J. Phys. Chem. **1989**, *93*, 3667–3673

Heterodinuclear Transition-Metal Cluster Ions in the Gas Phase. Thermochemistry and Reactivity of $NbFe^+$ and $NbFeL^+$ (L = O, CO, H_2O, and Alkenes)

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(Received: March 14, 1988; In Final Form: July 25, 1988)

We report on the gas-phase chemistry of $NbFe^+$. $NbFe^+$ was prepared by reacting laser-desorbed Nb^+ with $Fe(CO)_5$ to produce $NbFe(CO)_3^+$ and $NbFe(CO)_2^+$, which both undergo collisional activation by sequential loss of carbonyl ligands to produce $NbFe^+$. $NbFe^+$ is unreactive with small linear, cyclic, and branched alkanes, in contrast to the reactivity of Nb^+ and Fe^+. However, $NbFe^+$ is much more reactive than its first-row analogue, VFe^+, in that it reacts with alkenes larger than ethene, whereas VFe^+ is unreactive with linear C2–C6 alkenes. The presence of an allylic bond appears necessary in reactions with alkenes. Dehydrogenation is the main reaction pathway with C–C bond cleavage observed only for 3,3-dimethyl-1-butene, which contains no allylic C–H bonds. $NbFeL^+$ (L = alkene ligand) undergoes more extensive dehydrogenation in its reactions with alkenes than does $NbFe^+$, as has been observed for other dinuclear cluster ion species. Dehydrocyclization occurs in the reactions of $NbFe^+$ with linear C5 and C6 alkenes. Loss of Fe is observed in the reactions of the cluster with larger (C5–C7) cyclic alkenes, and bis(cycloalkene) cluster structures are formed in reactions with cyclopentene, methylcyclohexene, and cycloheptene. $NbFeC_7H_8^+$ generated from cycloheptene and methylcyclohexene yield different collision-induced dissociation (CID) spectra indicating isomeric structures. Reactions of $NbFe^+$ and $NbFeL^+$ (L = CO, O) with dioxygen and ethylene oxide indicate 85 kcal/mol < $D°(NbFe^+\text{–}O)$, and 119 kcal/mol < $D°(NbFeO_n^+\text{–}O)$ (n = 1, 2). $NbFeO_3^+$ undergoes an unusual reaction with ethylene oxide via abstraction of H_2O, indicating $D°(NbFeO_3^+\text{–}H_2O) > 9$ kcal/mol. The oxidized cluster ions are very stable toward collision-induced dissociation with products corresponding only to cleavage of the metal–metal bond resulting. However, $NbFeO_3H_2O^+$ undergoes facile loss of H_2O upon collision-induced dissociation. Other thermochemical limits derived from ion–molecule reactions and CID spectra include $D°(Nb^+\text{–}Fe) > 60$ kcal/mol, $D°(NbFe^+\text{–benzene}) > 30$ kcal/mol, $D°(Nb^+\text{–benzene}) = 66 \pm 7$ kcal/mol, $IP(NbC_7H_8) < 7.87$ eV, IP(NbFe) < 8.8 eV, and $IP(FeC_5H_6) > 6.9$ eV.

Introduction

Many new techniques have been developed recently for studying the reactivity of small metal clusters.[1] These developments have been spurred on by the prospect of gaining a deeper understanding of the fundamental processes involved in homogeneous and heterogeneous catalysis. Particularly important in studying the chemistry of small clusters is the ability to determine size-dependent properties. Gas-phase ionic clusters have advantages over neutral clusters in this respect, since neutral cluster techniques do not allow size selection and, in addition, fragmentation often occurs during the ionization process prior to detection. Also, many well-developed mass spectrometric techniques, including sequential reaction monitoring, kinetic energy selection, and ion trapping are available for the study of ionic clusters.

Previous studies have indicated that most dinuclear cluster ions are relatively unreactive compared to their atomic ion constituents.[2,3] Although the reasons for this are not completely understood at present, the origins of the reduced reactivity of most dinuclear cluster ions with alkanes ($CoFe^+$, VFe^+, $CuFe^+$, Co_2^+, Fe_2^+) is surely related to the electronic structure and bonding in these species.[2] As part of our continuing studies on heterodinuclear cluster ions, we report on the gas-phase chemistry of $NbFe^+$. These results yield a variety of thermochemical values including limits and absolute bond energies for $NbFe^+$, $NbFeL^+$, and NbL^+.

