

residues of the opposite pyrromethenone system. The solvent bridges the propionic acid and the pyrromethenone to form a structure which is perturbed from the usual intramolecular hydrogen-bonded conformation.

However, the resonance Raman spectra provide information about the chromophores only. The spectra contain no propionate or central bridge methylene bands or bands directly attributable to bound water or amino acid residues, if any. While Raman spectroscopy demonstrates that the intramolecular hydrogen bonds of the aqueous dianion are broken in the albumin complex, it does not directly reveal where the propionates are.

It is known that the primary bilirubin binding site is in the region of residues 190-240.^{8b} This region contains several lysines and arginines. It has previously been proposed that bilirubin

propionates bind to these sites.^{8,13} Our Raman spectra provide further evidence that this binding occurs, and that there are no new hydrogen bonds to the bilirubin lactam or pyrrole groups.

The recent circular dichroism studies of Lightner and co-workers¹⁵ may be interpreted as measuring the angle between extended pyrromethenone groups, rather than demonstrating retention of internal hydrogen bonds. With this interpretation, the circular dichroism can be reconciled with the model compound studies of Lauffer¹⁴ and with our own results.

Acknowledgment. This work was supported by National Science Foundation Grant CHE-8317861.

Registry No. 1a, 635-65-4.

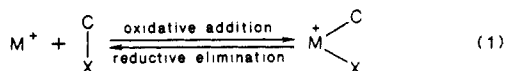
Mn(I)-Induced 1,6-Demethanation across the CC Triple Bond of Linear Alkynes in the Gas Phase. A Case for the Generation of Manganese Cycloalkynes?[†]

Christian Schulze and Helmut Schwarz*

Contribution from the Institut für Organische Chemie, Technische Universität Berlin, D-1000 Berlin 12, West Germany. Received June 15, 1987

Abstract: Complexes of Mn(alkynes)⁺ were generated in the gas phase and found to exhibit a reactivity which is even richer than that of the analogous Fe(alkyne)⁺ species. Among the many unimolecular dissociations, the Mn⁺-induced demethanation of 4-octyne is of particular interest. The study of isotopomers and the effects of alkyl chain lengths reveals the operation of an unprecedented 1,6-elimination mode across the CC triple bond, and the experimental results may be explained by invoking the intermediate generation of the as yet unknown metallacycloalkynes. The implications of the unexpected, rich gas-phase ion chemistry of Mn⁺ with regard to theoretical models are discussed.

The gas-phase chemistry of naked transition metal ions with organic substrates remains a major focus in quite different areas encompassing catalysis, organic, organometallic, and theoretical chemistry.¹ While most transition metal ions M⁺ readily undergo oxidative insertion (eq 1) in CX bonds (X = hydrogen, carbon,



halogen, nitrogen, oxygen, etc.), Mn⁺ shows a distinctly lower reactivity toward these substrates.^{1d,2,3} The decreased reactivity of Mn⁺ in comparison with, for example, Fe⁺, Co⁺, or Ni⁺ has been explained by using several qualitative theoretical concepts. Allison and Ridge^{1g,2c} ascribe the reduced reactivity of Mn⁺ to the quite high promotion energies to generate from the 3d⁵4s¹ ground-state configuration of Mn⁺ either a 3d⁴4s² or an 3d⁴4s¹4p¹ excited state, which may then be used to form two covalent bonds. Based on this concept and taking into account results from a generalized valence bond approach,⁴ it was indeed possible to establish an inverse relationship between the transition metal ion reactivity and the promotion energies of M⁺. Armentrout^{1f,2f} and Weisshaar^{2e} explain the low reactivity of Mn⁺ in terms of a frontier orbital MO concept, developed earlier by Saillard and Hoffmann.⁵ According to this, the metal insertion of a 3dⁿ4s⁰ configuration is favored over that with a 3dⁿ⁻¹4s¹ because of two favorable donor-acceptor interactions in the former. These are the interaction of the doubly occupied σ_{CX} orbital (donor) with the empty M⁺_{4s} (acceptor) and that of a doubly occupied d_{xz}, say, (donor) with

the empty σ*_{CX} (acceptor). Spin conservation also requires double occupancy of the d_{xz} which can only occur for metal ions (3dⁿ, high spin) with n > 6, i.e., for Fe⁺, Co⁺, and Ni, but not for the ground-state Mn⁺ ion.

