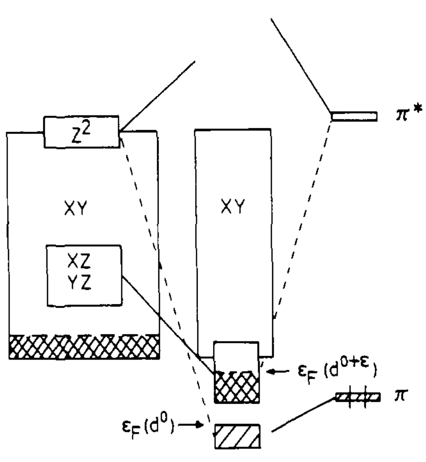
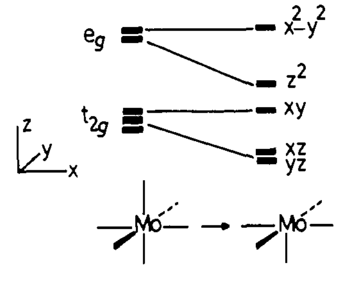


▩ $\pi^* \oplus$ xz/yz states

▨ $\pi \oplus z^2$ states

Figure 2. Schematic interaction diagram between the surface and the propene adsorbate, see text. The circled "plus" means "bonding".

Reduction of the surface, i.e., populating its d band, does not localize the electrons in the Mo_2 *xz* and *yz* π-type of hybrids despite the removal of an apical π-donor, see **2**. Rather, the *xy* states displaying Mo–Mo σ overlap parallel to the surface develops into a band wide enough for its bottom to lie below the protruding *xz*/*yz* hybrids and house the extra electron density. Figure 1 illustrates this point.



2

Sticking a propene above Mo_2 turns on a σ donation from π into z^2 as noted[4] by Anderson. However, bonding states are also generated between empty *xz*/*yz* of Mo_2 and π^* of C_2H_4. These states, empty in an overall d^0 surface, emerge below[13] the bottom of *xy* not involved in the adsorption and get filled by electron transfer in the reduced system. Figure 2 describes schematically this mechanism and is based on a DOS analysis of the overall system. Numerically the reduction process was simulated by injecting[14] one or two electrons in the unit cell starting from a d^0 system. With ϵ representing the averaged[15] extra electron population and Δ the variation of electron population between after and before adsorption, we have for $\epsilon = 0.333$, $\Delta(xy) = -0.324$, $\Delta(xz/yz) = +0.994$, $\Delta(z^2) = +0.138$, $\Delta(\pi) = -0.15$, and $\Delta(\pi^*) = +0.45$. Prereduction strengthens the C_2H_4/MoO_3 bonding; the averaged Mo–C overlap population goes from 0.10 ($\epsilon = 0$) to 0.25 ($\epsilon = 0.333$). The surface *xy* states act as a "reservoir", temporarily storing the electron density that it eventually pours into new surface/adsorbate bonding levels.[16] These electronic factors may constitute the *raison d'être* of the prereduction. These conclusions are drawn out of semiquantitative computations; further insight could be gained from more sophisticated calculations and perhaps by an experimental study of the catalytic properties of doped MoO_3.[17] Yet, our complementary calculations[9] on the (100) MoO_3/propene system point out that prereduction plays a crucial role in the rate-determining step, the first C–H scission, toward acrolein formation. This finding may be supported by infrared and ESR measurements showing[18] that the Mo atoms are reduced in the catalytic cycle with the $Bi_2Mo_3O_{12}$ system.

Acknowledgment. Thanks are due to E. Vignon for the typing and CIRCE for technical assistance.

---

[13] With a chemically reasonable Mo–C distance of 2.1 Å.

[14] The amount of electron density referred to is small enough to justify the rigid band model.

[15] $\epsilon = 0.3333$ means formally one d^4 Mo and five d^0 Mo per cell.

[16] A somewhat similar effect was described in: Silvestre, J.; Hoffmann, R. *Langmuir* **1985**, *1*, 621.

[17] $K_{0.30}MoO_3$ possesses a structure similar to that of MoO_3. Photoemission studies show a population of the Mo d bands: Wertheim, G. K.; Schneemeyer, L. F.; Buchanan, D. N. F. *Phys. Rev. B* **1985**, *32*, 3568.

[18] Praliaud, H.; Forissier, M., unpublished results.