Experimental Section

All experiments were carried out using a prototype Nicolet FTMS-1000 Fourier transform mass spectrometer previously described in detail.[4] Briefly, the instrument is equipped with a 5.2-cm cubic trapping cell with 80% transmittance stainless steel screens as the transmitter plates. The cell is situated between the poles of a Varian 15-in. electromagnet maintained at 0.9 T. Metal ions were produced by focusing the frequency-doubled beam (532 nm) of a Quanta Ray Nd:YAG laser onto a high-purity block of Nb supported on the transmitter screen nearest the laser.[5]

Reagent chemicals were obtained commercially in high purity and used as supplied except for multiple freeze–pump–thaw cycles to remove noncondensible gases. $Fe(CO)_5$ was introduced into the cell via a pulsed valve that has previously been described in detail.[6] The pulsed valve alleviates complicating secondary reactions between the cluster and the parent carbonyl by permitting the $Fe(CO)_5$ to be pumped away before isolation of the $NbFe^+$. Hydrocarbon and oxygen reagent gases were present in the cell at a total static pressure of $\sim 2 \times 10^{-7}$ Torr. Argon was present in the cell at a total static pressure of $\sim 2 \times 10^{-6}$ Torr. The argon was used as the collision gas for collision-induced dissociation (CID),[7] as well as for cooling any excited cluster ions with thermalizing collisions before reaction.[8] $NbFe^+$ undergoes ~50 thermalizing collisions with background gas prior to reaction. The temporal decay of $NbFe^+$ during reaction with 1-butene was observed to follow linear pseudo-first-order kinetics for ~2 half-lives of the parent intensity, supporting the proposal that the majority of the ions are thermalized. However, the presence of a small population of nonthermal ions cannot be completely ruled out.

$NbFe^+$ was prepared by a method developed in our laboratory.[9] Briefly, laser-desorbed Nb^+ reacts with $Fe(CO)_5$ by reactions 1

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and 2. The product carbonyl ions were then accelerated to permit collision-induced dissociation (CID) with the background argon resulting in sequential loss of the remaining carbonyls. Variations of CID product ion intensities for $NbFe(CO)_3^+$ and $NbFe(CO)_2^+$ as a function of collision energy are shown in Figures 1 and 2. The $NbFe^+$ was then isolated by swept double resonance ejection pulses[10] and allowed to react with the appropriate reagent gas.

$$\mathrm{Nb^+ + Fe(CO)_5} \begin{cases} \to \mathrm{NbFe(CO)_2^+ + 3CO} & 27\% \quad (1) \\ \to \mathrm{NbFe(CO)_3^+ + 2CO} & 73\% \quad (2) \end{cases}$$

The bare cluster ion and both cluster carbonyls react with $Fe(CO)_5$ to produce the trimeric carbonyls, reactions 3–8. Reactions 3 and 4 were sufficiently rapid to necessitate use of the pulsed valve.

$$\mathrm{NbFe^+ + Fe(CO)_5} \begin{cases} \to \mathrm{NbFe_2(CO)_3^+ + 2CO} & 14\% \quad (3) \\ \to \mathrm{NbFe_2(CO)_4^+ + CO} & 86\% \quad (4) \end{cases}$$

$$\mathrm{NbFe(CO)_2^+ + Fe(CO)_5} \begin{cases} \to \mathrm{NbFe_2(CO)_4^+ + 3CO} & 19\% \quad (5) \\ \to \mathrm{NbFe_2(CO)_5^+ + 2CO} & 81\% \quad (6) \end{cases}$$

$$\mathrm{NbFe(CO)_3^+ + Fe(CO)_5} \begin{cases} \to \mathrm{NbFe_2(CO)_5^+ + 3CO} & 52\% \quad (7) \\ \to \mathrm{NbFe_2(CO)_6^+ + 2CO} & 48\% \quad (8) \end{cases}$$

Product ion distributions are reproducible to within ±10% absolute. Secondary product distributions were determined by isolating the ion of interest by swept double resonance ejection pulses[10] and permitting it to react with reagent gas. Secondary product distributions for species which produce two primary products close in mass (e.g., difference of two mass units at 200 amu) were difficult to determine due to a number of experimental factors, including the low magnetic field, which resulted in poor "front-end" resolution.[11] Therefore, secondary product distributions for these ions are reproducible to within ±25%. CID experiments were attempted for all product ions in the present work. However, the close proximity of some of the high mass products also made CID experiments intractable.