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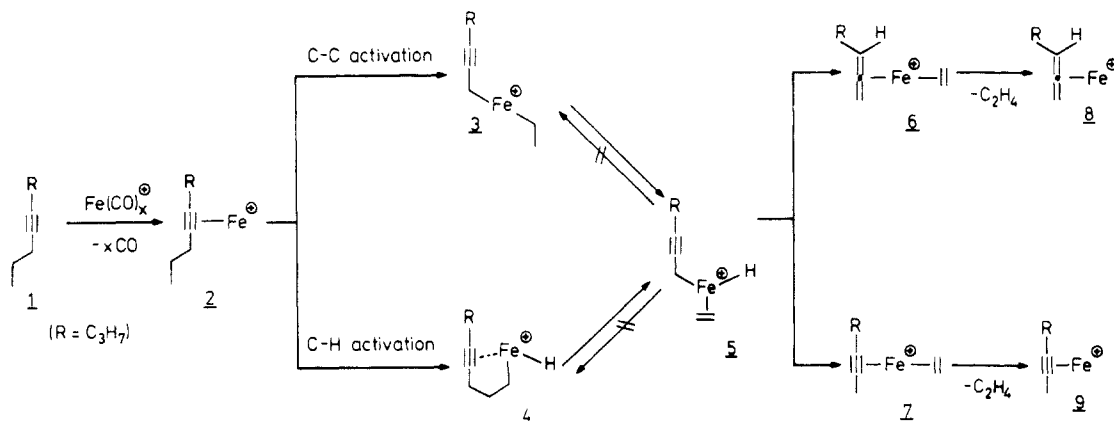
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[†] Dedicated to Professor Klaus Hafner, Darmstadt, on the Occasion of his 60th Birthday.

Scheme I



We describe here the unprecedented gas-phase reactions of Mn^+ with linear alkynes which reveal an unexpectedly rich chemistry. Among the many reactions observed, the unimolecular loss of CH_4 from $\text{Mn}^+(\text{alkyne})^+$ complexes is of particular importance as the products formed could be interpreted as first examples of the as yet unknown metallacycloalkynes with Mn^+ in a high oxidation state.⁶

Experimental Section

The experimental set-up has been described in earlier papers.^{1h,7} Briefly, Mn^+ is generated from either $\text{Mn}_2(\text{CO})_{10}$ or $\text{Mn}(\text{CO})_5(\text{CH}_3\text{-c-C}_3\text{H}_4)$ by electron impact ionization. In a typical experiment the organometallic compound and the alkynes (in a ratio 1:5–10) were introduced simultaneously via the gas inlet system in the chemical ionization source of a Vacuum Generator ZAB-HF-3F triple sector mass spectrometer of BEB configuration (B denotes magnetic and E electric sector).⁸ Experimental conditions were as follows: ionization energy, 100 eV; emission current, 0.5 mA; repeller voltage, 0 V; acceleration voltage, 8 kV; mass resolution, 2000–5000 (10% valley definition); ion source pressure, 10^{-5} mbar; ion source temperature, 200 °C. The Mn^+ /hydrocarbon complexes were formed by reaction of $\text{Mn}(\text{CO})_x^+$ ions and the appropriate hydrocarbon. The so-formed organometallic complexes, having 8 keV kinetic energy, were mass-selected and focused with B(1)E, and the unimolecular dissociations occurring in the field-free region between E and B(2) were monitored by scanning B(2). The data reported correspond to the average of 10–100 spectra which were accumulated using the VG 11/250 data system. All alkynes, including the D-labeled isotopomers, were purified by gas chromatography and fully characterized by NMR spectroscopy and mass spectrometry (MS). The deuterium content was determined by MS.

In view of the fact that electron impact ionization of $\text{Mn}_2(\text{CO})_{10}$ generates electronically excited Mn^+ ions⁹ having radiative lifetimes of the order of microseconds,¹⁰ we have generated Mn^+ species also by fast atom bombardment (FAB)¹¹ of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. This method, which is believed¹² to generate ground-state metal ions, has recently proved^{2d,13} to be a convenient means to generate metal ion complexes in the gas phase. To this end, Mn^+ is generated by bombarding a solid $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ target with 8 kV xenon atoms, and the sputtered Mn^+

(or Mn^+ complexes of higher mass) react in the gas phase with hydrocarbons to form the $\text{M}^+(\text{alkyne})^+$ complexes which, after extraction from the ion source, are mass-selected and analyzed as described above.

