

Bare Tetranuclear Transition-Metal Cluster Ions in the Gas Phase. Reactivity of Sc_4^+ with Small Molecules

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Abstract: In this paper we report the first studies on the reactivity of a bare tetranuclear cluster ion, Sc_4^+ , with a variety of small molecules in the gas phase using Fourier transform mass spectrometry (FTMS). This tetranuclear ion was generated directly by focusing the beam of a pulsed Nd:YAG laser into a small cavity drilled into a high-purity scandium rod. The Sc_4^+ is found to exhibit an extraordinary degree of reactivity toward alkanes. Particularly remarkable is the extent to which dehydrogenation occurs, much greater than is observed for any of the atomic transition-metal ions investigated to date including Sc^+ . Some carbon chain cleavage is also observed for alkanes larger than propane. Finally, the tetramer undergoes a variety of interesting reactions with oxygen, benzene, methanol, and ethylene sulfide.

The nature of the activation of small molecules by transition-metal cluster compounds has received considerable attention¹ in connection with their potential as versatile, selective catalysts.² Bare transition-metal clusters³ have, likewise, become the center of much attention as models for catalytic activity.⁴ Of particular significance is that the catalytic specificity of these clusters may be tailored by selectively varying their size as well as composition.⁵

Although gas-phase-ion techniques are ideally suited for studying size-selected metal cluster ions, relatively few studies have been performed due mainly to the lack of clean and efficient methods for generating the cluster ions. Naked transition-metal cluster ions can be generated in the gas phase by either electron impact⁶ or multiphoton⁷ ionization of polynuclear metal carbonyl complexes. While these methods have not been fully exploited for chemical studies, they are somewhat limited by the nature of the cluster compounds which can be introduced into the source. Smalley and co-workers have developed an elegant and convenient technique for generating clusters of various sizes for gas-phase studies.⁸ In addition, we recently demonstrated a two-step process for in situ synthesis of bare homonuclear and heteronuclear diatomic and triatomic transition-metal cluster ions in the gas phase using Fourier transform mass spectrometry-collision induced dissociation (FTMS-CID),⁹ which promises to expand the size and nature of the clusters accessible for study.

The reactivity of gas-phase cluster ions can be dramatically affected by their size. For example, both Co_2^+ ¹⁰ and CoFe^+ ¹¹ are unreactive with alkanes. In contrast, the trimer FeCo_2^+ reacts readily with alkanes by attacking C-H bonds.¹² Furthermore, the addition of ligands can effect reactivity as exemplified by the recent report that Co_2CO^+ attacks C-H bonds of alkanes.¹³ For comparison, the atomic ions, Fe^+ and Co^+ , are very reactive with alkanes predominantly attacking C-C bonds.¹⁴⁻¹⁸ These important differences in reactivity are not well understood at this time and will continue to be the subject of intense future investigation.

Here, we report the first studies on the reactivity of a bare tetranuclear cluster ion, Sc_4^+ , with a variety of small molecules in the gas phase using Fourier transform mass spectrometry (FTMS). This tetranuclear ion was generated directly by a novel laser ionization technique.¹⁹ Briefly, this method involves focusing the beam of a pulsed Nd:YAG laser down the center of a small-diameter hole drilled into a scandium rod. In contrast, laser ionization of flat metal surfaces generates predominantly atomic monopositive ions.²⁰ Cluster ions have been observed by laser microprobe mass analysis (LAMMA) of thin metal foils (Ag, Al, Au, and Fe),²¹ but the yields are not sufficient for study by FTMS.

A large relative abundance of Sc_4^+ was achieved by using the new configuration.

Experimental Section

The theory, instrumentation, and methodology of ion cyclotron resonance (ICR)²² spectrometry and Fourier transform mass spectrometry (FTMS)²³ have been discussed at length elsewhere. All experiments were

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Table I. Primary Reaction Product Neutral Losses for the Reaction of Sc_4^+ with Alkanes

alkane	percent neutral losses from reactant alkanes													
	H_2	2H_2	3H_2	4H_2	5H_2	CH_4 , H_2	CH_4 , 2H_2	CH_4 , 3H_2	C_2H_6	C_2H_6 , H_2	C_2H_6 , 2H_2	C_3H_8 , H_2	C_4H_{10}	C_4H_{10} , H_2
methane	100													
ethane	19	81												
<i>n</i> -propane		74	26											
<i>n</i> -butane		24	64	4		<i>a</i>	<i>a</i>		3	5				
2-methylpropane		55	42	3										
<i>n</i> -pentane		9	54	10			14		3	10				
2,2-dimethylpropane		36	25	9		4	21			5				
2-methylbutane		13	45	12			18			12				
<i>n</i> -hexane		4	24	37	5		3	3		9	5	4	3	3

^a Less than 2% of this product was observed.