Throughout this study we have used Stevenson's rule, which is based on the assumption that, in a dissociation, the fragment with the lowest ionization potential will retain the charge.[12] Wherever possible, we have made comparisons with thermochemical values obtained by other techniques and have found these results to be in good agreement.

Results and Discussion

Hydrocarbon Chemistry. The product distributions for the reactions of $NbFe^+$ with hydrocarbons are listed in Table I. The thermochemical information derived from the reactions and CID results is given in Table II. $NbFe^+$ is unreactive with linear, cyclic, and branched alkanes, in contrast to the behavior of the bare metal ions, Nb^+[13] and Fe^+.[14] Nb^+ is one of the most active metal ions toward C–H insertion in alkanes and alkenes, as exemplified by formation of product ions from alkanes corresponding to $NbC_nH_n^+$, and the sequential reactions of Nb^+ with ethene to produce $Nb(C_2H_2)_n^+$ ($n = 1$–6). Fe^+ is much less active toward C–H insertion, but does react with butane and larger alkanes predominantly by C–C bond activation.

This decreased reactivity of the bare metal dimer relative to the bare metal ions has been observed in a number of other systems, including Co_2^+,[2a,b] $CoFe^+$,[2c] VFe^+,[2d] and $CuFe^+$.[2e] One explanation for this was attributed to the energetics of the initial C–H insertion step.[2c] Previous results have indicated first-row M^+–H and M^+–CH_3 bonds are primarily of s character. Since metal–metal bonds in these dimers are believed to involve s electrons, the MM'^+–H and MM'^+–alkyl bonds were proposed to be weaker and the initial C–H insertion less thermodynamically favorable than for the atomic metal ions. However, recent results on the deprotonation of Fe_2H^+ indicate $D°(Fe_2^+–H) > 63$ kcal/mol,[15] while an endothermic threshold measurement of the Fe_2^+/ethane reaction indicates $D°(Fe_2^+–H) = 50 \pm 10$ kcal/mol.[16] These results, when compared to $D°(Fe^+–H) = 48$ kcal/mol,[17] suggest the cluster ion–hydride bond strengths are at least as strong as those for the atomic ion species. Also, Armentrout has observed Co_2^+ and Co^+ to react comparably with D_2 in an ion beam apparatus and has suggested $D°(Co_2^+–H)$ and $D°(Co^+–H)$ are quite similar.[18] The initial insertion into a C–H bond, however, clearly involves the formation of two σ bonds (alkyl–M_2^+–H). Thus, until values for two σ bonds to a cluster ion are determined, the energetics of the initial insertion will remain unknown. There is also the possibility that other factors such as electronic restructuring

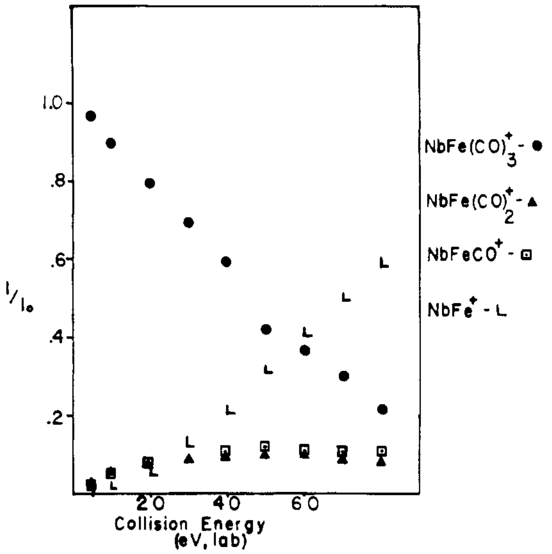

Figure 1. Variation of CID product ion intensities for $NbFe(CO)_3^+$ colliding with Ar at 0–80 eV laboratory collision energy.

