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Fourier Transform Ion Cyclotron Resonance Studies of Gas-Phase Reactions between Tungsten Ions and Hydrocarbons

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Summary: FT/ICR spectrometry has been used for gas-phase studies of the interaction between singly-charged positive tungsten ions and hydrocarbons (alkanes C_2–C_9, alkenes C_2–C_6, and cycloalkanes C_3–C_6). It is shown that this interaction results mainly in dehydrogenation products. The number of H_2 molecules eliminated depends upon the size and type of hydrocarbon and varies from 1 to 6. Significant amounts of C–C cleavage products have been found in the cases of cyclopropane and 2-methylpropene only.

Oxidative addition of a metal ion or its complex across C–H or C–C bonds is known to be an important step in hydrocarbon activation with metal complexes.[1] Analysis of the products formed from a hydrocarbon in the reaction with a particular metal complex or ion allows conclusions about the type of activation, C–H or C–C, that prevails.

Powerful methods for studying reactions of nonsolvated metal ions and complexes in the gas phase are mass spectrometry (MS) and ion cyclotron resonance spectrometry (ICRS).[2-4] Such studies can be important for catalysis, as metal ions or their complexes in the gas phase to a certain extent are models for the active centers of real catalysts.

In this work reactions between singly-charged positive tunsten ions W^+ and a series of hydrocarbons (alkanes C_2–C_9, alkenes C_2–C_6, and cycloalkanes C_3–C_6) have been studied.

Table 1. Composition of Products Formed in Reactions of W^+ with Hydrocarbons[a]

hydrocarbon	neutral loss	%	products
	Alkanes		
CH_4	no reacn[b]		
C_2H_6	H_2	80	$W(C_2H_4)^+$
	$2H_2$	20	$W(C_2H_2)^+$
C_3H_8	H_2	45	$W(C_3H_6)^+$
	$2H_2$	55	$W(C_3H_4)^+$
C_4H_{10}	H_2	60	$W(C_4H_8)^+$
	$2H_2$	40	$W(C_4H_6)^+$
C_5H_{12}	$2H_2$	37	$W(C_5H_8)^+$
	$3H_2$	63	$W(C_5H_6)^+$
C_6H_{14}	$3H_2$	40	$W(C_6H_8)^+$
	$4H_2$	60	$W(C_6H_6)^+$
C_7H_{16}	$4H_2$	100	$W(C_7H_8)^+$
C_8H_{18}	$4H_2$	50	$W(C_8H_{10})^+$
	$5H_2$	50	$W(C_8H_8)^+$
$CH_3CH(CH_3)(CH_2)_4CH_3$	$4H_2$	100	$W(C_8H_{10})^+$
C_9H_{20}[c]	$3H_2$		$W(C_9H_{14})^+$
	$4H_2$		$W(C_9H_{12})^+$
	$5H_2$		$W(C_9H_{10})^+$
	$6H_2$		$W(C_9H_8)^+$
	Cycloalkanes		
c-C_3H_6	H_2	41	$W(C_3H_4)^+$
	$2H_2$	27	$W(C_3H_2)^+$
	CH_4	12	$W(C_2H_2)^+$
	C_2H_4	20	$W(CH_2)^+$
c-$C_5H_9CH_3$	$3H_2$	100	$W(C_6H_6)^+$
c-C_6H_{12}	$3H_2$	100	$W(C_6H_6)^+$
	Alkenes		
C_2H_4	H_2	100	$W(C_2H_2)^+$
C_3H_6	H_2	55	$W(C_3H_4)^+$
	$2H_2$	45	$W(C_3H_2)^+$
1-C_4H_8	H_2	58	$W(C_4H_6)^+$
	$2H_2$	42	$W(C_4H_4)^+$
2-C_4H_8	H_2	75	$W(C_4H_6)^+$
	$2H_2$	25	$W(C_4H_4)^+$
i-C_4H_8	H_2	27	$W(C_4H_6)^+$
	$2H_2$	14	$W(C_4H_4)^+$
	CH_4,H_2	36	$W(C_3H_2)^+$
	C_3H_6	23	$W(CH_2)^+$
C_6H_{12}	$2H_2$	30	$W(C_6H_8)^+$
	$3H_2$	70	$W(C_6H_6)^+$

[a] Relative concentrations of various organometallic species were measured by taking into account the presence of all four major tungsten isotopes. The accuracy of measurements was ca. ±10%. [b] A small (no more than 5% of the initial concentration of W^+ ions) concentration of WCH_2^+ ions was observed. Perhaps, WCH_2^+ ions were formed in the reaction with the electronic excited W^+ ions that may be present in small amounts (see the text). [c] For C_9H_{20} the distribution of reaction products was not determined.

