dimerization was found to occur by a side reaction involving molecular oxygen; therefore, the catalytic reaction resulting in vanillin formation can be credited with at least 75% selectivity. The rate of dehydrodiisoeugenol formation in the uncatalyzed reaction with O_2 is about 10–20% as fast as the oxidation of substrate with CoSMDPT. Only at very low catalyst concentration or elevated reaction temperatures (≥60 °C) does the side reaction become important.

The formation of vanillin as a product has been unquestionably proven: NMR (singlet 9.8 ppm from Me_4Si), IR (carbonyl stretch), GC (co-injection experiment) and classical derivative analysis. Both the dinitropicrylhydrazyl, DNP, and semicarbazide derivatives of vanillin were prepared. The experimentally determined melting point of the DNP derivative and the semicarbazide derivative were found to be 268 and 227 °C, respectively, comparing favorably to the literature values of 271 and 230 °C.[9] Comparison of elemental analysis data for synthesized vanillin semicarbazide (VSC) to that for purchased reagent grade vanillin semicarbazide was very close (reagent grade VSC, 51.40% C, 5.55% H, and 20.02% N; synthesized VSC, 51.69% C, 5.24% H, 19.85% N). Verification of acetaldehyde as a second product was confirmed by using NMR spectroscopy, which showed two singlets in the aldehydic region for samples removed during the oxidation reaction. Intensity of the one aldehydic peak was increased considerably by spiking of the samples with acetaldehyde. The principal oxidation reaction that occurs in the cobalt catalyzed oxidation is shown in path 1.

Reaction parameters such as solvent, temperature, catalyst concentration, and O_2 pressure were varied in the study. Solvent effects indicate that methanol > toluene > CCl_4 for the reaction rate. Although the rate in methanol is fourfold greater than in CCl_4, the total absorption of dioxygen is about 25% less in methanol than in toluene or CCl_4. These variances in reaction rate may be attributed to diminished lifetime of the cobalt catalyst.

The reaction was found to be first order in CoSMDPT concentration (Table I), over a defined range, at different O_2 pressure levels while constant temperature was maintained. At low cobalt concentrations, the reported rate of oxygen uptake tended to be higher than expected for first-order kinetics which can be attributed to the competing dimerization reaction. With concentrations of catalyst up to 0.5 mg/mL solution, the rate was first order in cobalt(II). Oxygen dependence in the CoSMDPT reaction was found to be first order in nature, as was the substrate dependence. A rate law for the reaction over the pressure and concentration range described can be written by using the obtained information:

$$\text{product formation} = K_T[\text{CoSMDPT}][\text{isoeugenol}][O_2]$$

Aliquots from a reaction in progress were taken at regular intervals and studied by EPR. As the reaction progressed, the intensity of the cobalt dioxygen signal decreased and so did the rate of the reaction.[7] Addition of basic materials did not greatly alter the reaction, but the presence of acids or hydrogen bonding materials did inhibit the rate of vanillin formation. Thus, this reaction has many features in common with our earlier findings on the mechanisms of oxidation of substituted phenols by this catalyst system.[1]

By analogy to earlier studies we propose that the phenolic group of isoeugenol is converted to a phenoxy radical by our catalyst as demonstrated for the oxidation of 2,6-dimethylphenol to the substituted benzoquinone. In this latter system, $Co-O_2$ attack on the phenoxy radical was the next step leading to quinone formation.[1] Unpaired electron delocalization in the isoeugenol radical can lead to an allyl type of π system (consisting of the para carbon and the C=C of the α- and β-carbons of the substituent) for the substituent. At this point we can only speculate about a reaction path that leads to the observed products to provide a basis for further experiments. Attack by $Co-O_2$ at the β-carbon of the allyl substituent in the isoeugenol radical could occur leading to a dioxetane which decomposes into vanillin and acetaldehyde. By analogy with the substituted phenol oxidation the Co(III) resulting from this decomposition would then react with isoeugenol, forming the phenoxy radical and regenerating cobalt(II). Though speculative, the reaction sequence described above has precedence in the literature for all steps except the attack of the β-carbon by $Co-O_2$. Alternatively, a reaction sequence that involves conversion of dehydrodiisoeugenol to products may occur. Research is under way to establish the mechanism.

