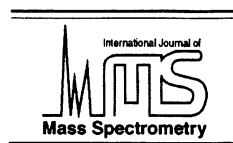




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C–H bond activation versus ring cleavage in the gas phase ion-molecule reactions of Nb^+ and Ta^+ with toluene and picoline

Steven W. Buckner^{a,*}, R. Marshall Pope^b^aDepartment of Chemistry and Geology, Columbus State University, Columbus, GA 31907, USA^bDepartment of Psychiatry, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599, USA

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Abstract

The reactions of Nb^+ and Ta^+ with toluene and picoline and their deuterium-labelled analogues were studied in a Fourier transform ion cyclotron resonance mass spectrometer. Methyl substitution completely changes the reactivities relative to benzene and pyridine. Both metals react to dehydrogenate toluene exclusively. In contrast to benzene, no ring cleavage is observed in the Ta^+ /toluene reaction. A simple explanation for this difference in reactivities is proposed based on the relative energies of the Hückel orbitals of benzene and toluene. The (b_1) symmetric antibonding orbital is higher in energy for toluene. Population of this orbital is necessary for formation of the metallanorbornadiene intermediate and does not occur at thermal energies. Reaction with ring labelled toluene- d_5 shows exclusive H_2 or D_2 elimination in reaction with Nb^+ and H_2 , HD, and D_2 elimination in reaction with Ta^+ . Reactions with the picolines show both dehydrogenation and ring cleavage. Isotope labelling studies show facile H/D scrambling occurs in the intermediate ion-molecule complexes with HCN and DCN both eliminated from the methyl- d_3 -2-picoline and 4-picoline. The metals react with picoline and pyridine by different mechanisms. The isotope labelling results suggest a metal-hydrido-azepinium structure for the intermediate complex. (Int J Mass Spectrom 182/183 (1999) 197–201) © 1999 Elsevier Science B.V.

Keywords: C–H bond activation; Ring cleavage; Gas phase ion-molecule reactions; Nb^+ and Ta^+ ; Toluene; Picoline

1. Introduction

Ben Freiser is remembered by many people for many reasons. Ben is remembered by his students for his kind-hearted attitude in personal issues, for his enjoyment in performing, analyzing, and discussing science, and for his always-timely humor in difficult situations. Ben will be remembered by the science community at large for his insights and contributions

to gas phase ion chemistry and mass spectrometry and, in particular, for his contributions which have furthered our understanding of fundamental inorganic chemistry. Ben will be missed.

The reactions of aromatic compounds with transition-metal-containing ions in the gas phase [1,2] has been a topic of long standing interest. A variety of interesting and unusual reaction pathways have been observed [3–23]. Dehydrohalogenation of halobenzenes and dehydration of phenol have been observed with many metals resulting in formation of metal-benzyne complexes [3–8,11,12]. These complexes can undergo further dehydrohalogenation with ligand

* Corresponding author.

Dedicated to the memory of Professor Ben Freiser.

coupling which produces metal-bound polyphenylene rings. Sc^+ and some second and third row metals and their complexes are found to directly dehydrogenate benzene to give metal-benzynes complexes. In contrast, the later first row metal-oxide cations are found primarily to hydroxylate benzene [14,15]. In an unusual reaction, we previously found Ta^+ to induce the retro-alkyne cyclotrimerization of benzene [16,17]. Further studies of gas phase cycloaddition reactions may be found in [18] and [19].

A few groups have recently studied the reactions of metal ions and metal-oxide ions with toluene. Bjarnason and Ridge observed the reactive early transition metal ions Sc^+ and Ti^+ to dehydrogenate toluene while ScO^+ , TiO^+ , V^+ , and VO^+ only form adducts with toluene [21]. Interesting selectivity is found for Sc^+ reacting with $\text{C}_6\text{H}_5\text{CD}_3$ to give 90% HD loss. Schwarz and co-workers [22,23] reported the reaction of FeO^+ with toluene produces primarily the benzylium ion with small amounts of oxidation and dehydrogenation. They also studied MoX_n^+ ($X = \text{O}, \text{S}$; $n = 2, 3$) and found a variety of reaction pathways including selective formation of the benzylium cation. In the current study we focus on the reactions of toluene and picoline with the highly reactive metals Nb^+ and Ta^+ . Previously, we found Ta^+ to induce ring cleavage in both benzene and pyridine, while Nb^+ cleaves the pyridine ring at thermal energies. The methyl substitution on the ring strongly modifies the reaction pathways for these metals in both cases.

