sistent with the N-η^1 orientation of pyrazine adsorbed on Ni.[2m] In addition to the spectroscopic data obtained in ultra-high vacuum, in situ laser Raman spectroscopy of pyridine adsorbed on roughened Cu, Ag, and Au electrodes in aqueous solution has been interpreted by some workers in terms of N-η^1 oriented pyridine molecules located at or near the electrode surface;[31] benzene does not adsorb on Cu or Ag to an appreciable extent.[2n] The above findings are not in disagreement with those of the present study. In fact, the degree to which these findings correlate is striking in view of the widely differing conditions employed.

Conclusions

The results of this study enable the formulation of certain rules regarding the orientation of adsorbed aromatic molecules. Perhaps these rules will serve as a summary of our findings and a target for future investigations.

Under the conditions of the present experiments: (i) Homocyclic aromatic ring systems are parallel to the surface, except as noted below. (ii) Chemisorbable functional groups tend to interfere with interaction of the homoaromatic framework with the surface. (iii) Bulky or electronegative substituents situated in four adjacent positions on the homoaromatic framework decrease the stability of the parallel orientation relative to other orientations. (iv) Inert electronegative substituents decrease the tendency of the homoaromatic framework to adsorb. (v) Inert flexible substituent chains of moderate length are situated as far from the metal surface as permitted by the chemisorbed functional groups. (vi) Nitrogen heteroaromatic rings (such as pyridine) are N-bonded perpendicularly to the surface, unless the N atom has been protonated or otherwise modified. (vii) Quinones adsorb in a way identical with their dihydroxyaromatic counterparts.

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Registry No. 1, 128-31-9; **2**, 106-51-4; **3**, 120-80-9; **4**, 95-71-6; **5**, 452-86-8; **6**, 1948-33-0; **7**, 98-29-3; **8**, 139-85-5; **9**, 1194-98-5; **10**, 608-43-5; **11**, 615-90-7; **12**, 150-78-7; **13**, 700-13-0; **14**, 527-18-4; **15**, 771-63-1; **16**, 87-87-6; **17**, 527-21-9; **18**, 87-66-1; **19**, 533-73-3; **20**, 636-32-8; **21**, 615-94-1; **22**, 608-80-0; **23**, 319-89-1; **24**, 527-31-1; **25**, 16867-04-2; **26**, 123-33-1; **27**, 5721-21-1; **28**, 1126-61-0; **29**, 81255-51-8; **30**, 1079-21-6; **31**, 21581-41-9; **32**, 81255-52-9; **33**, 81255-55-2; **34**, 41241-39-8; **35**, 571-60-8; **36**, 130-15-4; **37**, 574-00-5; **38**, 853-35-0; **39**, 853-68-9; **40**, 526-86-3; stearic acid, 57-11-4; 4-octadecylphenol, 2589-79-9; 4-octadecylresorcinol, 21093-23-2; 4-octadecyl-1,3,5-trihydroxybenzene, 81255-56-3; benzene, 71-43-2; toluene, 108-88-3; 1,3,5-trimethylbenzene, 108-67-8; pyridine, 110-86-1; Pt, 7440-06-4.

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Determination of the Orientation of Aromatic Molecules Adsorbed on Platinum Electrodes:[1] The Influence of Iodide, a Surface-Active Anion

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Abstract: Accurate measurements of the limiting coverages of species adsorbed on smooth platinum electrodes from solutions of aromatic compounds and iodide are reported. Comparison of the measurements with calculations describing various possible orientations of the adsorbed aromatic molecules defines the changes in orientation that occur as a result of coadsorption of iodide. Experimental data were obtained by electrochemical methods based upon the use of thin-layer electrodes, and calculations were based upon covalent and van der Waals radii tabulated by Pauling as described in the preceding article. A total of 28 compounds representing a variety of structures and chemical properties were included in this study: simple diphenols; alkyldiphenols; polyhydroxybenzenes and -quinones; halogenated diphenols; N-heteroaromatics; diphenols having surface-active side chains; polycyclic phenols and quinones; and a dihydroxythiophenol. The orientations prior to and following exposure to iodide solution were determined for each adsorbed compound.

Introduction

A method to determine the orientation of a molecule adsorbed on a smooth solid surface in solution has been described and employed to determine the orientations of 40 aromatic compounds adsorbed at smooth polycrystalline platinum electrodes in aqueous solution.[1] Experiments leading to selection of aqueous perchlorate as the supporting electrolyte for studies in the preceding article[1] revealed that orientation depends upon the identity of the electrolyte anion, a discovery that prompted the present study, an investigation of the interaction of oriented adsorbed aromatic molecules with iodide, a surface-active anion.

Interaction of iodide with clean platinum has been studied at polycrystalline and well-defined single-crystal surfaces in solution and in ultra-high vacuum.[2-4] Briefly, adsorption of aqueous or gaseous hydrogen iodide is dissociative, forming hydrogen gas and adsorbed iodine atoms:

$$\mathrm{HI} \xrightarrow{\text{Pt surface}} \mathrm{I\ (adsorbed)} + {}^{1}/_{2}\mathrm{H_2} \qquad (1)$$

Adsorption from vacuum produces a highly ordered layer (superlattice) of I atoms.[4] Maximum coverage from solution is the

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same as from vacuum ($\sigma_I = 14.1$ Å^2), which corresponds to one I atom per two surface Pt atoms.

Measurement of Adsorbed Iodine and Aromatics

Thin-layer electrochemical methodology for determination of the orientation of adsorbed aromatic molecules is described in the preceding article.[1] The thin-layer electrode has been described[5] and reviewed.[6,7] Only aspects unique to the present study will be included here.

