Activation of Hydrocarbons by W^+ in the Gas Phase

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The gas-phase reactivity of W^+ with hydrocarbons containing up to six carbon atoms has been studied by Fourier-transform ion cyclotron resonance mass spectrometry. W^+ is found to be one of the most reactive bare metal cations studied to date with *all* hydrocarbons except acetylene being activated at thermal energies. The observed reactivity is dominated by dehydrogenation, which is often multiple. Thus, reaction with propene leads to loss of two dihydrogen molecules (yielding $WC_3H_2^+$) and reaction with *n*-hexane leads to loss of 4 H_2 (yielding $WC_6H_6^+$). In *all* cases, the product ions are themselves reactive with the same neutral species, leading to reaction sequences of various lengths. Isotope labeling, collision-induced dissociation, and ligand exchange experiments have been extensively carried out in order to try to establish the structure of some of the intermediate and final product ions. It turned out that deriving structures from such experiments is much more difficult than for first-row transition metal ions. This is due to the higher reactivity and metal−ligand binding energies of tungsten.

I. Introduction

The gas-phase reactions of bare transition metal cations with small molecules have been actively studied in the last 20 years.[1] A major motivation for these studies is the ability of these highly unsaturated species to activate otherwise inert molecules such as alkanes. Extensive work on first-row metal cations has revealed a great variety of reactions, often with a high selectivity toward dehydrogenation, loss of small alkanes, alkenes, and so on. The reactivity of second- and third-row metals has been much less thoroughly investigated to date, even though recent studies have established that the most reactive metals are from the third row. Early work on Ta^+ [2] and Os^+ [3] showed that these cations are able to react with methane to form metal−methylidene complexes, a reaction which does not occur with any of the first- and second-row metals. A systematic study of the reactions of the third-row metals with methane[4] showed that, in fact, Hf^+, Ta^+, W^+, Os^+, Ir^+, and Pt^+ are all able to form MCH_2^+ complexes exothermically and with no activation barrier in excess of the energy of the reactants. Yet the reactivity of these metals with other hydrocarbons and other small molecules remain largely unexplored. Recent studies on W^+ [5−7] have begun to unravel a complex pattern of reactivity. In this paper, we describe the results of our experiments on the reactivity of W^+ with small hydrocarbons, using Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometry. This metal appears to be extremely reactive, and this reactivity is largely dominated by dehydrogenation, leading to the elimination of several H_2 molecules in many cases. Another prominent aspect is the ability of the product ions to react further with the same neutral molecule, leading to reaction chains. One of the major endeavors of our work has been to obtain a detailed description of these sequences of activation. Understanding the energetic and mechanistic details of each step remains a formidable challenge. As a step toward this goal, efforts were focused on the determination of the structure of the successive product ions.

II. Experimental Section

All reactions were studied using a Bruker Spectrospin CMS-47X Fourier-transform ion cyclotron resonance spectrometer described elsewhere.[8] Neutral reactants were generally introduced in the reaction cell through a leak valve (Balzers) and maintained at a constant pressure of 2×10^{-8} mbar except where otherwise specified. In order to carry out ligand displacement experiments, neutrals were also introduced through a pulsed valve. $W(CO)_x^+$ ions were produced by electron impact (50−70 eV) on $W(CO)_6$ in the external ion source. This produces a distribution of $W(CO)_x^+$ ions as described previously.[5e]

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$^{186}W^+$ was isolated in the ICR cell using standard radiofrequency (rf) ejection techniques. This is done first by selecting all W$^+$ ions. In order to identify the products of dehydrogenation reactions, it is desirable to work with a unique isotope of tungsten. The ^{186}W isotope was chosen since it is separated from its nearest congener by two mass units. Further on-resonance rf ejection pulses ($V_{pp} = 18V$) are then applied in order to select $^{186}W^+$ ions. Previous work has shown that ions produced this way have a significant amount of kinetic and electronic energy. In order to approach thermal conditions for ground state ions as much as possible, all reactions were studied in the presence of an argon bath, with a constant pressure of 10^{-6} mbar. Before any ion−neutral reaction was studied, a delay of at least 1 s was imposed on the selected $^{186}W^+$ ions, corresponding to an average of 50 thermalizing collisions. It has been previously shown for W$^+$ that such conditions ensure a distribution of ions close or equal to thermal and, in particular, that no detectable amounts of excited electronic states are present.[5e] This is facilitated for third-row metals such as W by large spin−orbit coupling constants which relax the forbiddenness of many electronic transitions. In cases where further relaxation seemed warranted, e.g. when there are small amounts of a product corresponding to a more energy-demanding reaction than the main peak, longer relaxation delays were used (2s or more) in order to establish whether the reaction is truly spontaneous. At the end of this delay, a final series of ejection pulses is applied until the desired ion is completely isolated. In particular, products of ion−hydrocarbon reactions taking place during the relaxation delay must be ejected since they reflect the behavior of excited ions. There are a few cases where such products are of masses close (a few Da away) to that of the ion to be studied. In such cases, both were isolated together in order to avoid off-resonance re-excitation of the thermalized ions. Variable reaction times, typically in the 1−20 s range, are then used to study the reactivity of the selected ions. Reaction sequences were further elucidated by examining changes in product ions distributions while continuously ejecting potential precursors.

The composition of all product ions was checked by recording high-resolution spectra. In this case the total pressure was lowered to ca. 10^{-7} mbar. Initial ion selection and the qualitative features of the reaction were verified not to be significantly altered by these conditions of less extensive relaxation.

In most cases, collision-induced dissociation (CID) or sustained off-resonance irradiation (SORI) spectra[9] were recorded in order to try to obtain structural information on the product ions. For CID experiments, the ions are kinetically excited by a rf pulse (with a center of mass (c.m.) energy in the 5−50 eV range) and allowed to collide with argon under quasi single collision conditions (Ar pressure 10^{-6} mbar, collision time 10 or 20 ms). For SORI experiments, ions are translationally excited using off-resonance excitation to maximum kinetic energies of up to 30 eV in the c.m. frame, for times of 1 or 2 s at Ar pressures of 5 10^{-7} mbar. All excitation energies specified in the text are given in the c.m. frame.

$W(CO)_6$ and all hydrocarbons were obtained commercially and used without further purification.

III. Results and Discussion

Results for the reactions of W$^+$ have been grouped by hydrocarbon size, i.e. number of carbon atoms. Since the reactivity is dominated by dehydrogenation, this makes it easier to follow the common features found with species of the same carbon number. All *primary* reactions are summarized in Table 1.

Table 1. Primary Ion Products Observed in the Reactions of W$^+$ with Hydrocarbons

neutral reactant	obsd reacns	comments
CH_4	$WCH_2^+ + H_2$	
C_2H_2	no reacn	
C_2H_4	$WC_2H_2^+ + H_2$	
C_2H_6	$WC_2H_4^+ + H_2$	
	$WC_2H_2^+ + 2H_2$	
C_3H_4	$WC_3H_2^+ + H_2$	both allene and propyne
C_3H_6	$WC_3H_2^+ + 2H_2$	
c-C_3H_6	$WC_3H_2^+ + 2H_2$	major
	$WC_2H_2^+ + CH_4$	minor
C_3H_8	$WC_3H_4^+ + 2H_2$	major
	$WC_2H_2^+ + CH_4 + H_2$	minor
C_4H_6	$WC_4H_4^+ + H_2$	major
	$WC_2H_2^+ + C_2H_4$	minor
	$WC_3H_2^+ + CH_4$	minor
C_4H_8	$WC_4H_4^+ + 2H_2$	major
	$WC_3H_2^+ + CH_4 + H_2$	minor
i-C_4H_8	$WC_3H_2^+ + CH_4 + H_2$	major
	$WC_4H_4^+ + 2H_2$	minor
n-C_4H_{10}	$WC_4H_6^+ + 2H_2$	
	$WC_4H_4^+ + 3H_2$	
	$WC_3H_4^+ + CH_4 + H_2$	*a*
	$WC_3H_2^+ + CH_4 + 2H_2$	*a*
i-C_4H_{10}	$WC_4H_6^+ + 2H_2$	major
	$WC_3H_2^+ + CH_4 + 2H_2$	minor
	$WC_3H_4^+ + CH_4 + H_2$	minor
1-C_5H_{10}	$WC_5H_6^+ + 2H_2$	
	$WC_5H_4^+ + 3H_2$	
	$WC_4H_4^+ + CH_4 + H_2$	
	$WC_3H_4^+ + [C_2, H_6]$	minor
2-methyl-1-butene	$WC_5H_6^+ + 2H_2$	
	$WC_5H_4^+ + 3H_2$	
	$WC_4H_4^+ + CH_4 + H_2$	
n-C_5H_{12}	$WC_5H_6^+ + 3H_2$	major
	$WC_4H_4^+ + CH_4 + 2H_2$	minor
C_6H_6	$WC_6H_4^+ + H_2$	
c-C_6H_{12}	$WC_6H_6^+ + 3H_2$	
n-C_6H_{14}	$WC_6H_8^+ + 3H_2$	major
	$WC_6H_6^+ + 4H_2$	
	$WC_5H_6^+ + CH_4 + 2H_2$	minor

[a] Minor channel, sensitive to initial thermalization of W$^+$, so that formation of this ion may be due to excited W$^+$.

A. C_2 Hydrocarbons. No reaction was observed with acetylene. In contrast, chains of activation were observed with both ethylene and ethane.

Ethylene. As described previously,[5a,6,7] W$^+$ reacts with ethylene via dehydrogenation, forming $WC_2H_2^+$ as the sole product. Experiments with C_2D_4 yield virtually identical results indicating that, unlike the situation found for CH_4, there is no deuterium isotope effect. The subsequent reactions observed are similarly dehydrogenations, as summarized by eq 1. The sequence stops

$$WC_{2n}H_{2n}^{\ +} + C_2H_4 \rightarrow WC_{2n+2}H_{2n+2}^{\ +} + H_2 \quad (n = 0-4) \quad (1)$$

after the fifth reaction forming $WC_{10}H_{10}^+$, such that even under conditions of extremely long time, no further reaction products are evident. This is in direct contrast to the results reported by Berg et al.,[7] who found that this sequence continued up to nine steps. However in that case, no attempt had been made to avoid any excess kinetic energy resulting from transfer of the ions from the external ion source. This may then have resulted in either different isomers being formed in the various reaction steps, or left successive product ions with sufficient internal energy to allow the reported sequence to proceed. In either case it is clear from the present

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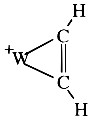
results that when W^+ is well thermalized there is no reaction beyond the fifth step.

Two low-energy structures can be readily imagined for the initial $WC_2H_2^+$ reaction product, a metallacyclopropene complex **1** and a metal—vinylidene structure **2**. The plausibility of these two structures is supported by the frequent observation of metal—vinylidene complexes in the liquid phase, including tungsten complexes.[10] In addition, *ab initio* calculations show that both of these types of bonding are comparable in energy for $F_4WC_2H_2$.[11]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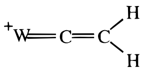
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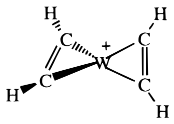
The energetic requirement for the dehydrogenation of ethylene to acetylene (42 kcal mol^{-1}) is easily accommodated by the minimum W^+—C_2H_2 interaction energy of 75 kcal mol^{-1} derived from the experiments with C_2H_6 (see below). Alternatively a vinylidene complex requires a metal—carbon bond energy of at least 86 kcal mol^{-1}.[12] This is also reasonable given the strength of the metal—carbon bond of at least 111 kcal mol^{-1} in WCH_2^+.[13]

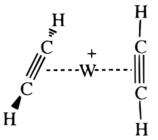
There appears to be only one case in the literature for which the question has received an answer. Reaction of Sc^+ with CH_2CD_2 yields ScC_2HD^+ exclusively, indicating a 1,2 dehydrogenation.[14] Ab initio calculations subsequently showed the vinylidene complex to be significantly higher in energy than the acetylene complex.[15] This experiment was not carried out with W^+ since the use of similar labelings for other hydrocarbons (see below) shows that partial or total H/D randomization occurs, precluding firm structural assignment for the product ion.

