

C-C Bond Activation: Cycloheptatriene Reaction on W(100), W(100)-(5×1)-C, and W(100)-(2×1)-O

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Abstract: The adsorption and reaction of cycloheptatriene ($c\text{-C}_7\text{H}_8$) was investigated on W(100), W(100)-(5×1)-C, and W(100)-(2×1)-O surfaces under ultra-high-vacuum conditions with use of thermal desorption spectroscopy and isotope exchange reactions. Irreversible dehydrogenation yielding gaseous H_2 was the only reaction observed on clean W(100). Cycloheptatriene dehydrogenation was suppressed on W(100)-(5×1)-C, allowing reactions involving C-C bond activation to proceed. Benzene formation was uniquely observed on the -(5×1)-C surface. Reaction of cycloheptatriene-7- d_1 on W(100)-(5×1)-C demonstrated that the 7 position was initially dehydrogenated, yielding a coordinated C_7H_7 adsorption intermediate which subsequently eliminated one carbon to yield benzene.

Tungsten-based materials, such as carbides and oxides, are used as catalysts for several reactions involving C-C and C-H bond activation in hydrocarbon molecules.¹ The rates and selectivity of hydrocarbon reactions are dependent on the presence, concentration, and structure of carbon or oxygen adlayers. Tungsten carbide and carbided surfaces of tungsten have been shown to exhibit greater reactivity for reactions involving C-C bond activation than clean tungsten.²

We have studied the reactivity of unsaturated hydrocarbons on W(100), W(100)-(5×1)-C, and W(100)-(2×1)-O surfaces under ultra-high-vacuum conditions, in order to probe for changes in the selectivity for C-H vs. C-C bond activation. Previously reported studies of C_2H_4 and C_2H_2 showed suppression of C-H bond activation on the -(5×1)-C and -(2×1)-O surfaces compared to clean W(100).³

In this work, the adsorption and reaction of cycloheptatriene on W(100), W(100)-(2×1)-O, and W(100)-(5×1)-C surfaces were investigated. C-H bond activation was suppressed on the -(5×1)-C and -(2×1)-O surfaces, analogously to the acetylene and ethylene chemistry. The -(5×1)-C surface uniquely effects benzene formation from cycloheptatriene. We propose that initial C-H bond scission occurs at the 7 position, producing a cyclic C_7H_7 adsorption intermediate, which undergoes further reaction to produce benzene.

Experimental Section

All experiments were performed in an ultrahigh-vacuum chamber with a base pressure of $\approx 2 \times 10^{-10}$ torr, described in detail previously.⁴

The W(100)-(5×1)-C overlayer was prepared by dosing 60 L of ethylene on clean W(100) maintained at a temperature of ≈ 1500 K. The W(100)-(2×1)-O structure was prepared by exposure of clean W(100) to 20 L of $\text{O}_2(\text{g})$ at ≈ 1250 K. The W(100) crystal was cleaned by cycles of oxygen treatment at $\approx 10^{-6}$ torr pressure and 1400 K crystal temperature and subsequent flashing in vacuum to 2500 K.⁴

The benzene (99% purity), toluene (99% purity), and cycloheptatriene (90% purity) were all obtained from Aldrich Chemical Co. The benzene and toluene were dried over sodium sulfate, degassed, vacuum distilled, and used without further purification. The cycloheptatriene was purified by preparative scale gas chromatography. The final purity of the cycloheptatriene was 99%: it was degassed and vacuum distilled prior to use. The cycloheptatriene-7- d_1 was synthesized from tropylium tetrafluoroborate (Aldrich) and sodium borodeuteride in D_2O .⁵ It was purified by vacuum distillation and characterized as >95% purity with NMR and mass spectrometry.

All gases were admitted to the vacuum system with use of a directed dosing system with a calibrated flux.⁴ The reactants were freshly ad-

Table I. Relative Cracking Fractions of Cycloheptatriene

mass/charge	ion identity	rel fraction
92	C_7H_8^+	0.42
91	C_7H_7^+	1.00
78	C_6H_6^+	0.04
2	H_2^+	0.11

mitted to the source for each experiment and the mass spectra of the gases admitted to the vacuum system were monitored in order to preclude reactions that may occur on the source or vacuum system walls from contributing to the observed chemistry. Gaseous hydrogen and oxygen were admitted through separate dosers from the hydrocarbons.