ESR Studies on the Radical Cation Mechanism of the Ring Opening of Cyclopropylamines

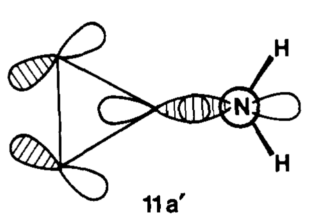
Xue-Zhi Qin and Ffrancon Williams*

Department of Chemistry, University of Tennessee
Knoxville, Tennessee 37996-1600

Received July 25, 1986

Cyclopropylamine radical cations have been implicated in the mechanism of inactivation of monoamine oxidase and cytochrome P-450 by cyclopropylamines.[1,2] The key step in the proposed mechanism is illustrated for the parent compound in Scheme I and consists of the ring opening of the aminium radical cation **1** to the carbon-centered radical **2** which subsequently attacks the active site of the enzyme.[2] Here we present ESR evidence for this ring-opening reaction and report that **2** is not converted to the nitrogen-centered radical **3** whereas the corresponding reaction for the neutral radical (**5** → **6** in Scheme II) proceeds to completion at similar temperatures. These results provide a firm basis for the radical cation mechanism of enzyme inactivation,[1,2] in keeping with the structural evidence that the inactivator is bound to the enzyme through carbon rather than nitrogen.[2]

The radical cation from cyclopropylamine was generated radiolytically in several Freon matrices,[3] $CFCl_3$ and CF_3CCl_3 being the most suitable for the study of the sequestered radical cation. Figure 1 shows the ESR spectrum of the ring-opened radical cation **2**,[4] the β-hydrogen hyperfine couplings differing significantly from those for neutral $CH_2CH_2CH{=}NR$ radicals[5] (Table I). The formation of **2** from **1** can be rationalized by considering the HOMO of cyclopropylamine,[6] the removal of an electron from this 11a′ orbital leading to a weakening of the C–C bonds. That



11a′

---

[1] Tullman, R. H.; Hanzlik, R. P. *Drug Metabolism Rev.* **1984**, *15*, 1163.

[2] (a) Silverman, R. B. *J. Biol. Chem.* **1983**, *258*, 14766. (b) Silverman, R. B.; Yamasaki, R. B. *Biochemistry* **1984**, *23*, 1322. Silverman, R. B.; Zieske, P. A. *Biochemistry* **1985**, *24*, 2128.

[3] For experimental details, see, e.g.: Snow, L. D.; Williams, F. *Faraday Discuss. Chem. Soc.* **1984**, *78*, 57.

[4] **2** is a distonic radical cation. For other examples, see: (a) Yates, B. F.; Bouma, W. J.; Radom, L. *J. Am. Chem. Soc.* **1984**, *106*, 5805. (b) Sack, T. M.; Cerny, R. L.; Gross, M. L. *J. Am. Chem. Soc.* **1985**, *107*, 4562.

[5] Maeda, Y.; Ingold, K. U. *J. Am. Chem. Soc.* **1980**, *102*, 328.

[6] Kimura, K.; Katsumata, S.; Achiba, Y.; Yamazaki, T.; Iwata, S. *Handbook of He I Photoelectron Spectra of Fundamental Organic Molecules*; Halsted: New York, 1981; pp 118, 119.

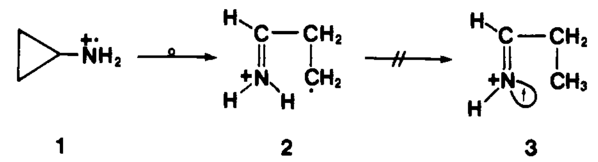
0002-7863/87/1509-0595$01.50/0

Table I. ESR Parameters for the Ring-Opened Radical Cation of Cyclopropylamine, Related $^{\bullet}CH_2CH_2CH{=}NR$ Radicals, and the Propan-1-iminyl Radical