Exposure of a Pt electrode to iodide–aromatic mixtures or treatment of an aromatic adsorbed layer with iodide solution led to adsorbed I atoms, adsorbed aromatics, and a solution containing aromatic molecules and I^- ions. As before, the amount of dissolved hydrocarbon was determined by thin-layer potential step coulometry and the adsorbed amount calculated by difference.[1] When electrolysis of iodide and hydrocarbon overlapped slightly, graphical integration of thin-layer linear scan voltammograms was employed; systems for which overlap was substantial were not pursued. Hydrocarbons desorbed by iodide exposure were also determined as above. Adsorbed I atoms were determined[2] as follows: the surface was rinsed with pure electrolyte to remove dissolved I^-; electrolytic oxidation at 1.2 V (vs. AgCl reference) converted adsorbed I to IO_3^- ions, which were determined by coulometric reduction at 0.7 V (eq 2). Γ_I was found from eq 3.

$$I_{ads} + 3H_2O \rightleftharpoons IO_3^- + 6H^+ + 5e^- \qquad (2)$$

$$\Gamma_I = (Q - Q_b)_{IO_3^-}/5FA \qquad (3)$$

Details of this procedure appeared previously.[2]

Experimental Section

Preparation of electrodes, electrolytes, and reagents is described in the preceding article.[1] Iodide solutions were prepared from analytical reagent grade sodium iodide (Mallinckrodt).

Results

When an adsorbed layer of aromatic molecules on a platinum thin-layer electrode is exposed to 5×10^{-4} M I^- in aqueous perchlorate media, two changes are directly observable: (a) adsorbed aromatic molecules are desorbed from the surface into the solution layer; (b) iodide is transferred from the solution to the surface.

Thin-layer current–potential curves illustrating this behavior appear in Figure 1. For instance, the solid curve in 1A was obtained after adding a single aliquot of I^- solution to a thin-layer electrode containing only a chemisorbed layer of 1,4-naphthohydroquinone (**24**), which is known to be flat[1] on the surface with ten equidistant carbons (the η^{10} orientation).[8] The peak at 0.20 V (vs. an AgCl reference electrode prepared with 1 M NaCl) is due to 1,4-napthohydroquinone displaced from the surface by the iodide treatment, and the peak at 0.46 V results from the excess dissolved iodide. The sharp peak near 1 V results from oxidation of dissolved iodine, and the broad peak above 1.1 V is due to oxidation of chemisorbed aromatic compound and chemisorbed I atoms. Reversal of the scan direction at 1.2 V leads to a peak at 0.78 V due to reduction of IO_3^- to I_2; this current is used for determination of adsorbed I as IO_3^-. Shown for comparison in Figure 1B are current–potential curves, for 1,4-naphthohydroquinone present in chemisorbed form only (dot–dashed curve) and in dissolved as well as chemisorbed forms (solid curve); the dotted curve is for the clean surface. Dissolved and chemisorbed forms of iodide and the aromatic compound are thus readily identifiable. Dissolved halogen is rinsed away prior to determination of adsorbed I atoms. Results of this type, Figure 1, were obtained for all 28 compounds studied. The results are summarized in Table I. Adsorption data are expressed in terms of Γ, the interfacial concentration (mol cm^{-2}), and σ, the average area (Å^2) occupied by a molecule in the adsorbed layer.

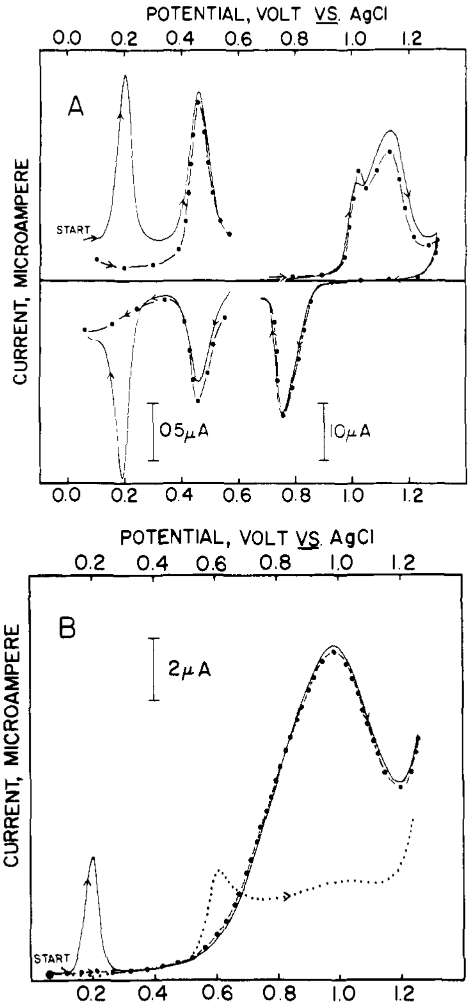

Figure 1. Current–potential curves for 1,4-naphthohydroquinone and iodide in 1 M $HClO_4$ at a Pt thin-layer electrode: (A) chemisorbed 1,4-naphthohydroquinone in a single aliquot of I^- solution (—), clean Pt electrode in a single aliquot of I solution (-··-); (B) electrode containing 1,4-naphthohydroquinone chemisorbed and in solution (—), chemisorbed 1,4-naphthohydroquinone only (-·-), clean Pt electrode in 1 M $HClO_4$ (···). Experimental conditions: 10^{-4} M naphthohydroquinone in 1 M $HClO_4$, 5×10^{-4} M NaI in 1 M $HClO_4$; thin-layer electrode volume, *V*, 4.08 μL; electrode area, 1.18 cm^2; potential scan rate, *r*, 2 mV/s; temperature, 296 ± 1 K.

Adsorption of I^- into the aromatic surface layer has at least four possible causes: (i) displacement of aromatic molecules from the surface (desorption); (ii) reorientation of aromatic molecules to a more compact arrangement; (iii) irreversible reactions of iodide with the adsorbed hydrocarbon species; (iv) insertion of iodide into voids of the hydrocarbon layer.

