. Stair, P. C.; Somorjai, G. A. *J. Chem. Phys.* **1977**, *67*, 4361.

(5) Hubbard, A. T. *CRC Crit. Rev. Anal. Chem.* **1973**, *3*, 201.

(6) (a) Tsai, M.-C.; Muetterties, E. L. *J. Am. Chem. Soc.* **1982**, *104*, 2534. (b) Tsai, M.-C.; Muetterties, E. L. *J. Phys. Chem.* **1982**, *86*, 5067. (c) Surman, M.; Bare, S. R.; Hofmann, P.; King, D. A. *Surf. Soc.* **1983**, *126*, 349.

0020-1669/85/1324-0073$01.50/0