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THERMODYNAMIC CHARACTERIZATION OF METAL PHTHALOCYANINES-HUMAN SERUM ALBUMIN INTERACTIONS

The temperature dependence of the binding constants for human serum albumin and sulfonated metal-phthalocyanines were estimated by fluorescence spectroscopy. Stern-Volmer's analysis and Chipman's fits provided binding data for van't Hoff calculations of the thermodynamic parameters governing these interactions. Results show that the formations of the HSA- phthalocyanine complexes are favorable processes by both the ΔH^o and ΔS^o. However, the formation of HSA-$AlPcS_4$ has a stronger dependence than HSA-$ZnPcS_4$on ΔS^o.

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A KINETIC STUDY OF THE OXIDATION-REDUCTION CHEMISTRY OF CYTOCHROME *C* BY UV-VISIBLE SPECTROPHOTOMETRY

The rate laws for oxidation of ferrocytochrome *c* (Fe^{2+}) to ferricytochrome *c* (Fe^{3+}) by O_2 in the air at ambient conditions have been studied at pH 3.5, 6.5, 7.5 and 8.5 by UV-visible spectrophotometry. The oxidation reactions conducted at pH 3.5, 6.5 and 7.5 were first-order in ferrocytochrome *c* (Fe^{2+}) with rate constants being 0.0207 min^{-1}, 0.0093 min^{-1}, and 0.0037 min^{-1}, respectively. At pH 8.5, no oxidation reaction took place. The first-order rate law demonstrates that the oxidation is resulted from interaction of only a single ferrocytochrome *c* (Fe^{2+}) molecule with O_2 on the molecule's heme iron. The kinetic study established a linear relationship between the rate constant of the oxidation reaction and the pH value of the cytochrome *c* solution:k (min^{-1}) = -0.00420 pH + 0.0355. This unprecedented relationship is accounted for as that the rate of electron transfer from ferrocytochrome *c* (Fe^{2+}) to O_2, which is proportional to the reduction potential of oxygen directly related to pH, dictates the rate constant for the oxidation reaction. Upon reaction with hydrogen peroxide at ~1 M, cytochrome c underwent denaturation likely due to formation of a Fe=O double bond in its heme iron.

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SURFACE STUDIES OF 2,5-BIS(N,N'-DIMETHYL)-1,4-BENZOQUINONE ON IRON, COPPER AND ALUMINUM

2,5-Bis(N,N'-dimethyl)-1,4-benzoquinone, an amine quinone monomer (AQM14a) is deposited by sublimation on iron, copper and aluminum foils in order to investigate the mechanism for corrosion inhibition. The molecule stores excess electron density in the carbonyl region of the molecule as demonstrated by its low stretching frequency of 1620 cm^{-1}. The 100 cm^{-1} carbonyl shift from thin film on iron and 1.9 eV shift up in the oxygen 1s electron feature seen by XPS indicates a strong electron donation to the surface from the monomer. This suggests that the molecule is donating its excess electron density into the bulk surface. The carbonyl feature does not appear to shift in the spectra taken on the thin films deposited on copper and aluminum.

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CARBON DEPOSITION OVER Pt/Al_2O_3 AND Pd/Al_2O_3 CATALYSTS IN THE DRY REFORMING OF METHANE WITH CARBON DIOXIDE REACTION

A thermal gravimetric analyzer was used to determine the amount of carbon deposition on Pt/Al_2O_3 and Pd/Al_2O_3 catalysts used in the dry reforming of methane with carbon dioxide. The rate of carbon deposition increased as temperature was increased from 700° to 900°C. The activation energies for carbon deposition were determined to be 97 kJ/mol for Pd/Al_2O_3 and 218 kJ/mol for Pt/Al_2O_3. Since coking is the major mode of catalyst deactivation for the dry reforming of CH_4 with CO_2, the Pt catalyst should exhibit a longer catalyst life than the Pd catalyst.