2. Experimental

All experiments were performed at the University of Arizona on a Fourier transform ion cyclotron resonance mass spectrometer [24–27]. A one cubic inch trapping cell was used for the experiments. The excite plates have been replaced with tungsten screens (transmittance >80%) to allow light into the cell for photodissociation and laser desorption/ionization experiments. The magnetic field was supplied by a Varian electromagnet regulated at ~ 1.2 T. Atomic metal ion precursors were generated by desorption/ionization from pure metal samples (V, Nb, Ta;

Goodfellow, Inc.) using 1064 or 532 nm radiation from a Spectra-Physics DCR-11 pulsed Nd:YAG laser [28]. The laser and mass spectrometer are interfaced using a previously described method [29].

High purity toluene was obtained from Aldrich, dried over molecular sieves, and placed through freeze-pump-thaw cycles to remove noncondensable gases. Methyl- d_3 4-picoline was purchased from Aldrich chemical. Methyl- d_3 2-picoline was synthesized from 2-methylpyridylacetate by a method adapted from Williams [30]. A modification of the procedure was required due to an omission in the original citation. Deuterium exchange of the two α -hydrogens is effected by 6 h reflux in $\text{Na}_2\text{CO}_3/\text{D}_2\text{O}$ solution. The solution remains an amber color for the first 3 h. At this point, an orange brine begins to appear. It is extremely useful to follow the reaction using TLC. An appropriate eluting solvent consists of 5% acetic acid, 1% NaCl, isopropyl alcohol, and ethyl acetate. The methyl group is cleaved from the ester at the end of the reflux period by addition of a strong NaOD liqueur. The pH is adjusted to ≈ 5 with DCl. (Note: $\text{C}_5\text{H}_4\text{NCH}_2\text{CO}_2^- \text{Na}^+$ irreversibly forms insoluble salts with sulfates and phosphates.) Gentle reflux drives off CO_2 . Diethyl ether is used to extract the product from basic solution. Purity was determined using GC/MS and ^{13}C NMR. Only α - d_3 picoline was detected.

3. Results and discussion

We have previously observed some early transition metal ions and their oxides to induce ring cleavage in reactions with benzene, pyridine, quinoline, and isoquinoline at thermal energies. The reaction with benzene is modelled by a mechanism involving formation of a metallanorbornadiene [structure (a) in Fig. 1] which decomposes by loss of acetylene [16]. Results for the pyridine and quinoline reactions are found to best fit a mechanism with an intermediate analogous to the metallacycloheptatriene [structure (b)] in Fig. 1 [17].

Table 1 shows the results for the reactions of Ta^+ and Nb^+ with isotopically labelled toluene (toluene-

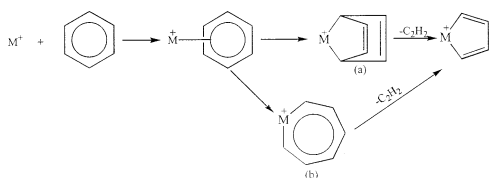


Fig. 1. Scheme for the reaction of a metal ion ($M^+ = \text{Nb}^+$ or Ta^+) with benzene. The two pathways resulting in ring cleavage may include a metallanorbornadiene ion (structure a) or a metallacycloheptatriene ion (structure b) intermediate.

d_5 , ring labelled). The only product observed is dehydrogenation. This contrasts with the heteroaromatic systems discussed below where methyl substitution does not block the ring-cleavage process. Higeshide et al. previously reported a molecular beam study of the reaction of Nb^+ with benzene and toluene [13]. They reported an enhanced rate of reaction for toluene relative to benzene (essentially the same result as that found for Cu^+ and V^+). They reported dehydrogenation for benzene but did not report on the product distribution for the toluene reaction. We clearly observe exclusive dehydrogenation for Nb^+ with toluene. Linear pseudo-first-order reaction kinetics were observed for the Nb^+ /toluene in our FT-ICR suggesting there is no contribution from translationally or electronically excited Nb^+ to the dehydrogenation process.