Thermal desorption data were collected with an IBM PC, allowing for monitoring of between one and eight separate masses in a single experiment. Radiative heating was used in all experiments described herein, resulting in heating rates in the range of 12–20 $\text{K}\cdot\text{s}^{-1}$.

Results

Clean W(100). The thermal desorption spectrum obtained subsequent to cycloheptatriene adsorption on clean W(100) is shown in Figure 1. (Table I lists the cracking fractions of relevant masses from cycloheptatriene for clarification.) Molecules adsorbed at low exposures (<0.6 L, $1 \text{ L} \equiv 10^{-6} \text{ torr}\cdot\text{s} = 10^{14} \text{ molecules}\cdot\text{s}^{-1}$) underwent irreversible C-H bond cleavage prior to 500 K, as evidenced by the desorption of molecular hydrogen and carbon remaining on the surface. No hydrocarbon desorption was observed below this exposure: 91, 78, 28, and 16 amu were monitored in order to probe for gaseous C_7H_8 , C_6H_6 , C_2 hydrocarbons, and CH_4 production, respectively. Higher exposures of cycloheptatriene resulted in desorption of C_7H_8 in two narrow, poorly resolved peaks at 170 and 190 K. These desorption features did not saturate: the 190 K peak appears first with both features increasing monotonically as a function of cycloheptatriene exposure. No deuterium incorporation into the desorbed C_7H_8 was observed when atomic deuterium was coadsorbed with cycloheptatriene. In these experiments, $\text{D}_2(\text{g})$ was dosed onto the clean W(100) surface at 120 K with exposures in the range of 0.5–10 L with a dose of >0.7 L of cycloheptatriene following. Thermal desorption resulted in low-temperature desorption of the parent (91 amu), as in Figure 1, and production of gaseous H_2 , HD, and D_2 , verifying that the preadsorbed deuterium remained on the surface subsequent to cycloheptatriene adsorption. No deuterium incorporation into the desorbed cycloheptatriene was detected. Thus, the observed 91-amu desorptions are attributed to sublimation of multilayers of condensed cycloheptatriene.

W(100)-(5×1)-C. The W(100)-(5×1)-C surface has been characterized previously.⁷⁻⁹ The -(5×1)-C overlayer involves

(1) See, for example: Oyama, S. T.; Haller, G. L. *Catalysis* **1982**, *5*, 333–364.

(2) Levy, R.; Boudart, M. *Science* **1973**, *181*, 547.

(3) Pearlstine, K. A.; Friend, C. M. *J. Vac. Sci. Technol. A* **1984**, *2*, 1021.

(4) Baldwin, E. K.; Friend, C. M. *J. Phys. Chem.* **1985**, *89*, 2576.

(5) Tsai, M.-C.; Stein, J.; Friend, C. M.; Muettterties, E. L. *J. Am. Chem. Soc.* **1982**, *104*, 3533.

(6) The parent ion, C_7H_8^+ , has a mass to charge ratio of 92. However, m/e 91 amu is the predominant ion in the mass spectrum of gaseous cycloheptatriene. In general, both 91 and 92 amu were monitored.

(7) Benziger, J. B.; Ko, E. I.; Madix, R. J. *J. Catal.* **1978**, *54*, 414.