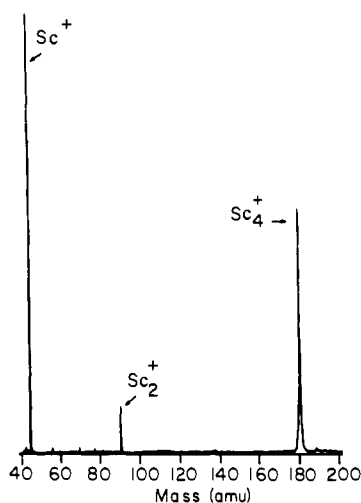


Figure 1. Mass spectrum obtained by focussing the beam of a pulsed Nd:Yag laser into a small cavity drilled into a high-purity scandium rod.

performed on a Nicolet prototype FTMS-1000 Fourier transform mass spectrometer previously described in detail²⁴ and equipped with a 5.2-cm cubic trapping cell situated between the poles of a Varian 15-in. electromagnet maintained at 0.9 T. The cell was constructed in our laboratory and includes a $1/4$ in. diameter hole in one of the transmitter plates which permits irradiation with various light sources. A high-purity scandium rod (6 mm \times 4 mm) containing a 1 mm diameter, 3 mm deep hole was supported on the opposite transmitter plate. Metal ions were generated by focusing the beam of a Quanta Ray Nd:YAG laser (frequency doubled to 530 nm) into the cavity of the scandium rod. The diameter of the focused laser beam was approximately 0.3 mm, and the laser power density was estimated to be about 10^9 W cm^{-2} . This power is somewhat higher than what is typically used for the generation of atomic metal ions.^{17,18} The spectrum obtained from laser ionization of the scandium rod is shown in Figure 1 and indicates that the tetramer can be generated in excellent yield. Details of this technique for cluster ion formation will appear elsewhere.¹⁹ Cluster ions generated in this way undoubtedly have a range of internal energies. The absence of any appreciable pressure effects, however, suggests that they are predominantly in their ground state.

Chemicals were obtained commercially in high purity and were used as supplied except for multiple freeze-pump-thaw cycles to remove noncondensable gases. Sample pressures were on the order of 1×10^{-7} torr. Argon was used as the collision gas for CID experiments at a total sample pressure of approximately 5×10^{-6} torr. A Bayard-Alpert ionization gauge was used to monitor pressure.

Details of the CID experiments have previously been discussed.²⁴⁻²⁶ The collision energy of the ions can be varied (typically between 0 and

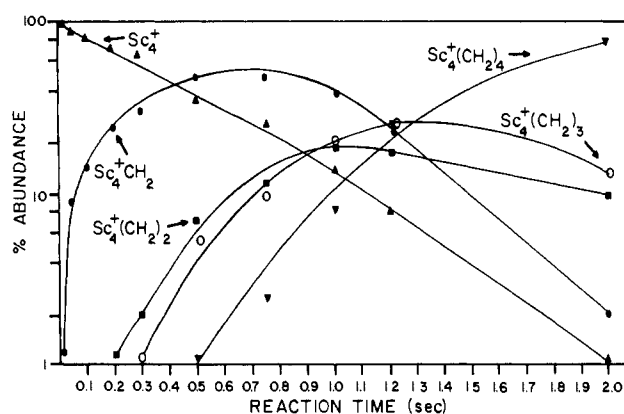


Figure 2. Temporal variation of ion abundances for the reaction of Sc_4^+ with methane at 4×10^{-7} torr.

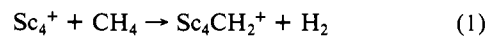
100 eV) from which plots of CID product ion intensities vs. ion kinetic energy can be made. These plots are reproducible to $\pm 10\%$ absolute and yield additional structural information. The spread in ion kinetic energies is dependent on the total average kinetic energy and is approximately 35% at 1 eV, 10% at 10 eV, and 5% at 30 eV.²⁷

Results and Discussion

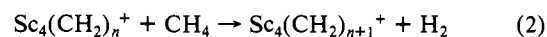
Nature of Sc_4^+ . The Sc_4^+ cluster does not undergo fragmentation upon collisional activation up to ~ 100 eV kinetic energy, indicating formation of a strongly bound unit. A tetrahedral arrangement of the scandium metals would yield the most stable configuration and, therefore, this cluster is believed to consist of a tetrahedral configuration.

Reactivity of Sc_4^+ with Alkanes. The primary product ions and neutral losses for the reactions of Sc_4^+ with small alkanes are summarized in Table I. This ion exhibits an extraordinary degree of reactivity toward alkanes. Particularly remarkable is the extent to which dehydrogenation occurs, much greater than is observed for any of the atomic transition-metal ions investigated to date including Sc^+ .²⁸

Methane. In marked contrast to atomic scandium cations, which are unreactive with methane,²⁸ Sc_4^+ reacts directly with methane, reaction 1. In addition to reaction 1, Sc_4CH_2^+ yields



secondary and higher order reactions, sequentially attaching up to four methylene units, reaction 2. The temporal variation of



$$n = 0-3$$

ion abundances for reaction of Sc_4^+ with methane is shown in Figure 2. Both Sc_4CH_2^+ and $\text{Sc}_4(\text{CH}_2)_3^+$ appear to react more rapidly than $\text{Sc}_4(\text{CH}_2)_2^+$.