A simple explanation for the absence of ring cleavage in the Ta^+ /toluene reaction may be found by considering the effect of methylation on the intermediate metallanorbornadiene ion. Fig. 2 shows a simple description of the Hückel orbitals of benzene and the perturbation introduced by methyl substitution. In the Hückel description of benzene, the two highest bonding pi states are degenerate and the two lowest

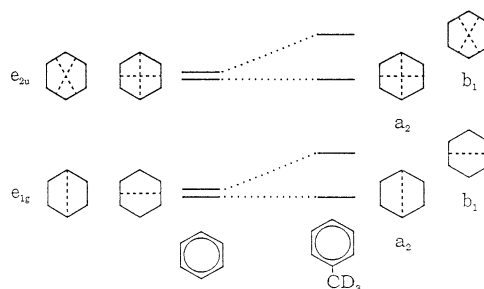


Fig. 2. Description of the Hückel orbitals of benzene and the perturbation introduced by methyl substitution.

antibonding pi states are degenerate. The electron-donating methyl group lifts this degeneracy. Molecular orbitals without a node at the substituted position on the ring are destabilized. The symmetric bonding orbital (b_1) becomes the HOMO and the antisymmetric antibonding orbital (a_2) becomes the LUMO.

In order to form the metallanorbornadiene intermediate which is proposed for the Ta^+ /benzene reaction [structure (a) in Fig. (1)], population of the symmetric *antibonding* orbital (b_1) with two electrons from the metal is required [31]. The symmetry of the antisymmetric a_2 LUMO is inconsistent with the localized double bonds of the metallanorbornadiene. The methyl substitution in toluene increases the energy of the b_1 symmetric antibonding orbital and makes it inaccessible to population by an electron pair from the incoming metal ion. The lower energy a_2 LUMO does not have the correct symmetry. Thus, the ring cleavage pathway is shut off.

Also of note in the results shown in Table 1 is the absence of HD loss in the reaction of Nb^+ with ring-labelled toluene. Recent work by Bjarnason and Ridge reveals dehydrogenation of toluene by Sc^+ and Ti^+ [21]. Isotope labelling studies show a mixture of H_2 , D_2 , and HD loss in both cases, though for Sc^+ HD elimination dominates. The reactions of FeO^+ with toluene were reported by Schröder et al. to give a small amount of dehydrogenation [14]. And again, isotope labelling shows the presence of an HD loss.

Observation of H_2 loss and absence of isotope scrambling in the Nb^+ reaction shows that both a 1,1-dehydrogenation to produce a metal-carbene [structure (c), Fig. 3] and a 1,2 ring dehydrogenation

Table 1

Product distributions for the reactions of Nb^+ and Ta^+ with isotopically labelled toluene ($\text{C}_6\text{D}_5\text{CH}_3$) (uncertainties in branching ratios are $\pm 10\%$)

Products	Nb^+	Ta^+
$\text{MC}_7\text{H}_3\text{D}_3^+ + \text{D}_2$	20	45
$\text{MC}_7\text{H}_2\text{D}_4^+ + \text{HD}$		15
$\text{MC}_7\text{HD}_5^+ + \text{H}_2$	80	40

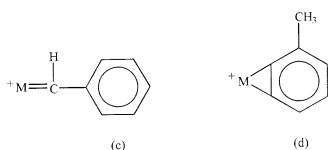


Fig. 3. Structures for the ion products in the reaction of Nb⁺ with toluene, (c) metal-carbene, (d) metal-benzyne.

to produce a metal-benzyne [structure (d), Fig. 3] are occurring. Activation of the methyl C–H bonds is greatly favored over the arene C–H bonds. This is likely due to the much lower C–H bond energy for the methyl group (372 kJ/mol for a methyl C–H bond in toluene versus 464 kJ/mol for a C–H bond in benzene [32]). Nb⁺ does not dehydrogenate CH₄ at thermal energies [2]. The observed thermal 1,1-dehydrogenation for toluene may be facilitated by the stability of the product carbene where the phenyl ring may interact with the highly unsaturated niobium center.