Figure 1 and Table I indicate that *the amount of aromatic displaced*, ΔΓ, is substantial and that displacement, i, accounts for at least part of the iodide uptake for almost all compounds studied. However, comparison of columns 3 and 4 of Table I reveals that *iodide uptake*, Γ_I, does not correlate solely with the amount of hydrocarbon displaced, ΔΓ, testifying to participation by factors such as ii–iv. Voltammetric data of the type illustrated by Figure 1, obtained for all compounds, indicate that the material released into the solution by displacement has identical voltammetric properties and therefore the same skeletal structure as the starting material, with the exception of **9**. *Adsorption of these aromatic compounds on platinum and subsequent displacement by iodide solution generally does not involve a chemical reaction between the iodide and the adsorbed aromatic.* Possibility iii is therefore eliminated. 1,4-Dimethoxybenzene (**9**), although adsorbed intact,[1] undergoes stepwise demethylation during desorption, forming a mixture of hydroquinone, 4-methoxyphenol, and

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Table I. List of Compounds and Adsorption Data[a]

compound	Γ, nmol cm^{-2}	σ_i, Å^2	$\Delta\Gamma$, nmol cm^{-2}	Γ_I, nmol cm^{-2}	σ_f, Å^2
1, hydroquinone	0.322 ± 0.007	51.6 ± 1.4	0.169 ± 0.016	0.630 ± 0.005	50.2 ± 2.4
pH 3	0.322 ± 0.007	51.6 ± 1.4	0.052 ± 0.002	0.449 ± 0.005	38.1 ± 2.1
pH 7	0.322 ± 0.007	51.6 ± 1.4	0.009 ± 0.002	0.388 ± 0.005	35.3 ± 2.1
2, pyrocatechol	0.296 ± 0.007	55.8 ± 1.4	0.207 ± 0.005	0.832 ± 0.010	54.4 ± 2.1
pH 3	0.296 ± 0.007	55.8 ± 1.4	0.099 ± 0.005	0.604 ± 0.010	41.0 ± 2.1
pH 7	0.296 ± 0.007	55.8 ± 1.4	0.033 ± 0.010	0.538 ± 0.010	33.9 ± 2.1
3, methylhydroquinone	0.258 ± 0.005	64.3 ± 1.4	0.047 ± 0.005	0.590 ± 0.010	38.9 ± 2.1
pH 7	0.258 ± 0.005	64.3 ± 1.4	0.005 ± 0.002	0.461 ± 0.010	39.6 ± 2.1
4, 4-methylpyrocatechol	0.258 ± 0.007	64.3 ± 2.1	0.056 ± 0.005	0.649 ± 0.009	36.7 ± 2.4
pH 7	0.258 ± 0.007	64.3 ± 2.1	0.009 ± 0.002	0.533 ± 0.009	36.7 ± 2.4
5, *tert*-butylhydroquinone	0.226 ± 0.007	73.5 ± 2.1	0.028 ± 0.002	0.538 ± 0.012	45.2 ± 2.8
pH 7	0.226 ± 0.007	73.5 ± 2.1	0.007 ± 0.002	0.470 ± 0.003	45.2 ± 2.8
6, 4-*tert*-butylpyrocatechol	0.226 ± 0.007	73.5 ± 2.1	0.059 ± 0.005	0.693 ± 0.012	41.0 ± 2.8
pH 7	0.226 ± 0.007	73.5 ± 2.1	0.019 ± 0.002	0.592 ± 0.014	39.6 ± 2.8
7, 2,5-dimethylhydroquinone	0.237 ± 0.009	69.9 ± 2.8	0.026 ± 0.002	0.620 ± 0.014	36.7 ± 2.8
8, 2,3-dimethylhydroquinone	0.320 ± 0.005	52.3 ± 1.4	0.045 ± 0.002	0.418 ± 0.005	38.9 ± 1.4
9, 1,4-dimethoxybenzene	0.221 ± 0.009	74.9 ± 2.8	0.139 ± 0.014	0.740 ± 0.004	70.6 ± 3.0
10, durohvdroquinone	0.207 ± 0.005	80.5 ± 2.1	0.028 ± 0.002	0.728 ± 0.016	35.3 ± 2.1
11, tetrafluorohydroquinone	0.148 ± 0.005	112.3 ± 3.5	0.009 ± 0.002	0.921 ± 0.020	26.1 ± 1.4
12, tetrachlorohydroquinone	0.150 ± 0.005	110.2 ± 3.5	<0.002	0.853 ± 0.019	30.4 ± 1.4
13, 1,2,4-benzenetriol	0.268 ± 0.007	62.2 ± 2.1	0.193 ± 0.007	0.815 ± 0.019	67.8 ± 2.1
14, hexahdroxybenzene	0.235 ± 0.005	70.6 ± 1.4	0.167 ± 0.005	0.806 ± 0.014	76.3 ± 2.1
15, tetrahydroxybenzoquinone	0.242 ± 0.005	68.5 ± 1.4	0.150 ± 0.005	0.731 ± 0.009	68.5 ± 2.1
16, 2,3-dihydroxypyridine	0.452 ± 0.014	38.9 ± 1.4	0.157 ± 0.005	0.646 ± 0.009	27.5 ± 1.4
pH 7	0.592 ± 0.012	28.3 ± 0.7	0.117 ± 0.002	0.449 ± 0.012	21.9 ± 1.4
17, 3,6-dihydroxypyridazine, pH 7	0.672 ± 0.014	24.7 ± 0.7	0.484 ± 0.007	0.860 ± 0.012	25.4 ± 1.4
18, allylhydroquinone	0.336 ± 0.005	49.5 ± 0.7	<0.002	0.395 ± 0.006	32.5 ± 2.1
19, 4-allylpyrocatechol	0.343 ± 0.007	48.7 ± 0.7	<0.002	0.362 ± 0.009	33.2 ± 2.1
20, 2-(1-hydroxy-5-hexenyl)hydroquinone	0.216 ± 0.007	77.0 ± 2.1	0.033 ± 0.002	0.778 ± 0.019	30.4 ± 1.4
21, phenylhydroquinone	0.190 ± 0.007	86.9 ± 2.8	0.330 ± 0.002	0.724 ± 0.009	40.3 ± 1.4
22, 2-(2-aminoethyl)hydroquinone	0.256 ± 0.005	65.0 ± 1.4	0.059 ± 0.005	0.169 ± 0.009	34.6 ± 3.2
pH 7	0.313 ± 0.009	53.0 ± 1.4	0.012 ± 0.002	0.282 ± 0.009	41.7 ± 3.0
23, 2-(2-aminoethyl)methylhydroquinone	0.216 ± 0.005	77.0 ± 2.1	0.052 ± 0.002	0.700 ± 0.014	40.3 ± 2.1
pH 7	0.261 ± 0.007	63.6 ± 2.1	<0.002	0.277 ± 0.009	48.7 ± 3.2
24, 1,4-dihydroxynaphthalene	0.249 ± 0.005	66.4 ± 1.4	0.141 ± 0.005	0.710 ± 0.020	61.5 ± 1.4
25, 1,4-naphthoquinone	0.258 ± 0.009	64.3 ± 2.8	0.153 ± 0.009	0.728 ± 0.019	63.6 ± 2.8
26, anthraquinone-1,5-disulfonic acid	0.117 ± 0.005	141.3 ± 5.6	0.066 ± 0.002	0.813 ± 0.024	98.9 ± 3.2
27, anthraquinone-2,6-disulfonic acid	0.127 ± 0.009	130.7 ± 5.6	0.077 ± 0.002	0.815 ± 0.019	103.1 ± 3.2
28, 2,5-dihydroxythiophenol	0.552 ± 0.019	30.4 ± 1.4	<0.002	<0.002	30.4 ± 1.4

