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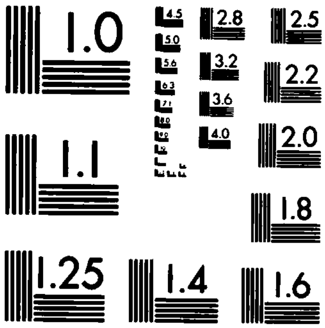

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The mission of this AFOSR project was to determine the structure, orientation, composition and reactivity of the surface molecular species which form spontaneously when metals come into contact with fluids, as in batteries, fuel cells, electronic circuits, marine environments and the atmosphere. All of these topics have been investigated as promised. A series of major discoveries have been made in this project and thus far forty-nine scientific articles have been published.

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Reprints and Preprints

Details of the reported research are contained in forty-nine research articles supplied to the U.S. Air Force Office of Scientific Research under separate cover. Additional copies are available upon request to the Principal Investigator.

ABSTRACT

The mission of this AFOSR project was to determine the structure, orientation, composition and reactivity of the surface molecular species which form spontaneously when metals come into contact with fluids, as in batteries, fuel cells, electronic circuits, marine environments and the atmosphere. All of these topics have been investigated as promised. A series of major discoveries have been made in this project and thus far forty-nine scientific articles have been published. These include:

- (i) determination of the spatial orientations and mode of attachment of typical organic molecules chemically bonded to electrode surfaces;
- (ii) discovery that each orientation of an adsorbed molecule reacts differently;
- (iii) identification and exploration of variables which influence adsorbate orientation (concentration, temperature, potential, electrolyte, solvent, substrate, surface structure, pH and hydrogen bonding);
- (iv) exploration of the influence of oriented adsorbates on electrode rates;
- (v) preparation of well-defined surfaces under atmospheric conditions;
- (vi) electrodeposition of highly ordered layers of Ag and Cu onto well-defined substrates;
- (vii) discovery of the orderedness of adsorbed ionic layers at well-defined surfaces;
- (viii) direct experimental exploration of the cation-selectivity of metal-solution interfaces.

These findings were made possible by a unique combination of surface research techniques in ultra-high vacuum and electrochemistry in solution, employed in a long-term systematic series of investigations.

REPORT OF RESEARCH (April, 1981 - April, 1985)

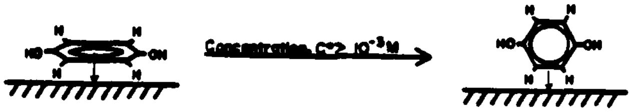
All of the topics covered by the grant proposal have been investigated as promised. Research during the period of this report has led to numerous discoveries which are briefly summarized here and described in detail in 49 publications acknowledging AFOSR support. A list of these publications is included at the end of the report. A number of promising avenues of research suggested by these findings are currently being investigated with a three-year renewal of our grant from AFOSR.

1. Comparative Reactivity of Adsorbed vs. Unadsorbed Molecules.

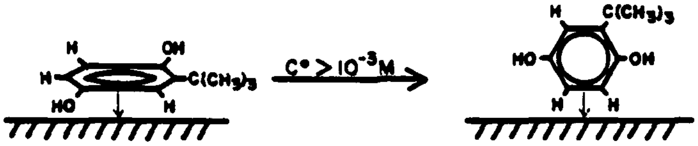
Thin-layer electrodes were employed to compare the electrochemical reactivities of the adsorbed and unadsorbed states of about 50 polyhydric phenols and quinones on annealed Pt surfaces (50). Contrary to conventional wisdom, most of the adsorbed states of these compounds were almost totally unreactive, yet the adsorbed material did not prevent the unadsorbed material from reacting at a very rapid rate. Only in rare instances did the adsorbed form display reversible electron transfer behavior. This basic observation is fundamental to an understanding of adsorbed intermediates in all of their manifestations, such as fuel cells, coatings and surface analysis methods based upon electrochemistry. Although aromatic compounds were an informative object of study, the lessons learned should be applicable to compounds of most types. Forty-four examples representing a wide variety of organic functional groups are discussed in Reference 40. Reasons for the observed differences in reactivity are revealed by results reported below.

2. Modes of Bonding of Aromatic Molecules to Surfaces.

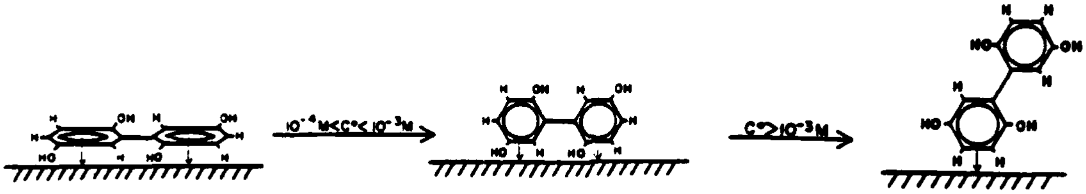
Accurate thin-layer electrochemical measurements of packing density of aromatic compounds on polycrystalline platinum electrodes were made (47,49). Twenty-six compounds representing various structures, functional groups and other molecular properties were studied. Each compound displayed one or more packing density plateaus. Comparison of the packing densities with molecular model calculations of the type described by Pauling (101) revealed that the plateau values correspond to specific orientations of the adsorbed species. Details are given in References 43, 47 and 49. For example, adsorption from solutions containing less than 10^{-4} M hydroquinone led to the flat adsorbed state. As the concentration was increased slightly to 3 x 10^{-4} M, the adsorbed layer was converted to edgewise adsorbed species:



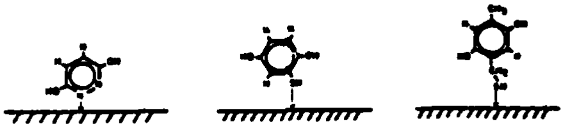
Adsorption went to completion in less than five seconds, while desorption required hours or days. Hence, these "cooperative" orientations have ample stability for practical applications as well as fundamental investigations. Evidence as to which edge was responsible for edgewise attachment was obtained by various methods described below, including observation that alkyl-substituents extend away from the surface:



Uncondensed polycyclic aromatics, such as biphenyl derivatives, underwent multiple orientational transitions:



Compounds containing strongly surface-active functionalities such as aromatic nitrogen or low-valent sulfur are attached through that moiety and therefore display a single, predominant orientation at all adsorbate concentrations:



As explained in Reference 64, these profound surface chemical bonding phenomena were obscured in the classical literature by experimental and interpretational deficiencies. Conversely, now that one has a clear view of the existence and nature of these adsorbed intermediates, one can seek practical applications by design rather than by chance, and one can intelligently plan a program of very significant future investigations. As discussed in Reference 62, orientational transitions of aromatic compounds have been overlooked in vacuum studies because the transitions occur above about 18 Torr, a pressure far above the range employed by previous workers.

Chirality influenced adsorbate packing. Accurate packing density measurements were made for the pure enantiomer L-3-(3,4-dihydroxyphenyl) alanine, L-DOPA, and a recemic mixture of D,L-DOPA (53). At concentrations where the edgewise orientation predominates, the pure enantiomer (L-DOPA) packs more densely than the racemic mixture. However, no difference in packing occurs with the flat adsorbed species. Evidently, the chiral amino acid side chains of neighboring molecules interact strongly for the edgewise orientation but not for the flat orientation.

Packing density and molecular orientation information obtained by electrochemical methods has been supplemented with quantitative Auger spectroscopic data (71) and reflection-absorption infrared spectra (71,72,78). For example, Auger intensities from C, S and O in hydroquinone sulfonic acid increased and those from Pt decreased in the manner expected when the adsorbate concentration was increased through the flat-to-edgewise orientational transition region (71). Intensity ratios also varied in the manner expected. Surface infrared spectra obtained in collaboration with Professor Jay B. Benziger of Princeton University likewise supported the electrochemical results. Observed in spectra for the edgewise hydroquinone adsorbate orientation but not for the flat orientation were three broad peaks between 2700 and 3000 cm^{-1} characteristic of hydrogen-bonded phenolic compounds (102) and a peak near 3030 cm^{-1} assignable to the aromatic C-H stretch (78). These IR spectral differences are consistent with adsorbate reorientation in light of the surface dipole selection rule (103). Taken together the electrochemical and spectroscopic evidence indicate that adsorption of benzoquinone or hydroquinone from dilute solutions ($C^o < 7.5 \times 10^{-5}$ M) produces flat-oriented adsorbate (ring parallel to the surface) in the quinone redox state, while adsorption from higher concentrations yields the 2,3-edgewise orientation di-sigma bonded in the diphenolic redox state (78).

3. Temperature Dependence of Adsorbed Orientation.

Accurate packing density measurements were made as a function of temperature for aromatic compounds in aqueous solutions at annealed polycrystalline Pt thin-layer electrodes (60). Eight compounds were studied: hydroquinone, 1; 2,5-dimethylhydroquinone, 2; 2,2',5,5'-tetrahydroxybiphenyl, 3; 1,4-naphthohydroquinone, 4; anthraquinone-1,5-disulfonic acid, 5; 2,5-dihydroxythiophenol, 6; 2,3-dihydroxypyridine, 7; and 3,6-dihydroxypyridazine, 8. The temperature dependence of adsorption of compounds, 1-4, for which adsorption was primarily due to interaction of the aromatic ring(s) with the Pt surface, was very striking:

(i) The stepwise transitions to higher packing density with increasing adsorbate concentration were most sharply defined at low temperatures (near 5°C);

(ii) At low concentrations of adsorbate, packing density increased with temperature but decreased with temperature at high concentrations;

(iii) An additional packing density plateau appeared near room temperature (between 25°C and 65°C); and,

(iv) Packing density transitions were barely noticeable at 65°C. Compounds 5-8, which were attached to the surface by a functional group other than a simple benzene ring, displayed virtually temperature independent adsorption behavior. Such results indicated for the first time the sharp temperature dependence of the mode of attachment of adsorbed benzene rings at Pt surfaces, and were an essential consideration in understanding a wide variety of chemical processes which involve adsorbed species. Fuel cells, catalytic reactors, protective coatings and adhesives are examples of the many areas in which this basic research can be applied.

4. Reactions of Oriented Adsorbed Molecules: Oxidation, Reversible Redox and Reductive Desulfurization.

Oxidation of each orientation of an adsorbed aromatic compound gave a different distribution of products (50). This remarkable result was obtained by measuring the number of electrons per molecule, n_{ox}, to oxidatively desorb each specific orientation. Twenty-nine compounds were studied, representing a variety of orientations, structures and chemical characteristics. In each case, an exact correlation existed between orientation and oxidative n-value, n_{ox}. In particular, n_{ox} was at least two-fold smaller for edgewise initial adsorbed orientation than for flat orientation. Since changes in number of electrons transferred per reacting molecule are generally associated with changes in reaction stoichiometry, the variation of n_{ox} with orientation is an indication of changes in oxidation product distribution. Isolation and identification of the products is in process at the moment.

Determination of n_{ox} was based upon precise measurements of packing density (by coulometric electrolysis of unadsorbed aromatic), rinsing the electrode and separate precise determination of the electrolytic charge Q_{ox} to oxidize and desorb the adsorbed material. The magnitude of n_{ox} is related to the measured Q_{ox} and Γ by the following equation:

$$n_{ox} = \frac{Q_{ox} - Q\ (\text{blank})}{FA\Gamma}$$

where Q (blank) was measured under identical conditions except that the adsorbate was absent. Rinsing the surface during oxidation did not influence n_{ox}. Oxidation at all potentials in the range from 0.85 to 1.35 volt (vs. AgCl reference) yielded identical values of n_{ox}, although the rate of oxidation varied, as expected. Oxidation led to complete removal of the hydrocarbons, as evidenced by the fact that the amount of platinum surface oxide formed was equal to that for a clean surface and by the fact that the voltammograms obtained following oxidation were identical to those for a clean surface.