Results and Discussion

The metastable ion (MI) mass spectrum of $\text{Mn}(\text{4-octyne})^+$ is given in Figure 1b, and for comparison we also give the MI spectrum of $\text{Fe}(\text{4-octyne})^+$ (Figure 1a). Unimolecular loss of C_2H_4 from the latter has been studied in great detail,^{1h,14,15} and the mechanism depicted in Scheme I accounts for all experimental findings.

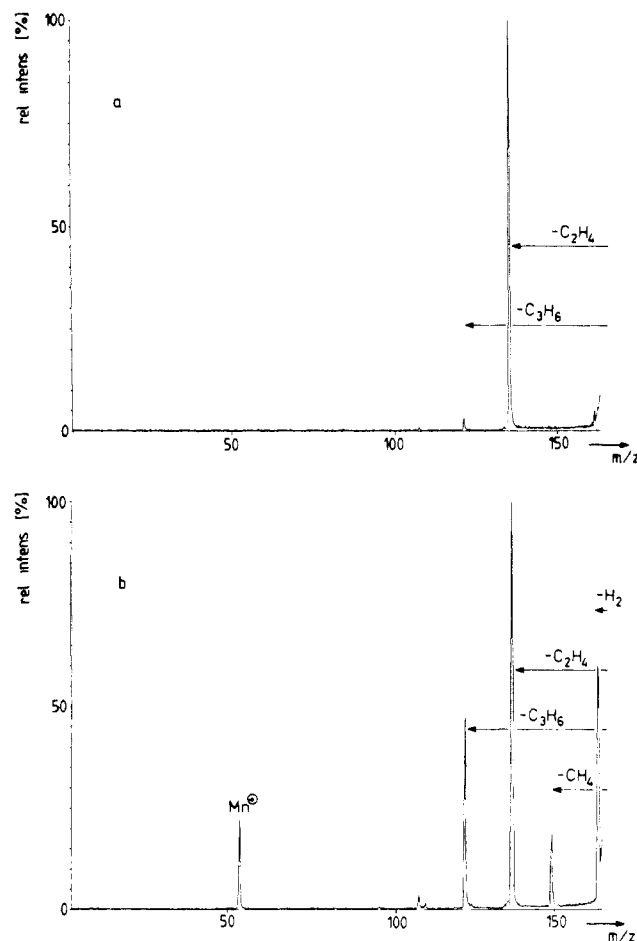


Figure 1. Metastable ion (MI) mass spectra of (a) $\text{Fe}(\text{4-octyne})^+$ (generated from $\text{Fe}(\text{CO})_5$ and 4-octyne according to ref 1h, 14) and (b) $\text{Mn}(\text{4-octyne})^+$ (generated from $\text{Mn}_2(\text{CO})_{10}$ and 4-octyne). It should be noted that, except for minor intensity differences, the same MI spectra were obtained when the $\text{Mn}(\text{4-octyne})^+$ complex was generated from $\text{Mn}_2(\text{CO})_{10}$, $\text{Mn}(\text{CO})_5(\text{CH}_3\text{-c-C}_6\text{H}_4)$ (both electron impact ionization) or $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (FAB).