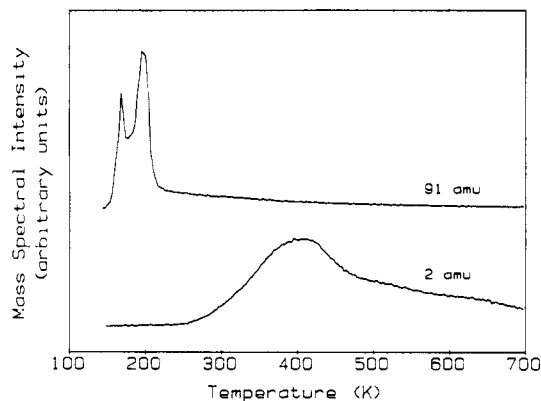


Figure 1. The thermal desorption spectrum obtained subsequent to adsorption of 10 L of cycloheptatriene on clean W(100) is shown in the figure. The adsorption temperature was ≈ 120 K and the heating rate used in this experiment was $20 \text{ K}\cdot\text{s}^{-1}$. The upper trace (91 amu) corresponds to desorption of the unreacted parent. Mass 91 corresponds to C_7H_7^+ , the predominant ion in the mass spectrum of cycloheptatriene. The same results were obtained when 92 amu, C_7H_8^+ , was monitored. The lower trace, 2 amu, corresponds to desorption of gaseous H_2 produced from irreversible decomposition of cycloheptatriene and subsequent hydrogen atom recombination on the surface. No hydrocarbon desorption, other than the parent, was observed.

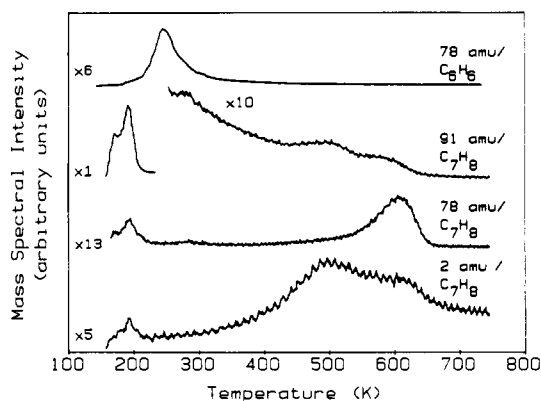


Figure 2. Thermal reaction of cycloheptatriene on W(100)-(5 \times 1)-C resulted in the lower three desorption spectra depicted here. The initial cycloheptatriene exposure was ≈ 3.8 L with a crystal temperature of 120 K. The three traces correspond to desorption of molecular H_2 (2 amu), benzene (78 amu), and C_7H_8 (91 amu) subsequent to cycloheptatriene adsorption and heating on the -(5 \times 1)-C surface. The top-most trace is the thermal desorption spectrum obtained subsequent to exposure of the -(5 \times 1)-C to 1.1 L of benzene at 120 K, reflecting the desorption temperature of molecularly adsorbed C_6H_6 . No decomposition accompanying the benzene desorption was observed. The heating rate in both experiments was $12 \text{ K}\cdot\text{s}^{-1}$.

reconstruction of the tungsten surface plane and incorporation of carbon atoms into the lattice. The initially proposed structure resembled WC, resulting in an hexagonal layer of tungsten atoms with carbon lying entirely under the top-most tungsten layer.⁷ Ultraviolet photoemission data comparing WC(0001) and the W(100)-(5 \times 1)-C are very similar,⁹ suggesting that the -(5 \times 1)-C does resemble WC. The alternative model that has been proposed is a W_3C_2 surface carbide which also invokes a reconstruction of the tungsten surface layer to a more close-packed structure.⁸ The carbon is proposed to be in the top-most layer as dimers with several rows of unobscured tungsten atoms.

The desorption spectrum obtained from thermal reaction of cycloheptatriene is depicted in Figure 2. Benzene formation is observed in a reaction-limited desorption peak at 600 K. Adsorption of benzene itself on the -(5 \times 1)-C surface results in a desorption-limited peak at 240 K (Figure 2). Coadsorption of