Sc_4CH_2^+ , formed in reaction 1, eliminates both $\text{H}\cdot$ and CH_2 upon collisional activation. Elimination of $\text{H}\cdot$ forming Sc_4CH^+

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dominates at low collision energy while formation of Sc_4^+ dominates at high collision energy. This is in contrast to CID of $\text{FeCo}_2\text{CH}_2^+$, formed in reaction 3, which eliminates predominantly



H_2 at low collision energy with CH_2 elimination dominating at high collision energy.²⁹

The above results indicate that the Sc_4CH_2^+ species may consist either of a methyldiene or a methyldiene-hydride structure. Both terminal and bridging methyldiene clusters are known³⁰ as well as hydride-carbonyl-methyldiene clusters.³¹ If Sc_4CH_2^+ consists of an intact methylene, then reaction 1 implies $D^\circ(\text{Sc}_4^+-\text{CH}_2) > 110$ kcal/mol.³² This value can be compared to $D^\circ(\text{Mn}^+-\text{CH}_2) = 94 \pm 7$ kcal/mol, $D^\circ(\text{Fe}^+-\text{CH}_2) = 96 \pm 5$ kcal/mol, $D^\circ(\text{Co}^+-\text{CH}_2) = 85 \pm 7$ kcal/mol, and $D^\circ(\text{Rh}^+-\text{CH}_2) = 94 \pm 5$ kcal/mol.^{33,34}

$\text{Sc}_4(\text{CH}_2)_2^+$, formed in reaction 2, yields elimination of H_2 and C_2H_4 to form $\text{Sc}_4\text{C}_2\text{H}_2^+$ and Sc_4^+ , respectively, upon collisional activation with the latter loss dominating at all collision energies. $\text{Sc}_4\text{C}_2\text{H}_4^+$, formed from ethane, yields the same CID fragmentations, suggesting that $\text{Sc}_4(\text{CH}_2)_2^+$ formed in reaction 2 actually consists of ethene bound to the cluster or that methyldiene coupling occurs upon collisional activation. Stable bis(methyldiene) cluster complexes are known.³⁵ These results suggest that Sc_4CH_2^+ formed in reaction 1 does consist of methylene bound to the cluster and that upon collisional activation, α -hydride abstraction occurs, resulting in Sc_4CH^+ formation.

Formation of $\text{Sc}_4\text{C}_2\text{H}_4^+$ in reaction 2 may proceed by initial formation of a hydrido-methyl-methyldiene species. Migratory insertion of methyl to methyldiene followed by subsequent elimination of hydrogen forms $\text{Sc}_4(\text{ethene})^+$. Migratory insertion of an alkyl to an alkylidene is well supported in solution for cationic mononuclear alkylidene/alkyl complexes.³⁶⁻⁴² In those studies the alkylidene/alkyl insertions were facilitated by a positive charge on the metal center. It has been suggested that the positive charge renders the unsaturated carbon electrophilic and accelerates a migratory insertion which is best regarded as a migration of the alkyl group with its bonding electron pair onto the unsaturated carbon.⁴² Such a process is analogous to the well characterized alkyl/carbonyl migratory insertions.⁴³ Alternatively, formation

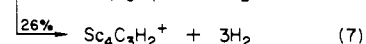
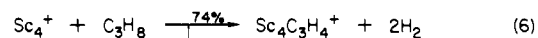
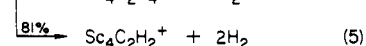
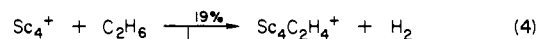
Table II. Neutral Product Losses for the Dehydrogenation Reaction of Sc_4^+ with *n*-Butane-1,1,1,4,4,4- d_6 (Losses of Less Than 2% Are Not Listed)

neutrals lost	% abundance
(H_2 , HD)	6
(H_2 , D_2) or 2HD	13
(HD, D_2)	8
(2H_2 , D_2) or (H_2 , 2HD) or 2D_2	11
(H_2 , HD, D_2) or 3HD	26
(H_2 , 2D_2) or (2HD, D_2)	26
(HD, 2D_2)	4
(2H_2 , 2D_2) or (H_2 , D_2 , 2HD) or 4HD	3

of $\text{Sc}_4(\text{ethene})^+$ in reaction 2 may proceed by initial formation of a bis(methyl) complex followed by formation of ethane which undergoes subsequent dehydrogenation.

