drocarbon (**7**). The close structural resemblance between the trinervitene soldier substances and the Neocembrane-A (nasutene),[8] reported to be a trail pheromone for an Australian *Nasutitermes* species, implicates cembrene-type intermediates in the biogenesis of the trinervitenes.

Acknowledgment. We are grateful to Professor J. Meinwald for discussions, and to Professor C. Djerassi's group for measurements of the 360-MHz spectrum of TG-2,[6] and to Ms. V. Parmakovich for MS measurements. We also wish to thank Mr. S. Ogendo for technical assistance, Drs. M. Kaib, O. Bruinsma (ICIPE), and Mr. R. Buxton (Tsavo Research Project, Voi, Kenya) for their help during collections.[9]

References and Notes

(1) Part 1 of this series appears as the preceding communication: G. D. Prestwich, S. P. Tanis, J. P. Springer, and J. Clardy, *J. Am. Chem. Soc.*, preceding paper in this issue.

(2) *T. gratiosus* was collected in Voi and in Kibwezi, Kenya; *T. bettonianus* was collected in Machakos and in Ruiru, Kenya. Most studies were carried out on the former species because of its optimal size and abundance as well as the simplicity of its major soldier secretion.

(3) Each trinervitene compound constituted 0.1–3% of the total body weight of the major soldiers. The chemical ecology of these secretions, including inter- and intraspecies differences, will be described elsewhere.

(4) P. Zanno, I. Miura, K. Nakanishi, and D. Elder, *J. Am. Chem. Soc.*, **97**, 1975 (1975), and references therein.

(5) The peaks could not be separated by the use of various NMR solvents and/or shift reagents; in spite of repeated attempts, no NOE was observable.

(6) Although the structural units elucidated by spectral methods were submitted to the Stanford CONGEN program, R. E. Carhart, D. H. Smith, H. Brown, and C. Djerassi, *J. Am. Chem. Soc.*, **97**, 5755 (1975), the information was not restrictive enough to arrive at a single final structure.

(7) J. Dillon and K. Nakanishi, *J. Am. Chem. Soc.*, **97**, 5417 (1975).

(8) A. J. Birch, W. V. Brown, J. E. T. Corrie, and B. P. Moore, *J. Chem. Soc., Perkin Trans 1*, 2653 (1972).

(9) Supported by United Nations Development Project grant to ICIPE and NIH Grant AI 10187 and National Science Foundation Grant MPS-75-06154 (Spex Model Ramalog 5 Laser Raman Spectrometer) to Columbia University.

(10) NIH postdoctoral fellow (1976–1977), Fellowship AI 05076.

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Inelastic Electron Tunneling Spectroscopy of Carbon Monoxide Chemisorbed on Alumina-Supported Transition Metals

Sir:

The first successful attempt to obtain infrared spectra of carbon monoxide on supported transition metals appears to have been performed by Eischens, Francis, and Pliskin, with the report of CO stretching modes (1800-2100 cm^{-1}).[1] Similar observations on the chemisorption of carbon monoxide with vibrational spectroscopy have been successfully made by other workers.[2] In most cases, however, the associated metal-carbon stretching vibrations and carbon-oxygen bending modes, which occur at lower frequency (800-200 cm^{-1}) cannot be observed, because the support material interferes strongly in the low frequency region. We wish to report here the successful application of inelastic electron tunneling spectroscopy[3] (IETS) for the observation of metal-carbon and carbon-oxygen vibrational modes of carbon monoxide chemisorbed on alumina supported transition metals.

In our experiments, an aluminum electrode is evaporated onto a glass slide and allowed to oxidize in air at 110 °C to form the necessary alumina insulating layer. After the alumina is cleaned in an argon glow discharge, a very thin layer of transition metal is evaporated onto it and exposed to carbon monoxide. The junction is completed with an evaporated top metal electrode of lead. The metal-insulator-metal junctions are formed at the intersections of crossed metal electrodes. See Figure 1.