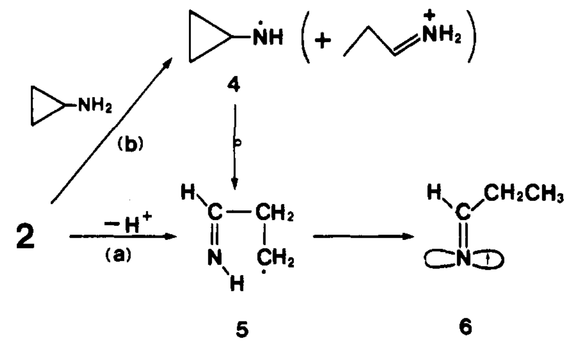
radical cation or radical	matrix or solvent	T/K	hyperfine couplings/G	g	ref
$^{\bullet}CH_2CH_2CH{=}NH_2^+$	CF_3CCl_3	80–140	22.6 (2 H_α), 17.0 (2 H_β)	2.0026	this work
	$CFCl_3$	80–160	22.5 (2 H_α), 17.0 (2 H_β)	2.0027	this work
$^{\bullet}CH_2CH_2CH{=}N$-*n*-Pr	*c*-C_3H_6	135–275	22.1 (2H_α), 29.2 (2 H_β)	2.0027	5
$^{\bullet}CH_2CH_2CH{=}N$-*i*-Pr	*c*-C_3H_6	135–275	22.1 (2 H_α), 29.2 (2 H_β)	2.0027	5
$CH_3CH_2CH{=}N^{\bullet}$	CF_3CCl_3	150	79.7 (1 H), 9.6 (1 N), 2.8 (2 H)	2.0028	this work
	$CFCl_2CF_2Cl$	125	80.5 (1 H), 9.7 (1 N), 3.0 (2 H)	2.0029	this work
	adamantane	room temp	78.5 (1 H), 9.5 (1 N), 2.77 (2 H)	2.0030	*a*
	adamantane	room temp	79.5 (1 H), 9.4 (1 N), 2.80 (2 H)	2.0030	11
	c-C_3H_6	223	79.5 (1 H), 9.6 (1 N), 2.76 (2 H), 0.45 (3 H)	2.0028	*b*

[a] Wood, D. E.; Lloyd, R. V.; Pratt, D. W. *J. Am. Chem. Soc.* **1970**, *92*, 4115. [b] Cooper, J. W.; Roberts, B. P.; Winter, J. N. *J. Chem. Soc., Chem. Commun.* **1977**, 320.

Scheme I



Scheme II



only **2** is formed can be ascribed to the stabilization of the cationic center through the formation of the protonated imine group. The ESR signal from **2** showed little or no decay from 80 to 160 K in $CFCl_3$ and from 80 to 140 K in CF_3CCl_3, the upper limits corresponding to the softening points of these matrices,

It was also of interest to study the conjugate base of **2**, and previous studies have shown that neutral secondary radicals can be generated in the more mobile $CFCl_2CF_2Cl$ matrix by deprotonation of the radical cation[7] or by hydrogen atom transfer from the neutral molecule to the radical cation.[8] Accordingly, the radicals expected by paths a and b of Scheme II are **5** and **4**, respectively, but the aminyl radical **4** could ring open[5] to also give **5**. However, the neutral radical produced in $CFCl_2CF_2Cl$ below 125 K (Figure 2 and Table I) is the propan-1-iminyl radical **6**[9] which can readily be formed from **5** by internal hydrogen transfer.[10] Similarly, only **6** is present at room temperature following the X-ray irradiation of cyclopropylamine in adamantane,[11] the likely path of formation being **4** → **5** → **6** in this case.[12]

This work therefore establishes a remarkable difference between the reactivities of the radical cation and the neutral radical over

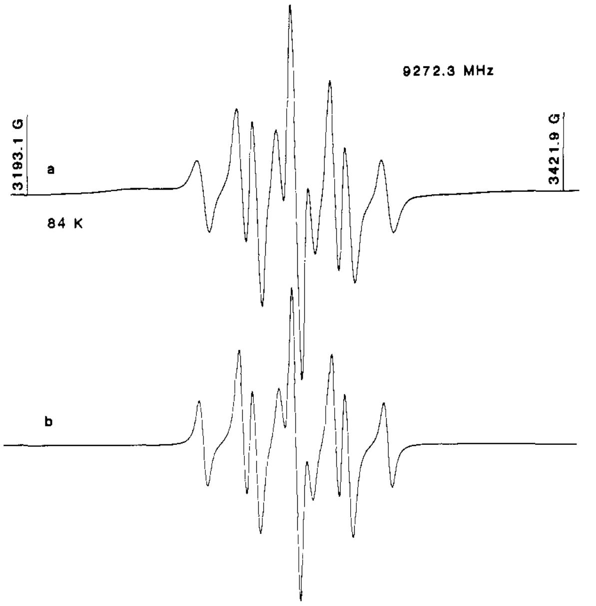


Figure 1. First-derivative ESR spectrum of the ring-opened cyclopropylamine radical cation in CF_3CCl_3 (a) and its simulation (b), using the parameters in Table I and a Lorentzian line width of 3.0 G.