Since the stoichiometry of electrochemical oxidation of adsorbed aromatic intermediates depends on the mode of attachment (50,51) which in turn is a sensitive function of orientation, we have made a study of the temperature dependence of n_{ox} (60). Two representative compounds were studied: hydroquinone and 1,4-dihydroxynaphthalene. The n_{ox} is indeed very strongly dependent upon temperature. As the temperature was raised from 5^{o} to 65^{o}C, the magnitude of n_{ox} (extent of oxidation of the adsorbed molecule) increases sharply. Furthermore, the selective oxidation of edgewise adsorbed intermediates to products other than CO_2 vanishes above 65°. Results of such measurements are vital to understanding the thermal stability of chemisorbed species and the temperature dependence of reactions involving adsorbed intermediates such as in energy generation/storage devices, formation of protective/insulative surface coatings, and bonding of adhesives to surfaces.

Reversible electrochemical redox couples formed by specific orientations of three compounds were studied (60): 2,2',5,5'-tetrahydroxybiphenyl, 3; 2,5-dihydroxythiophenol, 4; and 2,5-dihydroxy-4-methylbenzyl mercaptan, 5. Compounds 3 and 4, adsorbed exclusively through the -SH moiety in a single orientation at all packing densities (49), showed reversible redox reactivity analagous to the unadsorbed quinone-hydroquinone couples. Virtually all of the adsorbed material participated in the redox reaction, as judged by thin-layer coulometry. The voltammetric peak width for Compounds 4 was comparatively large, an effect attributable to coupling between adjacent redox centers and through the surface. Consistent with this explanation, Compound 5 in which the redox center is isolated from the Pt surface by a C-C single bond, showed the normal voltammetric peak width comparable to that of the unadsorbed compounds. The reversible reactivity of these adsorbed compounds, 4 and 5, persisted at all temperatures studied, from 5° to 65°C. In contrast, Compound 3, which is attached to the surface in three orientations depending upon packing density (both rings flat; both rings edgewise; or one ring edgewise and the other ring pendant, Reference 47), displayed reversible redox reactivity only when present in the edge-pendant orientation. Clearly, molecular orientation (i.e., mode of attachment to the surface) is a vital consideration in the reactivity of adsorbed intermediates. Furthermore, the fact that one of orientation is readily reactive and the others are not is one of a growing number of insufficiencies of voltammetric methods based upon semi-infinite diffusion (non-thin-layer methods) when used for measurement of adsorbed amounts. We shall return to this point in category 15, below. Furthermore, the fraction of reversibly electroactive adsorbed 3 varied with temperature; under conditions where temperature is influencing the proportion of edge-pendant material, this variation is correlated with the orientational transition, but within the single edge-pendant, orientation reactivity increases with temperature.

In view of the obvious importance of catalytic desulfurization for production of economical, clean fuels, we examined the reductive desulfurization of oriented adsorbed layers of compounds 4, 5 and pentafluoro-thiophenol, 6. Ease of reduction increased in the order 5 << 4 << 6. The degree of desulfurization increased with temperature up to 25°C, but at higher temperatures, efficiency began to decrease due to hydrogenation of the aromatic moiety.

5. Energy Barrier to Flat-to-Edgewise Transitions.

We have discovered that an appreciable barrier exists to re-orientation of adsorbed aromatics from the flat orientation (η^6, "pi-bonded" attachment) to an edgewise orientation (η^2, "di-sigma" attachment) (62). This barrier manifested itself for instance through the necessity of applying a much higher adsorbate concentration to convert flat states to edgewise than to form the edgewise states at the clean surface. Oriented adsorbed aromatic intermediates therefore enjoy kinetic as well as energetic (long-term) stability. Discovery of the reorientation barrier was based upon measurement of the adsorptive uptake of aromatic compounds by Pt thin-layer electrodes pre-coated with a layer of flat-oriented molecules of the same compounds. Four compounds were chosen for study: hydroquinone, 1; 1,4-naphthohydroquinone, 2; 2,3-dimethylhydroquinone, 3; and 2,5-dimethylhydroquinone, 4. Firstly, the clean electrode was treated with a dilute solution of the adsorbate shown previously to form the flat orientation and for which the packing density was known (47,49). Secondly, the pretreated surface was exposed to a more concentrated solution of the adsorbate and any additional uptake accurately measured. The results, expressed as total packing density, were compared with those for the unpretreated surface. The same edgewise orientations were eventually formed on the pretreated surface as on the clean surface. That is, η^6-to-η^2 transitions occurred as before. However, the transition was postponed to higher concentrations; this concentration barrier was higher for some of the compounds, 1-3, than others, 4. Furthermore, when pretreatment was with partially re-oriented ("tilted") intermediates, the adsorption profile was remarkably similar to that for the unpretreated electrode. Also, the hindered compounds, 3 and 4, were affected least by surface pretreatment. These results suggest that:

(i) adsorption of 1-3 at concentrations above 10^{-3} M on clean Pt leads at least primarily to direct edgewise attachment;

(ii) complete re-orientation from flat to edgewise states involves substantial kinetic as well as energy barriers;

(iii) the flat adsorbed state is a precursor to formation of the edgewise orientation of 4.

These findings help to explain the peculiar contradictions reached by earlier workers, particularly the Russian school (104), on the basis of radiotracer adsorption measurements which proceeded from low concentrations (flat adsorption) to high without intermediate cleaning of the surface.

6. Potential-Dependence of Aromatic Adsorption.

Accurate thin-layer coulometric measurements of packing density were made as a function of the electrode potential of the smooth Pt surface during adsorption (65). One compound, hydroquinone, has been studied thus far; work is continuing on other compounds.