Several experiments were attempted to distinguish between these two possibilities for $WC_2H_2^+$. The CID spectrum of $WC_2H_2^+$ shows loss of C_2H_2 exclusively. Although such a result is consistent with a metal—acetylene structure, it does not eliminate the metal—vinylidene possibility since collisional activation could simultaneously induce isomerization of vinylidene to acetylene. Ligand exchange experiments were carried out with benzene-d_6; however, no substitution was observed. The main product ion formed results from dehydrogenation with a dominant loss of HD and minor losses of H_2 and D_2, which deviates from statistical losses. There is also a much less abundant association of C_6D_6 without activation, whereby $WC_8D_6H_2^+$ is formed. In an attempt to generate a metal—acetylene complex, $WC_2H_2^+$ was obtained through ligand exchange in the reaction of WCO^+ with acetylene. The behavior of this $WC_2H_2^+$ ion under pulses of C_6D_6 turned out to be the same as that of the $WC_2H_2^+$ ion generated from the reaction of W^+ with ethylene.

Reaction of $WC_2D_2^+$, generated from reaction of W^+ with C_2D_4, with C_2H_2 was carried out in order to investigate the possibility of thermoneutral ligand exchange. Several reaction products were observed, including ions at one and two mass units less than that of the parent $WC_2D_2^+$. While formation of WC_2DH^+ must result from a process involving ligand coupling, the formation of $WC_2H_2^+$ could arise from either ligand coupling or direct ligand displacement. In any case, while both of these possibilities are compatible with structure **1**, this experiment does not allow structure **2** to be eliminated since ligand exchange might occur through an intermediate $W(C_2D_2)(C_2H_2)^+$ complex in which vinylidene to acetylene isomerization takes place. Thus while the possibility of a metal—vinylidene complex cannot be eliminated, all of the experimental data are most simply rationalized on the basis of a metal—acetylene complex.

The structure of $WC_4H_4^+$, the product of the second dehydrogenation step, was probed by both CID and ligand exchange experiments. Collisional activitation of $WC_4H_4^+$ leads to the loss of C_2H_2 and C_4H_4 with the former being dominant. In the presence of C_6D_6, sequential displacement of C_2H_2 units by C_6D_6 is observed. These results strongly suggest that the $WC_4H_4^+$ structure involves two C_2H_2 ligands. As with $WC_2H_2^+$, the simplest way to accommodate these results is by invoking a bis(metallacyclopropene) structure **3a**, which could also be viewed as a bis(acetylene) complex **3b**.


3a


3b

This conclusion is in contrast to that for $MC_4H_4^+$ ions formed in the analogous reactions of Ta^+ and Nb^+ with C_2H_4.[2] In both cases, the most favorable fragmentation upon CID was found to be H_2 loss, leading the authors to suggest metallacyclopentadiene or metal—butyne-3-ene complexes.

The CID spectrum of the product of the third reaction, $WC_6H_6^+$, shows a facile loss of H_2 and a minor loss of C_6H_6. Reaction of $WC_6H_6^+$ with C_6D_6 fails to give ligand displacement. This latter observation does not however disprove the existence of a metal benzene complex since both an exothermic hydrogen loss channel and a direct clustering channel are observed. In the former case losses of H_2 and D_2, in a ratio of 2:1, are observed with no observation of HD loss. This is thus strongly suggestive of a bis(benzene) intermediate which, upon complete randomization of the internal energy, can eliminate either H_2 or D_2 to give the two possible benzene—benzyne complexes accompanied by a deuterium isotope effect. This result is reproduced when the reaction is carried out with a $WC_6H_6^+$ complex which

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is known to have a W(benzene)$^+$ structure.[16] At sufficiently high pressures of C_6D_6 subsequent replacement of C_6H_6 by C_6D_6 in $W(C_6H_6)(C_6D_4)^+$ is also observed. These observations thus fairly conclusively establish the $W(C_6D_6)^+$ species as a metal−benzene complex.

On the basis of the observation that the third reaction of the sequence is exothermic, the resulting metal−benzene complex must be bound by at leaast 50 kcal·mol^{-1}. However, a considerably greater lower limit is established by the observation of the substitution of both CO's is $W(CO_2)^+$ by one molecule of benzene.

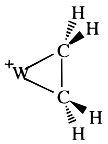
Several possibilities exist for the structure of the fourth product ion $WC_8H_8^+$. Given the W(benzene)$^+$ structure of $WC_6H_6^+$, the most likely possibilities are a two-ligand complex $W(C_6H_6)(C_2H_2)^+$ and a species containing a single C_8H_8 ligand. SORI experiments at variable energies show that at 20 eV the lowest energy dissociation process involves loss of H_2. At 30 eV SORI experiments reveal minor losses of $C_2H_2 + H_2$ and of C_6H_6. CID experiments also show a dominant loss of H_2 and significant losses of both $C_2H_2 + H_2$ and C_6H_6. These experiments thus strongly suggest that the structure of $WC_8H_8^+$ involves coordinated benzene and acetylene. This is supported by ligand exchange experiments in which C_6D_6 is observed to displace C_2H_2 from $WC_8H_8^+$, leading to $W(C_6H_6)(C_6D_6)^+$, which in turn undergoes a very slow ligand exchange to yield $W(C_6D_6)_2^+$.

The structure of the ultimate reaction product observed, $WC_{10}H_{10}^+$, was investigated similarly using SORI, CID, and ligand exchange. SORI and CID experiments show two comparable low-energy dissociations, the loss of H_2 and the loss of C_2H_2. These results thus strongly suggest a structure involving benzene and two acetylene ligands. Attempts to displace C_2H_2 by C_6D_6 showed no reaction. This cannot necessarily be considered to be in contradiction with the proposed structure since $WC_{10}H_{10}^+$ may already be sufficiently sterically encumbered to prevent addition of benzene. Consequently the reaction with C_2H_2 of $WC_{10}D_{10}^+$ generated in an analogous fashion using C_2D_4 was undertaken. Rather than ligand displacement, a simple addition was observed, which suggests the formation of a bis(benzene) complex. This poses the question however of why this ion is not observed in the reaction sequence with ethylene. One possible explanation is that the energy of complexation of ethylene to $WC_{10}D_{10}^+$ is insufficient to overcome the barrier to loss of H_2, while in the case of acetylene no H_2 loss is necessary to proceed to benzene formation. This would render the process feasible for acetylene but energetically inaccessible with ethylene.

Sequential dehydrogenations of C_2H_4 have already been observed with several transition metal cations. An intriguing outcome of an overview of these reactions is that all chains appear to stop at different points, even though H_2 loss is the exclusive pathway at each step. Thus the reaction with Os^+ produces $OsC_4H_4^+$ and a small signal corresponding to $OsC_6H_6^+$.[3] That of Nb^+ yields $NbC_{12}H_{12}^+$ for which a bis(benzene) structure has been proposed.[2] The reaction sequence with Ta^+ is the longest observed to date, involving 10 steps with final product ions of the form $TaC_{20}H_n^+$ ($n = 14, 16, 18$).[17] With U^+, the final product is $UC_6H_6^+$.[18] CID and ligand exchange experiments similar to those described in the present work were performed on the three successive product ions from the reaction of U^+. The results are significantly different, due to the higher reactivity of W^+. Although the conclusions are the same for the structures of $MC_2H_2^+$ and $MC_6H_6^+$ (M = U, W), the structure of $UC_4H_4^+$ was found to bear a single ligand, while we have found that $WC_4H_4^+$ is a $W(C_2H_2)_2^+$ species. The difference in rate of formation between $UC_4H_4^+$ (much slower than both other steps[18]) and $WC_4H_4^+$ (about as fast as the other steps, i.e. a significant fraction of the collision rate) may be indicative of different mechanisms.

Ethane. The reaction of W^+ with ethane involves both single and double dehydrogenation, leading to the formation of $WC_2H_4^+$ and $WC_2H_2^+$ in a ratio which is very sensitive to the W^+ kinetic energy. As above, the CID spectrum of $WC_2H_2^+$ shows exclusively loss of C_2H_2 which leads to the assumption of a W^+−acetylene structure. It must be noted however that under normal operating conditions where W^+ is relaxed for 1 s in 10^{-6} mbar of Ar after isolation, the ratio of single to double dehydrogation products is 1:2. This ratio reaches a value of 1.5:1 at a relaxation time of 5 s. This may then be consistent with the double dehydrogenation being very nearly thermoneutral. If however the rate of the second dehydrogenation is determined by the height of an intermediate barrier on the potential energy surface, then this value is a lower bound to the bond energy. It is also conceivable that the sensitive energy dependence of the ratio of single to double dehydrogenation is due to the formation of two different $WC_2H_4^+$ species, only one of which is able to undergo a second dehydrogenation.

The CID spectrum of $WC_2H_4^+$ shows a major loss of H_2 and a minor loss of C_2H_4. This is directly analogous to that found for $WC_2H_4^+$ derived from two sequential reactions of W^+ with methane.[5a] No definitive conclusion regarding structure can be obtained although the most likely possibility in both cases is a metallacyclopropane **4**. The other possible structures are a metal−ethylidene **5** and a metal−bis(methylidene) complex **6**.



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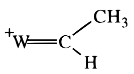

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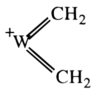

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The occurrence of both single and double dehydrogenation has also been observed in the reactions of Os^+,[3] Sc^+, Y^+, La^+,[19] and Ti^+.[20] Nearly exclusive loss of HD from CH_3CD_3 indicates the formation of an ethylene ligand. The double dehydrogenation reaction is unusual in that it apparently is the sum of an exothermic and

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[16] Reaction of $W(CO)_2^+$ with benzene can be used to generate W(benzene)$^+$ ions with little internal energy. The procedure is analogous to that described for other hydrocarbons in: Mourgues, P.; Ohanessian, G. *Rapid Commun. Mass Spectrom.* **1995**, *9*, 1201.

[17] Cassady, C. J.; McElvany, S. W. *J. Am. Chem. Soc.* **1990**, *112*, 4788.

[18] Heinemann, C.; Cornehl, H. H.; Schwarz, H. *J. Organomet. Chem.* **1995**, *501*, 201.

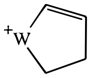
[19] (a) Reference 14a. (b) Sunderlin, L.; Armentrout, P. B. *J. Am. Chem. Soc.* **1989**, *111*, 3845.

[20] (a) Sunderlin, L.; Armentrout, P. B. *Int. J. Mass Spectrom. Ion Processes* **1989**, *94*, 149. (b) Tolbert, M. A.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 7509.

an endothermic channel. This would be consistent with our observation of a dependence of the $WC_2H_4^+/WC_2H_2^+$ intensity ratio upon relaxation of W^+. Possible explanations for the bimodal behavior of the formation of $MC_2H_2^+$ are (a) elimination of H_2 with or without one vibrational quantum, (b) formation of two different electronic states of $MC_2H_4^+$, only one of which undergoes further dehydrogenation, and (c) formation of two different structures of $MC_2H_4^+$, with again only one leading to formation of $MC_2H_2^+$.