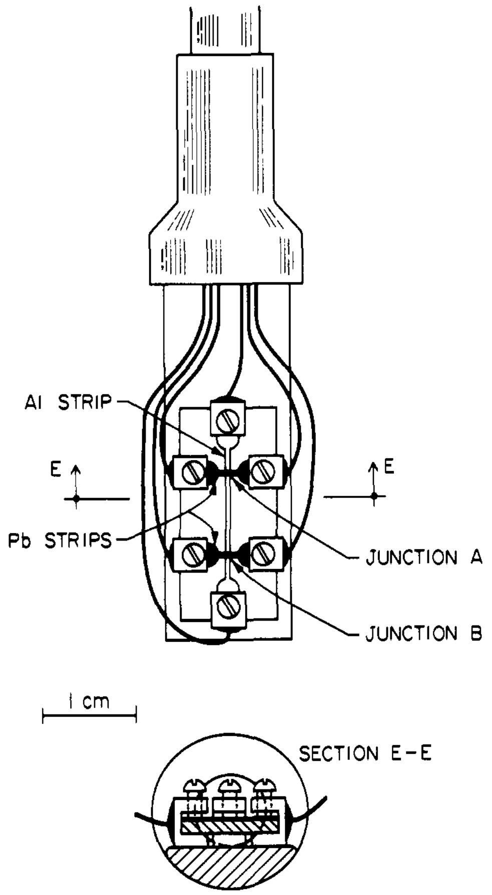

Figure 1. Two Al-oxide-Rh-CO-Pb junctions are formed at the intersections of the crossed metal films. Electrical contact to the junctions is made with brass screw clamps. Tunneling spectra are taken electronically with the sample inserted down the neck of a conventional helium storage Dewar.

Figure 2 shows a series of tunneling spectra for various coverages of rhodium metal on the alumina. The coverage was determined with an oscillating quartz crystal microbalance and, of course, represents an average over the surface; most of the coverages are submonolayer. The residual gas pressure before the Rh evaporation was in the range 4×10^{-8} to 2×10^{-7} Torr. The pressure was increased to 10^{-5} Torr of CO during the Rh evaporation to ensure that CO would dominate the residual gases. This pressure was maintained for 100 s after the Rh evaporation to give a total exposure of 10^3 Langmuirs of CO. (The spectra were insensitive to exposure >100 Langmuirs.)

The spectrum with Rh = 0 Å is free of any vibrational peaks due to CO; all these peaks are present in junctions not exposed to CO. They are due to vibrational modes of the alumina, OH groups bound to the surface of the alumina, and the aluminum electrode.[3]

Studies on rhodium carbonyls ($Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$)[4] suggest that rhodium-carbon stretching modes should be in the range 400-600 cm^{-1}. At low rhodium coverages (0.5 and 1 Å) we observe only one peak in this range: at 408 ± 5 cm^{-1}. As coverage increases, this peak grows in size and two new peaks appear: a sharp one at 454 ± 5 cm^{-1} and a broad one centered at 580 ± 10 cm^{-1}. The appearance of

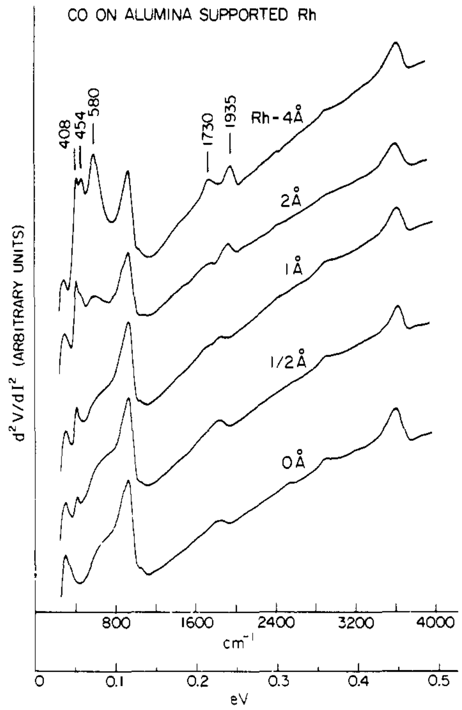

Figure 2. Tunneling spectra of CO adsorbed on various thicknesses of Rh evaporated on alumina. Note that new peaks appear as the thickness of Rh increases implying new types of bonding. For all these spectra the CO exposure was ≈10^3 Langmuir.