Acknowledgment. We acknowledge the support of this research by the National Science Foundation through Grant 84 08149.

---

[9] Roberts, R. M.; Gilbert, J. C.; Rodewald, L. B.; Wingrove, A. S. *Modern Experimental Organic Chemistry*, 2nd ed.; Holt, Rinehart, and Winston: San Francisco, CA, 1974.

Optical Coupling of Surface Chemistry. Photoluminescent Properties of a Derivatized Gallium Arsenide Surface Undergoing Redox Chemistry

Hal Van Ryswyk and Arthur B. Ellis*

Department of Chemistry
University of Wisconsin—Madison
Madison, Wisconsin 53706

Received December 23, 1985

Photoluminescence (PL) can be a powerful tool for examining semiconductor-derived interfaces. In recent studies, we have demonstrated that PL from semiconductor electrodes is influenced by applied potential[1] and that PL from semiconductors coated with Pd films is sensitive to hydrogen gas.[2] In both the semiconductor/liquid and semiconductor/metal interfaces, PL intensity conforms to a dead-layer model that permits the mapping of the electric field in the semiconductor: electron–hole pairs formed within a distance on the order of the depletion width do not contribute to PL.[3]

These results, which indicate that bulk PL can be influenced by interfacial chemistry, have prompted us to examine PL from a semiconductor/molecular interface. We report in this paper on the PL properties of n-GaAs derivatized with a redox-active film. In particular, we demonstrate that redox chemistry in the film can alter the depletion width of the underlying semiconductor by several hundred angstroms, as reflected in substantial changes in PL intensity satisfying a dead-layer model. Moreover, our results suggest a general strategy for designing optically coupled sensors with chemical specificity.

Samples of n-GaAs[4] were derivatized with (1,1′-ferrocenediyl)dichlorosilane by the method of Wrighton et al. to yield the idealized structure shown in Scheme I; some polymerization may also occur.[5] Surface attachment was verified by cyclic voltammetry under photoexcitation in CH_3CN with 0.1 M $[n\text{-}Bu_4N]BF_4$ as supporting electrolyte. Integration of the cyclic voltammetric waves shows the surface concentration of redox-active sites to be 1×10^{-9} mol cm^{-2}, corresponding to several monolayers. Samples were stored under Ar at −10 °C when not in use.

---

* Author to whom correspondence should be addressed.

(1) Ellis, A. B. In *Chemistry and Structure at Interfaces: New Laser and Optical Techniques*; Hall, R. B., Ellis, A. B., Eds.; VCH Publishers: Deerfield Beach, FL, 1986; Chapter 6.

(2) Carpenter, M. K.; Van Ryswyk, H.; Ellis, A. B *Langmuir* **1985**, *1*, 605.

(3) Hollingsworth, R. E.; Sites, J. R. *J. Appl. Phys.* **1982**, *53*, 5357 and references therein.

(4) Samples of n-GaAs:Te from Laser Diode Labs, Inc., had carrier concentrations of 3×10^{16} cm^{-3} and (100) orientation. Samples were etched in 4:1:1 H_2SO_4/H_2O_2 (30%)/H_2O at 50 °C for 30 s, rinsed in distilled water, immersed in 7 M KOH at 50 °C for 30 min, rinsed again, and air-dried prior to derivatization.

(5) Bolts, J. M.; Wrighton, M. S. *J. Am. Chem. Soc.* **1979**, *101*, 6179 and references therein.