No CID studies were carried out on $\text{Sc}_4(\text{CH}_2)_3^+$ and $\text{Sc}_4(\text{CH}_2)_4^+$ formed in reaction 2. Recently, carbon-carbon chain growth has been observed for methylene addition to cluster-bound unsaturates.⁴⁴ Absence of formation of more highly unsaturated products in reaction 2 *vide infra*, however, suggests that methylene addition to cluster-bound ethene is not occurring. The $\text{Sc}_4(\text{CH}_2)_4^+$ formed in reaction 2 may, therefore, consist of a bis(ethene) cluster structure.

Ethane and Propane. Both ethane and propane react with Sc_4^+ yielding exclusively dehydrogenation products, reactions 4-7. Absence of any C-C bond cleavage products indicates that oxidative addition of the cluster across C-C bonds is unfavorable.



Dehydrogenation reactions with aliphatic alkanes are characteristic of early transition-metal atomic cations;^{17,28,45} however, the large amount of unsaturation observed with Sc_4^+ is unusual. For example, Sc^+ reacts with ethane to yield 94% loss of H_2 and 6% loss of 2H_2 ,²⁸ whereas reaction with Sc_4^+ results in 81% elimination of 2H_2 . Increased reactivity toward hydrogen elimination in aliphatic alkanes has also been observed recently for the trinuclear cluster FeCo_2^+ ^{12,29} compared to the atomic species Fe^+ and Co^+ .¹⁴⁻¹⁸

Elimination of H_2 and C_2H_4 is the only fragmentation observed for collisional activation of $\text{Sc}_4\text{C}_2\text{H}_4^+$ produced from ethane. CID of $\text{Sc}_4\text{C}_2\text{H}_2^+$ generated from ethane yields efficient elimination of C_2H_2 as the only fragmentation. These results suggest formation of ethene and ethyne cluster ions with ethane. Recently, a novel rearrangement of a bis(methyldiene) cluster involving simultaneous coupling and decoupling of carbyne fragments has been reported.⁴⁶ In addition, a ruthenium cluster has been shown to cleave the C-N triple bond of an isocyanide ligand.⁴⁷ It appears, however, that the Sc_4^+ cluster is unable to cleave the triple bond of ethyne.

CID of $\text{Sc}_4\text{C}_3\text{H}_4^+$ formed from propane yields facile elimination of H_2 with some elimination of 2H_2 observed at high kinetic energy forming Sc_4C_3^+ , a polycarbide species.⁴⁸ Although there are several examples of carbido-metal clusters, there are only a few polycarbide clusters known.^{49,50} The above Sc_4C_3^+ species

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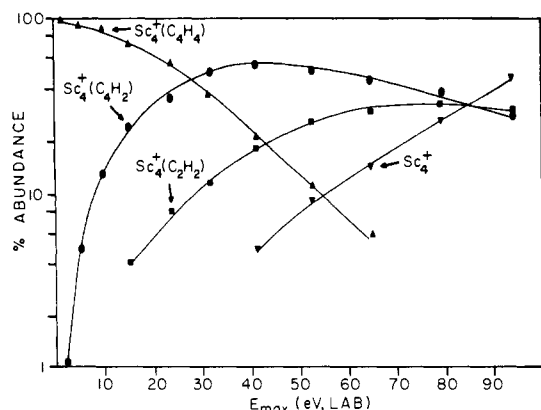
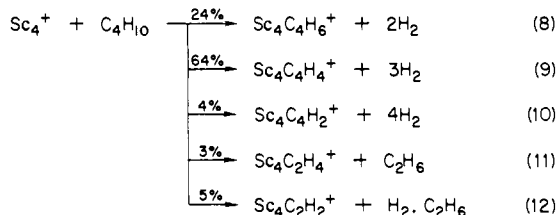


Figure 3. Variation of CID product ion intensities as a function of kinetic energy for $\text{Sc}_4\text{C}_4\text{H}_4^+$ formed in reaction 9.

probably consists of a peripheral tricarbide cluster rather than the more common cage carbides.⁵¹

Secondary reactions are observed with both ethane and propane. These reactions occur readily and appear to be dominated by hydrogen elimination. Multiple hydrogen losses are observed in the secondary chemistry, but they are much less abundant than those observed for the primary reactions. No carbon chain cleavages are observed in the secondary chemistry of either alkane.

Reactions with *n*-Butane. Multiple hydrogen elimination is the major process observed for the primary reaction of Sc_4^+ with *n*-butane, reactions 8–10. In addition, a small amount of carbon-carbon bond cleavage also occurs, reactions 11 and 12.