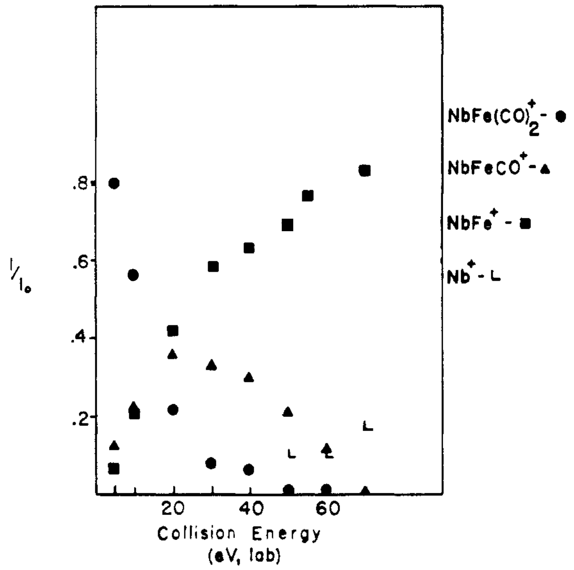

Figure 2. Variation of CID product ion intensities for $NbFe(CO)_2^+$ colliding with Ar at 0–80 eV laboratory collision energy.

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TABLE I: Distribution of Primary and Secondary Products for the Reactions of $NbFe^+$ with Small Hydrocarbons

	primary reactions			secondary reactions		
reactant	neutral loss	primary product	rel %	secondary loss	secondary product	rel %
linear alkanes		NR				
cyclic alkanes		NR				
ethene		NR				
propene	H_2	$NbFeC_3H_4^+$	100	H_2	$NbFeC_6H_8^+$	80
				$2H_2$	$NbFeC_6H_6^+$	20
1,3-butadiene	H_2	$NbFeC_4H_4^+$	100	H_2	$NbFeC_8H_8^+$	35
				$2H_2$	$NbFeC_8H_6^+$	35
				$3H_2$	$NbFeC_8H_4^+$	30
1-butene	H_2	$NbFeC_4H_6^+$	82	H_2	$NbFeC_8H_{12}^+$	11
				$2H_2$	$NbFeC_8H_{10}^+$	63
				$3H_2$	$NbFeC_8H_8^+$	26
	$2H_2$	$NbFeC_4H_4^+$	18	H_2	$NbFeC_8H_{10}^+$	37
				$2H_2$	$NbFeC_8H_8^+$	63
isobutene	H_2	$NbFeC_4H_6^+$	81	H_2	$NbFeC_8H_{12}^+$	41
				$2H_2$	$NbFeC_8H_{10}^+$	32
				$3H_2$	$NbFeC_8H_8^+$	27
	$2H_2$	$NbFeC_4H_4^+$	19	$2H_2$	$NbFeC_8H_8^+$	47
				$3H_2$	$NbFeC_8H_6^+$	27
				$4H_2$	$NbFeC_8H_4^+$	26
cis-2-butene	H_2	$NbFeC_4H_6^+$	35	H_2	$NbFeC_8H_{12}^+$	14
				$2H_2$	$NbFeC_8H_{10}^+$	86
	$2H_2$	$NbFeC_4H_4^+$	65	H_2	$NbFeC_8H_{10}^+$	47
				$2H_2$	$NbFeC_8H_8^+$	53
trans-2-butene	H_2	$NbFeC_4H_6^+$	40		NR	
	$2H_2$	$NbFeC_4H_4^+$	60	H_2	$NbFeC_8H_{10}^+$	100
1-pentene	$2H_2$	$NbFeC_5H_6^+$	100	$2H_2$	$NbFeC_{10}H_{12}^+$	33
				$3H_2$	$NbFeC_{10}H_{10}^+$	43
				Fe, $2H_2$, $H^\bullet$	$NbC_{10}H_{11}^+$	10
				Fe, $3H_2$	$NbC_{10}H_{10}^+$	14
1-hexene	$2H_2$	$NbFeC_6H_8^+$	69	$2H_2$	$NbFeC_{12}H_{16}^+$	25
				$4H_2$	$NbFeC_{12}H_{12}^+$	25
				Fe, $4H_2$	$NbC_{12}H_{12}^+$	50
	$3H_2$	$NbFeC_6H_6^+$	31	H_2	$NbFeC_{12}H_{16}^+$	12
				$3H_2$	$NbFeC_{12}H_{12}^+$	38
				Fe, $3H_2$	$NbC_{12}H_{12}^+$	50
3,3-dimethyl-1-butene	CH_4, H_2	$NbFeC_5H_6^+$	100	$3H_2$	$NbFeC_{11}H_{12}^+$	100
cyclopentene	H_2	$NbFeC_5H_6^+$	68	$2H_2$	$NbFeC_{10}H_{10}^+$	34
				Fe, $2H_2$	$NbC_{10}H_{10}^+$	66
	$2H_2$	$NbFeC_5H_4^+$	32	H_2	$NbFeC_{10}H_{10}^+$	5
				Fe, $H^\bullet$	$NbC_{10}H_{11}^+$	65
				Fe, H_2	$NbC_{10}H_{10}^+$	30
benzene		NR				
cyclohexene	$2H_2$	$NbFeC_6H_6^+$	100	Fe, $2H_2$	$NbC_{12}H_{12}^+$	100
toluene		NR				
1-methylcyclohexene	$2H_2$	$NbFeC_7H_8^+$	100	Fe, $2H_2$	$NbC_{14}H_{16}^+$	73
				$3H_2$	$NbFeC_{14}H_{14}^+$	27
cycloheptene	$2H_2$	$NbFeC_7H_8^+$	60	$3H_2$	$NbFeC_{14}H_{14}^+$	31
				Fe, $2H_2$	$NbC_{14}H_{16}^+$	69
	Fe, $2H_2$	$NbC_7H_8^+$	40			
cycloheptatriene	Fe	$NbC_7H_8^+$	100			