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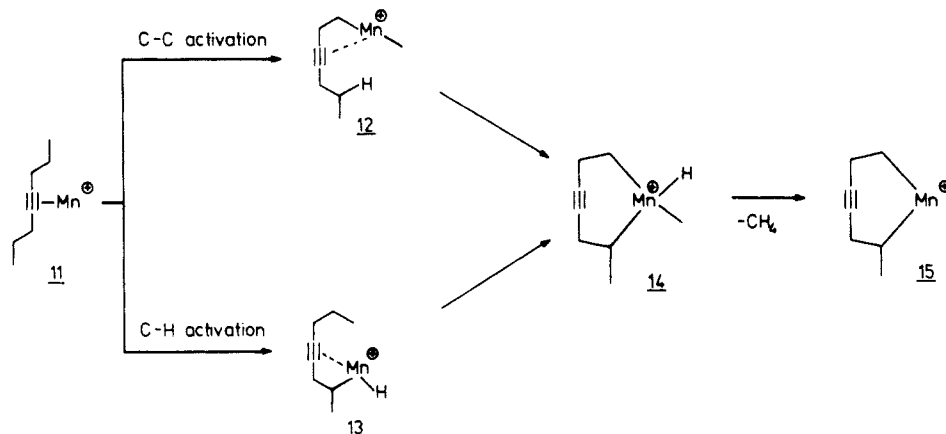
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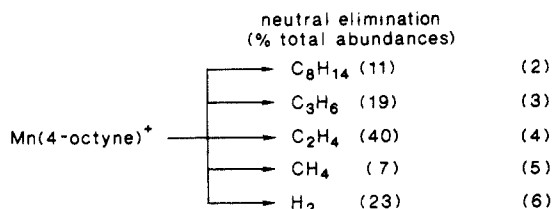
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Scheme II



The ethylene-hydrido complex **5** is, presumably, generated in competition via oxidative addition of the CC (**2** → **3**) or the CH bond (**2** → **4**) to the π -complexed Fe^+ , followed by irreversible hydrogen migration (**3** → **5**) or cleavage of the propargylic CC bond (**4** → **5**). By probing the structure¹⁶ of the ethylene decomposition products, Gross et al.¹⁵ were able to show that **8** and **9** are formed in an approximate ratio of 1.5:1. This implies that migration of the Fe^+ -bound hydrogen to the acetylenic carbon atom (**5** → **6**) is kinetically favored over migration to the propargylic carbon atom (**5** → **7**), a result which has also been observed in other cases.^{1h,15}

In view of the previously reported low reactivity of Mn^+ , the behavior of the $\text{Mn}(4\text{-octyne})^+$ complex is completely unexpected. At best, one might have expected detachment of Mn^+ to occur (eq 2), a reaction which is indeed observed. However, the majority of the $\text{Mn}(4\text{-octyne})^+$ ions decompose via a multitude of competing processes (eq 3–6). The branching ratios of these reactions are



practically insensitive to the mode of generation of the $\text{Mn}(4\text{-octyne})^+$ complexes.

By using the time-honored "labeling approach" we have tried to elucidate the mechanisms by which the various neutrals are formed from $\text{Mn}(4\text{-octyne})^+$. However, except for the loss of hydrogen, which involves to 83% the 1,2 and to 17% the 2,3 positions of 4-octyne (with an average kinetic isotope effect $k_{\text{H}_2}/k_{\text{HD}} = 1.70$), and which is described as a metal-induced 1,2-dehydrogenation, and that of CH_4 , the presently available set of data does not permit us to draw any definitive conclusions. Therefore, in the following we will refrain from any speculation concerning these reactions and will rather confine ourselves to a discussion of the Mn^+ -induced demethanation of 4-octyne. This reaction turned out to follow a quite remarkable mechanism.

From the data given in Table I the following conclusions can be drawn with regard to the loss of methane. (i) Methane is formed from a terminal methyl group, which is not surprising, and an additional hydrogen; the latter is provided by one of the methylene groups. Absence of loss of CH_3D in the spectrum of **10c** rules out that the fourth hydrogen is provided by the second methyl group. Thus, a formal 1,7-elimination is not operative.

(16) Suggested structures are hypothetical in nearly all cases studied in mass spectrometry; they are based on plausible considerations using as much direct and indirect evidence as available from experiments and model considerations. Strictly speaking, none of the structures are proven. Nevertheless, the heuristic values of such structural representations are undeniable in chemistry, as long as speculation remains within acceptable limits.