Table 2 shows product distributions for the reactions of Nb⁺ and Ta⁺ with 2-picoline. In this case, the presence of the methyl group does not significantly affect the ring cleavage process. For Ta⁺ only ring cleavage occurs whereas for Nb⁺ there is a very small amount of simple H₂ loss. For both metals, loss of HCN is most often coupled with loss of H₂. After HCN loss, a metallacyclopentadiene ion structure is presumably generated with a d² metal center. The complex then undergoes intramolecular C–H insertion and subsequent H₂ loss. For Ta⁺, this process occurs with 100% efficiency as seen by the absence of simple

Table 2

Product distributions for the reactions of Nb⁺ and Ta⁺ with 2-picoline. Previous results for pyridine and quinoline [17] are shown for comparison (uncertainties in branching ratios are ±10%).

Reactants	Neutral losses (shown as %)			
	H ₂	HCN	HCN + H ₂	CH ₃ CN
Nb ⁺ /picoline	4	11	74	11
Ta ⁺ /picoline			60	40
Nb ⁺ /pyridine	10	90		
Ta ⁺ /pyridine	15	85		
Nb ⁺ /quinoline	53	47		
Ta ⁺ /quinoline	10	90		

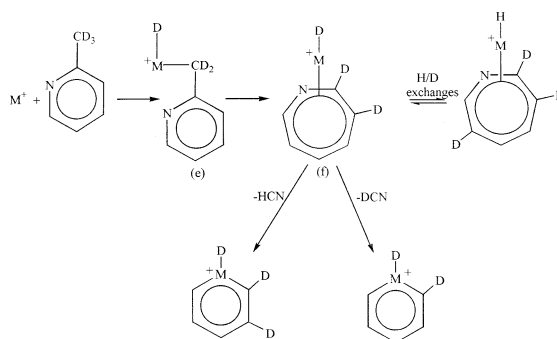


Fig. 4. Scheme for the reaction of 4-picoline with Ta⁺ or Nb⁺ (metal designated as M⁺).

HCN loss. As expected, for 2-picoline, methyl substitution results in competitive loss of CH₃CN.

Ring cleavage for the N-containing aromatic systems is expected. Previously we found that pyridine and the quinolines react through a metallacycloheptatriene intermediate [structure (b) in Fig. 1] [17]. The energy of this intermediate is not substantially affected by methyl substitution. Hence ring cleavage still remains. Labelling studies, however, reveal an interesting twist in this reaction. Reaction with methyl-d₃ labelled 2-picoline reveals isotope scrambling. A mixture of (3H + C + N), (2H + D + C + N), and (2D + H + C + N) loss is observed. For the methyl-d₃ labelled 4-picoline reaction with Nb⁺, both HCN and DCN loss are found. For the HCN + H₂ loss channel, a simple metallacycloheptatriene intermediate which decomposes by loss of HCN should give only D₂ loss. For the labelled 4-picoline, only HCN loss is expected with Nb⁺.

A mechanism which accounts for this scrambling may be found in analogy to the interconversion of the radical cations of tropylium and toluene upon electron impact [23,33]. This mechanism involves metal-ion mediated conversion of picoline to azepine. Fig. 4 presents a scheme for the reaction. After initial methyl C–D insertion, the ligand rearranges from a picolynyl [structure (e)] to an azepine structure [structure (f)]. This intermediate allows for rapid 1,2-sigmatropic shifts and H/D exchange on the ring prior to loss of HCN from the ring. DCN loss is explained by migration of the D atom to the α-position on the ring.

4. Conclusion

The reactions of aromatic rings with Nb⁺ and Ta⁺ are significantly altered by methyl substitution on the aromatic ring. In contrast to its reaction with benzene, Ta⁺ only reacts with toluene by dehydrogenation. The presence of the methyl substituent increases the energy of the lowest lying symmetric antibonding orbital. Population of this orbital is necessary for formation of the metallanorbornadiene intermediate on the pathway to ring cleavage. Nb⁺ shows competitive formation of metal-carbene and metal-benzyne ion complexes with toluene. Ring cleavage in the reaction of Nb⁺ and Ta⁺ with picoline is not significantly attenuated relative to pyridine. However, deuterium labelling experiments suggest the mechanism differs in the pyridine and picoline reactions. An intermediate metal-azepinium structure is proposed to exist on the reaction pathway leading to loss of HCN.

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