TABLE II: Thermochemical Values Derived from CID and Reaction Data (See Text)

$D°(Nb^+\text{–}Fe) > 60$ kcal/mol
$D°(NbFe^+\text{–}C_3H_4) > 39$ kcal/mol
$D°(NbFe^+$–cyclopentadiene$) > 32$ kcal/mol
$D°(NbFe($cyclopentadiene$)^+$–cyclopentadiene$) > 32$ kcal/mol
$D°(NbFe^+$–cyclohexadiene$) > 36$ kcal/mol
$D°(NbFe^+\text{–}O) > 85$ kcal/mol
$D°(NbFeO_n^+\text{–}O) > 119$ kcal/mol ($n = 1, 2$)
$D°(NbFe^+$–benzene$) > 30$ kcal/mol
$D°(NbFe^+$–cycloheptatriene$) > 47$ kcal/mol
$D°(Nb^+$–benzene$) = 66 \pm 7$ kcal/mol
$D°(Nb^+$–toluene$) = 61 \pm 12$ kcal/mol
$D°(Nb^+$–cycloheptatriene$) > 68 \pm 5$ kcal/mol
$D°(Nb^+\text{–}O) \sim 194$ kcal/mol

IP(Fe–cyclopentadiene) > 6.9 eV
IP(NbFe) < 8.8 eV
IP(NbO_2) ~ 7.9 eV
IP(NbO) ~ 6.5 eV
IP(Nb–cycloheptatriene) < 7.9 eV

of the cluster ion prior to reaction or overall reaction endothermicity due to a weak cluster ion–(π-ligand) bond strength may be responsible for the reduced reactivity.

Recently, $RhFe^+$, $RhCo^+$, and $LaFe^+$ were reported to react with alkanes via dehydrogenation.[19] The novel reactivity was attributed to the combination of a first- and a second- or third-row metal. It was proposed that this would result in reduced orbital overlap due to differences in constituent orbital size and energy. The resulting cluster ion would contain metals with more atomic character and would be more reactive. The present results would appear to be at odds with this, but $NbFe^+$ is much more reactive with alkenes than its first-row analogue, VFe^+.[2d] Thus, $NbFe^+$ appears to follow this type of reactivity pattern.

$NbFe^+$ reacts with alkenes larger than ethene predominantly by C–H insertion. Absence of reaction ($k^{II} < 1 \times 10^{-12}$ cm^3/(molecule·s)) of $NbFe^+$ with ethene, benzene, and toluene, (see Table I) and reaction with other alkenes, indicates that the presence of a weak allylic C–H bond is necessary for reaction with alkenes. The allylic position provides a place for initial bond activation of the alkene by the cluster ion.