[a] Experimental conditions as described in text. Unless otherwise indicated, the values reported were obtained at a single pH, 1 M $HClO_4$. pH 3 solutions contained 10^{-3} M $HClO_4$ in 1 M $NaClO_4$; the pH 7.0 buffer contained 10^{-2} M NaH_2PO_4, adjusted to pH 7 with NaOH, in 1 M $NaClO_4$.

starting material. The time allowed for the iodide-induced desorption was 180 s, although $\Delta\Gamma$ remained constant when the desorption time was varied from 15 to 300 s. Increasing the I^- concentration to 10^{-3} M did not affect the $\Delta\Gamma$ values, but in the interest of experimental precision in the measurement of $\Delta\Gamma$ an I^- concentration of 5×10^{-4} M was used.

Possibilities ii and iv require quantitative inspection of the data. The Γ, Γ_I, and $\Delta\Gamma$ data for each compound were used to determine σ_f, *the average surface area occupied by each hydrocarbon molecule remaining on the surface after contact with iodide solution* (the "final" orientation). The resulting values of σ_f were compared with calculated values of σ corresponding to various possible orientations. The magnitude of σ_f was determined from eq 4. Equation 4 is based on the fact that the sum of the areas

$$\sigma_f = \frac{(10^{16}/(6.023 \times 10^{23})) - \sigma_I\Gamma_I}{\Gamma - \Delta\Gamma} \qquad (4)$$

occupied by each adsorbed species must equal the electrode area, A (in cm^2):

$$10^{16}A = N_f\sigma_f + N_I\sigma_I \qquad (5)$$

N_j, the number of molecules of the jth adsorbed species, was obtained from the interfacial concentration Γ_j by using eq 6. Substitution of eq 6 into (5) gave eq 4.

$$N_j = (6.023 \times 10^{23})\Gamma_j A \qquad (6)$$

Studies of I adsorption on clean Pt surfaces[2-4] have determined that σ_I = 14.1 Å^2. The value calculated for a spherical I atom of van der Waals[9] radius 2.15 Å^2 is 14.5 Å^2; this agreement suggests that the adsorption of iodine on Pt is limited only by the size of the I atom. Because the I atom is spherical, the value of σ_I will be constant, 14.1 Å^2, whether I is adsorbed alone or with other surfactants.

Equation 4 does not include a contribution due to I atoms that find their way into voids of the original aromatic layer ($\Gamma_I > 0$, with $\Delta\Gamma = 0$ and $\sigma_f = \sigma_i$), possibility iv. However, eq 4 agrees with experiment for all compounds except **26** and **27** (see below), suggesting that such voids occur infrequently.

Experimental σ_f values are given in Table I; these can be compared with the corresponding theoretical σ values given in Table I of the preceding article[1] to obtain the probable orientations of adsorbed aromatics in the presence of iodide. The theoretical values were calculated for models of two-dimensional molecular packing based upon bond lengths, bond angles, and van der Waals distances tabulated by Pauling.[9] Reliability of these calculated values has been demonstrated.[1]

In addition to treatment of the aromatic layer with iodide solution as described above, σ_f was measured in *simultaneous* adsorption of iodide and aromatic compound from mixed solution (5×10^{-4} M aromatic compound and 1 M $HClO_4$). Compounds for which the dissolved form was electrolyzed at a potential well separated from that for iodide were selected for this purpose. The solution of I^- and aromatic was added to a clean thin-layer cell, and the electrolytic charge required for oxidation or reduction of dissolved aromatic for one and two fillings of the thin-layer

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[9] Pauling, L. C. "Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960; pp 221-264.