Both $WC_2H_4^+$ and $WC_2H_2^+$ converge to a common product, $WC_4H_6^+$, in reaction with a second molecule of ethane. The reactivity of $WC_4H_6^+$ at long reaction times appears to be consistent with the existence of two distinct forms, only one of which is able to react with a third ethane molecule, while the other remains essentially unreactive up to the longest reaction times examined. Given the possibility of the existence of two forms of $WC_4H_6^+$, it seemed likely that one would arise from reaction of $WC_2H_2^+$ and the other from reaction of $WC_2H_4^+$. In order to explore this possibility, experiments were carried out in which either $WC_2H_2^+$ or $WC_2H_4^+$ was continuously ejected during the entire reaction time after selection of W^+. Although this procedure may lead to off resonance excitation of the other ion, it is less dangerous in this respect than using short ejection pulses. The results of these experiments suggest that $WC_4H_6^+$ arising from $WC_2H_4^+$ is the species which does not react further with C_2H_6. In contrast $WC_4H_6^+$ formed by reaction of $WC_2H_2^+$ appeared to react completely with ethane to give $WC_6H_8^+$ and $WC_6H_{10}^+$.

Possibilities for these $WC_4H_6^+$ species include a metallacyclopentene **7**, a metal−butadiene complex **8**, and a metal−acetylene−ethylene or bis(metallacycle) complex **9**.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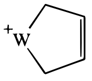
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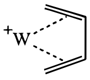
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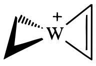
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It is tempting to suggest that the unreactive isomer has a more saturated structure such as **9**, while the reactive one bears a single C_4H_6 ligand. Attempts were therefore carried out to try to differentiate these possibilities. The CID spectra of $WC_4H_6^+$ show losses of H_2 and C_2H_4 and, at the highest collision energies used, also loss of C_4H_6. Further experiments were carried out in which isolated $WC_4H_6^+$ species formed in reaction of either $WC_2H_2^+$ or $WC_2H_4^+$ were allowed to react with C_6D_6. Unfortunately both of the isomeric structures reacted with C_6D_6 in exactly analogous fashion. These reactions included addition of benzene followed by either loss of H_2 or C_2H_4 or replacement of either C_2H_4 or C_2H_2 followed by loss of $2D_2$, $D_2 + HD$, or $D_2 + H_2$. It would appear that the addition of benzene to both $WC_4H_6^+$ species leads to an activation that is sufficient to lead to a common reactivity. Thus neither the CID nor the ligand displacement experiments permit a differentiation of the possible structures.

$WC_6H_{10}^+$ does not react further with ethane. However $WC_6H_8^+$ undergoes a further dehydrogenation reaction with ethane, terminating the reaction sequence by formation of $WC_8H_{12}^+$.

Interestingly, the reactivity of $WC_4H_6^+$ is reminiscent of that of W^+ since both give a mixture of single and double dehydrogenations with ethane. This similarity would be easily explained by a reactive form of $WC_4H_6^+$ with a single C_4H_6 ligand. The fact that the double dehydrogenation product $WC_6H_8^+$ reacts further via single dehydrogenation to yield an unreactive species suggests that the ultimate reaction product $WC_8H_{12}^+$ might have two C_4H_6 ligands.

The complete sequence of reactions observed with ethane is summarized as follows.

$$W^+ + C_2H_6 \rightarrow WC_2H_4^+ + H_2 \tag{2a}$$

$$\rightarrow WC_2H_2^+ + 2H_2 \tag{2b}$$

$$WC_2H_2^+ + C_2H_6 \rightarrow WC_4H_6^+ + 2H_2 \tag{3}$$

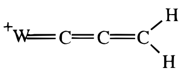
$$WC_2H_4^+ + C_2H_6 \rightarrow WC_4H_6^+ + H_2 \tag{4}$$

$$WC_4H_6^+ \text{ (from (3))} + C_2H_6 \rightarrow WC_6H_{10}^+ + H_2 \tag{5a}$$

$$\rightarrow WC_6H_8^+ + 2H_2 \tag{5b}$$

$$WC_6H_8^+ + C_2H_6 \rightarrow WC_8H_{12}^+ + H_2 \tag{6}$$

B. C_3 Hydrocarbons. Allene and Propyne. The reactions with C_3H_4 isomers have been described in detail previously.[5c] The primary product in the reaction of W^+ with both isomers of C_3H_4 is $WC_3H_2^+$. The similar behavior of this species produced by the two different reactions does not allow any of the four most probable structures **(10−13)** to be eliminated.



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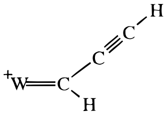

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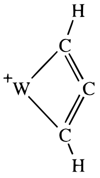

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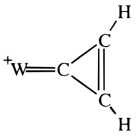

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Ab initio calculations show that the ground electronic states of the various isomers lie within less than 20 kcal mol^{-1},[21] so that either one or a mixture could be formed in the reactions of W^+ with C_3H_4.

The reaction of $WC_3H_2^+$ with both allene and propyne yields $WC_6H_4^+$ exclusively, for which the most likely structure is a metal−benzyne complex.[5c] Starting with the third reaction, two competing channels are observed, corresponding to the loss of C_2H_2 or CH_2. This pattern of reactivity is repeated at least up to the ninth reaction.[5c]

Propene. Compared to literature results with other metal cations, the reaction of W^+ with propene is unusual in that it occurs via double dehydrogenation. The product of this reaction, $WC_3H_2^+$, undergoes no fragmentation under CID conditions, even at the highest energies attempted. This suggests possible structures

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(21) Ohanessian, G. To be published.

Table 2. Primary Ion Products Observed in the Reactions of W^+ with Deuterium-Labeled Propene[a]

ions formed	3,3,3-d_3	1,1-d_2	2-d_1
$WC_3H_2^+$	10; 20; 10	29; 40; 30	56; 67; 100
WC_3HD^+	51; 60; 60	60; 53; 60	44; 33; 0
$WC_3D_2^+$	39; 20; 30	11; 7; 10	

[a] For each product, the percentages given correspond to the experimental observations, the prediction of the fully statistical model in which all hydrogen positions become equivalent, and that of the allylic mechanism, respectively.

analogous to those above (**10**−**13**). Similarly, none of these possibilities can be reasonably excluded.

Early first-row transition metal cations Sc^+,[22] Ti^+,[23] and V^+ [24] react with propene through single dehydrogenation, while late ones (Cr^+−Cu^+) are not reactive.[1a] Studies with other metal ions have been much less systematic. Mo^+ [25] and Rh^+ [26] generate a single H_2 loss, while La^+ leads to a mixture of H_2 and C_2H_4 losses.[27] Some of the lanthanide and actinide cations are also reactive, with losses of H_2 and C_2H_4 observed.[28] Thus W^+ appears to be the most reactive metal cation toward propene studied to date. It should be noted that the present results differ significantly from those reported by Kikhtenko et al.[6] since these authors described a mixture of single and double dehydrogenations of propene. Although good agreement is found for the reaction products with a number of hydrocarbons, significant discrepancies exist in several cases besides propene. The absence of relaxation gas in the latter experiments is the likely explanation for most of the differences of reactivity observed. Another complicating feature in the experiments of Kikhtenko et al.,[6] which is the likely cause of discrepancy with our results for propene, is that all tungsten isotopes were used together in ion−molecule reactions. The overlap between the groups of peaks corresponding to different degrees of dehydrogenation makes assignment of product ions more difficult.

This first double dehydrogenation reaction has also been studied using propene-3,3,3-d_3, -1,1-d_2, and -2-d_1, in order to attempt to elucidate the mechanism (see Table 2). The mechanism usually invoked in the literature to account for the activation of alkenes by other transition metal cations is termed "allylic".[29] In the case of propene, it starts with insertion of the metal into an allylic C−H bond, leading to a hydrido−allyl complex. This structure may result in the five terminal hydrogens becoming equivalent. Migration of the central hydrogen onto the metal then leads to H_2 loss via formation of a metal−allene complex. While this mechanism is in nearly perfect agreement with the observed products in the case of propene-1,1-d_2 (assuming statistical losses of H_2, HD, and D_2 in the second elimination), and in acceptable agreement with those observed with propene-3,3,3-d_3, it cannot account for the important fraction of WC_3HD^+ formed in the reaction with propene-2-d_1 since in this case the allylic mechanism predicts the exclusive formation of $WC_3H_2^+$. The results appear to be more consistent with a mechanism in which all of the hydrogens become equivalent before the first H_2 loss followed by a substantial deuterium isotope effect in the second elimination. This leads to product distributions which deviate slightly from statistical. The assumption of a statistical loss of hydrogens in the first step appears to be logical in view of the significant activation resulting from the association of W^+ with propene. After the first H_2 loss, the $WC_3H_4^+$ complex contains significantly less internal energy, and isotope effects can be expected to be more important in the second elimination of H_2. All of the data in Table 2 can be interpreted on the basis of statistical losses for the first elimination of H_2 followed by a HD/H_2 loss ratio of 0.54 and D_2/H_2 of 0.25. The second step of the reaction could be considered to be very similar to the reaction between W^+ and allene where deuterium substitution shows effectively statistical losses from H_2CCCD_2.[5c] The difference between the two situations is the much greater extent of internal energy resulting from the direct association of W^+ with allene. This greater activation results in a negligible isotope effect in the hydrogen loss.

Reaction with a further molecule of propene proceeds via a combination of single and double dehydrogenations giving $WC_6H_6^+$ and $WC_6H_4^+$. Although the relative intensities of these ions appear to be sensitive to the extent of initial relaxation of W^+, both are formed in all conditions used. CID experiments on $WC_6H_6^+$ show almost exclusive loss of H_2 with a very minor amount of loss of C_6H_6. In order to investigate the possibility that $WC_6H_6^+$ has a coordinated benzene structure, CID experiments were carried out on a true W(benzene)$^+$ species prepared in the manner described above. It also shows a dominant loss of H_2 but with a somewhat greater loss of C_6H_6. However this difference is not sufficient to eliminate the possibility that the species formed in the reaction with propene contains a coordinated benzene. The authentic metal−benzene complex was also allowed to undergo reaction with propene and exhibited both single and double dehydrogenations. In contrast, the $WC_6H_6^+$ formed in the sequential reaction of W^+ with propene showed only a double dehydrogenation. Thus it seems likely that $WC_6H_6^+$ formed in this way does not have a coordinated benzene structure.

The $WC_9H_8^+$ formed in the third sequential reaction with propene shows losses of one and two H_2, C_2H_2, C_2H_4, and C_6H_6 upon collisional activation. Although it is tempting to rationalize the loss of C_6H_6 on the basis of a benzene ligand, a W(benzene)$C_3H_2^+$ complex cannot easily explain losses of C_2H_2 and C_2H_4, since no such losses are observed in the CID spectra of either W(benzene)$^+$ or $WC_3H_2^+$. Therefore no definitive conclusion concerning the structure can be drawn. As described below, the possibility exists that a mixture of isomers is formed, which would explain the unusual features of the CID spectrum.

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(22) Lech, L. M.; Freiser, B. S. *Organometallics* **1988**, *7*, 1948.

(23) Guo, B. C.; Castleman, A. W. *J. Am. Chem. Soc.* **1992**, *114*, 6152.

(24) Buckner, S. W.; Gord, J. R.; Freiser, B. S. *J. Am. Chem. Soc.* **1988**, *110*, 6606.