Results of this study indicate a profound dependence of adsorbed amount on electrode potential. Packing density is relatively independent of potential from 0.0 to 0.4 volt vs. AgCl reference. Sight variation near 0.4 volt was observed in sulfate and phosphate electrolytes, probably due to potential dependent competitive adsorption of anions, but not in perchlorate. The sharp drop in adsorbed aromatic at potentials positive of 0.8 is due to competitive adsorption of oxygenous species, as expected from the surface oxidation features of voltammetric curves for Pt. Likewise, a decline at negative potentials correlates with hydrogen adsorption. The flat-to-edgewise transition of hydroquinone occurs in spite of competition from oxide or hydrogen. Incidentally, when the electrode potential was varied after formation of the adsorbed layer, only slight variations in packing density were observed, except at the extremes where oxidation ($E > 0.8$) or hydrogenation occurred ($E < -0.2$ volt vs. AgCl). It may be worth pointing out that from first principles, one expects to have these same electronic influences on adsorption phenomena in the gas phase due to the effects of hydrogen, oxygen, air, hydrocarbons and other fluid redox agents, but these are simply harder to control and less well understood from gas-solid experiments. Electrochemical experiments are thus very relevant to gas-solid studies and enjoy somewhat of an advantage in simplicity of both theory and practice.

Measurements of the oxidation n-value, n_{ox} were made as a function of the adsorption potential in order to disover how the potential-dependent orientational changes of adsorbed intermediates influence reactivity (65). Again, hydroquinone was the initial compound studied. Such studies are providing information regarding the reactivity of adsorbed intermediates and therefore an independent set of evidence concerning their adsorbed state. In particular, n_{ox} varies in the same way during the packing density transition near the positive and negative limits of the potential range studied, indicating that the usual flat and edgewise intermediates are present even at potentials for which the aromatic packing density is attenuated by competitive adsorption of hydrogen or oxygen.

Another very significant finding arising out of this study was that a barrier exists to orientational transition from edgewise to flat, even at low packing densities characteristic of flat orientation (64). This result was arrived at by first subjecting an edgewise adsorbed hydroquinone layer to rinsing with pure electrolyte at a range of potentials where partial desorption occured (negative or positive extremes of the potential range), followed by equilibration at 0.2 volt and then determination of n_{ox} at 1.2 volt. The magnitude of n_{ox} was unaffected by removal of various proportions of the adsorbed layer suggesting constancy of the adsorbed orientation.

7. Deficiencies of Adsorption Measurements Based on Hydrogen Co-Deposition or Anodic Oxidation.

Accurate measurements of the potential dependence of adsorption (64) point to severe deficiencies of two of the most common classical methods of adsorption measurement: conversion of hydrogen co-deposition data of anodic oxidation data to absolute packing densities or adsorbed molecule cross-sections requires assumptions which have proved to be incorrect at least for aromatic molecules. Those assumptions were: (a) that any change in the amount of adsorbed organic produced a corresponding change in sites available for adsorption of hydrogen; (b) that adsorption of hydrogen did not alter the nature or amount of adsorbed organic; and (c) that the electrolytic charge to oxidize an adsorbed molecule (n-value) was independent of the amount initially adsorbed. Assumption (a) is incorrect whenever the adsorbate molecules are adsorbed in different states (e.g., orientations) at different coverages. Assumption (b) is incorrect whenever reduction, desorption or re-orientation occurs as a result of a change in hydrogen adsorption or electrode potential; these are common occurrences. And, assumption (c) is false whenever the n-value for anodic oxidation is a function of adsorbed state (e.g., mode of attachment varies with coverage). A direct comparison of the correct adsorption data (thin-layer coulometry) with data obtained using the two previous methods has been made (64). Note that the hydrogen co-deposition methods not only failed to give absolute magnitudes of adsorbed amounts, but gave the wrong relative coverages, and even displayed incorrect qualitative coverage variation such that structural transitions were barely evident, or undetectable. Compounds studied were: hydroquinone, 1,4-dihydroxynapthalene, and 2,2',5,5'-tetrahydroxybiphenyl.

8. Influence of Anions on Aromatic Adsorption.

Studies were made of the adsorption, orientation (mode of attachment) and electrochemical oxidation of hydroquinone at smooth polycrystalline Pt electrodes in aqueous electrolytes having various degrees of surface activity towards Pt (44,63,66). In particular, we examined the influence of various anions on packing density, oxidation n-values (n_{ox}), and adsorption potential dependence. Ten electrolytes were studied: $HClO_4$, $NaClO_4$, $CsClO_4$, H_2SO_4, H_3PO_4, $NaPF_6$, NaF, NaCl, NaBr and NaI. Packing density, orientation and n_{ox} were barely affected by perchlorate, sulfate, phosphate, hexafluorophosphate, or fluoride media. n_{ox} decreased somewhat with increasing pH but there was no effect of Na^+ or Cs^+.

However, the three more strongly surface-active halides (Cl^-, Br^-, I^-) (24,38,41) had a profound effect on aromatic orientation. Experiments of three basic types were performed to characterize the influence of these ions on aromatic adsorption (44,66): (i) halide pretreatment prior to aromatic adsorption; (ii) halide in solution with the aromatic; or (iii) halide treatment of the adsorbed aromatic layer. All three types yielded similar results: Pretreatment of the Pt surface with dilute iodide (5×10^{-4} NaI) totally prevented chemisorption of hydroquinone. Pretreatment with 2×10^{-3} $\underline{M}$ Br^- severely attenuated hydroquinone adsorption (exposure for 180 sec.) at low concentrations but did little to prevent formation of an edgewise adsorbed layer at aromatic concentrations above 10^{-3} $\underline{M}$. Chloride ions had a moderate influence at low concentrations but were displaced almost completely by 3×10^{-3} $\underline{M}$ hydroquinone. It should be noted that halide displaced from the thin-layer electrode surface remains in the thin-layer cavity, such that these results reflect the competitive adsorption between halide and aromatic, starting from adsorbed aromatic. Similar adsorption profiles were obtained when a clean Pt surface was exposed to mixed solutions of aromatic and halide. Again Br^- had a stronger influence than Cl^- at the same concentration. The influence of 10^{-3} $\underline{M}$ halide was comparable to pretreatment with halide; use of higher halide concentrations led to sharply increased attenuation of aromatic adsorption.