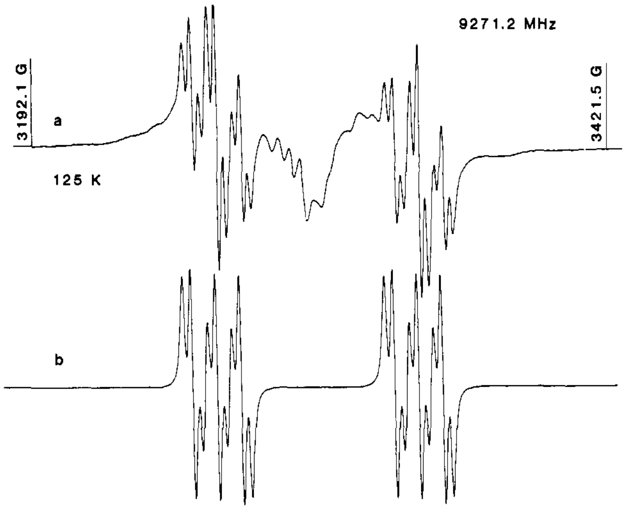


Figure 2. First-derivative ESR spectrum of the propan-1-iminyl radical in $CFCl_2CF_2Cl$ (a) and its simulation (b), using the parameters in Table I and a Lorentzian line width of 1.5 G.

a wide temperature range, the ring-opened and carbon-centered radical cation **2** showing no tendency to isomerize to **3** whereas its conjugate base **5** readily transforms to the nitrogen-centered radical **6**. Moreover, these relations are just the converse of those that apply to the *reverse* process of intramolecular hydrogen-atom abstraction by a nitrogen-centered radical to produce a carbon-

---

(7) Qin, X.-Z.; Williams, F. *J. Phys. Chem.* **1986**, *90*, 2292.

(8) Qin, X.-Z.; Williams, F. *Tetrahedron*, in press.

(9) Since the ESR spectrum of **6** in $CFCl_2CF_2Cl$ is anisotropic below 125 K, the precise temperature at which **6** is formed is difficult to establish. Radical **6** is also clearly detected in the CF_3CCl_3 matrix when **2** decays above the softening point (145 K) of this matrix, again indicating the role of ion–molecule reactions in neutral radical formation.

(10) An alternate path for the formation of **6** via **3** is, of course, excluded by the stability of **2** relative to **3** (vide infra).

(11) Danen, W. C.; West, C. T. *J. Am. Chem. Soc.* **1974**, *96*, 2447.

(12) The ambiguity concerning the radical produced by *tert*-butoxyl radical attack on cyclopropylamine at −60 °C[11] would seem to be resolved in favor of $CH_2CH_2CH{=}NOCMe_3$ rather than **5** in view of the present results showing that **6** is also formed to the exclusion of **5** at low temperatures.

J. Am. Chem. Soc. 1987, 109, 597-599

centered radical in the Hofmann–Löffler reaction.[13] In this latter case, the initially formed tricoordinate nitrogen radical cation analogous to **3** reacts to give a species such as **2** while the corresponding reaction for the neutral radical, which would be similar to **6** → **5**, is not observed. Thus, combining information from the two systems, it is clear that the preponderant radicals are of type **2** for the radical cation and of type **6** for the neutral radical irrespective of whether one starts from carbon-centered or nitrogen-centered radicals. This strongly suggests a thermodynamic basis for the difference in reactivity, radicals such as **2** and **6** being more stable than their respective isomers **3** and **5**.

In fact, thermochemical data for prototype reactions were used by one of us some 25 years ago to predict that a nitrogen-centered radical cation should be more reactive than its counterpart neutral radical in hydrogen atom abstraction, the argument being that a stronger N–H bond is formed in the former case.[14,15] A corollary is that for the reverse process of hydrogen atom transfer from nitrogen, the reaction of the neutral radical should be favored over that of the radical cation, and this case is clearly exemplified here by the facility of **5** → **6** in comparison with **2** → **3**.[16,17] Since the above prediction depends only on the relative heats of reaction, the origin of the reactivity difference can be kinetic or thermodynamic. Clearly the reaction selectivity will in general be greatest when thermodynamics controls the outcome, such that an endothermic hydrogen transfer to the radical becomes exothermic for the radical cation, and vice versa for the reverse process.[18] These simple principles are nicely illustrated by the present results and those previously obtained in studies of the Hofmann–Löffler reaction.[13]

Acknowledgment. We thank Professor Stephen F. Nelsen for his interest in the problem and for communicating the results of his computations on the reactions of interest. We are also indebted to a referee who encouraged us to expand our discussion to include a more explicit consideration of the information gained from the Hofmann–Löffler reaction. This research has been supported by the Division of Chemical Sciences, U.S. Department of Energy (Report DOE/ER/02968-163).