(25) (a) Schilling, J. B.; Beauchamp, J. L. *Organometallics* **1988**, *7*, 194. (b) Cassady, C. J.; McElvany, S. W. *Organometallics* **1992**, *11*, 2367.

(26) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 5870.

(27) Heinemann, C.; Schröder, D.; Schwarz, H. *Chem. Ber.* **1994**, *127*, 1807.

(28) (a) Schilling, J. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1988**, *110*, 15. (b) Reference 27. (c) Cornehl, H. H.; Heinemann, C.; Schröder, D.; Schwarz, H. *Organometallics* **1995**, *14*, 992.

(29) (a) Larsen, B. S.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 1912. (b) Peak, D. A.; Gross, M. L.; Ridge, D. P. *J. Am. Chem. Soc.* **1984**, *106*, 4307. (c) Peak, D. A.; Gross, M. L. *Anal. Chem.* **1985**, *57*, 115.

(30) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data Suppl.* **1988**, *17*, No. 1.

Subsequent reaction of $WC_9H_8^+$ occurs much more slowly than the preceding steps. Reaction products include ions resulting from both single and double dehydrogenation. Of these, $WC_{12}H_{12}^+$ appears not to react further, while $WC_{12}H_{10}^+$ reacts by simple addition of propene, leading to $WC_{15}H_{16}^+$ as the final product. Monitoring product formation as a function of reaction time also reveals that formation of $WC_{12}H_{10}^+$ occurs significantly more rapidly than that of $WC_{12}H_{12}^+$. This is consistent with the presence of two isomers of $WC_9H_8^+$ having different reactivities with propene. Although isolation of $WC_6H_4^+$ is not practical because of the presence of $WC_6H_6^+$, the latter can be eliminated by SORI excitation leading to dehydrogenation. This yields a significant intensity of $WC_6H_4^+$. Reaction of this ion with propene leads initially to the formation of $WC_{12}H_{10}^+$ and subsequently of $WC_{12}H_{12}^+$, $WC_{12}H_{14}^+$, and $WC_{15}H_{16}^+$. The latter three appear to be unreactive with propene. These results are consistent with the formation of two isomers of $WC_9H_8^+$, one of which arises from reaction of $WC_6H_4^+$ and the latter from reaction of $WC_6H_6^+$, although no direct proof of this filiation could be obtained.

The sequence of reactions with propene is summarized in reactions 7–12.

$$W^+ + C_3H_6 \rightarrow WC_3H_2^+ + 2H_2 \quad (7)$$

$$WC_3H_2^+ + C_3H_6 \rightarrow WC_6H_6^+ + H_2 \quad (8a)$$

$$\rightarrow WC_6H_4^+ + 2H_2 \quad (8b)$$

$$WC_6H_6^+ + C_3H_6 \rightarrow WC_9H_8^+ + 2H_2 \quad (9)$$

$$WC_6H_4^+ + C_3H_6 \rightarrow WC_9H_8^+ + H_2 \quad (10)$$

$$WC_9H_8^+ + C_3H_6 \rightarrow WC_{12}H_{12}^+ + H_2 \quad (11a)$$

$$\rightarrow WC_{12}H_{10}^+ + 2H_2 \quad (11b)$$

$$WC_{12}H_{10}^+ + C_3H_6 \rightarrow WC_{15}H_{16}^+ \quad (12)$$

Cyclopropane. The reaction sequence with cyclopropane is very similar to that with propene, except that an additional minor channel of CH_4 loss is observed. Thus the first reaction is mainly a double dehydrogenation leading to the formation of $WC_3H_2^+$, together with a small amount of $WC_2H_2^+$. While the latter species requires C–C insertion of the metal at some stage, it is not necessarily the case for the main channel since cyclopropenylidene c-C_3H_2 is the most stable isomer of C_3H_2 and is able to form a strong bond to W^+, leading to **13**. Reactions of bare transition metal cations with cyclopropane have not been as extensively studied to date as those of other small alkanes. Several first-row metals have been found not to react with c-C_3H_6.[1a] The second-row cation Rh^+, which is also known to react mainly through dehydrogenation, has been found to undergo mainly single H_2 loss at thermal energies.[31] The most reactive cations previously studied are Nb^+ and Ta^+.[2] Their reactivity is similar to that reported here since the main reaction product is $MC_3H_2^+$ in each case. However both Nb^+ and Ta^+ undergo minor reactions involving loss of carbon fragments, as $MC_2H_2^+$ and MCH_2^+ product ions are observed. Once again, W^+ appears to be among the most reactive metals studied to date and maybe the one with the strongest selectivity for dehydrogenation. Since these features apply to most reactions with other hydrocarbons reported below, further comparison with literature results will be done only in a few cases.

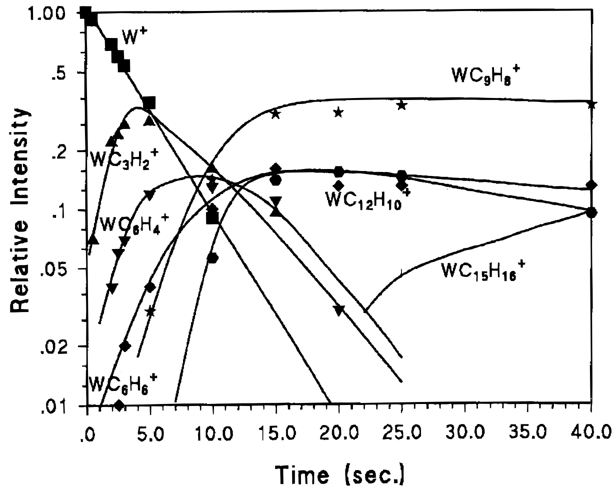

Figure 1. Kinetic plot for the reaction of W^+ with cyclopropane at a a pressure of 2×10^{-8} mbar in an argon bath of 10^{-6} mbar. Minor channels involving the formation $WC_5H_4^+$, $WC_8H_6^+$, $WC_{10}H_{10}^+$, $WC_{11}H_{10}^+$, and $WC_{13}H_{12}^+$ are not shown for clarity.

The reaction of $WC_3H_2^+$ with c-C_3H_6 leads to the formation of both $WC_6H_4^+$ and $WC_6H_6^+$ as with propene. Monitoring the third reaction while continuously ejecting either $WC_6H_4^+$ or $WC_6H_6^+$ shows that both ions lead to $WC_9H_8^+$ as with propene but with an additional minor formation of $WC_9H_6^+$ from $WC_6H_4^+$. $WC_9H_8^+$ is unreactive with cyclopropane at least in part (the formation of two isomers of this ion from $WC_6H_4^+$ and $WC_6H_6^+$ is possible, as discussed in the case of propene), while $WC_9H_6^+$ undergoes a dehydrogenation reaction to form $WC_{12}H_{10}^+$. A final addition of c-C_3H_6 leads to the appearance of $WC_{15}H_{16}^+$ at long reaction times (20 s or more with a c-C_3H_6 pressure of 2×10^{-8} mbar). However at the longest reaction time studied (40 s), the main peak is still due to $WC_9H_8^+$. These features are summarized in the kinetic plot for the main reaction channel shown in Figure 1.

The CH_4 loss channel leads to the competitive formation of minor ions such as $WC_4H_4^+$. The multiple possibilities for combining successive losses of H_2, 2 H_2, and CH_4 make it difficult to derive a definitive scheme for formation of further ions such as $WC_5H_4^+$, $WC_8H_6^+$, $WC_{11}H_{10}^+$, and $WC_{13}H_{12}^+$.

Propane. The first reaction of W^+ with propane proceeds via two channels, a major loss of two molecules of H_2 and a minor loss of CH_4 and H_2 in a ratio of 1:4. Propane is the smallest hydrocarbon for which loss of methane is observed in reactions of W^+. The analogous reaction with propane-2,2-d_2 shows a near statistical loss of 2 H_2, H_2 + HD, and 2 D_2 (2 HD). This suggests a mechanism involving initial insertion into any of the C–H bonds, followed by reversible β-H transfer to the metal prior to H_2 elimination (Scheme 1).[28c]

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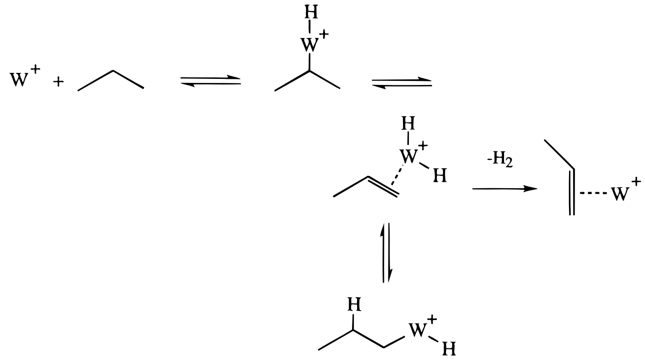
[31] (a) Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 5944. (b) Chen, Y.-M.; Armentrout, P. B. *J. Am. Chem. Soc.* **1995**, *117*, 9291.

Scheme 1



The metal−propene complex formed in this way eliminates a further H_2 as in the direct reaction of W^+ with propene. This second H_2 elimination thus likely leads to a metal−allene or metal−propyne complex. CID experiments on $WC_3H_4^+$ show only the loss of H_2, indicating that this ion likely does not have a $H_2CW(C_2H_2)^+$ structure, which would be expected to lose C_2H_2 upon collisional activation, in analogy with the loss of C_2H_2 upon CID of $WC_2H_2^+$ formed in the reaction with C_2H_4.

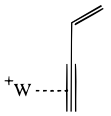
The parallel reaction of W^+ leading to the elimination of $CH_4 + H_2$ may proceed either via insertion into a C−C bond followed by *β*-H transfer or, alternatively, by insertion into a C−H bond followed by *β*-CH_3 migration. In either case, the subsequent loss of methane likely leads to the formation of a metal−ethylene complex which contains sufficient residual internal energy to undergo a further elimination of H_2. The alternative possibility of an initial elimination of H_2 to yield a metal−propene complex followed by loss of CH_4 is however the most probable in view of the common behavior observed for the reactions with linear alkanes as discussed below. In this connection, it is of interest to note that recent work on Rh^+,[32] a metal cation whose main reaction channels with alkanes involve dehydrogenation as for W^+, has lead to the suggestion of an alternative mechanism for H_2 loss. Instead of the classical oxidative addition−*β*-hydrogen migration−reductive elimination mechanism, this pathway involves a concerted migration of two hydrogen atoms onto the metal, leading to the direct formation of an intermediate dihydrido−alkene complex. This mechanism may account for the preference of Rh^+ and some other metal cations for dehydrogenation over elimination of small hydrocarbons.

In analogous fashion to the reaction of W^+, two ions are formed in the second reaction step, $WC_6H_8^+$ and $WC_5H_6^+$ by losses of 2 H_2 or $CH_4 + H_2$. Continuous ejection of $WC_2H_2^+$ establishes that $WC_5H_6^+$ is formed by reaction of both $WC_2H_2^+$ and $WC_3H_4^+$. The CID spectrum of $WC_6H_8^+$ shows primarily losses of H_2 and C_3H_6. This would appear to be incompatible with species such as a cyclohexadiene complex, a bis(allene) or bis(propyne) complex, or a structure containing both a propene ligand and a covalently bound C_3H_2 moiety, which would all be expected to lose two molecules of H_2 relatively easily. One possible structure compatible with this spectrum is a metallacyclobutane−vinylidene complex.