A Bruker CMS-47 Fourier transform ICR spectrometer[5] has been used in all experiments. The magnetic field was 4.7 T, and resolution (50%) was ca. 2×10^5. The capacity of the ion pump for the vacuum system was 160 L/s. The background pressure was 3×10^{-9} mbar. Ions were formed in the ICR cell by electron impact (70 eV) on tungsten hexacarbonyl vapors. The standard pulse sequence (quench/ionization/variable delay/RF pulse) described in the literature[5] was used to obtain ICR spectra. All reactions were studied at room temperature. A typical partial pressure of $W(CO)_6$ was 5×10^{-8} mbar, and that of hydrocarbons, $(1–2) \times 10^{-7}$ mbar. A Bayard–Alpert's ionization gauge was used to monitor pressure. All chemicals used were high-purity commercial samples ("Reakhim"). Prior to use, all hydrocarbons were treated with multiple freeze–pump–thaw cycles. Tungsten carbonyl with natural abundances of tungsten isotopes was used. Ions were monitored for periods of 0.1–10 s, which allowed observation of both primary and subsequent secondary reactions. With all hydrocarbons, the reactions were observed simultaneously for all four major tungsten

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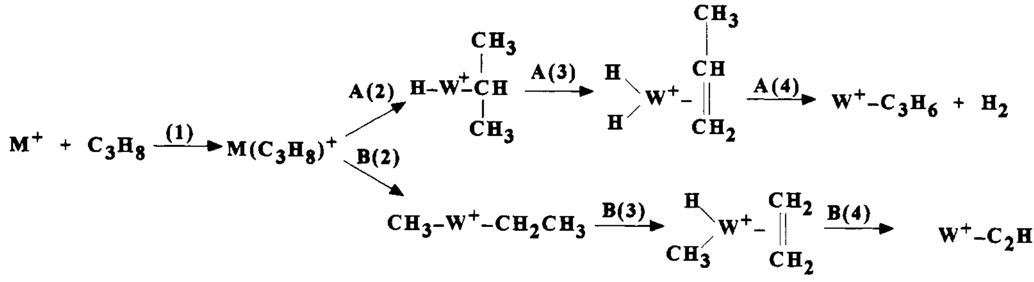
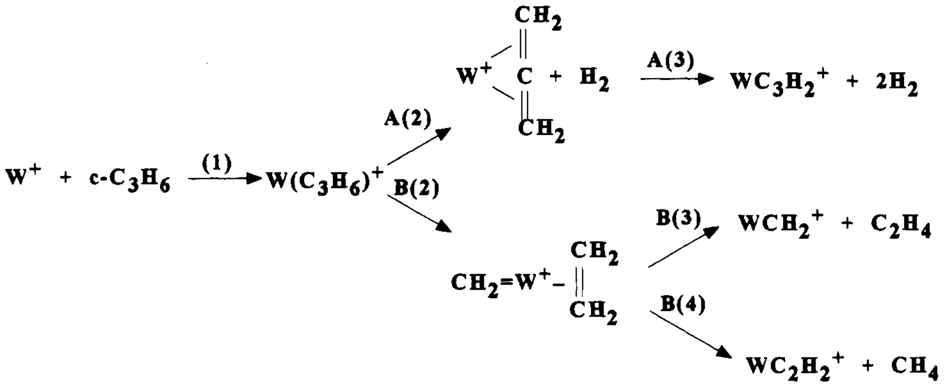
Scheme 1. Classical Pathways for the Reaction between M^+ Ions and C_3H_8: C–H (pathway A) or C–C (Pathway B) Insertion/Shift of β-H atom/H_2 (Pathway A) or Alkane (Pathway B) Elimination



Scheme 2. A Pathway for the Reaction between W^+ and c-C_3H_6



isotopes, i.e. $^{182}W^+$ (abundance 26.3%), $^{183}W^+$ (14.3%), $^{184}W^+$ (30.7%), and $^{186}W^+$ (28.6%).

It is known that ionization by electron impact can produce ions in electronically excited states. Electronic state-specific metal ion chemistry has been extensively studied; however, no quantitative studies have yet been performed on the state-specific chemistry of the second- and third-row transition metal ions.[6] In our work, the absence of the electron excited states of W^+ ions was probed with the method suggested in ref 7, i.e. by checking whether the decay of W^+ ions due to their reaction with tungsten carbonyl molecules was exponential. According to such tests, the excited ions constituted less than 5% of W^+ ions.

Reactions of hydrocarbons with singly-charged ions of other VIA group metals have been studied earlier.[8,9] An extreme unreactivity of the ground state Cr^+ has been reported.[8] The Mo^+ ion proved to be more reactive,[9] though cross sections of its reactions with alkanes, ethylene, and cyclohexane were rather small. Reactions of molybdenum ions with other cycloalkanes and alkenes have large cross sections. Dehydrogenation without carbon skeleton destruction is found to be the main pathway of Mo^+ reactions with hydrocarbons. As will be shown in the present paper, the same tendency is observed for W^+ as well. Reaction of W^+ ions produced by laser ablation of metal targets with methane was studied in ref 10.