The influence of halide on hydroquinone adsorption was also investigated as a function of electrode potential (66). Maximum interference by halide occurred near -0.1 volt vs. AgCl reference, although a moderate increase in halide influence was also observed at potentials more positive than 0.4 volt apparently due to electric field assisted specific adsorption of halide.

Desorption of pre-adsorbed aromatic compounds by halide increases in the order $Cl^- < Br^- \ll I^-$ (66), and is a function of halide concentration. Desorption of twenty-eight aromatic compounds by I^- solutions was investigated (44). <u>For all twenty-eight compounds, the material desorbed from the surface</u>

was identical to the starting material. This is conclusive evidence that under the conditions of our experiments, the aromatic compounds were adsorbed essentially intact, without appreciable changes in molecular frame-work. Recovery was greater than 90% when 10^{-2} M NaI was used (66). Only slight differences in ease of desorption were observed in comparisons between flat and edgewise adsorbed states (66).

When flat-adsorbed aromatics were treated with 10^{-3} M NaI for 180 seconds, the amount of halogen adsorbed exceeded that expected from the amount of aromatic desorbed (44). Granted that the area occupied by an I atom is constant, this suggested that the aromatic molecules remaining on the surface re-orient to take up less surface area. Indeed, quantitative comparison of the data with molecular models indicated that the adsorbed aromatic molecules were no longer in the flat orientation. The same edgewise orientations as were formed by concentration-induced transitions give an exact fit with experiment for all of the large number of compounds studied (44). A brief summary of these findings is as follows:

(i) aromatic molecules were re-oriented and eventually displaced from the Pt surface by I^- ions;

(ii) iodide uptake by the surface was most rapid in acidic media;

(iii) displacement of the aromatic by I^- was most nearly complete at -0.1 volt vs. the AgCl reference;

(iv) aromatic compounds having alkyl substituents were less readily desorbed by I^- ions;

(v) re-orientation favored edgewise structures occupying minimum surface area;

(vi) where possible a ring edge having only H atoms as substituents was closest to the surface;

(vii) biphenyl derivatives re-oriented with both rings edgewise to the surface;

(viii) compounds attached to the surface through strongly surface-active substituents such as -SH were not re-oriented by I^- ions.

9. Effect of Surface Roughness on Adsorbate Orientation and Reactivity.

Adsorbate orientation and anodic oxidation of hydroquinone have been studied at Pt thin-layer electrodes purposely roughened by platinization or mechanical polishing (79). Roughness factors, A/A_o, were determined by precise measurements of H adsorption and I adsorption packing densities. Isotherms, $\Gamma(C)$, and adsorbate-oxidation n-values, $n_{ox}(C)$, were determined for a range of surface roughnesses, $1.02 \leq A/A_o \leq 5$. Beyond $A/A_o > 5$, the orientation transition of HQ essentially vanished. Taken together with data concerning mode of bonding to smooth surfaces (97), the adsorption and oxidation data suggest that the suppression of the packing density transitions by surface roughness arises from inhibition of adsorption in the vertical orientation. The results account for the fact that packing-density (orientational) transitions were not observed in studies involving platinized or non-annealed Pt surfaces. Surface roughness effects are attributable to breakdown of cooperative adsorption/reorientation phenomena due to disruption of optimum conditions for stable bridge-bonding to the surface and intermolecular hydrogen-bonding in the edgewise orientation. Mechanical polishing with 0.25 micrometer diamond particles and electrochemical etching decreased surface roughness appreciably (down to $A/A_o = 1.4$), but did not produce sufficient smoothness for oriented adsorption comparable to high temperature annealing.

10. Ordered/Disordered Packing in Chemisorbed Mixtures.

Adsorptive competition between pairs of aromatic compounds at annealed polycrystalline Pt thin-layer electrodes in aqueous solution at room temperature has been studied (82,96,97).

When hydroquinone (HQ) and naphthohydroquinone (NHQ) were both present at concentrations below 10^{-4} $\underline{M}$, a mixed adsorbed layer was formed in which both compounds were oriented flat (82). However, when either concentration (or the total concentration) exceeded 10^{-3} $\underline{M}$, the mixed adlayer consisted of both adsorbates in the vertical orientation. NHQ was adsorbed more rapidly and strongly than HQ at all bulk concentrations studied. Precise comparisons of the mole fraction ratio in the adsorbed phase with that in the solution phase revealed that the mixed interactions between HQ and NHQ were very similar to the self-interactions of the pure compounds.

Likewise, accurate packing-density measurements were made for mixtures of NHQ with 2,2',5,5'-tetrahydroxybiphenyl (THB), and of NHQ with phenylhydroquinone (96). In contrast to the results reported above, the packing of structurally dissimilar pairs of compounds resulted in various degrees of disordered, inefficient packing. These observations correlated with the degree to which the edgewise-oriented structures would be expected to promote efficient intermolecular hydrogen bonding.

Order-disorder effects in competitive chemisorption were then examined in detail for NHQ and THB (97). Mixed adsorption profiles for these compounds showed minima in total packing density which resulted from decreased adsorption of NHQ. For example, with the edgewise orientations, traces of THB in an adlayer composed primarily of NHQ introduced disorder into the layer which lowered the packing density of NHQ. Electrochemical reactivity of the adlayer was sharply influenced by disorder.

