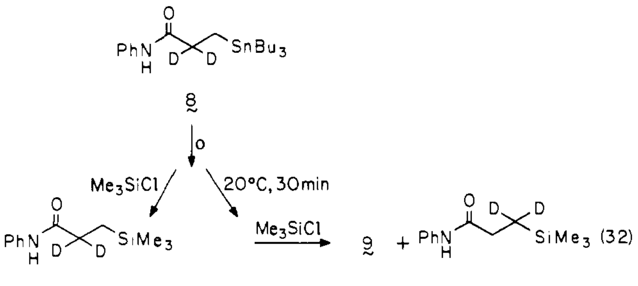
J. Am. Chem. Soc. 1983, 105, 7183-7185

Table I. Reactions of 1 and 2 with Various Electrophiles

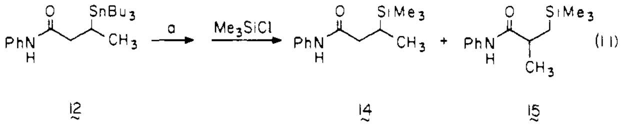
organo-lithium reagent	electrophile	product	yield, %
1	D_2O	**6**, E = D	84.5 (89 d_1)
1	Me_3SiCl	**6**, E = Me_3Si	72.0
2	D_2O	**7**, E = D	72.2 (95 d_1)
2	Me_3SiCl	**7**, E = Me_3Si	76.2
2	Bu_3SnCl	**7**, E = Bu_3Sn	64.0
2	$[CH_3(CH_2)_3]_2CO$	**7**, E = $[CH_3(CH_2)_3]_2COH$	67.2

Scheme I



(a) THF, 2 DABCO, 2 n-BuLi, -70°C, 10 min.

Scheme II

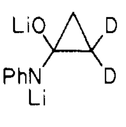


(a) THF, 2 DABCO, 2 n-BuLi, -70°C, 4 h.

To find out whether the rearrangement of **1** to **2** constitutes the migration of the phenyl ring or the involvement of a cyclopropane intermediate such as **3**, we prepared *N*-phenyl-3-(tri-*n*-butylstannyl)propionamide-*2-d*$_2$ (**8**).[8] Reactions of dilithio derivatives generated from **8** with chlorotrimethylsilane are described in Scheme I.[9] The formation of **10** indicates involvement of dilithiocyclopropane intermediate **11** in such a rearrangement.

An attempt to detect the cyclopropyl intermediate **3** by using ^{1}H NMR spectroscopy was unsuccessful. The initial dilithio derivative **1**, generated from **4**, was stable below −40 °C. New signals,[10] consistent with the rearranged acyclic dilithio species **2**, started appearing at −40 °C. The rearrangement was complete in 1 h at this temperature, and quenching the reaction mixture with chlorotrimethylsilane produced **7** (E = $SiMe_3$). Consequently, the acyclic derivative **2**, rather than the cyclopropane **3**, is the major reactive species responsible for the formation of **7**.[11]

The tin–lithium exchange of **12** to produce the corresponding secondary dilithio derivative **13** was very slow at −70 °C (80% in 4 h).[12] Quenching the reaction mixture with chlorotrimethylsilane produced a 1:1 mixture of **14** and **15** (Scheme II). Tin–lithium exchange of **12** was much faster at −10 °C (complete within 30 min), but pure rearranged product **15** was isolated from the reaction mixture upon addition of chlorotrimethylsilane. We are considering other ways of generating such dilithiocyclopropane derivatives as well as attempting to trap these intermediates with other substrates.[13]



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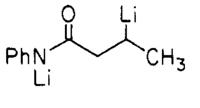

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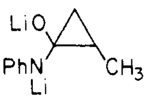

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Acknowledgment. We thank Larry W. Kelts and Dr. J. John Uebel for obtaining the low-temperature ^{1}H NMR spectra of the organolithium reagents.