0002-7863/86/1508-2454$01.50/0

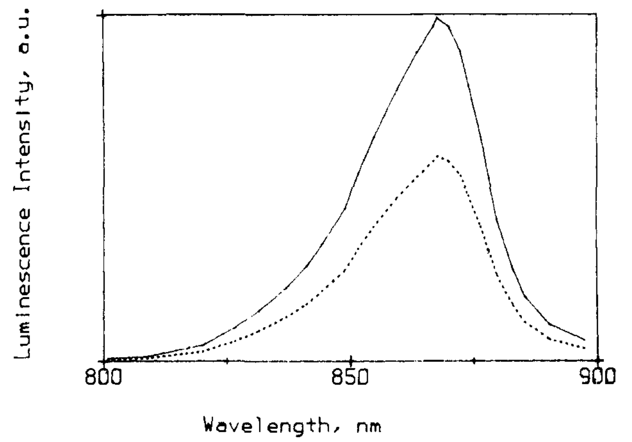
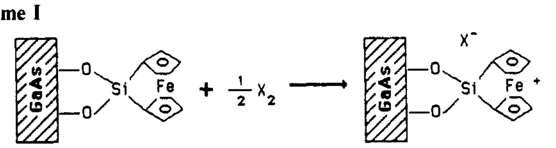


Figure 1. Uncorrected PL spectra of a derivatized n-GaAs sample before (solid line) and after (dotted line) treatment with I_2 vapor in flowing N_2. Following the reaction with I_2, treatment with gaseous N_2H_4 regenerates the solid curve. The sample was excited with the 457.9-nm line of an Ar^+ laser.

Scheme I



Excitation of the derivatized sample with ultraband gap 457.9-nm light ($E_g \sim 1.4$ eV) in an atmosphere of N_2 produces edge emission at 865 nm, as shown in Figure 1. No change in the PL spectrum is observed when the sample is subsequently exposed to H_2, O_2, CO, CH_4, and H_2O vapor. However, introduction of a volatile oxidant such as I_2 by sublimation in a flow of N_2 produces rapid quenching of the PL intensity; within a few seconds, the limiting 40% quenching shown in the figure is reached. A slightly greater degree of quenching is observed with dry, gaseous Br_2.[6] That quenching corresponds to oxidation of the ferrocene derivative, as shown in Scheme I, is supported by the restoration of the original PL signal by chemical or electrochemical reduction. In the former case, the gaseous reductant N_2H_4 rapidly reverses the effect of I_2; the PL changes were reversible during 10 cycles of alternate exposure to I_2 and N_2H_4.[7] Alternatively, use of the I_2-treated sample as an electrode evidences the expected ferricenium dark reduction wave at −0.25 V vs. SCE in the aforementioned electrolyte, concomitant with the return of PL quenching by gaseous I_2. In control experiments, PL from n-GaAs samples that were either only etched or etched and treated with $(CH_3)_2SiCl_2$ showed no effect upon exposure to I_2, dry Br_2, or N_2H_4.

The PL spectral changes induced by I_2 are indicative of an expansion in the electric field in the semiconductor; on electrostatic grounds, such an effect is consistent with the presence of negatively charged (poly)halide ions near the semiconductor surface, as shown in Scheme I. By regarding the region supporting the electric field as being completely nonemissive, i.e., a dead layer, a quantitative expression for relative PL intensity is obtained, eq 1; this treatment

$$\Delta D = \frac{-\ln\,(PL_{ox}/PL_{red})}{\alpha'} \qquad (1)$$

assumes that the n-GaAs surface recombination velocity is either very large or insensitive to the oxidant.[8] In eq 1, PL_{red} and PL_{ox} are the PL intensities before and after the addition of the oxidant, ΔD is the corresponding change in dead-layer thickness, and $\alpha' = (\alpha + \beta)$ with α and β the solid's absorptivities for the exciting and emitted light. A quantitative test of the dead-layer model is the calculation of a constant value for ΔD using several interrogating wavelengths of varying optical penetration depth. We find that the PL quenching observed with 457.9-, 514.5-, and 632.8-nm excitation yields, using literature absorptivities,[9] a consistent value for ΔD of 260 Å. The satisfactory accord with the dead-layer model is consistent with an electrostatic origin of PL quenching. Alternatively, the quenching may reflect the shift in the redox potential of the surface monolayers; a concomitant shift in the semiconductor's Fermi level would also produce these PL effects.