11. Influence of Non-Aqueous Solvents on Aromatic Adsorption.

The chemisorption behavior of NHQ at annealed polycrystalline Pt thin-layer electrodes has been studied from aqueous solutions containing preselected amounts of benzene, benzoic acid or HQ in order to explore the influence of non-aqueous solvents (91). Adsorption profiles were found to be extremely sensitive to the presence of any of these model aromatic "solvents". As little as 10^{-5} $\underline{M}$ (1 ppm) of these compounds in water was sufficient to alter the adsorption profile of NHQ by suppressing the orientational transitions in favor of the fully edgewise orientation. At concentrations above 10^{-3} $\underline{M}$ the edgewise orientation of NHQ was completely suppressed.

Moving further in the direction of aromatic adsorption and reactivity at Pt surfaces in non-aqueous solutions, studies were made of the chemisorption of NHQ and THB at annealed polycrystalline Pt thin-layer electrodes from aqueous solutions containing preselected amounts of acetonitrile (93), a widely-used non-aqueous solvent. Acetonitrile, CH_3CN, was found to influence the adsorption profiles of NHQ and THB to a moderate extent: coadsorption of CH_3CN promoted edgewise aromatic adsorption even at concentrations of aromatic for which the flat orientation would otherwise have occurred. As a result, CH_3CN acted as a promotor of the distinctive reactivity of edgewise-oriented adsorbed aromatic intermediates such as the distinctive, reversibly-electroactive edge-pendant ($4,5-\eta^2$) orientation of THB (93).

12. Gas-Phase and Electrochemical Hydrogenation of Ethylene.

Rates of hydrogenation of ethylene to ethane under gas-solid (GS) and liquid-solid (LS) conditions at well-defined Pt(111) and annealed polycrystalline Pt surfaces were measured and compared (75). Comparison of the rate laws under appropriate conditions showed that the hydrogenation proceeded by different reaction mechanisms at the two different interfaces. We have employed a combination of solution and ultrahigh vacuum surface analysis procedures (low-energy electron diffraction, Auger electron spectroscopy, high-resolution electron energy-loss spectroscopy, temperature programmed desorption and electrochemistry) to characterize the adsorbed species formed under GS and LS reaction conditions and to gain insight into the reaction mechanisms. The results suggested that in hydrogenation at the LS interface ethylene was reduced on the Pt surface by adsorbed H atoms, while in hydrogenation at the GS interface H atoms were transferred from the Pt surface through a layer of irreversibly adsorbed ethylene to ethylene that is adsorbed on top of this layer.

13. Effect of Low-Level Surface-Active Impurities on Aromatic Adsorption.

Changes in the adsorption profiles of NHQ on annealed polycrystalline Pt thin-layer electrodes in aqueous 1 M $HClO_4$ brought about by varying levels of surface-active organic impurities (typified by HQ and benzene) have been observed (84). As little as 10^{-5} M HQ or benzene (1 ppm) was sufficient to alter the adsorption profile of NHQ. Similar results were produced by traces of iodide ion (44). The profound influence of traces of surface-active impurities may help to account for the marked discrepancies among adsorption measurements for aromatic compounds reported in the literature by various workers.

14. Influence of Oriented Adsorbates on Electrode Rates.

We have explored the influence of single, oriented, adsorbed layers on the electrode kinetics of unadsorbed uncharged redox couples at annealed polycrystalline Pt thin-layer electrodes in aqueous solutions (87,88). Redox couples investigated were: cis-dinitrodiammino-trans-dichloroplatinum (IV) and cis-dinitrodiammineplatinum (II); benzoquinone and hydroquinone; naphthoquinone and hydroquinone; t-butyl-benzoquinone and t-butyl-hydroquinone; or duroquinone and durohydroquinone. Stable, irreversibly-attached monolayers were formed by pretreating the Pt electrode with: KCl; KI; KCN; KSCN; K_2S; dimethylsulfoxide; pyridine; hydroquinone sulfonic acid; hydroquinone; naphthohydroquinone; t-butyl-hydroquinone; durohydroquinone; pentafluorothiophenol or phenyltriethylammonium perchlorate. Profound enhancement or retardation of the subject redox rates were observed depending upon the surface layer which had been applied. In a majority of cases the redox rate law (mechanism) was altered by the presence of a pre-adsorbed layer. The results could be understood in terms of three types of phenomena: steric blocking of reactive surface sites; adlayer dielectric thickness effects; and interionic (double-layer) effects between the adsorbed layer and the reaction intermediates.

15. Electrodeposition onto Well-Defined Surfaces.

The Pt(111)($\sqrt{7}$x$\sqrt{7}$)R19.1^{o}-I superlattice, which formed spontaneously at room temperature when the Pt(111) surface was exposed to I_2 or HI vapor (35,38), was used as a well-defined starting point for studies of the structure of silver electrodeposited from aqueous solutions (52,54). LEED patterns were obtained after removal of the electrode from solution at various points along the cyclic current-potential curves. The iodine atomic layer was stable in aqueous $AgClO_4/HClO_4$ electrolytes at open circuit, and nicely served the purpose of protecting the surface from attack by electrolyte and residual gases. When electrodeposition was commenced, the LEED pattern began to show (3x3) beams due to an electrodeposited layer in addition to the ($\sqrt{7}$x$\sqrt{7}$) beams of the iodine layer. After completion of the first deposition peak, the LEED pattern was exclusively (3x3). Auger spectra obtained at this point confirmed the silver coverage based upon the electrochemical data. The most probable structure was deduced from the data. LEED patterns indicative of an ordered surface were obtained at all stages of the silver electrodeposition process. Likewise, lattices consistent with the unequal sizes of Pt and Ag atoms were obtained at silver coverages of a monolayer and above. Quantitative data and possible structures are presented in References 52 and 54.