The products of W^+ reactions with hydrocarbons are summarized in Table 1. It can be seen from the table that unless some hindrances to dehydrogenation exist, primary and subsequent deeper dehydrogenations (i.e. cleavage of C–H bonds) comprise the only reaction pathway. Measurable amounts of C–C cleavage products were found for cyclopropane and 2-methylpropene only. While for cyclopropane, the notable skeleton destruction may be due to the large C_3 ring strain energy (27.6 kcal/mol);[11] in the case of 2-methylpropene, the difficulty of the rearrangement needed for dehydrogenation must be the main reason for the relatively large yield of the C–C cleavage products.

No clear tendencies in alteration of product ratios for different alkanes can be seen. The same can be said about alkenes. Indeed, the overall alteration of dehydrogenation products ratios along the row of alkanes allows two different treatments: (i) This ratio keeps constant along the row, while C_2H_6, C_4H_{10}, and C_7H_{16} are exceptions. (ii) This ratio decreases along the row, while C_3H_8, C_7H_{16}, and C_8H_{18} are exceptions. It is also not clear why the ratio alters from 1-butene to 2-butene. Note that the depth of dehydrogenation within a family of hydrocarbons with the same number of carbon atoms (e.g. C_3H_8, C_3H_6, c-C_3H_6, or C_6H_{14}, C_6H_{12}, c-C_6H_{12}) may be controlled by four factors, namely: (i) the free energy of formation for the hydrocarbon, i.e. the chemical energy stored in it; (ii) the free energy of formation for the organometallic products formed upon dehydrogenation; (iii) the probability of energy loss in the form of vibrational excitation of the abstracted H_2 molecules; (iv) the probability of dehydrocyclization that depends on internal rotations inside the organometallic intermediates. This factor may become important for higher hydrocarbons (C_5 and larger).

For most of the hydrocarbons studied in this work, no evidence for pathways other than the classical ones (C–H or C–C insertion/shift of β-H atom/H_2 or alkane elimination;[2] Scheme 1) can be seen from the data of Table 1. However, for c-C_3H_6 and i-C_4H_8, reaction product distributions suggest that certain deviations from these classical

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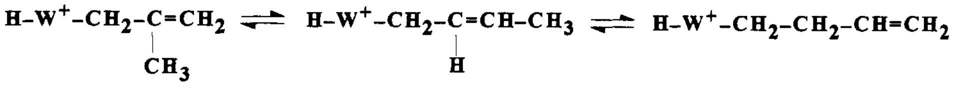
Scheme 3. Rearrangements of 2-Methylpentene in the Dehydrogenation Process



$$H\text{-}W^{+}\text{-}CH_2\text{-}\underset{CH_3}{\underset{|}{C}}{=}CH_2 \rightleftharpoons H\text{-}W^{+}\text{-}CH_2\text{-}\underset{H}{\underset{|}{C}}{=}CH\text{-}CH_3 \rightleftharpoons H\text{-}W^{+}\text{-}CH_2\text{-}CH_2\text{-}CH{=}CH_2$$

mechanisms are observed. In particular, for c-C_3H_6 and i-C_4H_8 the structure of such products as $W(C_4H_4)^+$, $W(C_3H_4)^+$, and $W(C_3H_2)^+$ is not clear. In ref 8, an allene structure has been suggested for the C_3H_4 fragment in organometallic reaction intermediates and products. This is indeed very probable for propane and propene, but for cyclopropane the formation of $W(CH_2)^+$ and $W(C_2H_2)^+$ as products can be more easily explained by formation of a carbene–ethylene intermediate rather than an allene intermediate. A similar carbene intermediate has been proposed earlier for reactions of iron and cobalt ions with cycloalkanes.[2] Both pathways for c-C_3H_6 transformation, i.e. via the allene C_3H_4 ligand and carbene plus ethylene ligands, are shown in Scheme 2.

The hydrocarbon 2-methylpropene has no H–C–C–H fragments. Therefore, the usual dehydrogenation involving a β-H shift is impossible for 2-methylpropene. A rearrangement is needed to result in $W(C_4H_6)^+$ and $W(C_4H_4)^+$ (neutral losses of H_2 and 2 H_2). The mechanism of skeletal rearrangement of 2-methylpropene through the formation of trimethylenemethane and methylcyclobutane complexes was discussed in ref 12. An alternative to this rearrangement may be the CH_3-group migration to the terminal carbon atom as shown in Scheme 3.

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