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(8) Acetyl-d_3 chloride was purchased from KOR Isotopes. Compound **8** was prepared from (iodomethyl)tri-*n*-butyltin and the 1,3-dilithio derivative derived from acetanilide-d_3.

(9) The unequal amounts of **9** and **10** (3:2) obtained may signify the incomplete formation of the intermediate **11** under the reaction conditions.

(10) The observed characteristic signals of **2**: ^{1}H NMR (THF-d_8) δ 2.42 (t, 1, J = 6.1 Hz, LiCH), 2.73 (d, 2, J = 6.1 Hz, CH_2), 5.10 (t, 1, J = 6.7 Hz, para H), 5.59 (d, 1, J = 7.3 Hz, ortho H), 5.94 (d, 1, J = 7.3 Hz, ortho′ H), 6.16 (appt, 1, J = 7.3, 6.7 Hz, meta H), 6.31 (appt, 1, J = 7.3, 6.7 Hz, meta′ H). DABCO was not present in this reaction mixture. Ortho and meta protons were nonequivalent up to 10 °C, above which **2** decomposed. Sandel, V. R.; McKinley, S. V; Freedman, H. H. *J. Org. Chem.* **1968**, *33*, 495–497.

(11) It is possible that **3**, even though present in low concentration, is the true reactive species for the formation of the rearranged products **7**. This is unlikely, as **2**, generated independently from **7** (E = $SnBu_3$) under conditions where cyclopropane formation is not expected (THF, 2 DABCO, 2 BuLi, −70 °C, 10 min), reacts with electrophiles such as Me_3SiCl to give exclusively **7** (E = $SiMe_3$).

(12) Compound **12** was prepared by the reaction of dilithioaniline with ethyl 3-(tributylstannyl)butyrate in THF.

(13) All compounds gave satisfactory spectral and analytical data.

Orientation of Complex Molecules Chemisorbed on Metal Surfaces: Near-Edge X-ray Absorption Studies

Allen L. Johnson and E. L. Muetterties*

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California—Berkeley
Berkeley, California 94720

J. Stöhr*

Corporate Research Science Laboratories
Exxon Research and Engineering Company
Linden, New Jersey 07036

Received September 6, 1983

Structural definition of chemisorbed states is essential to a molecular understanding of surface chemistry.[1] A large family of molecules of great significance in surface chemistry has in common π and π^* molecular orbitals that interact strongly with surfaces.[2] We describe here the general structural utility of a surface technique to the chemisorption states and surface reaction intermediates derived from such molecules. The technique is NEXAFS, which is based on the analysis of the polarization dependence of the *n*ear-*e*dge- *X*-ray-*a*bsorption *f*ine *s*tructure of the 1s core excitation of chemisorbed species. This technique has been previously applied to chemisorbed atoms[3] and diatomic molecules.[4,5]

The theory and technique of NEXAFS have been described previously.[3-5] In brief, the crystal is exposed to a monochromatic, linearly polarized beam of X-rays, and the X-ray absorption coefficient is measured as a function of X-ray beam angle with respect to the surface plane in the region near the K edge of an atom (e.g., C or N) in the adsorbed molecules. Absorption in this region is dominated by resonant transitions into bound (usually π^*) and pseudobound (usually σ^*) molecular orbital states. It has been shown for cylindrically symmetric molecules such as CO that the polarization dependence for transitions from an s initial

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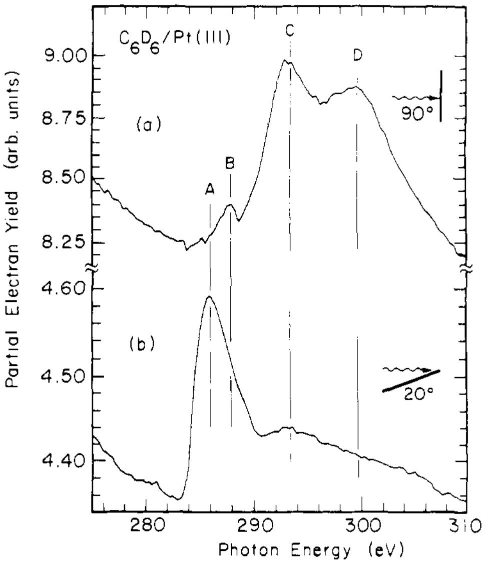