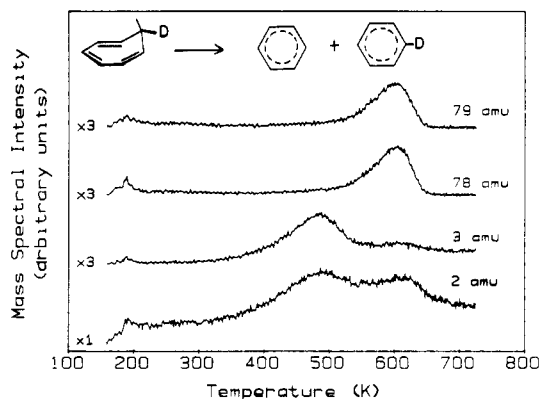


Figure 3. Reaction of cycloheptatriene-7- d_1 on W(100)(5 \times 1)-C with a heating rate of $12 \text{ K}\cdot\text{s}^{-1}$ resulted in the desorption data shown here. The top two spectra correspond to desorption of $\text{C}_6\text{H}_7\text{D}$ (79 amu) and C_6H_6 (78 amu), uncorrected for fragmentation in the mass spectrometer. The intensity in these spectra observed at < 200 K is the result of fragmentation of parent cycloheptatriene-7- d_1 which exhibits a desorption, not pictured, in the range of 150–200 K. The two lower traces are the result of production of gaseous HD (3 amu) and H_2 (2 amu) from the reaction of the cycloheptatriene-7- d_1 on the -(5 \times 1)-C surface. No desorption of gaseous D_2 (4 amu) or benzene- d_2 to - d_6 (80–84 amu) was detected. The exposure of cycloheptatriene-7- d_1 was ≈ 1.1 L with an initial crystal temperature of ≈ 120 K.

a 1:1 mixture of C_6H_6 and C_6D_6 did not result in any H-D exchange: only gaseous C_6T_6 and C_6D_6 were desorbed. In addition, benzene did not undergo decomposition on the -(5 \times 1)-C surface: only molecular desorption was observed. Two small, poorly resolved, $\text{H}_2(\text{g})$ desorption features of approximately equal magnitude are observed at 500 and 630 K following reaction of $\text{c-C}_7\text{H}_8$. A small 91-amu desorption peak, coincident with the 500 K gaseous H_2 desorption, is also evident. The benzene and two molecular hydrogen features are all present at low $\text{c-C}_7\text{H}_8$ exposures (≈ 0.6 L): their intensities simultaneously increase up to a saturation exposure of 3.3 L. At high cycloheptatriene exposures, two large, narrow, 91-amu desorption features are observed at 190 and 150 K. The 190 K desorption peak appears first, with exposures greater than 1.7 L resulting in desorption at 170 and 190 K. These two low-temperature cycloheptatriene desorptions are attributed to sublimation of a condensed multilayer. No other hydrocarbons were produced from reaction of the cycloheptatriene: methane and C_2 fragments were searched for.

Reaction of cycloheptatriene-7- d_1 was used to determine the stoichiometry of adsorption intermediates leading to benzene formation. The resulting thermal desorption spectrum is shown in Figure 3. No desorption of D_2 (4 amu) or d_2 - d_6 benzenes was observed. The two key results obtained from reaction of the cycloheptatriene-7- d_1 are the lack of deuterium desorption in the higher temperature molecular hydrogen feature at 630 K and the production of both benzene- d_0 and benzene- d_1 in a relative ratio of $\approx 1:1.2$, corrected for mass spectral fragmentation. The lack of gaseous D_2 (4 amu) is the result of a relative excess of H vs. D atoms in the monodeuteriocycloheptatriene molecule. Thus, all deuterium is desorbed as gaseous HD or as benzene- d_1 . Experiments where significant concentrations of atomic deuterium and cycloheptatriene were coadsorbed could not be performed due to the low dissociation probability for H_2 (D_2) on the carbide surface.¹⁰

Toluene adsorption was also investigated on the W(100)-(5 \times 1)-C surface, as it is a possible surface stable intermediate,

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(10) (a) A small amount of atomic deuterium could be adsorbed on the -(5 \times 1)-C after prolonged exposure to gaseous D_2 . No H-D exchange in the desorbed $\text{c-C}_7\text{H}_8$ or C_6H_6 was observed in these experiments. The low dissociation probability for H_2 on the -(5 \times 1)-C has been previously reported.^{10b} Attempts to atomize deuterium with use of a hot filament resulted in significant levels of CO and H_2O contamination as well as D atoms, precluding careful study. No H-D exchange was observed in these limited sets of deuterium coadsorption experiments. (b) Benziger, J. B.; Ko, E. I.; Madix, R. J. *J. Catal.* **1978**, *54*, 414.