Table II. Adsorption Data for Mixed Aqueous Solutions of Aromatic Compounds and Iodide[a]

compound	Γ, nmol cm^{-2}	Γ_I, nmol cm^{-2}	σ_f (mixture), Å^2	σ_f (aromatic-coated surface), Å^2
1, hydroquinone, pH 7	0.204 ± 0.005	0.693 ± 0.009	33.2 ± 1.4	35.3 ± 2.1
2, pyrocatechol, pH 7	0.183 ± 0.009	0.693 ± 0.009	37.4 ± 1.4	33.9 ± 2.1
3, methylhydroquinone, pH 7	0.216 ± 0.007	0.616 ± 0.009	36.7 + 2.1	39.6 ± 2.1
4, 4-methylpyrocatechol, pH 7	0.216 ± 0.007	0.620 ± 0.009	36.4 ± 2.1	36.7 ± 2.4
5, *tert*-butylhydroquinone, pH 7	0.143 ± 0.009	0.728 ± 0.014	43.8 ± 2.8	45.2 ± 2.8
6, 4-*tert*-butylpyrocatechol, pH 7	0.143 ± 0.009	0.743 ± 0.014	42.4 ± 2.8	39.6 ± 2.8
10, durohydroquinone	0.169 ± 0.007	0.717 ± 0.033	38.1 ± 2.1	35.3 ± 2.1
24, 1,4-naphthohydroquinone	0.108 ± 0.005	0.698 ± 0.009	62.2 ± 2.1	61.5 ± 1.4
26, anthraquinone-1,5-disulfonic acid	0.061 ± 0.005	0.717 ± 0.023	106.0 ± 3.2	98.9 ± 3.2

[a] Experimental conditions as described in text. Unless otherwise indicated, the solutions contained 5×10^{-4} M NaI and 10^{-4} M aromatic compound in 1 M $HClO_4$ supporting electrolyte. A pH of 7.0 was maintained by a phosphate buffer in 1 M $NaClO_4$.

cavity determined. Aromatic interfacial concentration, Γ, was obtained from eq 4 of the preceding article.[1] In a separate trial the thin-layer cavity was rinsed and 1 M $HClO_4$ after one filling with the reactant mixture and Γ_I determined as IO_3^- (eq 3). σ_f was found from Γ and Γ_I by means of eq 4 (this paper), with $\Delta\Gamma = 0$. Values of σ_f obtained for iodide–aromatic mixtures appear in Table II (σ_f values from the sequential method are given for comparison). Values of σ_f obtained under the two sets of conditions agree rather closely, and no divergent trends are evident.

The relative adsorbed amounts of I and aromatic are dependent on the I^-/aromatic concentration ratio in solution: increasing the I^- concentration increases Γ_I. However, *the final orientation of adsorbed aromatic is independent of the* I^- *aromatic concentration ratio.* The concentrations stated above were chosen primarily to afford the best precision in measurement of Γ and Γ_I.

When the iodide layer was formed first and then exposed to the aromatic compound, no adsorption of the aromatic compound occurred (on the exposure time scale of these experiments, up to 300 s). This indicates that iodide solutions react with aromatic-coated surfaces but the opposite process, reaction of a dissolved aromatic compound with adsorbed iodide, does not occur at an appreciable rate. Also, the rate of iodide adsorption must be less than or comparable to that of the aromatic, since iodide, once adsorbed, would prevent adsorption of aromatic compounds. The rates and mechanisms of these displacement and coadsorption processes have not been investigated. Accordingly, the mechanism by which the stoichiometry of iodide-induced desorption stops short of complete removal of the aromatic layer is not known. Equilibrium has been ruled out as the cause by our observation that mutiple rinses with iodide solution do not significantly increase iodide uptake. The slowness with which hydrocarbons are displaced from the Pt surface by iodide and other surfactants has been reported.[10,11] It is very probable that iodide coadsorption leads to formation of a mixed superlattice, a stoichiometric surface layer resistant to further change. The tendency of iodine and other strong surfactants to form such superlattices on Pt surfaces has been noted in recent articles from this laboratory and elsewhere.[3,4] In particular, a closely analogous result was obtained in vacuum: dimethyl sulfoxide vapor adsorbed on Pt (111) to form a close-packed superlattice which, when treated with I_2 vapor, formed a new superlattice structure containing one iodine atom/dimethyl sulfoxide molecule, after which iodine uptake ceased.[10]

Inspection of σ_f and calculated σ values in Table I of the preceding article[1] shows that σ_f corresponds to σ for a definite orientation in all cases but two, the disulfonated anthraquinones (**26** and **27**). This is perhaps related to the large size and irregular shape of these compounds, which may lead to imperfect packing. Allowing for 10% void area leads to σ_f in agreement with the observed (σ_i) and calculated (σ for flat orientation) values for these two compounds.

The influence of pH on the interaction between adsorbed aromatics and iodide solutions has been explored for nine of the subject compounds. The amount of iodide uptake by the aromatic layer decreases with increasing pH (0–7) in all cases, due to a decrease in the amount of aromatic desorbed. This result is in keeping with the fact that I^- adsorption involves reduction of H^+ (eq 1).[2,4] For the alkyl-substituted compounds **3–6**, σ_f was constant, but for the remainder of the compounds, **1**, **2**, **16**, **22**, and **23**, σ_f was smaller at larger pH, indicating a greater degree of iodide-induced reorientation.

Discussion

1. Adsorbed Compounds for which Iodide Interaction Is Minimal. The simplest case is that of **28**, for which exposure of the adsorbed layer to iodide solution has no effect ($\Gamma_I = 0$, $\Delta\Gamma = 0$, $\sigma_i = \sigma_f$). This is not surprising in view of the strength of adsorption of the thiol moiety,[12] which leads to very efficient packing (σ_i = 30.4 ± 1.4 Å^2 compared with a theoretical value of 31.1 Å^2).