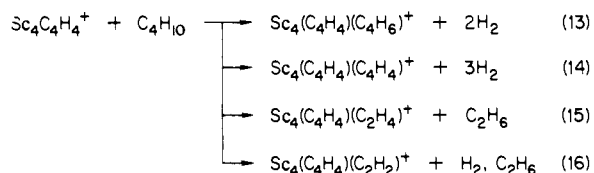


Reaction of Sc_4^+ with *n*-butane-1,1,1,4,4,4- d_6 results in a considerable amount of deuterium scrambling, Table II. Although the results of this experiment provide minimal structural and mechanistic information, they do suggest that fast, reversible hydrogen shifts probably occur in this complex.⁵²

Compared with the atomic metal ion Sc^+ , the chemistry of Sc_4^+ with *n*-butane is significantly different. The atomic metal ion dehydrogenates alkanes to a lesser degree and forms a greater abundance of carbon-carbon bond cleavage products than does the cluster. The most striking difference is the complete absence of the bis-methyl complex ($\text{H}_3\text{C}-\text{Sc}_4^+-\text{CH}_3$), which is seen as a major product in the reaction of the atomic ion with butane.²⁸

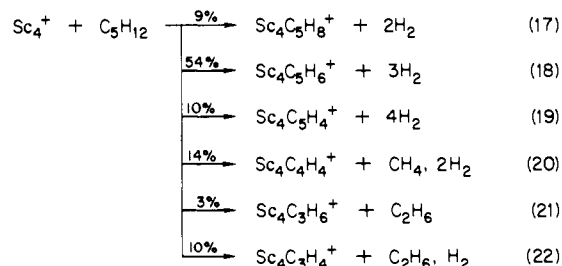
CID of $\text{Sc}_4\text{C}_4\text{H}_4^+$ generated by reaction 9 gives the loss of H_2 exclusively at low energies. At higher energies, the loss of C_2H_2 and C_4H_4 become competitive routes for ion fragmentation as shown in Figure 3. The $\text{Sc}_4\text{C}_4\text{H}_2^+$ formed by reaction 10 did not undergo collision-induced dissociation within the energy range of our FTMS.

Secondary reactions also occur readily for the primary ions formed in reactions 8–12. For example, $\text{Sc}_4\text{C}_4\text{H}_4^+$ reacts with *n*-butane to generate the products shown below, reactions 13–16.



It is interesting to note that carbon-chain cleavage is much more abundant in the secondary chemistry than in the primary chemistry of *n*-butane.

***n*-Pentane and *n*-Hexane.** Although hydrogen elimination is still the major reaction pathway, both *n*-pentane and *n*-hexane yield a significant percentage of carbon-carbon bond cleavage products when reacted with Sc_4^+ . The primary reactions of pentane are given below (reactions 17–22). For reactions with *n*-hexane, refer to Table I.

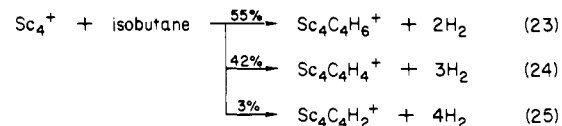


With the larger alkanes, multiple-loss fragments form the greatest percentage of the carbon-chain cleavage products, generating complexes with small, highly unsaturated hydrocarbon ligands bound to the metal cluster ion. Reaction 18 may involve a dehydrocyclization generating formally a cyclopentadiene cluster complex.⁵³ Both CoFe^+ and FeCo_2^+ appear to induce dehydrocyclizations in linear C_5 and C_6 hydrocarbons.^{11,12,29}

As is the case with the smaller alkanes, both *n*-pentane and *n*-hexane undergo secondary reactions with their respective neutrals. These processes are dominated by the loss of one or more hydrogen molecules from the neutral alkane. Some carbon-chain cleavage is also observed in the secondary chemistry of both of these alkanes.

As was found to be the case with *n*-butane, the extent of dehydrogenation produced by Sc_4^+ is greater than that for the corresponding atomic ion, Sc^+ . Although both the cluster and the atomic metal ions generate multiple losses in conjunction with carbon-chain cleavage, once again the cluster ion does not form any of the dialkyl ions which are abundantly formed with the atomic scandium ion.²⁸

2-Methylpropane. Reactions with the simplest of the branched alkanes, 2-methylpropane (isobutane), give a primary product distribution which is intermediate between that of *n*-propane and *n*-butane as can be seen from reactions 23–25. Multiple hydrogen losses are more abundant for 2-methylpropane than for *n*-propane; however, no carbon-carbon bond cleavage is observed as it is with *n*-butane (about 8%). The loss of 2 molecules of hydrogen is the



most abundant product, possibly forming a metal-trimethylene methane species. Alternatively, rearrangement to a linear C_4 backbone may occur.⁵⁴

2,2-Dimethylpropane and 2-Methylbutane. Both 2,2-dimethylpropane (neopentane) and 2-methylbutane react readily with Sc_4^+ . The behavior of these two alkanes is very similar to

(50) (a) Brice, M. D.; Penfold, B. R. *Inorg. Chem.* **1972**, *11*, 1381. (b) Brice, M. D.; Penfold, B. R. *Inorg. Chem.* **1972**, *11*, 3152. (c) Albano, V. G.; Braga, D.; Ciani, G.; Marginengo, S. *J. Organomet. Chem.* **1982**, *213*, 293.