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Secondary reactions of $\mathrm{NbFe^+}$ with olefins show more extensive neutral losses than the primary reactions. This "increased" reactivity of ligated cluster ions has been observed in a number of other systems including $\mathrm{Co_2CO^+}$,[2b] CoFe(olefin)$^+$,[2c] CuFe(olefin)$^+$,[2e] and Ag_n(*sec*-butylamine)$_2^+$ (n = 3, 5).[20] Two explanations have been proposed for this effect. First, the polarization of the metal–metal bond by the π-bound ligand and a subsequent increase of positive charge on the unbound metal may cause an increase in reactivity, or second, the ligand may reduce the electronic symmetry of the cluster and render it more reactive.

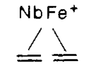
Further discussions in this section will center on possible structures for various NbFe(olefin)$^+$ product ions and the thermochemistry of these species derived from their collision spectra.

C2–C4 Alkenes. CID of $\mathrm{NbFeC_3H_4^+}$, produced by reacting $\mathrm{NbFe^+}$ with propene, yields loss of $\mathrm{H_2}$ and $\mathrm{C_3H_4}$, even at low energy.

$$\mathrm{NbFeC_3H_4^+} \xrightarrow[40\ \mathrm{eV}]{\mathrm{Ar}} \begin{cases} \mathrm{NbFeC_3H_2^+ + H_2} & 63\% & (9) \\ \mathrm{NbFe^+ + C_3H_4} & 37\% & (10) \end{cases}$$

Reasonable structures for $\mathrm{NbFeC_3H_4^+}$ are I and II. The formation of $\mathrm{NbFeC_3H_4^+}$ from propene indicates $D°(\mathrm{NbFe^+–C_3H_4})$ > 39 kcal/mol for structure I and $D°(\mathrm{NbFe^+–C_3H_4})$ > 41 kcal/mol for structure II.[21] The closeness of these values precludes determination of structure by thermochemistry, but formation of II appears more likely on mechanistic grounds. Formation of II would proceed by initial insertion into a weak allylic bond, followed by a β-hydrogen atom shift and reductive elimination of $\mathrm{H_2}$, whereas I would require initial insertion into a stronger vinylic C–H bond.

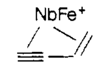
I



II

cis-Butadiene reacts to produce $\mathrm{NbFeC_4H_4^+}$ by loss of $\mathrm{H_2}$, reaction 11. CID of $\mathrm{NbFeC_4H_4^+}$ regenerates the bare cluster ion, probably ruling out a bis(acetylene) structure. While reaction 11 is not conclusive evidence, structure III is consistent with the CID results. Several isomeric $\mathrm{ScC_4H_4^+}$ species have recently been studied, one of which has been proposed to be analogous to structure III.[22]

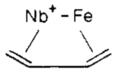
$\mathrm{NbFe^+}$ +  $\xrightarrow[-\mathrm{H_2}]{} \mathrm{NbFe^+–C_4H_4} \xrightarrow[\substack{55\ \mathrm{eV} \\ (\mathrm{lab})}]{\mathrm{CID(Ar)}} \mathrm{NbFe^+}$ (11)



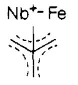
III

The isomeric butenes yield products corresponding to loss of one and two molecules of $\mathrm{H_2}$. $\mathrm{Fe^+}$ has been observed to be unreactive with isobutene,[23] but $\mathrm{Nb^+}$ reacts with isobutene multiple times with C–C cleavage also observed.[13] No C–C cleavage occurs for acyclic alkanes smaller than five carbons in reactions of $\mathrm{Nb^+}$ with alkanes. Since no C–C cleavage occurs for $\mathrm{NbFe^+}$ with alkenes, other than with 3,3-dimethyl-1-butene which contains no allylic C–H bonds, skeletal rearrangements appear unlikely and CID data, when available, substantiate this.

If the carbon skeleton remains intact, possible structures for $\mathrm{NbFeC_4H_6^+}$ from 1-butene and isobutene are IV and V. Unfortunately, attempts to probe these structures by collision-induced dissociation were unsuccessful.

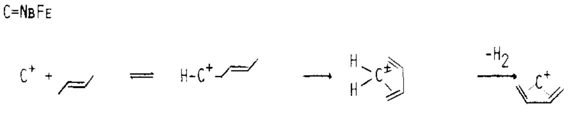


IV



V

SCHEME I



The reactions of *cis*- and *trans*-2-butene reveal some information about a possible mechanism for reaction of the cluster with alkenes. *trans*-2-Butene is observed to react at a rate ~25% of the other isomeric butenes (which react at approximately 20% of the collision rate). It is unlikely that the reaction of *trans*-2-butene is significantly less exothermic than the other butenes. More likely, the transition state involves a kinetically difficult δ-H abstraction step, as in Scheme I.