Tetrafluoro- and tetrachlorohydroquinone (**11** and **12**) do not form a close-packed layer from 10^{-4} M solution, based upon σ_i values much larger than theory for any possible orientation. Since the heavily fluorinated or chlorinated benzene ring is not strongly adsorbed on Pt,[12] the moderate adsorbability of **11** and **12** is probably due primarily to attachment through one or both OH groups.[1] These two compounds are not displaced by I^- ($\Delta\Gamma \approx 0$); therefore, filling of voids, possibly accompanied by reorientation, accounts for the iodide uptake. It may seem strange that a molecule that is only weakly adsorbed is not displaced by I^-. However, it is important to realize that the initial coverages of **11** and **12** are comparatively low. Even without displacement of the halogenated aromatics, the amount of I^- adsorbing on the unoccupied area is nearly 80% of that for a clean surface and much higher than when aromatics are present. Also, since the modes of attachment of the halogenated and nonhalogenated compounds differ, the rates and mechanisms of displacement by iodide would be expected to differ.

2. Compounds Displaced without Reorientation. About one-third of the compounds studied [**1** (pH 0), **2** (pH 0), **9**, **13–16**, **17** (pH 7), and **24–27**] are desorbed to a major extent ($\Delta\Gamma \approx {}^2/_3$) without reorientation ($\sigma_f = \sigma_i$). The unifying trait of these compounds is that none have alkyl substituents on the aromatic rings. Referring to Table I, compare hydroquinone ($\Delta\Gamma$ = 0.169 nmol cm^{-2}) with its alkyl derivatives methylhydroquinone ($\Delta\Gamma$ = 0.047), *tert*-butylhydroquinone ($\Delta\Gamma$ = 0.028), 2,5-dimethylhydroquinone ($\Delta\Gamma$ = 0.026), 2,3-dimethylhydroquinone ($\Delta\Gamma$ = 0.045) and durohydroquinone ($\Delta\Gamma$ = 0.028). This difference in inertness toward displacement is probably due to an inductive effect in which the alkyl groups donate electron density to the aromatic moiety, which in turn is acting as a donor towards the platinum surface.[13] A similar effect has recently been reported for benzene and toluene adsorbed on well-defined nickel surfaces; benzene is readily displaced by trimethylphosphine whereas toluene is not.[14]

3,6-Dihydroxypyridazine (**17**) does not reorient (σ_i = 24.7 ± 0.7, σ_f = 25.4 ± 0.2 Å^2) under the influence of iodide at pH 7 because in neutral or alkaline solutions this molecule is already

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present in its optimally space-efficient N-η^1 orientation.[1] Similar behavior is displayed by 2,3-dihydroxypyridine (**16**), except that the initial aromatic layer is not present exclusively in a (vertical) η^1 orientation ($\sigma_i = 28.3 \pm 0.7$, $\sigma_f = 21.9 \pm 1.4$, $\sigma_{calcd} = 23.3$ Å^2).

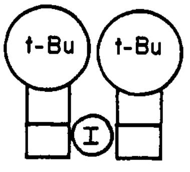
3. Compounds Reoriented by Iodide. For the rest of the compounds studied, the amount of iodide-induced desorption in molar acid is much less than that expected from the amount of iodide adsorbed. Since the area σ_I occupied by an I atom is constant, this strongly suggests that the aromatic remaining on the surface reorients to take up less space.

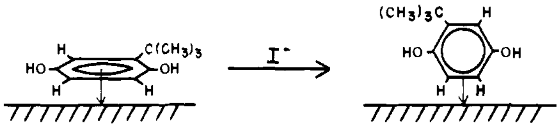
(a) Compounds without Nonaromatic Surface-Active Substituents. Compounds **3–8**, **10**, and **21–23** belong to this category; a unifying feature of these compounds that reorient rather than desorb in acidic I$^-$ solution is the presence of alkyl groups on the benzene ring.

In addition, in neutral (pH 7) I$^-$ solution, hydroquinone (**1**) and pyrocatechol (**2**) (the only compounds studied in this regard) undergo minimal desorption and complete reorientation; in contrast, in molar acid, extensive desorption and no reorientation occurs. Compounds **3–6**, likewise, show lesser desorption in neutral than in acidic I$^-$ solutions, but the reorientations are not pH dependent. This suggests that reorientation may be a general characteristic of flat-adsorbed aromatics in neutral I$^-$. The extent of iodide uptake by a benzene-coated surface decreased similarly with pH (Γ_I decreased from 0.728 to 0.503 to 0.329 nmol cm^{-2} as the pH was increased from 0 to 3 to 7, respectively). Since the pH dependence of displacement by I$^-$ is observed also for benzene, which contains no functional groups, it cannot be due to the influence of OH on other functional groups; instead, it probably stems from the involvement of protons in the I$^-$ adsorption process (eq 1).

Comparison of σ_f values for compounds in this category (Table I) with measured σ_i and calculated σ values in Table I of the preceding article[1] shows that the remaining adsorbed species are no longer in the η^6 orientation. η^1 orientations are also ruled out since the σ_f values are consistently and significantly large than those calculated for the various endwise orientations; furthermore, η^1 binding is observed only for molecules containing a single strongly surface-active atom such as low-valent N or S.[1] Therefore, edgewise orientations are the remaining possibilities.