In summary, chemistry occurring within a few monolayers can modulate the electric field thickness of an underlying semiconductor by several hundred angstroms, producing corresponding variations in PL intensity. This coupling of a molecular species to a semiconductor substrate represents a general contactless method for monitoring changes in surface chemistry. Futhermore, by exploiting molecular reactivity patterns, semiconductor/molecular interfaces with targeted chemical specificity can be designed for use as optically coupled sensors.

Acknowledgment. We are grateful to the Office of Naval Research, the Army Research Office, and the 3M Co. for generous support of this research. We thank Dr. Alan C. Thomas for experimental assistance and a reviewer for helpful comments.

Registry No. I_2, 7553-56-2; Br_2, 7726-95-6; N_2H_4, 302-01-2.

---

[6] Water vapor had no effect upon the I_2-initiated quenching (and restoration of PL with N_2H_4), but trace amounts of water present in the gaseous Br_2 led to etching of the surface.

[7] PL from derivatized samples stored in either oxidation state under Ar at −10 °C for a week remained sensitive to redox chemistry, although the magnitude of the effect diminished by a few percent.

[8] Hobson, W. S.; Ellis, A. B. *J. Appl. Phys.* **1983**, *54*, 5956.

[9] An absorptivity of 4.35 × 10^4 cm^{-1} at 632.8 nm was interpolated from: Sturge, M. D. *Phys. Rev.* **1962**, *127*, 768. Absorptivities of 9.38 × 10^4 and 1.99 × 10^5 cm^{-1} were used at 514.5 and 457.9 nm, respectively; these values were obtained via dead-layer analysis of PL quenching from samples operating in photoelectrochemical cells: Burk, A. A., Jr.; Johnson, P. B.; Hobson, W. S.; Ellis, A. B. *J. Appl. Phys.* **1986**, *59*, 1621.

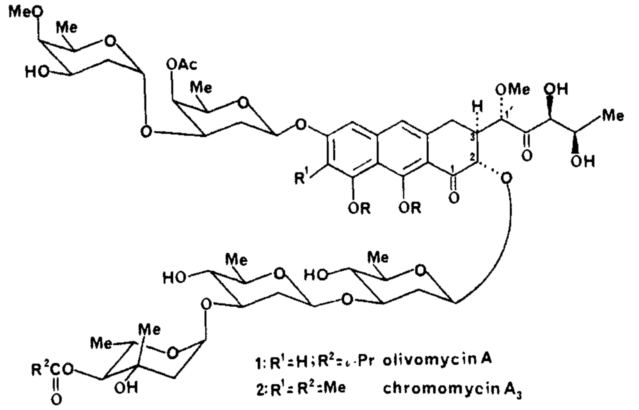
Stereoselective Total Synthesis of the Natural Enantiomer of Olivin Trimethyl Ether

R. W. Franck,* V. Bhat, and C. S. Subramaniam

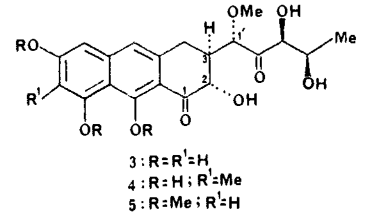
Chemistry Department, Hunter College/CUNY
New York, New York 10021

Received November 29, 1985

The olivomycins, an example being olivomycin A (**1**), produced



1: R¹=H; R²=i-Pr olivomycin A
2: R¹=R²=Me chromomycin A3



3: R=R¹=H
4: R=H; R¹=Me
5: R=Me; R¹=H

by *Streptomyces olivoreticuli*, belong to the aureolic acid family