Subsequent reactions of $WC_6H_8^+$ and $WC_5H_6^+$ occur, leading to products such as $WC_8H_8^+$, $WC_8H_{10}^+$, $WC_8H_{12}^+$, and $WC_9H_{10}^+$. Due to the extremely slow rate of each of the reactions in the propane sequence, further characterization of these species was not possible. However, in several cases processes involving triple dehydrogenation appear to be required, which would suggest the formation of particularly strong metal−ligand bonds.

The reaction of W^+ with propane, and indeed all of the linear C_3 hydrocarbons, can be understood on the basis of the qualitative potential energy profile shown on Figure 2, assuming that the intermediate ions with the same formulas formed in the various reactions have the same structure. The binding energy of W^+ to propane is assumed to be approximately 15 kcal mol^{-1} on the basis of the experimental value for Fe^+−propane[33] which also has a ground state based on an s^1d^{n-1} configuration. The value for the bond strength between W^+ and propene has been taken to be greater than 59 kcal·mol^{-1} on the basis of the observation of three successive dehydrogenations of methane by W^+.[4,5a] For either allene or propyne structures, the binding energy of W^+ to C_3H_4 can be taken as greater than 71 kcal mol^{-1} on the basis of the observation that the double dehydrogenation of propane by W^+ readily occurs. The failure to observe a third dehydrogenation of C_3H_8 only establishes the minimum energy of the highest barrier in the transformation of $WC_3H_4^+$ to $WC_3H_2^+$ as being above that of the initial separated reactants. The occurrence of a double dehydrogenation of C_3H_6 places this barrier and the final $WC_3H_2^+$ product at a position lower in energy than separated W^+ and C_3H_6.

C. C_4 Hydrocarbons. Butadiene. The reaction of W^+ with butadiene yields $WC_4H_4^+$ as the major product corresponding to H_2 loss, with a minor amount of $WC_2H_2^+$ and traces of $WC_3H_2^+$. Reaction with butadiene-1,1,4,4-*d*$_4$ yields a major loss of D_2 and a somewhat smaller loss of HD, a ratio which is not compatible with a statistical H/D scrambling on all positions. This result can be explained by the superposition of a 1,2 dehydrogenation, accounting for the loss of HD and leading to **14**, and a 1,1 or a 1,4 mechanism accounting for the loss of D_2, leading to **15** and **16**, respectively. Alternatively, a single mechanism associated with partial H/D randomization can be invoked.



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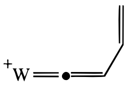
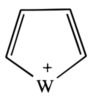
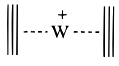


15



16



17

Several experiments were carried out in order to distinguish between these scenarios and between the possible structures of the $WC_4H_4^+$ product. CID spectra of $WC_4H_4^+$ at variable collision energies show losses of H_2, C_2H_2, and C_4H_4 with similar intensities. On the basis of the lack of fragmentation of ions such as WCH_2^+ and $WC_3H_2^+$, in which a W═C double bond is likely to be present, structure **15** can be regarded as less probable. **14**, **16**, and **17** are all compatible with these observations.

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(32) (a) Perry, J. K. Ph.D. Thesis, California Institute of Technology, 1994. (b) Reference 31b.

(33) Schultz, R. H.; Armentrout, P. B. *J. Am. Chem. Soc.* **1991**, *113*, 729.

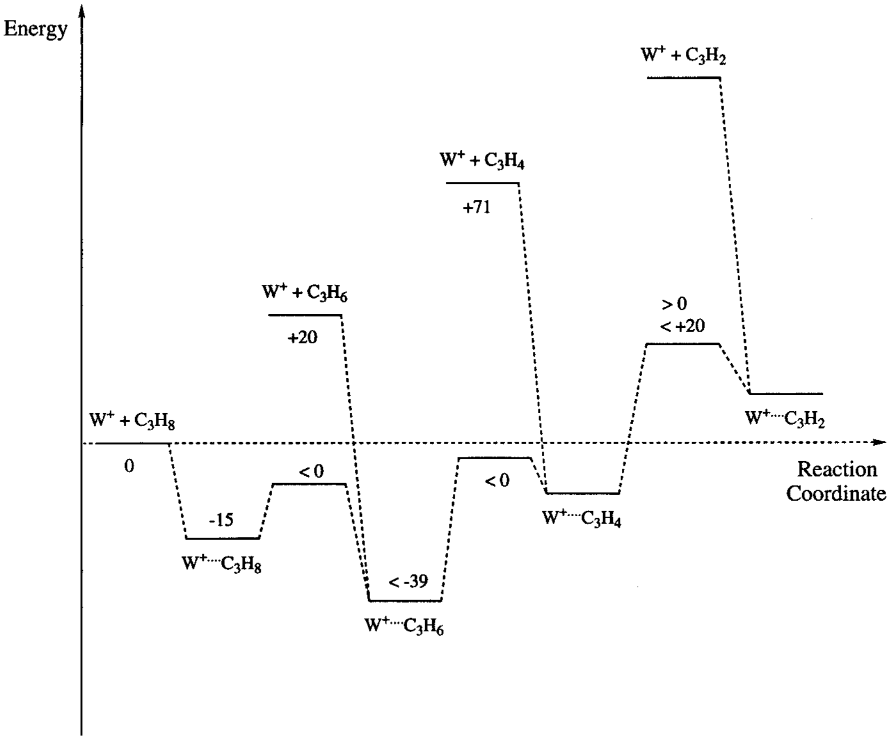
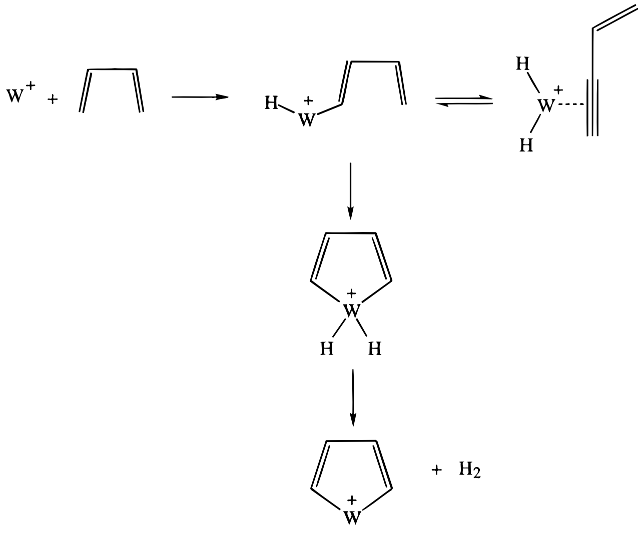


Figure 2. Qualitative potential energy profile for the reactions of W^+ with C_3 hydrocarbons. Enthalpies of formation of C_3H_n are taken from ref 30.

In another experiment, $WC_4H_4^+$ was selected after 4 s of reaction of W^+ with butadiene and subjected to one or two pulses of C_6D_6. This lead to the successive formation of $WC_8D_6H_2^+$ and $WC_{12}D_{12}^+$, showing that two molecules of benzene will each substitute a C_2H_2 moiety. This is most easily explained if $WC_4H_4^+$ has structure **17**. However this structure might be formed by isomerization of another $WC_4H_4^+$ isomer initially formed, within the $WC_4H_4(C_6D_6)^+$ complex, since complexation with benzene is likely to furnish an important energy reservoir. This hypothesis is supported by similar substitution patterns by C_6D_6 for $WC_4H_4^+$ ions formed in reactions with several other C_4 hydrocarbons (vide infra). $WC_4H_4^+$ is also formed in the reaction of WCO^+ with butadiene, presumably with less internal energy since its formation is now associated with CO detachment. When subjected to C_6D_6 pulses, the same substitution pattern was observed as above. Structure **16** could also be invoked to explain this pattern, as it is expected that its isomerization into **17** should be a facile process.

The presence of a mixture of $WC_4H_4^+$ isomers might be detectable in the outcome of their further reaction with butadiene. The reaction of $WC_4H_4^+$ with a second molecule of butadiene yields both $WC_8H_8^+$ and $WC_8H_6^+$, corresponding to a single and a double dehydrogenation. As discussed in detail above for the reaction of W^+ with ethane, the coexistence of such products could be due to the presence of two isomers of $WC_4H_4^+$ each reacting differently with butadiene or to a single isomer formed with a distribution of internal energies broad enough that only part of them are able to undergo the second H_2 loss. When labeled butadiene is used, the peaks corresponding to single dehydrogenation show the same proportions of losses of D_2 and HD from $WC_4H_2D_2^+$ and $WC_4HD_3^+$ as in the first reaction, suggestive of the same mechanism. In this respect it is of interest to note that the rate constants for reaction of W^+ and $WC_4H_4^+$ with butadiene are of the same order ($(3 \pm 2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}). This is most consistent with the presence of a single isomer. It should be noted that if the double dehydrogenation products arise from those of single dehydrogenation with the same H/D pattern, then the observed peaks imply a nearly exclusive loss of HD in the second step.

Scheme 2



The easiest way to account for the above results is by invoking a 1,4 dehydrogenation mechanism leading to **16**, accompanied by partial randomization of the hydrogens on the 1 and 2 positions on one hand and on the 3 and 4 positions on the other as shown in Scheme 2.

While $WC_8H_6^+$ is formed more rapidly than $WC_8H_8^+$, both are reactive with a third molecule of butadiene and completely consumed at long reaction times, forming $WC_{12}H_{12}^+$ and $WC_{12}H_{10}^+$, respectively, together with minor amounts of $WC_{10}H_{10}^+$ and $WC_{10}H_8^+$. $WC_{12}H_{12}^+$ appears to be unreactive with butadiene, while reaction of $WC_{12}H_{10}^+$ yields $WC_{16}H_{14}^+$ as the major product, plus $WC_{16}H_{16}^+$ and a minor amount of $WC_{14}H_{12}^+$. This difference in reactivity, which is similar to that observed for ions with the same formulas formed in the reaction with propene, suggests that $WC_{12}H_{10}^+$ and $WC_{12}H_{12}^+$ have different types of structures. It is of course tempting to explain the lack of reactivity of the latter by a bis(benzene) structure, whose lack of reactivity with larger hydrocarbons will be established below.

The full reaction sequence with butadiene is described in reactions 13−18.

$$W^+ + C_4H_6 \rightarrow WC_4H_4^+ + H_2 \qquad (13a)$$

$$\rightarrow WC_2H_2^+ + C_2H_4 \qquad (13b)$$

$$WC_4H_4^+ + C_4H_6 \rightarrow WC_8H_6^+ + 2H_2 \qquad (14a)$$

$$\rightarrow WC_8H_8^+ + H_2 \qquad (14b)$$

$$WC_2H_2^+ + C_4H_6 \rightarrow WC_6H_4^+ + 2H_2 \qquad (15)$$

$$WC_8H_6^+ + C_4H_6 \rightarrow WC_{12}H_{10}^+ + H_2 \qquad (16a)$$

$$\rightarrow WC_{10}H_8^+ + C_2H_4 \qquad (16b)$$

$$WC_8H_8^+ + C_4H_6 \rightarrow WC_{12}H_{12}^+ + H_2 \qquad (17a)$$

$$\rightarrow WC_{10}H_{10}^+ + C_2H_4 \qquad (17b)$$

$$WC_{12}H_{10}^+ + C_4H_6 \rightarrow WC_{16}H_{14}^+ + H_2 \qquad (18a)$$

$$\rightarrow WC_{16}H_{16}^+ \qquad (18b)$$

$$\rightarrow WC_{14}H_{12}^+ + C_2H_4 \qquad (18c)$$

1-Butene. The reaction of W^+ with 1-butene yields $WC_4H_4^+$ and $WC_3H_2^+$ in an approximate ratio of 2:1. These correspond to losses of two H_2 and of CH_4 plus H_2, respectively. As summarized in Scheme 3, this can be explained by initial insertion of W^+ into an allylic C−H or C−C bond. In the former case, 3,4 dehydrogenation leads to an intermediate metal−butadiene complex, which can itself proceed to a metallacyclopentadiene or bis(acetylene) product as in the reaction of W^+ with butadiene. Analogous experiments were carried out as in the latter case on the $WC_4H_4^+$ product ion.

