reduced to a poorly resolved singlet, but with a very similar overall width to that observed at the higher temperature. This is consistent with the freezing-out of the rotational motions of the methyl groups in this sterically hindered radical, giving a broad range of conformations, and consequently a spread of hyperfine couplings, hence the low resolution.

The ESR spectrum of the HMD•$^+$ cation indicates that the SOMO is essentially the $^2B_2$ orbital of the parent Dewar benzene molecule.[9] This was also the conclusion drawn from the nature of the polarizations observed in a photo-CIDNP study of HMD with excited (triplet) electron acceptors.[10] However, polarization of the protons on the bridge-head methyl groups was also observed, which leads these workers to conclude that the most likely explanation for this was the simultaneous formation of a second cation ($^2A_1$) via. a competing pathway, with its spin density confined mainly to the transannular bond.

The idea of competing pathways was borne out by the results obtained with different electron acceptors, which caused variations in the relative polarizations of the olefinic and bridge-head methyl groups. This is reasonable since calculations on the parent Dewar benzene molecule indicate that the $^2B_2$ and $^2A_1$ orbitals are of very similar energy. Our results, however, show only the presence of the $^2B_2$ cation.

It is of interest to consider why the $CFCl_3$ matrix is so successful in stabilizing the obviously highly unstable HMD•$^+$ cation. We feel that the most reasonable explanation is that the $CFCl_3$ molecules pack tightly and rigidly around the substrate molecule so that when it is ionized to its radical cation, although there is a large driving potential for rearrangment to the HMB•$^+$ cation, the molecular framework cannot relax to achieve the necessary planar arrangement. On annealing, softening of the rigid matrix allows the rearrangement to occur. A similar effect was proposed previously to account for changes in the optical spectra of radical cations on annealing the solid matrix in which they were isolated.[11]

Acknowledgment. I thank Prof. Symons for access to ESR facilities.

---

(9) Jorgensen, W. L.; Salem, L. *The Organic Chemists Book of Orbitals*; Academic: New York, 1973.

(10) Roth, H. D.; Schilling, M. L. M.; Raghavachari, K. *J. Am. Chem. Soc.* **1984**, *106*, 253.

(11) Bally, T.; Haselbach, E.; Lanyiova, Z.; Baertschi, P. *Helv. Chim. Acta* **1978**, *61*, 2488.

Surface Photochemistry: Products Retained on Pt(111) during Photolysis of Adsorbed CH_3Br

Y. Zhou, W. M. Feng, M. A. Henderson, B. Roop, and J. M. White*

Department of Chemistry, University of Texas
Austin, Texas 78712

Received March 8, 1988

The photochemistry of molecules at the gas–solid interface has been successfully investigated in a number of laboratories,[1-11] but very little work has shown photochemistry on *clean metal* surfaces. Previous work from this research group[12] showed that the photolysis of methyl halides (CH_3Br, CH_3Cl) adsorbed on Pt(111) lead to a detectable amount of methane (290 K), but no other hydrocarbons, in TPD. For CH_3Br, Br desorbed as atoms between 720 and 950 K. Significantly, these two methyl halides show no thermal chemistry on Pt(111).