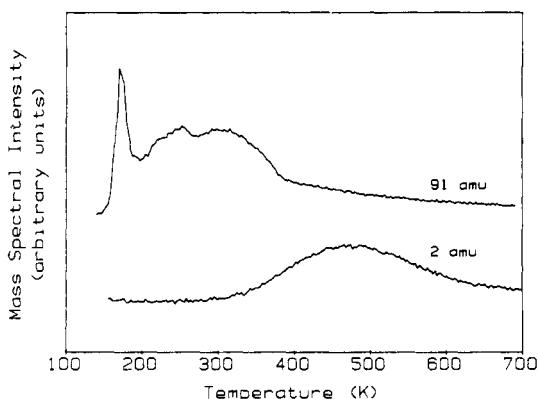


Figure 4. The thermal desorption spectrum obtained subsequent to a 6.6-L exposure of cycloheptatriene on W(100)-(2 \times 1)-O at 120 K is represented in the Figure. The upper trace (91 amu) corresponds to desorption of C₇H₈. The lower spectrum (2 amu) is produced from decomposition of the cycloheptatriene on the surface. No hydrocarbon formation was observed: 78, 16, and 28 amu, not pictured, were monitored for benzene, methane, and C₂ or greater noncyclic hydrocarbons, respectively.

resulting from cycloheptatriene isomerization.¹¹ The spectrum obtained from thermal treatment of a toluene multilayer resulted in parent 91-amu desorptions at \approx 190 and 280 K and a small, broad, featureless H₂ desorption in the range of 350–650 K. No formation of benzene, CH₄, or C₂ hydrocarbons was detected.

W(100)-p(2 \times 1)-O. The W(100)-(2 \times 1)-O surface has been extensively studied with a range of techniques.^{12–15} As in the case of the -(5 \times 1)-C, the surface tungsten atoms undergo a reconstruction with some incorporation of oxygen beneath the top-most metal layer.^{12–15}

Cycloheptatriene adsorbed on W(100)-(2 \times 1)-O yielded the desorption spectrum shown in Figure 4. Low exposures of cycloheptatriene resulted in a small, broad desorption of 2 amu above 425 K and 91-amu desorption at \approx 325 K. Exposures greater than 6.0 L yielded cycloheptatriene at \approx 250 and \approx 180 K. The amount of gaseous H₂ did not increase with increasing cycloheptatriene exposure above 6.0 L.

Toluene and benzene exhibited desorption behavior analogous to that of cycloheptatriene on the -(2 \times 1)-O surface: molecular desorption below 350 K and a limited amount of dehydrogenation above 400 K¹⁶ which did not increase with increasing hydrocarbon exposure. Molecular toluene desorbed at \approx 180 and \approx 300 K subsequent to toluene adsorption and molecular benzene desorbed at 170 and 260 K subsequent to benzene adsorption. In both cases, the higher temperature desorption appeared initially as a function of hydrocarbon exposure, with the lower temperature parent desorptions appearing at higher exposure, attributable to multilayer sublimation.

Discussion

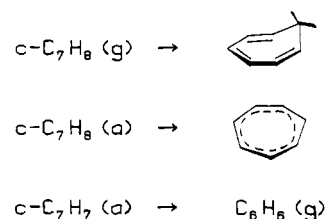
Irreversible C–H bond cleavage in adsorbed cycloheptatriene is predominant on clean W(100). C–H bond activation is suppressed on both the -(2 \times 1)-O and -(5 \times 1)-C surfaces. This is analogous to chemistry observed with other unsaturated hydrocarbons, where the predominant reactions are irreversible dehydrogenation on clean W(100) and reversible molecular adsorption on the carburized and oxidized surfaces.³

The most striking aspect of this cycloheptatriene chemistry is the benzene formation reaction observed on W(100)-(5 \times 1)-C. Directly analogous chemistry was previously observed on Ni(100).⁵

Clearly, suppression of extensive dehydrogenation is important in allowing for the C–C bond breaking and making reactions to be productive on tungsten-based surfaces. Extensive dehydrogenation on tungsten surfaces does not, in general, lead to hydrocarbon products but yields gaseous H₂ and strongly adsorbed carbon. Suppression of C–H bond activation in cycloheptatriene is not sufficient to generate gaseous benzene, as demonstrated by the inactivity of the -(2 \times 1)-O surface even though C–H bond scission is not predominant.