Figure 1. Polarization dependence of NEXAFS of the carbon K edge for Pt(111)-C_6D_6 at saturation coverage at 25 °C. Curve (a) is the normal incidence spectrum and (b) the glancing incidence spectrum. Peak A at 286 eV corresponds to a $1s \rightarrow \pi^*$ bound-state transition and peaks C and D at 293.5 and 299.5 eV to $1s \rightarrow \sigma^*$ pseudobound-state transitions (shape resonances). Peak B is due to CO. Note that NEXAFS studies are applicable to multiple chemisorption states. For example, the conversion of the pervasive flat benzene chemisorption state on atomically flat metal surfaces to a tipped or normal orientation might be effected by other adatoms or admolecules. This possibility can be unambiguously addressed through NEXAFS studies.

state to a pure σ^* or π^* state respectively follows $\cos^2$ and $\sin^2$ functions of the angle between the electric field vector and the molecular axis. As we show below, molecular orientation can be most easily inferred from the π^* resonance absorptions because of their intensity and sharpness. Experimental procedures are presented in the supplementary material.

The NEXAFS spectra for benzene (C_6D_6) adsorbed on Pt(111) are shown in Figure 1. There is a strong π^* resonance at 286 eV for grazing X-ray incidence (20°) and essentially none at normal incidence. Clearly, benzene lies in a plane parallel to the surface plane as has been proposed in studies based on other surface science techniques.[6] Extensions to toluene and hexafluorobenzene adsorbed on Pt(111) established orientations analogous to that of benzene. Benzonitrile also had the aromatic ring plane parallel to the surface plane. Polarization dependence of the π^* resonances associated with the CN group (K edge for N and C) indicates that the CN vector is in the C_6 ring plane or displaced slightly from the plane.

In sharp contrast to aromatic hydrocarbon orientation on Pt(111), pyridine is oriented in a plane near the surface normal as shown in Figure 2. The structural characterization, presently limited to high or saturation coverages for Pt(111)-NC_5H_5 at 25 °C, is analogous to that proposed for Ni(100)-NC_5H_5[7] and Cu(111)-NC_5H_5[8] at intermediate or high pyridine coverages. The equilibrium Ni(100)-$NC_5H_5 \rightleftharpoons$ Ni(100)-H + Ni(100)-2-pyridyl is established at +70 °C or below;[7] accordingly, there may be some 2-pyridyl species on Pt(111) at 25 °C.

Toluene is thermally reactive on nickel group metals. Scission of C-H bonds is regiospecific on Ni(111) and Ni(100) with all aliphatic C-H bonds cleaved at temperatures below that at which aromatic C-H bond scission begins.[9] This dehydrogenation is also regiospecific on Pt(111) but the degree is less than that observed for nickel surfaces.[10] Regiospecificity could be the result of C_6H_5CH and C_6H_5C intermediates in which the phenyl ring is tipped away from the surface.[11] Examination of this intermediate region by NEXAFS showed significant π^* resonances at both normal and glancing incidence (Figure 3). Clearly, some "intermediates" with the C_6 ring and oriented normal or largely normal to the surface were present, supporting the postulated C_6H_5CH and C_6H_5C "intermediates".