C5 Alkenes. $\mathrm{NbFe^+}$ reacts with cyclopentene to form $\mathrm{NbFeC_5H_6^+}$ and $\mathrm{NbFeC_5H_4^+}$, which further react with cyclopentene via two types of reactions, formation of bis(cycloalkene) cluster ions and splitting of the cluster with loss of Fe, reactions 12–16.

$$\mathrm{NbFe(c\text{-}C_5H_6)^+ + c\text{-}C_5H_8} \longrightarrow \begin{cases} \mathrm{NbFeC_{10}H_{10}^+ + 2H_2} & 34\% & (12) \\ \mathrm{NbC_{10}H_{10}^+ + (Fe + 2H_2)} & 66\% & (13) \end{cases}$$

$\mathrm{NbFeC_5H_4^+}$ + 
$\longrightarrow \mathrm{NbFeC_{10}H_{10}^+ + H_2}$ 5% (14)
$\longrightarrow \mathrm{NbC_{10}H_{11}^+ + (Fe + H)}$ 65% (15)
$\longrightarrow \mathrm{NbC_{10}H_{10}^+ + (Fe + H_2)}$ 30% (16)

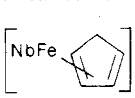
1-Pentene reacts with $\mathrm{NbFe^+}$ to produce $\mathrm{NbFeC_5H_6^+}$, which undergoes CID via loss of $\mathrm{H_2}$ and, presumably, $\mathrm{FeC_5H_6}$, reactions 17 and 18. These results imply a value of $\mathrm{IP(FeC_5H_6) > IP(Nb)}$ = 6.9 eV.

$$\mathrm{NbFeC_5H_6^+} \xrightarrow{\mathrm{CID(Ar)}} \begin{array}{llll} & \text{low energy} & \text{high energy} & \\ \mathrm{NbFeC_5H_4^+ + H_2} & 27\% & 63\% & (17) \\ \mathrm{Nb^+ + (FeC_5H_6)} & 73\% & 37\% & (18) \end{array}$$

Loss of Fe is one of the main reaction pathways in the secondary reactions of $\mathrm{NbFe^+}$ with cyclic alkenes, as illustrated above in the secondary reactions of $\mathrm{NbFe^+}$ with cyclopentene. Secondary reactions of $\mathrm{NbFe^+}$ with 1-pentene also yield loss of Fe, as well as formation of NbFe (bis(olefin)) ions, reactions 19–22.

$$\mathrm{NbFeC_5H_6^+} + \text{1-pentene} \longrightarrow \begin{cases} \mathrm{NbFeC_{10}H_{12}^+ + 2H_2} & 33\% & (19) \\ \mathrm{NbFeC_{10}H_{10}^+ + 3H_2} & 43\% & (20) \\ \mathrm{NbC_{10}H_{11}^+ + (Fe + H + 2H_2)} & 10\% & (21) \\ \mathrm{NbC_{10}H_{10}^+ + (Fe + 3H_2)} & 14\% & (22) \end{cases}$$

The formation of secondary products which correspond to loss of Fe is consistent with $\mathrm{C_5H_6}$ in $\mathrm{NbFeC_5H_6^+}$ being cyclopentadiene, indicating thermal dehydrocyclization of 1-pentene upon reaction with $\mathrm{NbFe^+}$. Thermal dehydrocyclization has been observed for atomic metal ions,[13] as well as for $\mathrm{FeCo_2^+}$,[24] and collisionally activated dehydrocyclization has been observed with $\mathrm{CoFe^+}$.[2c] Structure VI is consistent with the reaction results and the loss of $\mathrm{FeC_5H_6}$ in the CID spectrum of $\mathrm{NbFeC_5H_6^+}$, generated from reaction with cyclopentene. However, absolute structure assignment using low-energy multiple-collision CID is not unambiguous as rearrangement prior to fragmentation is possible. Values of $D°(\mathrm{NbFe^+–C_5H_6})$ > 32 kcal/mol and $D°(\mathrm{NbFeC_5H_6^+–C_5H_6})$ > 32 kcal/mol are implied from the reaction of $\mathrm{NbFe^+}$ with 1-pentene, assuming $\mathrm{C_5H_6}$ is cyclopentadiene.