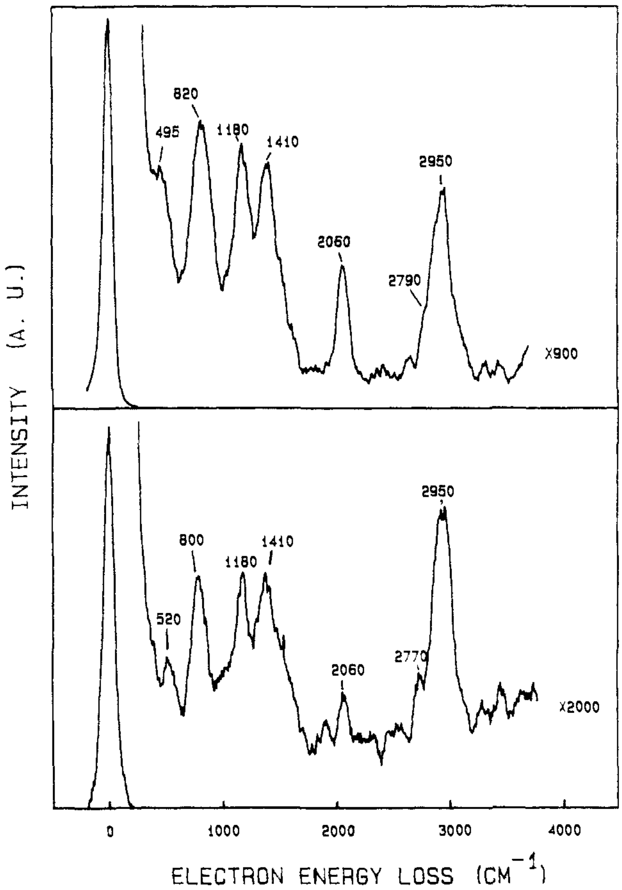

Figure 1. Specular (upper panel) and off-specular (lower panel) HREELS taken after irradiation for 90 min of a submonolayer of $CH_3Br/Pt(111)$ and flashing briefly to 220 K to remove remaining molecular CH_3Br.

The results suggest that, as in the gas phase, CH_3X (X = Br, Cl) absorbs UV light and forms an electronically excited state that is repulsive and, with significant probability, cleaves the C–X bond even though other relaxation paths exist.[14]

In this communication we identify, using vibrational spectroscopy, the adsorbed species formed during UV irradiation of CH_3Br on Pt(111). By comparison with measurements on CH_3I, which thermally decomposes to CH_3(a) and I(a),[15] we identify adsorbed methyl as the hydrocarbon fragment formed and retained during the photolysis.

A detailed description of the ultra-high-vacuum (UHV) system has been given elsewhere.[16] The Pt(111) surface was cleaned by Ar$^+$ ion sputtering, oxidation, and high-temperature annealing until no impurities were detected in Auger electron spectroscopy. With the sample at 100 K, purified CH_3Br was dosed through a 3 mm i.d. tube positioned 6 mm from the sample. A CH_3Br coverage slightly less than a monolayer was produced by warming multilayer $CH_3Br/Pt(111)$ to 135 K, which desorbs the multilayer

---

(1) Ehrlich, D. J.; Tsao, J. Y. *J. Vac. Sci. Technol.* **1983**, *B1*, 969.

(2) Chuang, T. J. *Surf. Sci.* **1986**, *178*, 763.

(3) Chuang, T. J. *Surf. Sci. Rep.* **1983**, *3*, 1.

(4) Osgood, R. M., Jr. *Annu. Rep. Phys. Chem.* **1983**, *34*, 77.

(5) Marsh, E. P.; Tabares, F. L.; Schneider, M. R.; Cowin, J. P. *J. Vac. Sci. Technol.* **1987**, *A5*, 519.

(6) Grassian, V. H.; Pimentel, G. C. *J. Chem. Phys.*, in press.

(7) Bourdon, E. B. D.; Cowin, J. P.; Harrison, I.; Polanyi, J. C.; Segner, J.; Stanners, C. D.; Young, P. A. *J. Phys. Chem.* **1984**, *88*, 6100.

(8) Tabares, F. L.; Marsh, E. P.; Bach, G. A.; Cowin, J. P. *J. Chem. Phys.* **1987**, *86*, 738.

(9) Roop, B.; Costello, S. A.; Greenlief, C. M.; White, J. M. *Chem. Phys. Lett.* **1988**, *143*, 38.

(10) Celii, F. G.; Whitmore, P. M.; Janda, K. C. *Chem. Phys. Lett.* **1987**, *138*, 257.

(11) Chuang, T. J.; Domen, K. *J. Vac. Sci. Technol.* **1987**, *A5*, 473. Domen, K.; Chuang, T. J. *Phys. Rev. Lett.* **1987**, *59*, 1484.

(12) Costello, S. A.; Roop, B.; Liu, Z.-M.; White, J. M. *J. Phys. Chem.* **1988**, *92*, 1019.

(13) Calvert, J. C.; Pitts, J. N. *Photochemistry*; Wiley: New York, 1966.

(14) Campion, A.; Gato, A. R.; Harris, C. B.; Robota, H. J.; Whitmore, P. M. *Chem. Phys. Lett.* **1980**, *73*, 447.

(15) Henderson, M. A.; Mitchell, G. E.; White, J. M. *Surf. Sci.* **1987**, *184*, L325.

(16) Mitchell, G. E.; Radloff, P. L.; Greenlief, C. M.; Henderson, M. A.; White, J. M. *Surf. Sci.* **1987**, *183*, 403.