these two new peaks implies the existence of new types of bonding. The broad band centered at 580 ± 10 cm^{-1} may contain contributions from carbon-oxygen bending vibrations.[4]

The intensity of the peaks in the carbon-oxygen stretching region is surprisingly small and partially obscured by the second harmonic of the strongest peak in the background spectra. Furthermore, a relatively large peak shift due to the top metal electrode would be expected because of the large dipole derivative of the carbon-oxygen bond (possibly comparable to the 2% downward shift seen in the hydrogen-oxygen stretching frequency).[5] We do not understand why the CO stretching modes are weak relative to the lower energy modes. (It may possibly be due to an orientation effect; the peaks would be expected to be weak if the CO were oriented parallel to the oxide surface.)[3,5] For these reasons we will not discuss these peaks except to note that background subtraction[6] shows that only the higher energy peak, at 1935 ± 10 cm^{-1}, appears only at higher rhodium coverages. This suggests that the adsorbed species that is present only at higher rhodium coverages has a weaker carbon-oxygen bond.

The initial stages of thin film growth based on nucleation theory and electron-microscope observations are first the formation of adsorbed monomers, then the formation of dimers, trimers, etc., leading to the formation of critically sized nuclei that deplete the monomers in the capture zone around them.[7] Thus, an interpretation that is consistent with our data is that at the lowest coverages (much less than a monolayer average coverage) there are adsorbed monomers, i.e., isolated Rh atoms, to which CO can bond in only one way. As coverage increases, small clusters form to which CO can bond in more ways (e.g., possibly in bridged configurations between adjacent rhodium atoms).

Similar experiments on nickel yield only one peak in the nickel-carbon stretching region, at 400 ± 5 cm^{-1}. In contrast to the rhodium experiments, no new peaks form as the coverage of nickel is increased. This suggests that the bonding of CO to small nickel clusters is fundamentally different than to small rhodium clusters.

Though this work is only a start, it illustrates the potential of IETS for the study of chemisorbed species on supported metals. We are especially interested in the investigation of catalytic reactions on supported metals.

Acknowledgments. We gratefully acknowledge support from the Materials Research Division of the National Science Foundation and the Office of Research Development, University of California, Santa Barbara.

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(8) Alfred P. Sloan Foundation Fellow.

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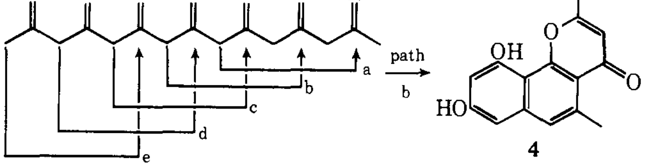
Biogenetic-Type Syntheses of Emodin and Chrysophanol

Sir:

For some time we have been studying the biogenetic-type synthesis of phenolic natural products from β-polycarbonyl compounds in a program directed toward the eventual synthesis of pretetramid in this manner.[1] The control of cyclization processes becomes a formidable problem with the higher polycarbonyl compounds.[2] For example, heptaketone **1** might undergo five aldol cyclizations (a–e); all of which with the exception of e look relatively probable.[3] Each of the initial cyclization products can undergo further cyclizations. As one approach to controlling these cyclizations, we have investigated derivatives **2** and **3** in which the terminal keto groups of **1** were protected as ketals.[2b] The ketals blocked cyclizations a and e and retarded d, so that only b and c remained. Cyclizations of **2** and **3** went primarily by path b, leading after two additional



4

1, R = O; R′ = O
2, R = $-OCH_2CH_2O-$; R′ = O
3, R = $-OCH_2C(CH_3)_2CH_2O-$; R′ = O
6, R = O; R′ = $-OCH_2CH_2O-$
19, R = O; R′ = H, $\overline{CH_2CH_2CH_2CH_2N}-$