(51) For the first example of a peripheral dicarbide metal carbonyl cluster see: Gervasio, G.; Rossetti, R.; Stanghellini, P. L.; Bor, G. *Inorg. Chem.* **1984**, *23*, 2073.

(52) Reversible β -hydride transfers have been observed previously in gas-phase metal ion chemistry. See for example: (a) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1976**, *98*, 7445. (b) Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1979**, *101*, 4998. (c) Reference 26b. (d) Reference 15c. (e) Reference 16a. (f) Carlin, T. J.; Sallans, L.; Cassady, C. J.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 6320.

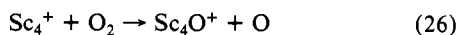
(53) Dehydrocyclizations are commonly observed on surfaces. See, for example: (a) Zoltan, P. *Adv. Catal.* **1980**, *29*, 272. (b) Bragin, O. V.; Krasavin, S. A. *Russ. Chem. Rev.* **1983**, *52*, 625.

(54) Co^+ dehydrogenates 2-methylpropane forming the rearrangement product $\text{Co}(\text{butadiene})^+$ and not $\text{Co}(\text{trimethylene})^+$. Hettich, R. L.; Jacobson, D. B.; Freiser, B. S., unpublished results.

that of *n*-pentane, giving almost identical product distributions (see Table I). This is somewhat unusual, particularly for the case of 2,2-dimethylpropane, since there are no β -hydrogens available for dehydrogenation by a 1,2-elimination. Reversible methyl shifts leading to rearrangement of the alkane could provide an explanation in analogy to the observation of rearrangement of 2,2-dimethylpropane to 2-methylbutane observed on surfaces.⁵⁵ The presence of carbon-carbon bond cleavage products suggests that C-C bond insertion is a competitive process.

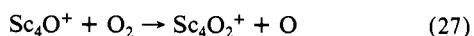
Reactions with Miscellaneous Compounds. In addition to the alkanes, a few other compounds were also reacted with Sc_4^+ in order to gain a better overall perspective of the cluster's chemical behavior. These compounds include oxygen, benzene, methanol, and ethylene sulfide.

Oxygen. Reaction of Sc_4^+ with dioxygen occurs readily at a pressure of 2×10^{-7} torr, eliminating O exclusively, reaction 26.



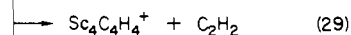
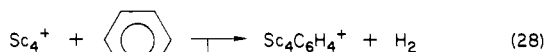
This indicates that $D(\text{Sc}_4^+-\text{O}) > 119 \text{ kcal mol}^{-1}$.³² Attempts to dissociate this ion by CID were unsuccessful as might be expected due to the strong metal-oxygen bond. The dimers Mn_2^+ , Fe_2^+ , Co_2^+ , and CoFe^+ all abstract an oxygen atom from dioxygen.^{56,57}

The Sc_4O^+ formed by reaction 26 reacts again with O_2 to generate Sc_4O_2^+ as the only product, reaction 27. After the

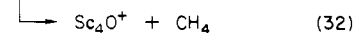
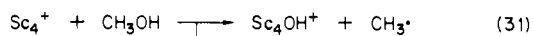


attachment of the second oxygen atom to the cluster ion, no further reaction was observed to occur, even at elevated pressures (5×10^{-6} torr) and long trapping times (2 s). No CID products were observed for the dioxide cluster ion within the energy range available with the FTMS, indicating that a coupling of oxygen atoms forming dioxygen does not occur.

Benzene. Benzene reacts with the scandium tetramer ion to produce hydrogen elimination as well as ring cleavage products. Stable benzyne complexes have been reported for nickel,⁵⁸ tantalum,^{58,59} and niobium⁶⁰ and are known for several cluster compounds.⁶¹ Although the dehydrogenation of benzene has been observed with Y^+ ,⁶² cleavage of the ring structure is quite unusual and attests to the highly reactive nature of this cluster ion. Reactions 28-30 occur readily at a sample pressure of 2×10^{-7} torr. Each of the primary reaction product ions reacts further with benzene to eliminate H_2 .



Methanol. Because of its strong metal-oxygen bond, the reactions of Sc_4^+ with methanol are, not surprisingly, dominated by cleavage of the C-O bond. Both a metal hydroxide and a metal oxide species are generated in the primary reactions 31 and 32.



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(56) Armentrout, P. B.; Loh, S. K.; Ervin, K. M. *J. Am. Chem. Soc.* **1984**, *106*, 1161.

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(58) Gowling, E. W.; Kettle, S. F. A.; Sharples, G. M. *Chem. Commun.* **1968**, 21.

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(60) McLain, S. J.; Schrock, R. R.; Sharp, P. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 263.

(61) (a) Brown, S. C.; Evan, J.; Smart, L. E. *J. Chem. Soc., Chem. Commun.* **1980**, 1021. (b) Deeming, A. J.; Rothwell, I. P.; Hursthouse, M. B.; Backer-Dirks, J. D. *J. Chem. Soc., Dalton Trans.* **1981**, 1879. (c) Adams, R. D.; Katahira, D. A.; Yang, L.-W. *Organometallics* **1982**, *1*, 235. (d) Arce, A. J.; Deeming, A. J. *J. Chem. Soc., Dalton Trans.* **1982**, 1155.