Table I. Unimolecular Loss of $\text{CH}_{4-x}\text{D}_x$ ($x = 0-4$) from Labeled $\text{Mn}(4\text{-octyne})^+$ complexes^a

$\text{CH}_{4-x}\text{D}_x$	$\text{C}_3\text{H}_7\text{C}\equiv\text{CR}^b$				
	10	10a	10b	10c	10d
CH_4	100	85.1	61.4	58.7	10.0
CH_3D		14.9	38.6		41.4
CH_2D_2					
CHD_3				41.3	48.6
CD_4					

^a Data are given in % $\Sigma\text{CH}_{4-x}\text{D}_x$. Errors are $\pm 2\%$ of reported data.
^b **10**, R = C_3H_7 ; **10a**, R = $\text{CD}_2\text{C}_2\text{H}_5$; **10b**, R = $\text{CH}_2\text{CD}_2\text{CH}_3$; **10c**, R = $(\text{CH}_2)_2\text{CD}_3$; **10d**, R = $\text{CH}_2\text{CD}_2\text{CD}_3$.

Table II. Metastable Ion Spectra of $\text{Mn}(\text{alkyne})^+$ Complexes^a

neutral lost	$\text{C}_3\text{H}_7\text{C}\equiv\text{CR}^b$			
	10	16	17	18
H_2	23	23	7	12
CH_4	7	5		
C_2H_4	40	36	37	21
C_3H_4			1	
C_3H_6	19	13	2	
Alkyne	11	23	53	67

^a Data are given in % Σ neutrals. ^b **10**, R = C_3H_7 ; **16**, R = C_2H_5 ; **17**, R = CH_3 ; **18**, R = H.

Similarly, the absence of CD_4 loss in the spectrum of **10d** suggests that a 1,1-elimination, by which a manganese-carbyne complex would have been generated, can also be ruled out. (ii) The losses of CH_3D (14.9%) from **10a** and CH_4 (10%) from **10d** can be interpreted as the result of either a conventional 1,2-elimination mode or a 1,5-elimination across the CC triple bond. A distinction between these mechanistic variants cannot be achieved by the present set of labeling data. (iii) The elimination of CH_3D (41.4%) from **10d** leaves no doubt that $>83\%$ of the total methane loss is due to an *unprecedented 1,6-elimination*. A mechanism which is in keeping with this unexpected labeling result is depicted in Scheme II. Addition of either a CC (**11** → **12**) or a CH bond (**11** → **13**) to the complexed manganese ion **11** generates intermediates which may further rearrange to the manganese-cycloheptyne cation **14**; the latter would then serve as direct precursor for the reductive elimination of methane to generate **15**. While metallacycles are often invoked or experimentally indicated to act as intermediates in gas phase reactions of transition metal ions,^{1b,c,g,6,7,17} we are fully aware that in none of the previously reported cases were CC multiple bond containing metallacycles involved. We, therefore, stress that the labeling results do not prove the existence of **14** and **15**, although it is difficult to conceive other, chemically more reasonable, pathways which would account for the unusual 1,6-elimination mode. As suggested by a referee it is interesting to note that each step of the mechanism proposed

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in Scheme II is consistent with the latest values for the Mn^+-H and Mn^+-CH_3 bond energies.^{2f,g} By using these values and average bond energies for $(\text{CH}_2)-\text{H}$ and $(\text{CH}_2)-\text{CH}_3$ bonds, we estimate an upper limit on strain energy for the manganese-cycloheptyne species **14** of 18 kcal/mol.

The Mn^+ -induced demethanation across the triple bond of acetylenes is also reflected if one generates $\text{Mn}(\text{alkyne})^+$ complexes with shorter alkyl chain length. This can be clearly seen from the data of the $\text{Mn}(\text{alkyne})^+$ complexes given in Table II. While CH_4 loss is found for both **10** and **16**, the reaction is not observed for **17** and **18**. This is, presumably, a direct consequence of the fact that for smaller alkynes the formation of metallacycles analogous to **14** is no longer possible. Instead, reactions dominate in which either the ligand is detached from the $\text{Mn}(\text{alkyne})^+$ complex or processes occur which involve the C_3H_7 unit (loss of H_2 and C_2H_4) only.