$WC_4H_4^+$ was isolated after 4 s of reaction of W^+ with C_4H_8 and allowed to collide with Ar. The CID spectrum at 20 eV collision energy shows a major loss of C_2H_2 and a minor loss of H_2. At 40 eV, another large peak corresponds to loss of C_4H_4. The SORI spectra of $WC_4H_4^+$ at 15 and 20 eV maximum energies display a dominant loss of C_2H_2 and minor losses of H_2 and C_3H_2. It is likely that the latter is made possible only in multiple collision conditions, due to a significant barrier associated with ligand rearrangement.

When subjected to one or two pulses of benzene, $WC_4H_4^+$ reacts dominantly to form $WC_8H_8^+$ and $WC_{12}H_{12}^+$ successively. This corresponds to two substitutions of C_2H_2 by C_6H_6, which, together with the collision spectra, argues in favor of structures **16** or **17**. Thus both types of experiments suggest that the $WC_4H_4^+$ ions formed in the reactions of W^+ with butadiene and 1-butene have the same structure.

The minor $WC_3H_2^+$ product may arise from initial insertion of the metal into the allylic C−C bond, yielding a metal−allene complex which undergoes a further dehydrogenation leading to the formation of $WC_3H_2^+$, as in the reactions with C_3H_6, c-C_3H_6, and both C_3H_4 isomers.

Reaction of WCO^+ with 1-butene exclusively yields a $WC_4H_6^+$ product ion. It is likely that inital H_2 loss is followed by CO detachment, leaving a $WC_4H_6^+$ ion without enough internal energy to undergo a second H_2 loss, contrary to what happens in the direct reaction of W^+ with 1-butene. Since W^+ and WCO^+ both have ground sextet spin states,[34] it may be assumed that the initial H_2 loss follows a common mechanism in both cases. It might then be considered that this experiment allows the $WC_4H_6^+$ intermediate of the $W^+ + C_4H_8$ reaction to be trapped.

Collisional activation of $WC_4H_6^+$ shows a dominant loss of H_2, plus less abundant losses of C_2H_2, CH_4, and C_4H_6. When subjected to a pulse of benzene, this ion undergoes two competitive reactions: (i) formation of $WC_{10}H_{10}^+$, which can be attributed to, e.g., dehydrogenation of C_4H_6 enabled by the energy gained through complexation with benzene, and (ii) successive substitutions of first a C_2H_4 and then a C_2H_2 unit by benzene molecules. Although the latter result would be most simply explained by invoking a metal−ethylene−acetylene structure, it may also arise from a metal−butadiene complex undergoing first H_2 loss as in (i) above and then successive substitution of two C_2H_2 units by C_6H_6 as in the case of the $WC_4H_4^+$ complex.

Further reaction of $WC_4H_4^+$ with 1-butene yields $WC_8H_8^+$ as the major product, plus minor amounts of $WC_6H_8^+$ and $WC_6H_6^+$, the latter two being of approximately equal intensity. Reaction of $WC_3H_2^+$ forms a single product, $WC_7H_6^+$. The third reactions are listed in reactions 19−22.

$$WC_8H_8^+ + 1\text{-}C_4H_8 \rightarrow WC_{12}H_{12}^+ + 2H_2 \quad \text{(major)} \qquad (19a)$$

$$\rightarrow WC_{12}H_{14}^+ + H_2 \quad \text{(minor)} \qquad (19b)$$

$$WC_6H_6^+ + 1\text{-}C_4H_8 \rightarrow WC_{10}H_{10} + 2H_2 \quad \text{(major)} \qquad (20a)$$

$$\rightarrow WC_{10}H_{12}^+ + H_2 \quad \text{(minor)} \qquad (20b)$$

$$WC_6H_8^+ + 1\text{-}C_4H_8 \rightarrow WC_{10}H_{12}^+ + 2H_2 \qquad (21)$$

$$WC_7H_6^+ + 1\text{-}C_4H_8 \rightarrow WC_{11}H_{10}^+ + 2H_2 \qquad (22)$$

2-Butene. The reactions observed with 2-butene (*E*, *Z*, or a mixture of both) are essentially identical to those described above for 1-butene. Attempts were made to identify minor differences which could be meaningful. The first reaction seems to proceed slightly more slowly with 2-butene, but this difference may be small enough to fall within experimental uncertainty. The ratio of

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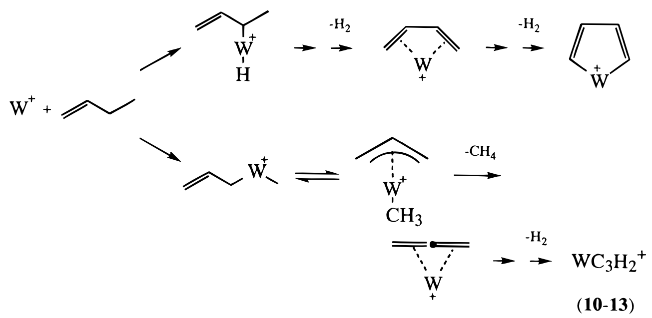
(34) Büker, H. H.; Maitre, P.; Ohanessian, G. To be published.

Scheme 3



$WC_3H_2^+$ to $WC_4H_4^+$ produced with 2-butene seems to be smaller than with 1-butene. Finally, in the reaction of $WC_8H_8^+$ with 2-butene, $WC_{12}H_{14}^+$ is more abundant than $WC_{12}H_{12}^+$, while the reverse is true with 1-butene. Overall, these differences are small enough that the reactions of 1- and 2-butene may be considered to be identical.

Isobutene (2-Methylpropene). Most products observed in the sequence of reaction with isobutene are the same as with 1- and 2-butene. However, the relative intensities are widely different, which suggests that this similarity may be only formal. The reactions observed are as follows:

$$W^+ + i\text{-}C_4H_8 \rightarrow WC_3H_2^+ + CH_4 + H_2 \quad \text{(major)} \qquad (23a)$$

$$\rightarrow WC_4H_4^+ + 2H_2 \quad \text{(minor)} \qquad (23b)$$

$$WC_3H_2^+ + i\text{-}C_4H_8 \rightarrow WC_7H_6^+ + 2H_2 \quad \text{(major)} \qquad (24a)$$

$$\rightarrow WC_7H_8^+ + H_2 \quad \text{(minor)} \qquad (24b)$$

$$\rightarrow WC_6H_4^+ + CH_4 + H_2 \quad \text{(minor)} \qquad (24c)$$

$$WC_4H_4^+ + i\text{-}C_4H_8 \rightarrow WC_8H_8^+ + 2H_2 \qquad (25)$$

$$WC_7H_n^+ + i\text{-}C_4H_8 \rightarrow WC_{11}H_m^+ + ((n + 8 - m)/2)H_2 \quad (n = 6, 8;\ m = 10, 12) \qquad (26)$$

$$WC_8H_8^+ + i\text{-}C_4H_8 \rightarrow WC_{12}H_{14}^+ + H_2 \quad \text{(major)} \qquad (27a)$$

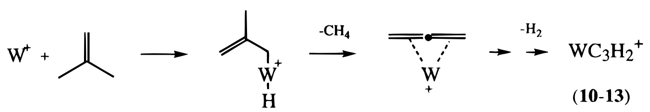
$$\rightarrow WC_{12}H_{12}^+ + 2H_2 \quad \text{(minor)} \qquad (27b)$$

$$\rightarrow WC_{11}H_{12}^+ + CH_4 \quad \text{(minor)} \qquad (27c)$$

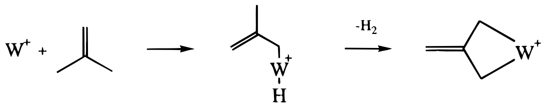
$$WC_{11}H_n^+ + i\text{-}C_4H_8 \rightarrow WC_{15}H_{16}^+ + ((n + 8 - 16)/2)H_2 \quad (n = 10, 12) \qquad (28)$$

Inversion of the relative abundances of $WC_3H_2^+$ and $WC_4H_4^+$ compared to 1- and 2-butene is explained if the allylic mechanism is dominant for all alkenes and C−H insertion is more facile than C−C insertion. This latter preference clearly emerges from the overall pattern of reactivity reported in the present paper. Indeed, the only allylic bonds are C−H bonds in isobutene, and following such an insertion, β-methyl migration enables loss of CH_4 leading to a metal−allene complex, which further eliminates H_2 as shown in Scheme 4.

Scheme 4



Scheme 5



Devising a scheme for double dehydrogenation is more difficult. While the first may be thought to lead to a metal−trimethylenemethane complex (see Scheme 5) as already postulated in the reaction of Sc^+ with toluene,[22] the second H_2 loss appears to require extensive rearrangements.

CID spectra of $WC_4H_4^+$ are similar to those of the same ions formed in the reactions with butadiene and 1-butene, except for a minor loss of CH_2 in addition to losses of C_2H_2 and C_4H_4. When $WC_4H_4^+$ is subjected to a benzene pulse, the same substitution pattern of C_2H_2 by C_6H_6 is observed as in previous cases. It is impossible at present to conclude whether rearrangement to a structure such as **16** or **17** occurs during formation of the ion or within the complex formed with benzene.

Another puzzling result was obtained when reacting isobutene with WCO^+. As before, such an experiment is considered to "stop" the usual elimination of two neutral molecules after the first. While the above considerations suggest that the product formed should correspond to loss of methane, it actually is loss of H_2 that is observed. This may then mean that the dominant pathway in the reaction of W^+ with isobutene first involves loss of H_2 and then loss of CH_4 rather than in the reverse order. When the resulting $WC_4H_6^+$ ion was subjected to benzene pulses, a slightly different picture was obtained compared to that of the $WC_4H_6^+$ ion arising from the reaction of WCO^+ with butene described above. In addition to the successive replacements of C_2H_4 and C_2H_2 by two benzene molecules, dehydrogenation was also observed to occur to a significant extent. Pulsing C_6D_6 showed that H_2 loss arises exclusively from the C_4H_6 ligand(s).

***n*-Butane.** The primary reaction of W^+ with *n*-butane yields a mixture of $WC_4H_6^+$ and $WC_4H_4^+$, corresponding to double and triple dehydrogenation, respectively. The relative amounts of products formed are sensitive to initial thermalization of W^+, and $WC_4H_6^+$ is found to be dominant when W^+ is thermalized during 4 s in 10^{-6} mbar of Ar before reaction. However here again there is no doubt that both channels are exothermic and involve no energy barrier higher than the energy of reactants. Small amounts of $WC_3H_2^+$ and $WC_3H_4^+$ are also detected but probably correspond to slightly endoergic channels or, alternatively, channels which have an activation barrier with an energy very close to that of the reactants. As for ethane and propane, the above reactivity is very similar to that observed with Os^+.[3] Other transition metal cations known to induce dehydrogenation, such as Ru$^+$ and Rh$^+$, induce a mixture of single and double H_2 losses.[35]

The CID spectra of $WC_4H_6^+$ at various collision energies are similar to those of the ions with the same formula formed in the secondary reactions with ethane, except for a minor additional fragmentation corresponding to methane elimination. This is suggestive of similar structures. Since a significant amount of $WC_4H_6^+$ is still present after 20 s of reaction with *n*-butane, a mixture of two different structures having different reactivities with *n*-butane, analogous to that established in the case of ethane, is also possible. The CID spectra of $WC_4H_4^+$ show losses of C_2H_2 and C_4H_4, compatible with structures **16** and **17**.