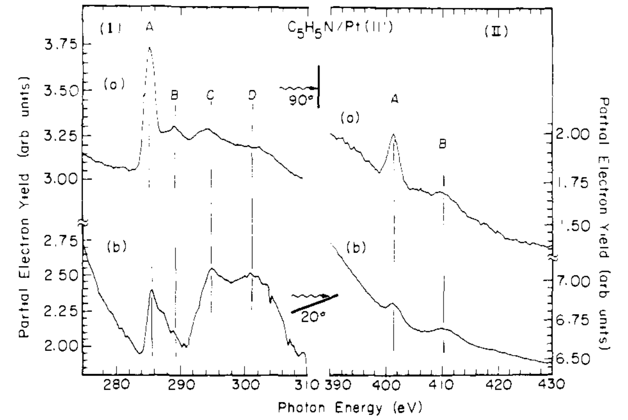

Figure 2. Carbon K edge (I) and nitrogen K edge (II) absorption spectra for Pt(111)-NC_5H_5 at 25 °C are depicted above for normal (a) and glancing (b) X-ray incidence. Significant is the opposite polarization dependence and the smaller width of the $1s \rightarrow \pi^*$ transition at ~286 eV (peak A) as compared to C_6D_6 (Figure 1) indicating that π orbitals are parallel to the surface and are not involved in the chemisorption bond. Peaks C and D correspond to transitions to quasibound σ^* shape resonances.

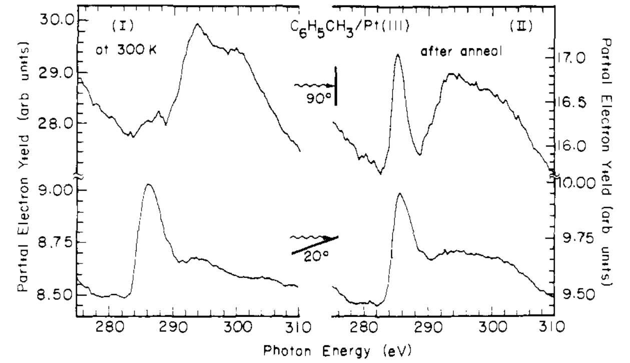

Figure 3. Carbon K edge NEXAFS spectra that illustrate the application of this technique to surface reaction chemistry. Toluene decomposition on many clean metal surfaces exhibits regiospecificity in that aliphatic C-H bonds are broken before those of the aromatic system. Suspected intermediates include phenylmethylene and phenyl-substituted methylidyne which would leave the C_6 ring tipped and normal, respectively, with reference to the surface plane. This supposition is strongly supported by NEXAFS data for Pt(111)-toluene and Pt(111)-toluene annealed in the region where dehydrogenation first begins. Notable in these studies are the widths of the π^* resonances and change in polarization dependence for Pt(111)-toluene at 25 °C *after* annealing in the region where dehydrogenation first begins (II).

NEXAFS applied to chemisorbed molecules or radicals with π systems should prove to be an important structural technique with respect to orientational features. Also, as discussed elsewhere,[5] energy separations between π^* and σ^* transitions can provide a good measure of bond-length parameters. Our toluene results illustrate the application of NEXAFS to surface reaction chemistry, potentially one of the most important contributions of NEXAFS to surface science.

Acknowledgment. This research was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy,

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under Contract DE-AC03-76SF00098. The work reported here was done at SSRL, which is supported by the Office of Basic Energy Sciences of DOE and the Division of Materials Research of NSF. We are especially indebted to the University of California, Berkeley, Graduate Division, for partial support of the work and to D. Outka, J. Gland and R. Koestner for assistance in the data collection.

Supplementary Material Available: Experimental procedure and analysis and Figure 4 for NEXAFS spectra for benzonitrile chemisorbed on Pt(111) (3 pages). Ordering information is given on any current masthead page.

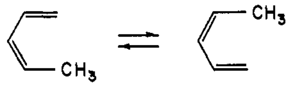
Ab Initio Study of the Transition Structure of the [1,5]-Sigmatropic Hydrogen Transfer in *cis*-1,3-Pentadiene

B. Andes Hess, Jr.,* and L. J. Schaad*

Department of Chemistry, Vanderbilt University
Nashville, Tennessee 37235

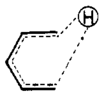
Received July 21, 1983

The simplest symmetry-allowed[1] [1,*n*]-sigmatropic rearrangement that can be readily observed thermally is the [1,5] hydrogen transfer in *cis*-1,3-pentadiene (**1**). In 1966 Roth and König using