Isomerization of cycloheptatriene to toluene on the surface can be eliminated as a possibility on the basis of the lack of correspondence between desorption spectra obtained from toluene and cycloheptatriene. Thus, the observed chemistry is the result of surface reaction of cycloheptatriene.

The studies of the cycloheptatriene-7-*d*₁ reaction on W(100)-(5 \times 1)-C and the fact that the benzene desorption is reaction limited have allowed us to formulate a mechanism for this reaction, which is outlined below. This mechanism is the same as that previously proposed for the cycloheptatriene–Ni(100) reaction system.⁵ Initial adsorption of cycloheptatriene is proposed



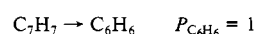
to occur via the π system of cycloheptatriene as shown in step 1. There is precedent for this type of coordination in organometallic complexes, such as cycloheptatriene–Cr(CO)₃.¹⁷ The coordination of the cycloheptatriene to the surface must be fairly robust given that no desorption occurs up to temperatures of \approx 400 K.¹⁸

Step 2 of the mechanism involves selective C–H bond scission at the 7 position. This step is predicated on the hydrogen desorption spectrum obtained from reaction of cycloheptatriene-7-*d*₁ on W(100)-(5 \times 1)-C. The desorption spectra (Figure 3) yielded gaseous HD only in the 500 K feature, whereas gaseous H₂ is produced at both 500 and 650 K. The 500 K molecular hydrogen feature is desorption limited, while the 650 K peak is reaction limited; thus, dehydrogenation at the 7 position occurs below 450 K. The proposed hydrocarbon intermediate is a cyclic C₇H₇ intermediate, where all carbons are equivalent. This is proposed on the basis of the ratio of C₆H₆ and C₆H₅D: the statistical isotopic ratio, assuming no H–D kinetic isotope effect, is 8:6 for C₆H₆:C₆H₅D.¹⁹ The large fraction of C₆H₅D produced requires randomization of the ring prior to benzene formation. This type of coordination also has precedent in the organometallic literature where dinuclear Fe and Ru complexes and mononuclear Rh exhibit analogous coordination to a cyclic C₇H₇ ring.^{20–23}

(17) See, for example: Stone, F. G. A. *Compr. Organomet. Chem.* **1982**, 3, 60.

(18) (a) The activation energy desorption may be crudely estimated by using several simplifying assumptions. For a first-order desorption, E_d for desorption occurring at 400 K is \approx 23 kcal/mol.^{18b} (b) King, D. A. *Surf. Sci.* **1975**, 47, 384.

(19) The ideal C₆H₆:C₆H₅D ratio is calculated by using the following scheme:



$$P_{\text{C}_6\text{H}_6} = (1/2)(1) + (1/2)(1/7) = 4/7$$

$$P_{\text{C}_6\text{H}_5\text{D}} = (1/2)(6/7) = 6/14$$

$$P_{\text{C}_6\text{H}_6}:P_{\text{C}_6\text{H}_5\text{D}} = 8:6$$

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(14) Prigge, S.; Niehus, H.; Bauer, E. *Surf. Sci.* **1978**, 75, 635.

(15) Alnot, P.; Behm, R. J.; Brundle, C. R., unpublished results.

(16) Carbon remained on the -(2 \times 1)-O surface subsequent to thermal desorption of benzene, toluene, and cycloheptatriene as detected by Auger electron spectroscopy.