0002-7863/88/1510-4447$01.50/0 © 1988 American Chemical Society

Table I. HREELS Frequencies of Chemisorbed CH_3Br and H_3

C_s symmetry	CH_3 photochemical from CH_3Br[a]	CH_3 thermal from CH_3I[b]		CH_3Br[b]
$\nu(CH_2)$	2950	2925		
$\nu(CH)$	2770[c]	2775	$\nu_s(CH_3)$	3015
$\delta(CH_2)$	1410	1425	$\delta_a(CH_3)$	1420
$\omega(CH_2)$	1180	1165	$\delta_s(CH_3)$	1285
$\tau(CH_2)$	NO[d]	NO		
$\rho(CH_2)$	NO	NO	$\rho(CH_3)$	945
$\delta(CH)$	820	790		
$\rho(CH)$	NO	NO		
$\nu(PtC)$	495	520		
			$\nu(C-Br)$	565
			$\nu(Pt-Br)$	NO

[a] This work. [b] Reference 15. [c] Resolved only in off-specular geometry. [d] NO = not observed.

and part of the first monolayer. The UV light, generated from a focused 100 W Hg arc lamp, passed through a neutral density filter and then a quartz window at the vacuum chamber wall. The incident angle was approximately 30 deg off the sample normal. In our experiments, the temperature reached during irradiation never exceeded 135 K and the radiant power on the sample was between 0.30 and 0.35 W. High-resolution electron energy loss spectroscopy (HREELS) was used to measure the vibrational spectra of adsorbed species and was taken with a primary beam energy of 7.0 eV and an elastic peak full width at half maximum of 95 cm^{-1}.

To take HREELS of the species formed and retained during irradiation, we irradiated a submonolayer of CH_3Br for 90 min, flashed the sample to 220 K, and then cooled the sample to 100 K to take the spectrum. As indicated by several experiments where TPD was done before and after HREELS, flashing to 220 K removes all the molecular methyl bromide that remains after photolysis.

Figure 1 (upper panel) shows the HREELS of monolayer CH_3Br after photolysis and flashing to 220 K. Except for the band at 2060 cm^{-1}, which is due to background CO, all other bands (2950, 1410, 1180, 820, and 495 cm^{-1}) can be attributed to CH_3 groups adsorbed on Pt(111).[15] The band assignments are listed in Table I with comparisons to CH_3Br on Pt(111) and to CH_3 generated from the thermal decomposition of CH_3I on Pt(111).[15] Assignments of the latter bands were confirmed with use of CD_3I.[15] Because the intensities are relatively weak and long data accumulation times are required, we did not systematically vary the irradition time.

The symmetric C–H stretches of methyl halides are above 3000 cm^{-1} regardless of coverage, while that of the adsorbed methyl group is below 3000 cm^{-1} (2925 cm^{-1} for CH_3 derived from CH_3I[15]). The C–H stretching frequency (2950 cm^{-1}) shown in Figure 1 is also below 3000 cm^{-1}, supporting the assignment as $CH_3(a)$. The fact that there is no band at 560 cm^{-1} attributable to C–Br stretching also indicates C–Br bond cleavage during photolysis. While it is not well-resolved in the specular direction, there does appear to be a "soft" C–H stretching mode in the 2775–2790-cm^{-1} region, as in CH_3I decomposition on Pt(111)[15] and in activated decomposition of CH_4 on Ni(111).[17] The Br-metal stretching frequency probably lies within the tail of the elastic peak. Thus, we conclude that methyl groups accumulate on the surface during photolysis.

Comparing the specular (Figure 1, upper panel) and off-specular (lower panel) HREELS, we conclude that all the observed modes are dipole allowed. Applying the HREELS dipole selection rule, this methyl group has symmetry less than C_{3v}, probably C_s,[15] as indicated in Table I.

In conclusion, these results show that the photolysis of submonolayer amounts of methyl bromide, adsorbed on Pt(111), leads to adsorbed methyl groups. These have a C_s symmetry and are the precursor to the methane observed in post-irradiation TPD. Methane formation involves background H_2 chemisorption and some methyl decomposition.[12]

Acknowledgment. This work was supported in part by the National Science Foundation Materials Research Group Program (DMR 8418086).

---

(17) Lee, M. B.; Yang, Q. Y.; Tang, S. L.; Ceyer, S. T. *J. Chem. Phys.* **1986**, *85*, 1693.