Since the double dehydrogenation of *n*-butane may be though of as leading to a butadiene complex, further dehydrogenation would be analogous to that described in the direct reaction of W$^+$ with butadiene. However the possibility of a mixture of $WC_4H_6^+$ isomers cannot be excluded as discussed above, in which case the formation of $WC_4H_4^+$ might be possible only from one of these isomers.

The main product of the second reaction is $WC_8H_8^+$, accompanied by less abundant $WC_8H_{12}^+$ ions and a much smaller $WC_8H_{10}^+$ peak. A minor channel leads to the formation of $WC_7H_8^+$ and a small amount of $WC_7H_{10}^+$, corresponding to loss of two H_2 molecules from the minor primary products $WC_3H_2^+$ and $WC_3H_4^+$. No significant further reaction was observed after a reaction delay of 20 s with a pressure of *n*-butane of 2×10^{-8} mbar.

The reaction sequence with *n*-butane is summarized in eqs 29−31.

$$W^+ + n\text{-}C_4H_{10} \rightarrow WC_4H_6^+ + 2H_2 \quad (29a)$$

$$\rightarrow WC_4H_4^+ + 3H_2 \quad (29b)$$

$$\rightarrow WC_3H_2^+ + CH_4 + 2H_2 \quad \text{(minor)} \quad (29c)$$

$$\rightarrow WC_3H_4^+ + CH_4 + H_2 \quad \text{(minor)} \quad (29d)$$

$$WC_4H_n^+ + n\text{-}C_4H_{10} \rightarrow WC_8H_8^+ + ((n+2)/2)H_2 \quad (n = 4, 6) \quad (30a)$$

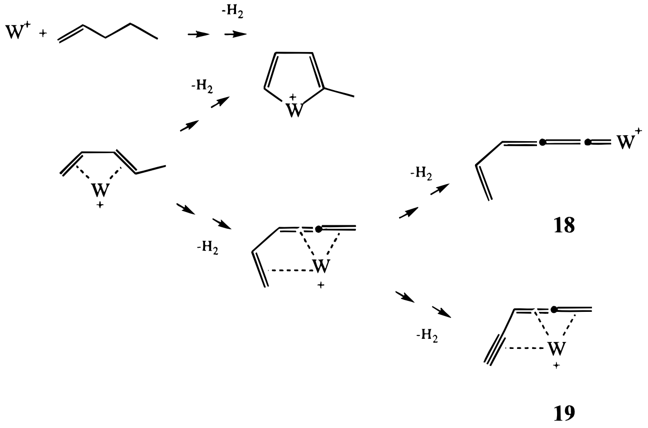
$$\rightarrow WC_8H_{10}^+ + (n/2)H_2 \quad (30b)$$

$$\rightarrow WC_8H_{12}^+ + ((n-2)/2)H_2 \quad (30c)$$

$$WC_3H_m^+ + n\text{-}C_4H_{10} \rightarrow WC_7H_8^+ + ((m+2)/2)H_2 \quad (m = 2, 4) \quad (31a)$$

$$\rightarrow WC_7H_{10}^+ + (m/2)H_2 \quad (31b)$$

Scheme 6



Isobutane. The primary products observed with isobutane differ from those observed with *n*-butane, since a major formation of $WC_4H_6^+$ and minor formations of $WC_3H_2^+$ and $WC_3H_4^+$ are observed. If 1,2 dehydrogenation is assumed to occur initially as usual, the resulting metal−isobutene complex formed may evolve by either loss of CH_4 plus H_2 leading to $WC_3H_2^+$ as in the direct reaction of W$^+$ with isobutene or by loss of H_2 leading to a complex with a trimethylenemethane ligand (see Scheme 5). Since the additional H_2 loss observed with isobutene is only a minor channel, it is not unexpected that it does not occur with isobutane since the initial complexation provides less internal energy available in this case.

The main secondary ion $WC_4H_6^+$ reacts with a second molecule of isobutane by double and triple dehydrogenation forming $WC_8H_{12}^+$ and $WC_8H_{10}^+$, plus loss of methane and H_2 forming $WC_7H_{10}^+$. Both of the minor secondary ions $WC_3H_2^+$ and $WC_3H_4^+$ converge to a common $WC_7H_8^+$ product in their respective reactions. The final ions observed are $WC_{11}H_{14}^+$ and $WC_{12}H_{20}^+$, the latter being formed by a slow clustering reaction of isobutane with $WC_8H_{10}^+$, while $WC_8H_{12}^+$ appears not to react further.

There is a remarkable similarity in the primary reactions of W$^+$ with all C_4 hydrocarbons in that $WC_4H_4^+$ appears to be a ubiquitous entity. This would suggest a significant energy minimum for a species of this composition such that, whatever the reactant C_4 hydrocarbon, all reactions lead via one or more rearrangements to this species. As discussed above, a metallacyclopentadiene structure appears to be compatible with all observed reactions, CID spectra, and ligand exchange processes. In a similar study of $ScC_4H_4^+$,[22] Lech and Freiser concluded that a single isomer is formed in the reactions with ethylene and butadiene, while another one results from the double dehydrogenation of cyclobutane. Evidence was also obtained for the formation of two isomers of $ScC_4H_6^+$. In the case of scandium, isomer differentiation was made easier by the significant extent of simple condensation in the reactions of some isomers. Unfortunately, the higher reactivity observed with tungsten complexes makes this technique less demonstrative.

D. Larger Hydrocarbons. The reactions with larger hydrocarbons were studied mainly in order to derive trends for the reactivity of W$^+$ in primary reactions. The reaction sequences are sometimes rather complex, and therefore, only that with 1-pentene will be given as an example.

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[35] Tolbert, M. A.; Mandich, M. L.; Halle, L. F.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 5675.

1-Pentene and 2-Methyl-1-butene. The reaction sequence with 1-pentene is described below (eqs 32–37). As before, filiations in secondary reactions were established by continuously ejecting each primary ion product in turn throughout a given reaction time.

$$W^+ + 1\text{-}C_5H_{10} \rightarrow WC_5H_6^+ + 2H_2 \qquad (32a)$$

$$\rightarrow WC_5H_4^+ + 3H_2 \qquad (32b)$$

$$\rightarrow WC_4H_4^+ + CH_4 + H_2 \qquad (32c)$$

$$\rightarrow WC_3H_4^+ + [C_2, H_6] \quad \text{(minor)} \qquad (32d)$$

$$WC_5H_4^+ + 1\text{-}C_5H_{10} \rightarrow WC_{10}H_{10}^+ + 2H_2 \qquad (33a)$$

$$\rightarrow WC_8H_8^+ + [C_2, H_6] \qquad (33b)$$

$$WC_5H_6^+ + 1\text{-}C_5H_{10} \rightarrow WC_{10}H_{10}^+ + 3H_2 \qquad (34)$$

$$WC_4H_4^+ + 1\text{-}C_5H_{10} \rightarrow WC_9H_8^+ + 3H_2 \qquad (35a)$$

$$\rightarrow W_7C_8^+ + [C_2, H_6] \qquad (35b)$$

$$WC_3H_4^+ + 1\text{-}C_5H_{10} \rightarrow WC_8H_8^+ + 3H_2 \qquad (36)$$

$$WC_8H_8^+ + 1\text{-}C_5H_{10} \rightarrow WC_{13}H_{14}^+ + 2H_2 \qquad (37)$$

The first reaction can be described as a combination of the various reactive channels described for smaller hydrocarbons. Insertion of W^+ into an allylic C–H bond is the dominant process, forming a 1-methylbutadiene complex after H_2 loss. This can undergo a 1,4 dehydrogenation leading to a methyl–metallacyclopentadiene $WC_5H_6^+$ complex. Alternatively, another insertion into an allylic C–H bond would yield a pentadienyl complex which can undergo H_2 loss to form a vinylallene $WC_5H_6^+$ isomer. The latter may lose a third H_2 molecule by activating either the allene or the vinyl moiety, to form either of **18** and **19** as shown in Scheme 6.

Loss of methane is likely to proceed via a mechanism analogous to that for 1-butene. Finally, the marginal loss of $[C_2, H_6]$ probably results from insertion of the metal into the allylic C–C bond followed by migration of a β-H onto the metal or, less probably, from insertion into a C–H allylic bond followed by migration of the β-ethyl fragment. The latter possibility can be disregarded since this channel is not observed in the reaction with 2-methyl-1-butene.

The reaction with 2-methyl-1-butene bears strong similarities with that with 1-pentene. As mentioned above, the marginal formation of $WC_3H_4^+$ is no longer observed, a sign that the latter arose from initial insertion into the allylic C–C bond. The relative intensities of the three major products are slightly different, with $WC_4H_4^+$ slightly more intense and $WC_5H_4^+$ slightly smaller than $WC_5H_6^+$, while the reverse was true with 1-pentene. Overall these differences are too small to be taken to correspond to significant changes in reactivity.

***n*-Pentane and *n*-Hexane.** The reaction of W^+ with *n*-pentane leads to a mixture of losses of either 3 H_2 or of $CH_4 + 2H_2$ in a ratio of 2:1, respectively. The reaction with *n*-hexane shows a mixture of triplet and quadruple loss of H_2 plus loss of $CH_4 + 2H_2$ in a ratio of 2:4:1. The $WC_6H_6^+$ product formed in the quadruple dehydrogenation channel does not show loss of C_6H_6 under CID conditions and thus likely does not have a coordinated benzene structure.

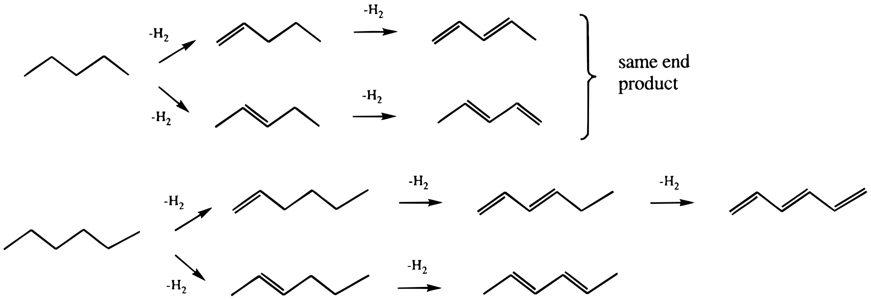
Putting together the primary reactions observed with propane, *n*-butane, *n*-pentane, and *n*-hexane (see Table 1) allows some generalizations to be made for linear alkanes. In all cases, multiple dehydrogenation is the dominant channel, with a minor amount of loss of methane plus one or two hydrogen molecules. In the dehydrogenation channel, propane and *n*-pentane yield a single product corresponding to loss of 2 H_2 and 3 H_2, respectively, while *n*-butane and *n*-hexane give a mixture of products. Thus linear alkanes appear to fall into two different classes, depending on whether they have an even or odd number of carbon atoms.