(62) Wise, M. B. Ph.D. Thesis, Purdue University, 1984.

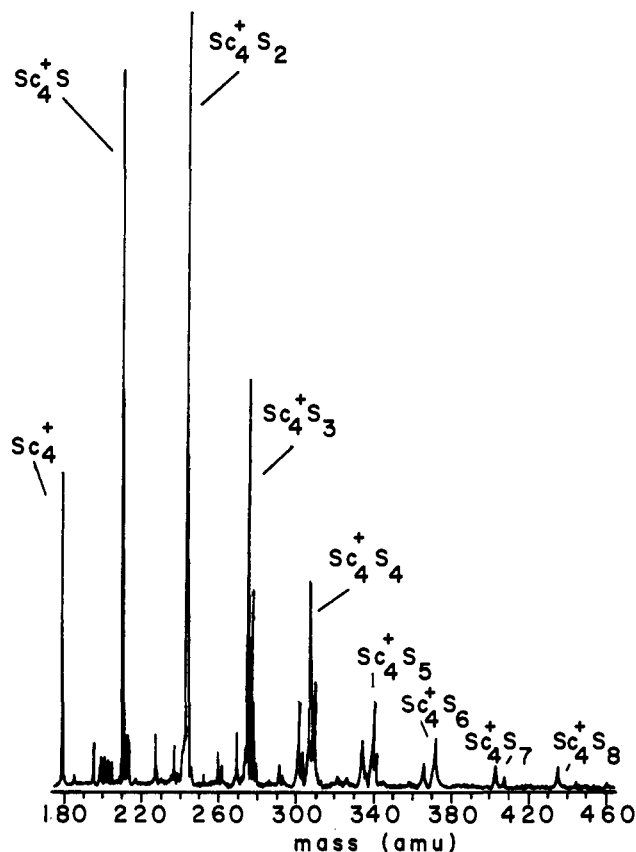
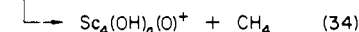
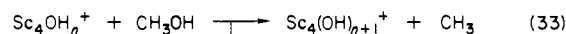


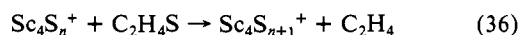
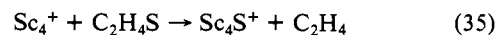
Figure 4. Mass spectrum of the products generated from Sc_4^+ and ethylene sulfide at 2×10^{-7} torr and 400 ms trapping time.

The primary ions, formed in reactions 31 and 32, undergo subsequent reactions of the same type with methanol, attaching up to six ligands (combinations of oxygen and hydroxides) to the metal cluster, reactions 33 and 34. These reactions are similar



to those observed when alcohols are reacted with atomic transition-metal ions such as Ti^+ ⁶³ and Y^+ .⁶²

Ethylene Sulfide. Reactions of most of the atomic transition-metal ions with ethylene sulfide have been found to form metal-polysulfide ions, with some metals attaching up to nine sulfur ligands.⁶⁴ Similar behavior is observed when the scandium tetramer is reacted with this compound at a pressure of 2×10^{-7} torr, reactions 35 and 36. It is interesting to note that a maximum



of only eight sulfur atoms can be attached to the metal cluster since one might expect that a metal cluster would be able to coordinate more ligands than an atomic metal ion. A spectrum of the reaction products observed at 2×10^{-7} torr and 400 ms trapping time is shown in Figure 4.

Conclusions

The Sc_4^+ cluster does not undergo fragmentation upon collisional activation up to ~ 100 eV kinetic energy, suggesting that it has a stable tetrahedral configuration. In its primary and secondary reactions with alkanes, Sc_4^+ exhibits an unusual propensity to form products resulting from multiple dehydrogenations. In marked contrast to Sc^+ , the cluster ion reacts with methane. Furthermore, the dialkyl products, which are so prevalent in the reactions of Sc^+ with alkanes, are totally absent in the cluster

(63) Byrd, G. D. Ph.D. Thesis, Purdue University, 1982.

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chemistry. Although dehydrogenation predominates, products arising from C-C insertion are observed for alkanes larger than propane, particularly in the secondary reactions. The Sc_4^+ cluster is observed to sequentially add 2 oxygen atoms from dioxygen and 8 sulfur atoms from ethylene sulfide. In addition to dehydrogenating benzene, formation of ring cleavage products affirms the highly reactive nature of Sc_4^+ . Finally this work demonstrates that the laser ionization-cavity source holds promise as a convenient and clean method of generating metal cluster ions for further study by FTMS.