Observation of a Transition-Metal–Enol Complex and Stereoselective Keto–Enol Tautomerization in Transition-Metal–Acyl Compounds

Joseph M. O'Connor* and Roger Uhrhammer

Department of Chemistry, D-006
University of California, San Diego
La Jolla, California 92093

Received February 16, 1988

Interest in the properties and reactivity of transition metal–acyl complexes stems from the central role that metal–acyl species play in catalytic reactions of industrial importance[1] and from recent advances in the use of metal–acyl complexes as stoichiometric reagents for organic synthesis.[2] The chemistry of organic carbonyl compounds is often influenced by keto–enol tautomerization processes;[3] yet, such a phenomenon has not previously been observed for a transition metal–acyl compound. Here we report the formation of a transition metal–enol complex $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(\mu\text{-}\eta^1,\eta^2\text{-}\overline{COCHCOH)}Re(CO)_4$, **1-Re**, and observation of kinetic, stereoselective tautomerization in the acyl-bridged compounds $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(\mu\text{-}\eta^1,\eta^2\text{-}\overline{COCH_2CO)}M(CO)_4$, [M = Re, **2-Re**; M = Mn, **2-Mn**].

We recently reported the synthesis of the novel acyl-bridged bimetallic complexes **2-Re** and **2-Mn** from reaction of $(\eta^5\text{-}C_5Me_5)Re(NO)(PPh_3)(COCH_2Li)$ and $M(CO)_5(OSO_2CF_3)$ [M = Mn, Re].[4] The ^1H NMR spectrum of **2-Re** in $CDCl_3$ exhibits doublets at δ 2.48 and 3.13 (J_{HH} = 20.7 Hz) assigned to the diastereotopic methylene hydrogens.[5] We have now observed that THF-d_8 solutions of **2-Re** give rise to three additional distinct resonances in the ^1H NMR spectrum, which we attribute to formation of transition metal–enol complex **1-Re**; singlets at δ 6.28 (1 H), 8.91 (1 H), and 1.73 (15 H) are assigned to the vinyl, hydroxyl, and $\eta^5\text{-}C_5Me_5$ hydrogens, respectively.[6] The intensity

---

(1) (a) Casey, C. P. *J. Chem. Educ.* **1986**, *63*, 188. (b) Henrici-Olive, G.; Olive, S. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 136. (c) Hermann, W. A. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 117. (d) Masters, C. *Adv. Organomet. Chem.* **1979**, *17*, 61. (e) Muetterties, E. L.; Stein, J. *Chem. Rev.* **1979**, *79*, 479. (f) Parshall, G. W. *Homogeneous Catalysis*; Wiley: New York, 1980; Chapter 5. (g) Sneeden, R. P. A. In *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, 1982; Vol. 8, p 19. (h) Tkatchenko, I. *Ibid.* p 101.

(2) (a) Burkhardt, E. R.; Doney, J. J.; Stack, J. G.; Heathcock, C. H.; Bergman, R. G. *J. Mol. Catal.* **1987**, *41*, 41 and references therein. (b) Liebeskind, L. S.; Welker, M. E.; Fengl, R. W. *J. Am. Chem. Soc.* **1986**, *108*, 6328 and references therein. (c) Davies, S. G.; Dordor-Hedgecock, I. M.; Sutton, K. H.; Walker, J. C. *Tetrahedron* **1986**, *42*, 5123 and references therein. (d) Brinkman, K.; Helquist, P. *Tetrahedron Lett.* **1985**, *26*, 2845.

(3) (a) Forsen, S.; Nilsson, M. In *The Chemistry of the Carbonyl Group, II*; Patai, S., Ed.; Wiley Interscience: New York, 1970. (b) Zimmerman, H. E. *Acc. Chem. Res.* **1987**, *20*, 263 and references therein. (c) Nadler, E. B.; Rappoport, Z.; Arad, D.; Apeloig, Y. *J. Am. Chem. Soc.* **1987**, *109*, 7873 and references therein. (d) Hine, J.; Miles, D. E.; Zeigler, J. P. *J. Am. Chem. Soc.* **1983**, *105*, 4374. (e) Hine, J. *Acc. Chem. Res.* **1978**, *11*, 1. (f) Capon, B.; Siddhanta, A. K.; Zucco, C. *J. Org. Chem.* **1985**, *50*, 3580.

(4) O'Connor, J. M.; Uhrhammer, R.; Rheingold, A. L. *Organometallics* **1987**, *6*, 1987.

(5) Additional resonances for **2-Re** are observed in the ^1H NMR spectrum ($CDCl_3$) δ 1.75 (s, 15 H), 7.30 and 7.43 (m, 15 H); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 289.8 (d, J_{CP} = 7.4 Hz), 275.6, 194.9, 191.6, 191.4, 190.9, 133.3 (br), 130.9, 128.8, 128.7, 103.6, 95.7, 9.9.

0002-7863/88/1510-4448$01.50/0