Conclusions

In contrast to previous reports, Mn^+ is not necessarily an unreactive transition metal ion in the gas phase. In the present system its reactivity with alkynes is even higher than that of the analogous $\text{Fe}(\text{alkyne})^+$ complexes which were previously thought of having the highest reactivity. Our results imply that either the hitherto used concepts for the oxidative addition of CX bonds to transition metal ions deserve a reconsideration of, alternatively, that the Mn^+ ions generated upon both electron impact (EI) and fast atom bombardment (FAB) are electronically excited, thus generating reactive species. While the formation of electronically excited Mn^+ upon electron impact ionization has been reported earlier,^{2f,g,18}

this possibility has not yet been considered for the FAB experiments.^{2d,12} The identical behavior of the $\text{Mn}(\text{4-octyne})^+$ complexes, generated via EI or FAB, strongly suggests that metal ions of the same electronic state distribution are formed, in which the excited ones are likely to cause the CH and CC activation.¹⁸

Mn^+ -induced demethanation of 4-octyne follows to >83% a formal 1,6-elimination.¹⁹ This unprecedented result could be interpreted by the formation of as yet unknown metallacycloalkyne intermediates. The study of labeled isotopomers and of the effects of chain length is in keeping with this interpretation.

Acknowledgment. We gratefully acknowledge support of our work by the following institutions: Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie, Stiftung Volkswagenwerk, and Technische Universität Berlin.

Registry No. **10**, 1942-45-6; **10a**, 108686-71-1; **10b**, 108686-72-2; **10c**, 81186-40-5; **10d**, 108686-73-3; **16**, 2586-89-2; **17**, 764-35-2; **18**, 107-00-6; $\text{Mn}(\text{CO})_3(\text{CH}_3-\text{c}-\text{C}_3\text{H}_4)$, 12108-13-3; $\text{Mn}_2(\text{CO})_{10}$, 10170-69-1; Mn^+ , 14127-69-6; CH_4 , 74-82-8; CH_3D , 676-49-3; CHD_3 , 676-80-2; H_2 , 1333-74-0; C_2H_4 , 74-85-1; C_3H_4 , 74-99-7; C_3H_6 , 115-07-1.

(18) Beauchamp et al. (Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 962) mention very briefly in a footnote that the reactivity of excited-state Mn^+ (produced by electron impact of $\text{Mn}_2(\text{CO})_{10}$) with alkanes differs markedly from the reactions of ground-state ions.

(19) Co(I)-induced 1,5-demethanation of *n*-hexane does not, as interpreted by Allison (ref 1c), result in the formation of a saturated cobalt metallacycle. Instead, deuterium-labeling data are interpreted in the original paper⁶ in terms of the conventional reaction sequence, i.e., a combination of CC and CH insertion reactions, thereby bypassing high oxidation states of Co⁺.

Chemisorption on Size-Selected Metal Clusters: Activation Barriers and Chemical Reactions for Deuterium on Aluminum Cluster Ions

Martin F. Jarrold* and J. Eric Bower

Contribution from AT&T Bell Laboratories, Murray Hill, New Jersey 07974.

Received July 6, 1987

Abstract: We describe a new approach to investigating chemisorption on size-selected metal clusters. This approach involves investigating the collision-energy dependence of chemisorption using low-energy ion beam techniques. The method provides a direct measure of the activation barrier for chemisorption and in some cases an estimate of the desorption energy as well. We describe the application of this technique to chemisorption of deuterium on size-selected aluminum clusters. The activation barriers increase with cluster size (from a little over 1 eV for Al_{10}^+ to around 2 eV for Al_{27}^+) and show significant odd-even oscillations. The activation barriers for the clusters with an odd number of atoms are larger than those for the even-numbered clusters. In addition to chemisorption of deuterium onto the clusters, chemical reactions were observed, often resulting in cluster fragmentation. The main products observed were $\text{Al}_{n-1}\text{D}^+$, Al_{n-2}^+ , and Al^+ for clusters with $n < 10$, and Al_nD^+ and $\text{Al}_{n-1}\text{D}^+$ for the larger clusters.

I. Introduction

Metal clusters might be considered as microscopic surfaces, and while there is an obvious relationship between chemisorption on surfaces and on bare metal clusters, we might anticipate that size, electronic properties, and geometric structure could influence chemisorption on the clusters. Since the application of the fast-flow reactor techniques to studying the chemistry of metal clusters¹⁻³ many cases have been identified in which the reaction

rates show a strong cluster-size dependence. Several attempts have been made to account for these changes in reactivity, invoking either the electronic properties⁴⁻⁷ or geometric structure.⁸ The cluster-size dependence presumably results from changes in the height of the activation barrier associated with chemisorption, or changes in the stability of the adduct. However, it is often difficult to determine which of these factors is responsible.

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