Acknowledgment is made to the Division of Chemical Sciences in the Office of Basic Energy Sciences in the United States Department of Energy (DE-AC02-80ER10689) and the National Science Foundation (CHE-8310039) for supporting the advancement of FTMS methodology.

Registry No. Sc_4^+ , 94669-91-7; methane, 74-82-8; ethane, 74-84-0; propane, 74-98-6; butane, 106-97-8; 2-methylpropane, 75-28-5; pentane, 109-66-0; 2,2-dimethylpropane, 463-82-1; 2-methylbutane, 78-78-4; hexane, 110-54-3; butane-1,1,1,4,4,4- d_6 , 13183-67-0; oxygen, 7782-44-7; benzene, 71-43-2; methanol, 67-56-1; ethylene sulfide, 420-12-2.

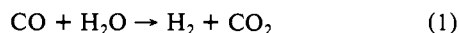
Kinetics of the $\text{Cr}(\text{CO})_6$ and $\text{W}(\text{CO})_6$ Catalyzed Water Gas Shift Reaction: Photoinitiated Formate Decomposition as a Probe of the Catalytic Cycle

Bruce H. Weiller, Jian-Ping Liu,[†] and Edward R. Grant*

Contribution from the Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853. Received September 4, 1984

Abstract: The catalytic cycle for the water gas shift reaction is initiated under mild conditions (5–65 °C) by the pulsed laser (337 nm) irradiation of $\text{M}(\text{CO})_6$ ($\text{M} = \text{Cr}, \text{W}$) in basic water/methanol solution. CO is supplied to the reaction as NaO_2CH . The cycle displays conventional saturation behavior in formate substrate concentration. The formate saturated rate (R_{max}) is enhanced by visible irradiation and is sensitive to deuterium substitution in formate ($R_{\text{max}}^{\text{H}}/R_{\text{max}}^{\text{D}} = 3.4 \pm 0.9$ and 4.4 ± 0.2 for Cr and W, respectively, at 25.0 °C). No CO inhibition in the catalytic cycle is observed, but the rate is inhibited by increasing water concentration. These observations are interpreted in terms of reversible reactions with H_2O that precede both entry into the cycle and rate-limiting decarboxylation/hydride migration within the cycle. Activation energies for the cycle are 26.0 ± 1.4 and 24.8 ± 0.8 kcal mol⁻¹ for Cr and W, respectively, and are attributed to the decarboxylation step. Rate constants for formate binding and decarboxylation along with equilibrium constants for water reactions are reported. This work demonstrates the importance of water as a coordinating ligand in the water gas shift catalytic cycle.

The water gas shift reaction (WGSR)



figures importantly in manufacturing practice, both as a means for the enrichment of synthesis gas streams in H_2 and as a side reaction of significance in hydroformylation and Fischer-Tropsch processes.¹ In industry water gas shift is promoted by heterogeneous catalysts, typically Fe_2O_3 , at high temperature and pressure ($T \approx 400$ °C, $P \approx 30$ atm).² However, several homogeneous systems exist that require less severe conditions.³ Among these are laboratory systems based on the groups 6 and 8 metal carbonyls.

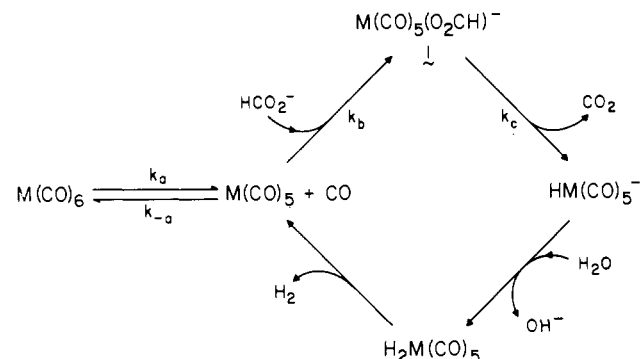
The properties of the group 6 systems are of particular interest because in basic water-methanol solution, catalysis apparently proceeds via a formate complex⁴ analogous to surface-bound formates observed in heterogeneous water gas shift.⁵ A resistance to sulfur poisoning adds further significance to this homogeneous system.⁶

The kinetics of thermally initiated catalysis of the water gas shift reaction by group 6B metal carbonyls has been thoroughly studied by King and co-workers.^{4a} They find the mechanism in Scheme I to be consistent with the data. Hydrogen evolution in this system is observed to follow a simple rate law

$$\frac{d[\text{H}_2]}{dt} = \frac{k_a k_b [\text{HCO}_2^-][\text{M}(\text{CO})_6]}{k_{-a} [\text{CO}] \quad (2)$$

The form of this expression for the rate of a catalytic process is significant. By explicitly including terms in $[\text{HCO}_2^-]$ and $[\text{CO}]$,

Scheme I



it emphasizes competitive CO dissociation/rebinding and reaction with formate by the metal complex in the *initiation* of the catalytic cycle. However, as evidenced by the absence of a term yielding saturation in formate, neither the method nor the kinetic analysis

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