---

(13) The Hofmann–Löffler reaction has an extensive bibliography. Some leading references to the history, mechanism, and synthetic utility of this reaction are: (a) Wolff, M. E. *Chem. Rev.* **1963**, *63*, 55. (b) Wawzonek, S.; Thelen, P. H. *J. Am. Chem. Soc.* **1950**, *72*, 2118. (c) Wawzonek, S.; Nelson, Jr., M. F.; Thelen, P. J. *J. Am. Chem. Soc.* **1951**, *73*, 2806. (d) Corey, E. J.; Hertler, W. R. *J. Am. Chem. Soc.* **1960**, *82*, 1657. (e) Neale, R. S.; Walsh, M. R. *J. Am. Chem. Soc.* **1965**, *87*, 1255. (f) Neale, R. S. *Synthesis* **1971**, *1*. (g) Deno, N. C. In *Methods in Free Radical Chemistry*; Huyser, E. S., Ed.; Marcel Dekker: New York, 1972; Vol. 3, Chapter 3, pp 135–154. (h) Chow, Y. L.; Danen, W. C.; Nelsen, S. F.; Rosenblatt, D. H. *Chem. Rev.* **1978**, *78*, 243–274. (i) Green, M. M.; Moldowan, J. M.; Armstrong, M. W.; Thompson, T. L.; Sprague, K. J.; Hass, A. J.; Artus, J. J. *J. Am. Chem. Soc.* **1976**, *98*, 849.

(14) Williams, F. *J. Am. Chem. Soc.* **1962**, *84*, 2895.

(15) By means of a simple thermochemical cycle, the difference between the $-\Delta H$ values for **3** → **2** and **6** → **5** can also be related to the difference between the proton affinities or basicities of **5** and **6**. Another useful relation obtained by coupling these reactions together is that, at equilibrium,

$$\log_{10} \frac{[\mathbf{2}][\mathbf{6}]}{[\mathbf{3}][\mathbf{5}]} = pK_a(\mathbf{2}) - pK_a(\mathbf{3})$$

(16) Computations by Nelsen using the AM1 program show that the reaction

$$\mathbf{3} + \mathbf{5} \rightarrow \mathbf{2} + \mathbf{6}$$

is exothermic by 20.6 kcal mol^{-1}, in agreement with the principle of our discussion here and elsewhere:[14] Nelsen, S. F., private communication.

(17) Neale and Walsh[13e] have criticized our earlier brief consideration[14] of the Hofmann–Löffler reaction by stating that contrary to our thesis, the basicity of Bu_2N may be greater than that of the parent amine Bu_2NH, since there is evidence that the basicity of the anilino radical C_6H_5NH exceeds that of aniline (Land, E. J.; Porter, G. *J. Chem. Soc.* **1961**, 3540). We believe that this comparison is inappropriate and emphasize that our considerations are not applicable to delocalized radicals. Curiously, Neale and Walsh also seem to doubt the validity of this comparison in footnote 13 of their paper. More recently, it has been shown that the basicity of Me_2NH exceeds that of Me_2N (Fessenden, R. W.; Neta, P. *J. Phys. Chem.* **1972**, *76*, 2857), and this is in fact the general rule for localized nitrogen-centered radicals.[13h]

(18) For simplicity, we assume that the contribution of entropy changes, which should be minimal for hydrogen-transfer reactions of the type considered here, through $T\Delta S$ to the position of thermodynamic equilibrium can be neglected in comparison with ΔH.