Comparison of Auger intensities for Pt, Ag and I at various stages of electrodeposition revealed that the iodine atomic layer was always the outermost layer. The silver electrodeposit was located underneath the iodine layer; when the silver was redissolved by anodic dissolution at controlled potential, the iodine remained on the surface. Deposition of up to one hundred layers has been studied. Accordingly, iodine atoms protect the substrate and electrodeposit from attack by solvent and electrolyte without interferring appreciably with the electrodeposition process. This indicates a promising direction for future research having to do with non-aqueous batteries: determination of the extent to which halides and other simple adsorbates are able to prevent solvent molecules and contaminants from interfering with electrodepositon in recharging of practical battery systems.

Similar results were obtained in a study of the electrodepositon of copper onto the well-defined Pt(111) surface pretreated with I_2 (55).

Silver electrodeposited onto a variety of iodine adlattices on Pt(100) was investigated by LEED, Auger spectroscopy and thermal desorption mass spectroscopy (56). The iodine adlattices were: Pt(100)[c($\sqrt{2}$x2$\sqrt{2}$)]R45^{o}-I (35,38), for which $\theta_I = 0.50$; Pt(100)(incommensurate)R45^{o}-I, for which $\theta_I = 0.52$ (35); and Pt(100)[c($\sqrt{2}$x5$\sqrt{2}$)]R45^{o}-I, $\theta_I = 0.60$, a new adlattice formed when Pt(100) was heated with I_2 vapor at atmospheric pressure (57). The I Auger signal was not appreciably affected by Ag deposition, indicating that the I atoms were located in the topmost layer of the surface at all Ag coverages. Electrodeposition proceeded very differently on the three I adlattice structures. Deposition onto Pt(100)[c($\sqrt{2}$x2$\sqrt{2}$)]R45^{o}-I proceeded in two separate, narrow underpotential peaks to form two highly ordered new superlattices, Pt(100)($\sqrt{2}$x$\sqrt{2}$)R45^o-(Ag,I) and Pt(100)($\sqrt{34}$x$\sqrt{34}$)R31^o-(Ag,I). Deposition onto the Pt(100)(incommensurate)R45^o-I surface was vastly different, spanning a wide range of underpotentials and producing diffuse electrodeposited layers; this illustrates the high degree of sensitivity of the electrodeposition process to substrate atomic structure. Deposition onto the Pt(100)[c($\sqrt{2}$x5$\sqrt{2}$)]R45^o-I adlattice likewise occurred over a wide range of potentials, forming islands of silver rather than monoatomic layers. Ion-bombardment or electrochemical redox cycling of the surface also led to structurally diffuse Ag electrodeposition behavior. Thermal desorption mass spectroscopy revealed that the halogen desorbs first, as I atoms, followed by Ag atoms, bulk silver preceeding UPD silver. Silver iodide thermal desorption (234 and 236 AMU) did not occur from electrodeposited samples.

We have also studied the adlattices (ordered adsorbed layers) and superlattices (crystalline deposited films) which occurred when the Pt(s)[6(111)x(111)] step terrace surface was exposed to I_2 vapor and when Ag was electrodeposited onto the I_2-pretreated surface (67). Although ultra-high vacuum studies of step-terrace surfaces have been reported (thirty articles are cited in Reference 67), ours was the first study of structures formed at atmospheric pressure and the first study of metal electrodeposition on a well-defined step-terrace surface.

Treatment of Pt(s)[6(111)x(111)] with I_2 vapor at atmospheric pressure or in ultra-high vacuum produced the same structure in about the same quality: Pt(s)[6(111)x(111)][7$\sqrt{3}$x step]R30^o-I, $\theta_I = 0.44$. This is a nearly hexagonal array of I atoms on the nearly hexagonal step-terrace substrate surface. Programmed heating of this structure in Ar or vacuum produced somewhat diffuse (3x step) and ($\sqrt{3}$x step) LEED patterns but not the slightest hint of the $\sqrt{7}$ structure which is characteristic of Pt(111). Programmed desorption mass spectroscopy and Auger spectroscopy did not detect any tendency for iodine to adsorb selectively at the steps. Electrodeposition onto the $7\sqrt{3}$ adlattice occurred in three narrow, well-separated UPD peaks. Iodine atoms form the top layer based upon Auger spectroscopy. The three UPD peaks led to formation of three new superlattice structures: Pt(s)[6(111)x(111)](3x terrace)-(Ag,I) at $\theta_{Ag} = \theta_I = 0.44$; Pt(s)[6(111)x(111)](1x terrace)-(Ag,I) at $\theta_{Ag} = 0.9$ and $\theta = 0.44$; and Pt(s)[6(111)x(111)]-(17x terrace)-(Ag,I) at $\theta_{Ag} = 1.8$. These three superlattices resemble in one dimension those for smooth Pt(111), but with the important differences that the steps completely alter the periodicity in the other dimension. There was no observable tendency for Ag deposition or thermal desorption to occur uniquely or selectively at steps. These findings indicate that a major role of steps in practical electrode reactions is to break up the long range order which would otherwise be expected on the crystal planes of the electrode material.

16. Preparation of Well-Defined Surfaces at Atmospheric Pressure.

We have recently discovered a means of producing well-ordered single-crystal surfaces at atmospheric pressure, and of verifying that the desired structure has been formed without the necessity of LEED or other elaborate ultra-high vacuum procedures (57,58). This initial work employed Pt substrates in halogen vapor for surface preparation, and linear scan voltammetry for surface structure verification, but we expect that many other equally useful examples will be found. This approach should lead to rapid progress in the study and application of well-defined surfaces by making such surfaced available to laboratories (the vast majority) which do not have facilities for manipulation of well-defined surfaces under practical chemical/electrochemical reaction conditions.