1

deuterium-labeled derivatives of **1** reported that the hydrogen transfer from C-5 to C-1 in **1** occurs in the gas phase with an activation enthalpy of 35 kcal/mol and a k_H/k_D of 12.2.[2] From this they concluded that the rearrangement proceeds through the symmetric transition structure **2**. Recently Kwart and Acheson



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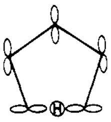
have suggested that the data of Roth and König[2] demand that the transition structure for the [1,5]-sigmatropic rearrangement of **1** have a collinear arrangement of the two terminal carbons and the migrating hydrogen (**3**).[3] Their conclusion was based[4]



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on the fact that the temperature dependence of k_H/k_D and an A_H/A_D ratio of 1.15 found by Roth and König are in line with the values predicted for a collinear hydrogen transfer by Schneider and Stern.[5]

Since Schneider and Stern used relatively simple model calculations in making their prediction, we thought it useful to undertake an ab initio study of the transition structure of the [1,5]-sigmatropic hydrogen transfer in **1**. The proposed collinear transition structure **3** as depicted by Kwart and Acheson has C_{2v} symmetry, while that of Roth and König (**2**) is of C_s symmetry. A third possible transition structure has C_2 symmetry, but this would involve the forbidden[1] antarafacial hydrogen transfer. In fact Roth and König have shown[6] that for a substituted 1,3-pentadiene the hydrogen transfer proceeds in a suprafacial fashion which could occur either via **2** or **3**. Since both **2** and **3** are of higher symmetry than the reactant (**1**), the task of locating the transition structure is greatly simplified. By imposing these higher symmetries the two potential transition structures can be readily located by energy minimization.

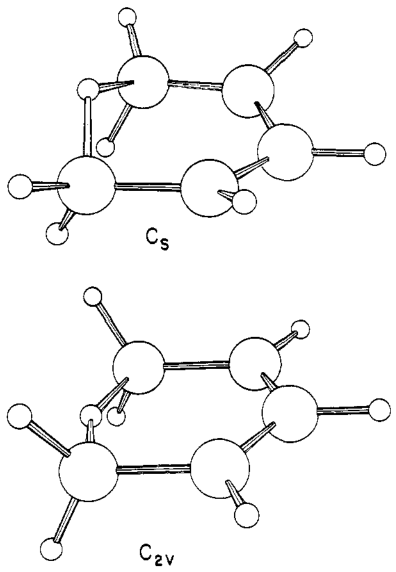

Figure 1. ORTEP drawings of the two transition structures considered.

Table I. Energies[a] (kcal/mol) of the Two Possible Transition Structures in the [1,5]-Sigmatropic Hydrogen Transfer in *cis*-1,3-Pentadiene

basis set	C_s	C_{2v}
3-21G	+54.6	+122.3
6-31G*	+58.7	+123.7

[a] Energies are given relative to the calculated *s-trans,cis*-1,3-pentadiene energy (3-21G: −192.87958 au; 6-31G*: −193.95625 au).

We have carried out these two minimizations with a 3-21G[7] wave function using the DEC 10 version of GAUSSIAN80.[8] The ORTEP[9] drawings in Figure 1 show the best C_{2v} and C_s structures. Single-point SCF energies and gradients were computed with the 6-31G* basis[10] at the best 3-21G geometries. The value of the gradient at these two points indicated, based on our experience, that these 6-31G* energies are most likely within 1 kcal/mol of the actual minima with this basis. Results are summarized in Table I where the energies of the proposed transition structures are given relative to that of the reactant **1**.[11] It is immediately seen that the proposed transition structure of C_{2v} symmetry is of considerably higher energy than that (C_s) suggested by Roth and König. The CHC angle of the migrating hydrogen in the C_s structure was found to be 129.9°. Further, this best C_{2v} structure

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[11] The energies of *cis*-1,3-pentadiene were obtained in a fashion similar to that of the two transition structures.

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