Isolation and Characterization of Vinylidene from the Dehydrogenation of Ethylidyne on the Ru(001) p(2×2)O Surface

M. M. Hills, J. E. Parmeter,[†] and W. H. Weinberg*

Division of Chemistry and Chemical Engineering
California Institute of Technology
Pasadena, California 91125

Received August 28, 1986

Although the structure and bonding of a variety of adsorbed species on transition-metal surfaces have been compared to those of similar ligands in homogeneous metal compounds, the chemical reactions which these two entities undergo have not been related. This connection represents the logical and necessary next step in relating the organometallic chemistry of homogeneous compounds with that of extended surfaces, i.e., the relationship between homogeneous catalysis by organometallic compounds and heterogeneous catalysis by metallic surfaces. It has been found that ethylene reacts with $Os_3(CO)_{12}$ to form a μ-vinylidene complex, $H_2Os_3(CO)_9(CCH_2)$, which can be hydrogenated to a μ-ethylidyne complex, $H_3Os_3(CO)_9(CCH_3)$.[1-3] Similarly, ethylene adsorbed on the hexagonal Ru(001),[4] Pt(111),[5] Pt(100),[6,7] Pd(111),[9] and Rh(111)[10] surfaces at room temperature forms ethylidyne, which dehydrogenates at higher surface temperatures. However, vinylidene has been neither isolated nor unambiguously identified as an intermediate in either the formation or the decomposition of adsorbed ethylidyne.[11] This paper reports the first conclusive spectroscopic identification of adsorbed vinylidene, which was observed following the annealing of adsorbed ethylidyne on the Ru(001) p(2×2)O surface.[12]

The high-resolution electron energy loss spectroscopic (EELS) measurements were carried out in an ultrahigh vacuum system that has been described in detail previously.[14] The p(2×2) oxygen overlayer on the Ru(001) surface, which is depicted in Figure 1a, corresponds to a fractional surface coverage of atomic oxygen of 0.25. The existence of this ordered overlayer was confirmed by EEL spectra which exhibit a $\nu_\perp$(Ru–O) mode at 535 cm^{-1} and a phonon mode characteristic of the ordered overlayer at 250 cm^{-1}.[15]

Exposure of the Ru(001) p(2×2)O surface to ethylene at temperatures below 240 K results in the adsorption of π-bonded molecular ethylene.[13,16] Upon annealing to 250 K, the π-bonded

---

[†] AT&T Bell Laboratories Predoctoral Fellow.

(1) Deeming, A. J.; Underhill, M. *J. Chem. Soc., Chem. Commun.* **1983**, 277.

(2) Deeming, A. J.; Underhill, M. *J. Chem. Soc., Dalton Trans.* **1974**, 1415.

(3) Andrews, J. R.; Kettle, S. F. A.; Powell, D. B.; Sheppard, N. *Inorg. Chem.* **1982**, *21*, 2874.

(4) Hills, M. M.; Parmeter, J. E.; Mullins, C. B.; Weinberg, W. H. *J. Am. Chem. Soc.* **1986**, *108*, 3554.

(5) Steininger, H.; Ibach, H.; Lehwald, S. *Surf. Sci.* **1982**, *117*, 685.

(6) Ibach, H. In *Proceedings of the Conference on Vibrations in Adsorbed Layers*, Jülich, 1978.

(7) The Pt(100) surface reconstructs to a slightly buckled, close-packed (5×20) superstructure.[8]

(8) Heilman, P.; Heinz, K.; Müller, K. *Surf. Sci.* **1979**, *83*, 487.

(9) Gates, J. A.; Kesmodel, L. L. *Surf. Sci.* **1983**, *124*, 68.

(10) Koel, B. E.; Bent, B. E.; Somorjai, G. A. *Surf. Sci.* **1984**, *146*, 211.

(11) Indeed, *no intermediate* has been observed in the reaction of molecularly adsorbed ethylene to ethylidyne. Likewise, no intermediate in the decomposition of adsorbed ethylidyne has been observed heretofore in which carbon–carbon bonding is preserved.

(12) The ethylidyne is a stable intermediate in the dehydrogenation of π-bonded, molecular ethylene on the Ru(001) surface on which an ordered p(2×2) overlayer of oxygen adatoms is present.[13]

(13) Hills, M. M.; Parmeter, J. E.; Weinberg, W. H., manuscript in preparation.

(14) Thomas, G. E.; Weinberg, W. H. *Rev. Sci. Instrum.* **1979**, *50*, 497.

(15) Rahman, T. S.; Anton, A. B.; Avery, N. R.; Weinberg, W. H. *Phys. Rev. Lett.* **1983**, *51*, 1979.

0002-7863/87/1509-0597$01.50/0