The final step in benzene formation must involve excision of one of the carbons from the π -coordinated C_7H_7 ring. The labeling experiments described herein do not provide insight into this step. Analogous ring contraction has been observed for reaction of 7-exo-substituted cycloheptatriene-Cr(CO)₃ complexes.²⁴ However, a detailed mechanism for this reaction has not been proposed.

Spectroscopic studies are required to characterize the adsorption structure of cycloheptatriene and the proposed C_7H_7 intermediate. Near edge X-ray absorption fine structure measurements in the

C(1s) region are planned. These studies will determine the molecular orientation with respect to the surface.²⁵ Gross differences in adsorption structure may yield insight into the chemical differences observed on the three W(100)-based surfaces.

Acknowledgment. C.M.F. acknowledges support from an IBM faculty development award (1983-1985) and an NSF Presidential Young Investigator Award. K.A.P. thanks the American Vacuum Society for an AVS Scholarship, 1983-1984. We also thank Professor T. N. Rhodin and the Cornell Materials Research Laboratory for the W(100) crystal. This work was supported in part by PRF-ACS Grant No. 14577-G5, Cottrell Grant No. 9787, and the Harvard Materials Research Laboratory, NSF DMR-80-20247.

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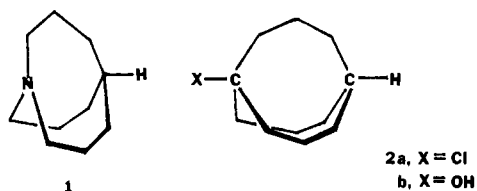
Photoelectron, Infrared, and Theoretical Study of 1-Aza-5-boratricyclo[3.3.3.0^{1,5}]undecane and Related Compounds

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 Received April 2, 1985

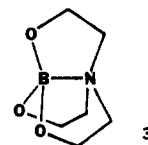
Abstract: 1-Aza-5-boratricyclo[3.3.3.0^{1,5}]undecane, **5**, has been studied by photoelectron spectroscopy and its association behavior studied by IR spectroscopy. The photoelectron results were interpreted with recourse to MNDO calculations on **5** and indicate a B-N bond similar electronically to that of Me₃N-BH₃. The previously reported photoelectron spectrum of 1-aza-4,6,11-trioxa-5-boratricyclo[3.3.3.0^{1,5}]undecane, **3**, has been reassigned based on MNDO calculations. The possibility that self-association of **5** in solution might involve extended p-orbital arrays has been ruled out based on IR spectra in a variety of solvents and in the gas phase. The B-N stretch is now believed to occur at 1039 cm⁻¹ rather than at 1271 cm⁻¹ as was earlier assigned. Despite reports that **5** did not form complexes, evidence for the existence of **5**·BBR₃ was obtained by NMR.

The bicyclo[3.3.3] skeleton is an inherently interesting ring system.¹ In manxine, **1**, various lines of evidence²⁻⁴ are indicative of planarity at nitrogen, an effect attributable to the idiosyncratic bicyclo[3.3.3]skeleton. The tertiary chloride **2a** undergoes sol-



volysis to the alcohol **2b** 10⁴ times faster than *tert*-butyl chloride under the same conditions,⁵ indicating that the planarity resulting from creation of a bridgehead carbonium ion is a welcome relief of angle strain present in the parent. A bridgehead-bridgehead attractive interaction allows both bridgeheads to pyramidalize

inward, as, for example, in boratran, **3**, where the X-ray structure⁶



reveals that the sum of angles around nitrogen and boron are 342.8° and 346.4°, respectively, and that these atoms are connected by a 1.693-Å bond. It is intriguing to visualize an intermediate situation in which the internal attractive interaction is weakened, resulting in bridgehead atoms sufficiently near planarity to take part in attractive intermolecular interactions. Such a possibility has been mentioned for **3**⁷ as well as **4**^{8,9} (eq 1). A report¹⁰ of the synthesis and properties of 1-aza-5-boratricyclo[3.3.3.0^{1,5}]undecane, **5**, included the observation that while **5** was monomeric in the gas phase, it was approximately hexameric in nonpolar solvents (Rast method), eq 2. Compound **5** thus

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