Pt(100) monocrystal surfaces purposely disordered by ion bombardment or electrochemical redox are restored to an ordered state by programmed heating in an Ar atmosphere containing I_2 vapor (57). (Electrochemical redox is the classical method by which Pt electrodes are cleaned or "activated" prior to use.) LEED and Auger studies showed that the initial product is a $Pt(100)[c(\sqrt{2}x5\sqrt{2})]45^{o}-I$ adlattice $\theta_I = 0.6$, consisting of a nearly hexagonal, centered rectangular array of I atoms on a simple Pt(100) substrate surface. Programmed heating of this adlattice led to stepwise desorption of halogen, forming a series of derivative adlattices previously observed in vacuum. One of these, $Pt(100)[c(\sqrt{2}x2\sqrt{2})]-R45^{o}-I$, at $\theta_I = 0.50$, proved to be particularly amenable to identification, without LEED, by means of its unusually distinctive cyclic voltammogram for Ag electrodeposition. A remarkable aspect of this discovery is that the quality of the structures formed at atmospheric pressure is superior to that of the same structures when formed in ulta-high vacuum. Apparently, the higher pressure of halogen allows each structure to approach more closely to the ideal state of minimum energy.

Similarly, Pt(111) surfaces purposely disordered by ion-bombardment or redox also were restored to a well-ordered state by heating in I_2 vapor at atmospheric pressure (58). Again a new adlattice, Pt(111)$(3\sqrt{3}x3\sqrt{3})R^{o}$-I, θ = 0.6, was formed from treatment with I_2 at atmospheric pressure. This is an hexagonal array of I atoms on a simple Pt(111) substrate surface. Programmed heating of this adlattice in Ar led to stepwise desorption of halogen, again forming a series of lower coverage I atom adlattices: Pt(111)[3x3]-I, θ_I = 0.44; Pt(111)$(\sqrt{7}x\sqrt{7})R19.1^{o}$-I, observed also in vacuum, θ_I = 0.43; and Pt(111)$(\sqrt{3}x\sqrt{3})R30^{o}$-I, θ_I = 0.33, observed in vacuum, also. The quality of these structures was far superior to that of the same structures formed in ultra-high vacuum. Accordingly, this discovery provides greater quality as well as convenience for preparation of well-defined surfaces.

17. Discovery of the Orderedness of Adsorbed Ionic Layers.

We have discovered that when a Pt(111) surface is immersed into an aqueous ionic solution an ordered adsorbed layer is spontaneously formed (76). On the basis of LEED the following structures were formed by various salts as indicated: Pt(111)$(2\sqrt{3}x2\sqrt{3})R30^{o}$-(KCN); Pt(111)(2x2)-(KSCN); Pt(111)(diffuse 1x1)-(K_2S); Pt(111)(3x3)-I, from KI; and Pt(111)(3x3)-(KBr). KI solutions yielded a layer of neutral I atoms requiring no cationic counterion, in agreement with our thin-layer electrochemical studies (24). All ionic concentrations from 10^{-4} to 10^{-1} M yielded the same adlattice structures, although 10^{-5} M KI gave the Pt(111)$(\sqrt{7}x\sqrt{7})R19.1^{o}$-I structure reported from dosing with HI or I_2 vapor in vacuum (35,38). The adsorbed layer functioned as a cation-exchanger: K^+ ions were quantitatively replaced by H^+ or Ca^{2+}.

However, Auger spectroscopy revealed that the packing density of cations was much lower than that of the chemisorbed layer; that is, the adsorbed layer was only partially ionized.

18. Cation-Selectivity in the Electrical Double-Layer.

Characterization of the Pt(111)$(2\sqrt{3}\times2\sqrt{3})R30^{\circ}$ structure which formed when Pt(111) was immersed into aqueous KCN solutions at controlled potential and pH by LEED, Auger spectroscopy and thermal desorption mass spectroscopy revealed that it consisted of isolated adsorbed CN^- ions surrounded by adsorbed CNH molecules and K^+ counterions (86). When immersed into aqueous solutions of simple chloride salts this surface underwent cation-exchange without loss or rearrangement of the CN^-/HCN layer, based upon Auger spectroscopy and LEED. Experiments in which cations were made to adsorb competitively from mixtures of chloride salts revealed that a remarkable degree of selectivity exists in the interaction of cations with this CN^- layer. Highly-charged cations predominated. Among cations of the same charge, those least strongly hydrated and those of relatively small size predominated. At the cyanide-pretreated Pt(111) surface the order of preference for cations was: $La^{3+} >> Ba^{2+} > Ca^{2+} >> Mg^{2+} >> K^+ > Na^+ = Cs^+ > NH_4^+ > H^+ >> Li^+ >> NR_4^+$. Quaternary ammonium cations were strongly excluded from the double-layer, even when present in solution at 100-fold excess over other cations.

19. Discovery of Electrode Surface Polyprotic Acidity.

Measurements were made for the first time of the extent of Cs^+ retention (surface acid-base neutralization) of adsorbed CNH molecules at the Pt(111) surface as a function of solution pH (89,92). The first stage of acid dissociation occurred readily as for an unadsorbed strongly acidic molecule. This layer resisted ionization up to about pH 9. At higher pH a second stage of dissociation was observed. The resistance to full ionization is attributable to formation of a surface lattice (adlattice) consisting of adjacent, mutually-repelling anions. Packing density of cations was measured by means of quantitative Auger electron spectroscopy (30).

Similar studies were carried out for surfaces containing adsorbed SCNH (76) molecules. Acid-base behavior analogous to that for adsorbed CNH was found (89).

When Ca^{2+} was the counter-ion surface ionization was limited to a single transition below pH 3 due to the larger size of the Ca^{2+} cation which remained heavily hydrated after adsorption, emersion and evacuation (89).

Experiments were also carried out in which pH was held constant at 9.2 and electrode potential was varied from -1 to +1 volt vs. Ag/AgCl (89). Structure of the CNH/CN^- layer was potential-dependent: reconstruction of the $Pt(111)(2\sqrt{3}x2\sqrt{3})R30^\circ$ adlattice occurred negative of -0.45 V with slight loss of CNH from the surface to form a $Pt(111)(\sqrt{13}x\sqrt{13})R14^\circ$ adlattice. Cation packing density was nearly independent of electrode potential, except at potentials where oxidation of the surface occurred.

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