As discussed previously, several possibilities exist for explaining a mixture of multiple H_2 losses. One of them is that the parent W^+ ions may have a distribution of kinetic energy wide enough that only part of them are able to proceed up to the last step. However the occurrence of such a mixture for several compounds would mean that the reaction is very close to threshold in each case, which seems rather unlikely. This suggests that the two channels correspond to two distinct mechanisms. This can be rationalized on the basis of a series of facile 1,2 dehydrogenations, leading in a stepwise fashion to conjugated polyenes. For alkanes with an odd number of carbons, this leads to a single polyene, while, for cases with an even number of carbons, two different channels are generated, with different numbers of steps, depending of which bond is dehydrogenated first. This is illustrated on Scheme 7 for *n*-C_5H_{12} and *n*-C_6H_{14}. This mechanism is based on the assumption that the sequence of dehydrogenations is driven by the special stability of coordinated conjugated polyenes and that alkene isomerization cannot effectively compete with dehydrogenation at each step.

A final dehydrogenation occurs, which may be considered to be analogous to that described for butadiene, leading to unsaturated metallacycles or bis(alkyne) structures analogous to **16** and **17**.

The minor channel leading to loss of methane plus one or several hydrogen molecules is also informative. If loss of methane is assumed to occur prior to dehydrogenation(s), it can be accounted for by either insertion of the metal into a C–H bond followed by a β-alkyl shift or by insertion into a C–C bond followed by a β-H shift. However this would lead to loss of alkane fragments larger than methane in the reaction of alkanes larger than propane. The complete absence of such losses for all linear alkanes studied implies that methane loss occurs *after* dehydrogenation(s). This scenario is consistent with the observation that this channel is more important for alkanes with an odd number of carbons, for which the series of 1,2 dehydrogenations leaves an intact terminal methyl group, than for alkanes with an even number of carbons for which such methyl groups are present only in one of the two dehydrogenation channels. The final loss of methane may then be analogous to that observed with linear butenes. Although the reactions reported for Nb^+ and Ta^+ [2] are similar to those for W^+, the specific patterns described above do not emerge for these other metals.

Scheme 7



In summary, the products observed with linear alkanes suggest that a sequence of 1,2 dehydrogenations first occurs, yielding a single polyene−metal intermediate if the number of carbon atoms is odd and a mixture of two if this number is even. At this point, there is a competition between an additional dehydrogenation and a demethanation, with the former being dominant.

In similar experiments, Kikhtenko et al. found mixtures of multiple dehydrogenations for all linear alkanes except C_7H_{16}.[6] As mentioned above, this might be due to the fact that no relaxation bath of argon was used to ensure efficient initial thermalization of W^+. Another important difference with the present work is that all W^+ isotopes were considered, which makes it rather difficult to identify minor peaks derived from multiple dehydrogenations.

Neopentane. The primary reaction products with neopentane show an unusually complex pattern, since five ions are formed in similar amounts (reactions 38a−e).

$$W^+ + \text{neo-}C_5H_{12} \rightarrow WC_5H_8^+ + 2H_2 \qquad (38a)$$

$$\rightarrow WC_5H_6^+ + 3H_2 \qquad (38b)$$

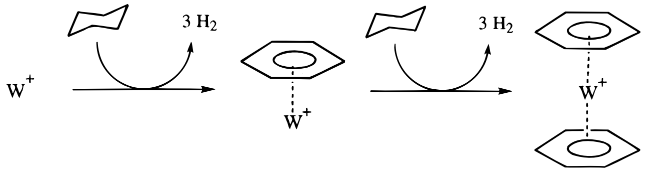
$$\rightarrow WC_4H_6^+ + CH_4 + H_2 \qquad (38c)$$

$$\rightarrow WC_4H_4^+ + CH_4 + 2H_2 \qquad (38d)$$

$$\rightarrow WC_3H_2^+ + [C_2, H_{10}] \qquad (38e)$$

In the absence of the usual 1,2 dehydrogenation channel, initial insertion of W^+ into either a C−H or a C−C bond may be invoked, followed by the migration of a β-methyl or of a β-hydrogen onto the metal, respectively. This leads to a metal−isobutene intermediate species, from which elimination of 2 H_2 and of CH_4 plus H_2 may be anticipated by analogy with the direct reaction of W^+ with isobutene. Since there is less energy available in the present case, further loss of only one H_2 molecule is also observed. There are many possibilities for the products of the double and triple dehydrogenation reactions. Since the structure of neopentane is unique among the hydrocarbons studied, it is not possible to authoritatively speculate on the extent to which significant skeletal rearrangements might be involved. It should however be noted that the rate constant for the primary reaction is very close to that for the reaction with *n*-pentane. In the present case, this means that the reaction efficiency is insensitive to the mechanism since after initial C−H insertion, no β-H's are available in neopentane.

Scheme 8



Cyclohexane. The reaction sequence observed with c-C_6H_{12} is simple since it consists in two successive triple dehydrogenations leading to $WC_6H_6^+$ and $WC_{12}H_{12}^+$. It most likely corresponds to the formation of metal−benzene and bis(benzene) complexes, as depicted in Scheme 8. A similar sequence has been described with Os^+.[36a] The same primary reaction has also been observed with a number of other metal cations, among which are Nb^+ and Ta^+,[2] Sc^+, Y^+, and La^+,[36b] V^+,[36c] and Rh^+.[36d]

Benzene. The reaction with benzene yields a $WC_6H_4^+$ ion as the exclusive primary product. Only few transition metal cations are able to undergo this reaction (in the first transition row, Sc^+ is the only case[1a]), which has been postulated to lead to the formation of a metal−benzyne complex. The metal−ligand binding energy is found to be high in this case since the CID spectra of $WC_6H_4^+$ at various energies do not show any fragmentation. This is consistent with the lower limit of 85 kcal mol^{-1} which is required for exothermic dehydrogenation of benzene. The secondary reaction proceeds by a mixture of simple clustering forming $WC_{12}H_{10}^+$, which likely is a benzene−benzyne complex, a smaller amount of dehydrogenation forming $WC_{12}H_8^+$ which may be viewed either as a bis(benzyne) or a biphenylene complex, plus a minor amount of acetylene loss forming $WC_{10}H_8^+$. $WC_{12}H_{10}^+$ appears not to be reactive (suggesting the two-ligand structure mentioned above), while $WC_{12}H_8^+$ undergoes both clustering and dehydrogenation reactions with a third benzene molecule, yielding $WC_{18}H_{14}^+$ and $WC_{18}H_{12}^+$ as final products. A minor amount of $WC_{16}H_{14}^+$ is also observed, which arises from $WC_{10}H_8^+$ through simple clustering. The fact that $WC_{12}H_8^+$ is able to induce H_2 elimination from benzene argues against a bis(benzyne) structure, which would be expected to be rather saturated. The reactivity of $WC_{12}H_8^+$, which is similar to that of $WC_6H_4^+$, appears to be more consistent with a one-ligand structure such as a metal−biphenylene. CID experiments were carried out on $WC_{12}H_8^+$ and $WC_{12}H_{10}^+$. Although their small mass difference precludes isolation of each of them

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[36] (a) Xiang, X.; Tollens, F. R.; Marshall, A. G. *Organometallics* **1995**, *14*, 542. (b) Huang, Y.; Wise, M. B.; Jacobson, D. B.; Freiser, B. S. *Organometallics* **1987**, *6*, 346. (c) Jackson, T. C.; Carlin, T. J.; Freiser, B. S. *J. Am. Chem. Soc.* **1986**, *108*, 1120. (d) Reference 31a.

in turn, meaningful experiments were made possible by the observation of a strong isotope effect in the second reaction with C_6D_6. In fact, the reaction of $WC_6D_4^+$ with C_6D_6 yields $WC_{12}D_{10}^+$ nearly exclusively. This is consistent with the dehydrogenation of the second benzene molecule occurring very close to threshold. CID experiments could be run on isolated $WC_{12}D_{10}^+$, showing losses of D_2, 2 D_2, and C_2D_2. Further CID experiments on $WC_{12}H_8^+$ and $WC_{12}H_{10}^+$ isolated together then showed that the former exclusively undergoes H_2 loss. These fragmentation patterns are consistent with the structures proposed above, although they cannot rule out other possibilities. A similar sequence has been observed with Os^+,[36a] but the use of all osmium isotopes did not allow for a clear distinction between ions such $OsC_{12}H_8^+$ and $OsC_{12}H_{10}^+$.

Conclusion

The reactions of W^+ with hydrocarbons have been found to proceed mainly via dehydrogenation, leading to the elimination of several molecules in most cases. W^+ is one of the most reactive of all transition metal cations, and this high reactivity carries over to the primary products of its reactions with hydrocarbons. This leads to reaction sequences of various lengths. Most often three or four molecules are successively activated before the reactions stops, but longer chains have also been observed, e.g. with C_3H_4 isomers. This high reactivity can be attributed to the strength of the metal−ligand bonds which are formed during the reactions. This enables the formation of stable intermediates, which then have sufficient internal energy available for rearrangement to products. This type of reactivity, dominated by dehydrogenation, makes W^+ resemble early first-row metal cations such Sc^+ and Ti^+ and late second-row cations such as Ru^+ and Rh^+, although all of these induce less extensive dehydrogenations in most cases. The metal ions with reactions most similar to those of W^+ are the early second-row metal Nb^+ and the third-row metals Ta^+ and Os^+. It is likely that this tendency to increasing reactivity when going down a column of the periodic table is related to the increasing metal−ligand binding energies.[37]

The high activation ability of W^+ results in the observation of several unprecedented reactions such as those with C_3H_6 and C_3H_4. It is likely that the multiple dehydrogenations observed correspond to the formation of complexes with highly unsaturated ligands, thereby making ion products themselves reactive. All C_4 hydrocarbons appear to lead to the same $WC_4H_4^+$ product ion, for which a metallacyclopentadiene or a bis(acetylene) structure can be proposed. By contrast, the $WC_6H_6^+$ ions formed in the reactions with ethene, propene, cyclohexane, and *n*-hexane might not be the same. Although extensive evidence for a metal−benzene structure could be obtained in the case of ethene, experiments aimed at structural determination point toward a different structure in the cases of propene and *n*-hexane.

Activation of alkenes probably involves the allylic mechanism described previously in the literature, although the observed reactions are significantly more complicated with W^+. Competition between allylic C−H and C−C bond insertion if any is yet another example of the strong bias of W^+ in favor of insertion into C−H bonds. Activation of alkanes appears to proceed preferentially via 1,2 dehydrogenation to yield highly unsaturated products, but when such a mechanism is impossible, as with neopentane, other channels are open with similar rate constants.

Isotope labeling was found to be only partly conclusive, since partial or total H/D randomization is generally observed. Again this may be attributed to the high stability of intermediates which can interconvert easily before elimination of a neutral molecule. For analogous reasons, ligand exchange experiments are less revealing than for many other metals: In many cases, the incoming molecule is itself activated, instead of reacting by simple displacement of another ligand. Finally, CID spectra often show ligand activation rather than detachment, leading to frequent H_2 losses which are similar to the processes observed in the reaction themselves.

Understanding the detailed mechanism for reaction propagation and termination remains a formidable challenge. Two general reasons can be invoked to explain the lack of reactivity of product ions: Either the metal no longer bears the appropriate number of nonbonding electrons for inserting into another covalent bond or else the coordination sphere around the metal is filled and leaves no room for an incoming molecule to interact strongly with the metal. In either case, this reasoning assumes that the metal remains the reactive center at each step, which might not always be true, especially when highly unsaturated ligands are present. In any case, the sequences of reactions observed imply extensive ligand coupling, and the formation of extended hydrocarbon structures such as PAH's can be postulated for some of the product ions.

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OM960616Q

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[37] Ohanessian, G.; Goddard, W. A. *Acc. Chem. Res.* **1990**, *23*, 386.