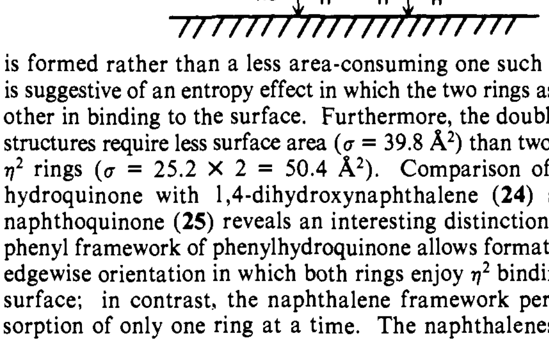
The σ values calculated for alternative η^2 orientations differ by as little as 0.7 Å^2 in some cases, compared with experimental standard deviation of about 2.1. However, for compounds containing bulky substituents, calculated η^2 σ values often differ substantially, allowing basic patterns to be recognized. Still other orientation assignments can be made tentatively on the basis of steric hindrance and/or chemical bonding considerations. For example, *tert*-butylhydroquinone (**5**) would be expected to adopt a η^2 orientation that places the *tert*-butyl group away from the Pt surface for the following reasons: Alkyl moieties are not as active toward Pt surfaces as are aromatic rings.[1,12] If placed toward the Pt surface, the bulky *tert*-butyl group would act primarily to interfere with attachment of the aromatic ring. On the other hand, placement of the *tert*-butyl group parallel to the Pt surface would require more surface area than is found experimentally. This leaves two equally possible orientations, 4,5-η^2 and 5,6-η^2, in which the *tert*-butyl group is placed along the ring edge farthest from the surface. Another interesting feature of the *tert*-butyl derivatives is that the *tert*-butyl group has a thickness, based upon van der Waals distances of closest approach, of 7 Å, which is greater than that of the phenyl ring, 3.4 Å. Accordingly, **5** and **6** must close pack in an interlocking manner if they are to avoid forming voids of size sufficient to accommodate an adsorbed I atom (see I). These voids are evidently occupied since σ_f (45.2 ± 2.8 Å^2) is smaller than calculated for a uniform thickness of 7 Å (52.3–70.6 Å^2) by a margin much too large to be ignored. Values of σ calculated for **5** allowing for the packing shown in I give excellent agreement for the unhindered 5,6-η^2 orientation [$\sigma(5,6) = 43.7$, $\sigma(4,5) = 42.9$, $\sigma(1,6) = \sigma(3,4) = 52.5$ Å^2) (see eq 7). Likewise, 4-*tert*-butylpyrocatechol (**6**), evidently reorients from η^6 ($\sigma = 72.1$ Å^2) to an interlocking η^2 orientation ($\sigma_f = 41.0 \pm 2.8$ Å^2). The 1,2-η^2 orientation leads to good agreement [$\sigma(1,2) = 42.4$; $\sigma(2,3) = \sigma(5,6) = 61.5$; $\sigma(1,6) = 45.8$ Å^2) and places the bulky *tert*-butyl group farthest from the surface. Similarly, on the basis of least steric hindrance and close agreement between experimental and calculated σ, plausible η^2 orientation assignments may be attempted for the other compounds such as 5,6-η^2-4-methylpyrocatechol ($\sigma_f = 36.7 \pm 2.4$; $\sigma_{calcd} = 36.4$ Å^2). 2,5-Dimethylhydroquinone (**7**) does not have a pair of adjacent unsubstituted positions with which to form an unhindered η^2 structure. The result is a σ_f value (36.7 ± 2.8 Å^2 intemediate between two possible structures: 3.4-η^2 ($\sigma = 39.2$ Å^2) affords lesser hindrance, while 2,3-η^2 ($\sigma = 33.6$ Å^2) requires less surface area. Durohydroquinone (**10**), likewise, has no unhindered η^2 structures; in this case, however, σ_f (35.3 ± 2.1 Å^2) corresponds more closely to the orientation that requires the least surface area: 2,3-η^2 [$\sigma(2,3) = 33.6$; $\sigma(1,2) = 39.2$ Å^2].





(7)

Phenylhydroquinone (**21**) is adsorbed initially with both phenyl rings flat on the surface ($\sigma_i = 86.9 \pm 2.8$ Å^2). Under the influence of iodide, it reorients to form a 3,4,2′,3′-η^4 structure ($\sigma_f = 40.3 \pm 1.4$; $\sigma_{calc:} = 39.8$ Å^2) (see eq 8). The fact that a η^4 structure is formed rather than a less area-consuming one such as 5,6-η^2 is suggestive of an entropy effect in which the two rings assist each other in binding to the surface. Furthermore, the double-ring η^4 structures require less surface area ($\sigma = 39.8$ Å^2) than two separate η^2 rings ($\sigma = 25.2 \times 2 = 50.4$ Å^2). Comparison of phenylhydroquinone with 1,4-dihydroxynaphthalene (**24**) and 1,4-naphthoquinone (**25**) reveals an interesting distinction: the biphenyl framework of phenylhydroquinone allows formation of an edgewise orientation in which both rings enjoy η^2 binding to the surface; in contrast, the naphthalene framework permits adsorption of only one ring at a time. The naphthalenes are not reoriented by acidic iodide solution. Likewise, the anthracene derivatives (**26** and **27**) do not reorient.



(8)

(b) Compounds Having Nonaromatic Surface-Active Substituents. Although alkenes are strongly adsorbed on Pt surfaces,[15,16] olefinic substituents of aromatic compounds compete only weakly with the phenyl ring for interaction with the surface. Nevertheless, in the presence of I$^-$, some influence by the alkene function can be detected. For instance, **18** and **19** are not desorbed by iodide. This is due at least in part to an inductive effect, as noted above, but may also stem from chemical bonding between the alkene and the platinum surface. Several possible η^2 orientations have very similar theoretical σ values, preventing a conclusive assignment on the basis of σ_f data. However, in each case the orientation representing the best compromise between steric hindrance and packing density agrees most closely with experiment: 5,6-η^2-