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DEGRADATION ANALYSIS OF POLYCYCLIC AROMATIC HYDROCARBONS BY MYCOBACTERIUM PRY-1 WITH EXCITATION EMISSION FLUORESCENCE SPECTROSCOPY

Fluorene, 2-ethyl naphthalene and 1-methyl naphthalene, all polycyclic aromatic hydrocarbons (PAHs) found in petroleum mixtures, were exposed to Mycobacterium PRY-1 and extracted after a series of increasing time intervals to determine the relative rates of degradation with excitation emission matrix (EEM) spectroscopy. While past researchers have documented the usefulness of utilizing fluorescence analysis to characterize petroleum contaminated sites, spectra is often hard to interpret due to complications we discuss. Information on how a specific PAH does degrade can be used to yield a better understanding of these systems. Serial dilutions of the extracts were produced and spectra were obtained from various concentrations to match our past work on petroleum mixtures. Total molecule degradation seems to vary over a 14 week period and thus the rates may not be uniform as we suggested could be the case for specific PAH's in our previous publication with motor oil under the same conditions.

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SYNTHESIS AND CHARACTERIZATION OF *fac*-DICARBONYL-NITROSYLTRIS(1-METHYL-IMIDAZOLE) MOLYBDENUM(0) HEXAFLUOROPHOSPHATE

The novel coordination compound [*fac*-$(MeIm)_3Mo(NO)(CO)_2]PF_6$ (MeIm = 1-methylimidazole) was synthesized from [(bpy)$(MeIm)Mo(NO)(CO)_2]PF_6$ (bpy = 2,2'-bipyridyl) in 63% yield. It was characterized by IR, ^{1}H NMR, and ^{13}C NMR spectroscopy, as well as combustion analysis and cyclic voltammetry. The structure was confirmed by single-crystal x-ray diffractometry. It is hoped that this compound will serve as a precursor to a novel π-basic dearomatization agent. An improved synthesis of [(bpy)(MeIm)$Mo(NO)(CO)_2]PF_6$ is also reported.

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EVIDENCE FOR ENERGY TRANSFER IN ISOMERIC METHYLNAPHTHALENE MIXED EXCIMERS ON Al_2O_3(0001)

Methylnaphthalene has been shown to form amorphous adlayers when vacuum deposited onto a cryogenically cooled surface of Al_2O_3. When optically excited, amorphous methylnaphthalene adlayers form excimers in the excited state, whose fluorescence is characteristically red-shifted, broad and featureless in the visible spectrum. If the surface temperature is linearly ramped by resistive heating, translational and rotational degrees of freedom allow the adlayer molecules to rearrange and undergo disorder-to-order transition. When a bilayer of both 1-methylnaphthalene and 2-methylnaphthalene was prepared, an increase in emission intensity was observed at a temperature near desorption and has been tentatively attributed to the formation of mixed excimers. Energy transfer was also expected from one to the other molecule of the mixed excimer, and the results indicated that for this system of 2-methylnaphthelene and 1-methylnaphthalene, the energy transfer was from the former to the latter molecule.

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DISUBSTITUTIONAL EFFECT ON NAPHTHALENE FLUOROPHORES ON Al_2O_3(0001)

Optical emission spectroscopy is a sensitive method by which thermally induced changes in the morphology of adlayer molecules on surfaces can be monitored. If sufficient thermal energy is applied to a surface composed of amorphously adsorbed molecules, the molecules have been found to undergo translational and rotational motion to rearrange to lower energy configurations, assuming that such low energy configuration exist. As thermal energy is given to the surface, the molecules will either undergo ordering transition if dispersion forces are substantial; if not, then the molecule will remain disordered through desorption. Molecules that have large surface areas have sufficient dispersion forces to interact with nearest neighbor molecules and they will tend to undergo disorder-to-order transition. For disubstituted naphthalenes, substitution on the carbon b to the bridgehead positions will cause the dispersion forces to become substantial. Otherwise, the molecule does not undergo the disorder-to-order transition and will exhibit excimer fluorescence through desorption.

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