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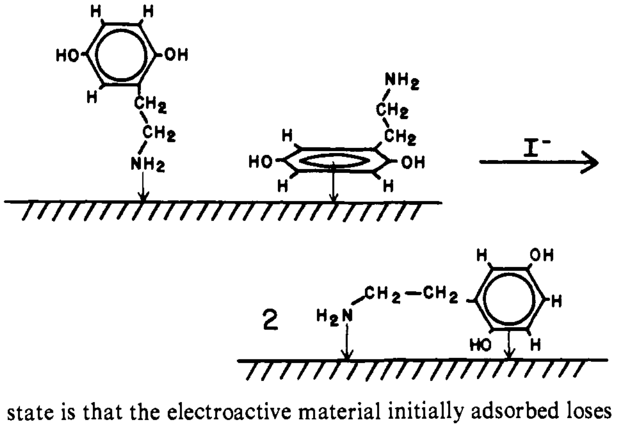
allylhydroquinone, ($\sigma_f = 32.5 \pm 2.1$; $\sigma_{calcd} = 33.6$ Å^2), and 1,6-η^2-4-allylprocatechol, ($\sigma_f = 33.2 \pm 2.1$; $\sigma_{cald} = 31.6$ Å^2). Compound **20** has a longer alkene side chain (hexene). However, the initial coverage ($\sigma_i = 77.0 \pm 2.1$ Å^2) and the absence of reversible electroactivity of the adsorbed layer indicate that it is initially adsorbed exclusively in the η^6 orientation, with the side chain extended away from the surface ($\sigma = 74.2$ Å^2). Under the influence of iodide, this structure reorients most probably to a 4,5-η^2 orientation in which the chain remains extended away from the surface ($\sigma_f = 30.4 \pm 1.4$; $\sigma_{calcd} = 29.6$ Å^2).

Compounds **22** and **23** have amine side chains, and at pH 7, a small fraction of the initial adsorption occurs through the amine nitrogen.[1] For these compounds, unlike all of the other compounds studied, *larger* values of σ_f are obtained at pH 7 than in acid (41.7 vs. 34.6 Å^2 for **22**; 48.8 vs. 40.3 Å^2 for **23**), although σ_f remains smaller than σ_i. This can be understood if attachment of dangling amine groups and aromatic rings accompanies reorientation of η^6-bonded aromatic rings to the more space-efficient η^2 orientations. The final structure is attached to the surface in two places (see eq 9). Further evidence for double attachment in the final state is that the electroactive material initially adsorbed loses its electroactivity as a result of iodide exposure. Since 20% of the initially adsorbed material was found to be reversibly electroactive[1] (and therefore presumably N attached), the observed σ_i can only be accounted for if the remaining 80% adopted a η^6 orientation in which the amine chain was positioned away from the surface. Therefore, double attachment occurs only after exposure to iodide. This situation is not analogous to that of phenylhydroquinone since the latter is always double attached, even in the initial flat orientation.



(9)

Conclusions

The results of the present study reveal that changes in coverage, orientation, and/or mode of attachment occur when a parallel-oriented adsorbed layer of aromatic compounds is exposed to a solution of a strongly surface-active anion such as iodide. Under these conditions (10^{-4} M aromatic and/or 5×10^{-4} M iodide in 1 M perchlorate electrolyte): (i) Displacement of adsorbed aromatic molecules from the platinum surface by iodide solution is greatest in acidic media. (ii) Alkyl substituents stabilize adsorbed aromatic compounds toward displacement by iodide. (iii) Monocyclic aromatic molecules adsorbed in a flat orientation *reorient* to an edgewise orientation unless they are extensively desorbed when exposed to iodide solution. (iv) The more stable η^2 oriented structures are those that occupy minimal electrode surface area and for which the ring edge closest the electrode does not contain bulky substituents. (v) Fused polycyclic aromatic molecules adsorbed parallel to the surface do not reorient under the influence of acidic iodide, although they undergo some desorption. (vi) The biphenyl moiety adsorbed with both rings parallel to the surface undergoes reorientation by iodide such that both rings are edgewise to the surface. (vii) Aromatic molecules attached to the surface by an SH group are not displaced by iodide. (viii) In general, reorientations induced by iodide convert structures making inefficient use of surface area into orientations occupying smaller surface area.

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Registry No. 1, 128-31-9; **2**, 120-80-9; **3**, 95-71-6; **4**, 452-86-8; **5**, 1948-33-0; **6**, 98-29-3; **7**, 615-90-7; **8**, 608-43-5; **9**, 150-78-7; **10**, 527-18-4; **11**, 771-63-1; **12**, 87-87-6; **13**, 533-73-3; **14**, 608-80-0; **15**, 319-89-1; **16**, 16867-04-2; **17**, 123-33-1; **18**, 5721-21-1; **19**, 1126-61-0; **20**, 81255-51-8; **21**, 1079-21-6; **22**, 21581-41-9; **23**, 81255-52-9; **24**, 571-60-8; **25**, 130-15-4; **26**, 117-14-6; **27**, 84-50-4; **28**, 2889-61-4; I^-, 20461-54-5; Pt, 7440-06-4.

Paramagnetic Carbon-13 Shifts Induced by the Free Radical 2,2,6,6-Tetramethylpiperidinyl-1-oxy. 1. Simple Aromatic and Paraffinic Hydrocarbons

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Abstract: Using the free radical 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) as a shift reagent, both apparent and true molar paramagnetic shifts of 22 compounds are reported. Paramagnetic shifts increase monotonically with measures of conjugation and aromaticity. The nonalternant hydrocarbons experience greater effects than the corresponding alternant systems. Steric hindrance effects become important factors in various methyl derivatives. As previously supposed the shifts do not appear to relate primarily with either the frontier spin densities or with π-charge densities. Therefore, the direct charge-transfer or spin delocalization proposals requiring a strong intermolecular interaction of the π-stacking variety is felt not to be attractive. Linear correlation exists between these and Morishima's data and between the data for TEMPO and 4-OH-TEMPO. In each case TEMPO is more effective as a shift reagent than the other two nitroxide free radicals. A shift model involving a pseudocontact interaction during the existence of a transient weak complex is supported by these data.

Chelated lanthanide compounds have been widely used as shift reagents in NMR.[1] Recently Morishima et al.,[2] Sysoeva et al.,[3] and Draney and Kingsbury[4] have obtained similarly interesting results on the paramagnetic shifts and relaxation behavior in a

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