VI

C6–C7 Alkenes. No reaction between the cluster ion and benzene or toluene occurs, in contrast to $\mathrm{CoFe^+}$ and $\mathrm{CuFe^+}$ which both react by displacement of a metal atom to form metal$^+$–

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[22] Lech, L. M.; Freiser, B. S. *Organometallics* **1988**, *7*, 1949.

[23] Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 7484.

[24] Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 5351.

benzene and metal$^+$–toluene complexes.[2c,e] A lower limit on $D°(\mathrm{Nb^+–benzene})$ of 60 kcal/mol is indicated by reaction 23.

$$\mathrm{Nb^+} + n\text{-hexane} \rightarrow \mathrm{NbC_6H_6^+} + 4\mathrm{H_2} \qquad (23)$$

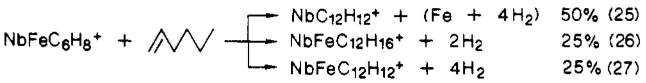
Absence of displacement of Fe by benzene indicates $D°(\mathrm{Nb^+–Fe}) > 60$ kcal/mol, which is in agreement with $D°(\mathrm{Nb^+\text{-}Fe}) = 68 \pm 5$ kcal/mol obtained from photodissociation threshold measurements.[25] Reversing the argument suggests $D°(\mathrm{Nb^+–benzene}) < 68 \pm 5$ kcal/mol, which, combined with the lower limit from reaction 23, indicates $D°(\mathrm{Nb^+–benzene}) = 66 \pm 7$ kcal/mol.

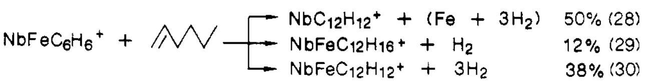
Cyclohexene reacts with NbFe$^+$ to form $\mathrm{NbFeC_6H_6^+}$, exclusively, which undergoes CID to regenerate the cluster ion, reaction 24. The CID results, also consistent with $D°(\mathrm{Nb^+–Fe}) > D°(\mathrm{Nb^+–benzene})$, imply $\mathrm{IP(NbFe)} < \mathrm{IP(C_6H_6)} = 9.25$ eV.

$$\mathrm{NbFeC_6H_6^+} \xrightarrow{\mathrm{CID(Ar)}} \mathrm{NbFe^+} + \mathrm{C_6H_6} \qquad (24)$$

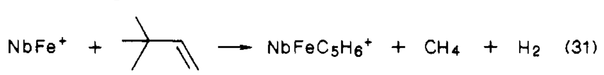
$\mathrm{NbFeC_6H_6^+}$ reacts with cyclohexene to form the niobium bis(benzene) ion. Surprisingly, no bis(benzene) cluster ion is formed. Since collisional activation of $\mathrm{NbFeC_6H_6^+}$ produces loss of $\mathrm{C_6H_6}$, while reaction of $\mathrm{NbFeC_6H_6^+}$ with cyclohexene produces loss of (Fe + $2\mathrm{H_2}$), the actual neutral products are most likely $\mathrm{FeH_2}$ and $\mathrm{H_2}$.[2c,25] All other cyclic alkenes containing one double bond form some amount of the bis(alkene) cluster ion. This indicates $\mathrm{Nb(C_6H_6)_2^+}$ is very stable. For comparison, $\mathrm{VFe(C_6H_6)_2^+}$ is observed to undergo collisional activation to form $\mathrm{V(C_6H_6)_2^+}$ by loss of Fe and is consistent with the high stabilities of early-transition-metal bis(benzene) complexes.[2d]

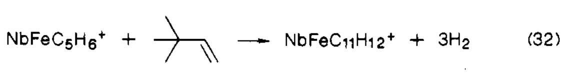
1-Hexene reacts to produce $\mathrm{NbFeC_6H_8^+}$ and $\mathrm{NbFeC_6H_6^+}$, which both react with 1-hexene to split the cluster ion as one reaction pathway, reactions 25 and 28. Reactions 25 and 28 are indicative of cyclic structures for $\mathrm{NbFeC_6H_6^+}$ and $\mathrm{NbFeC_6H_8^+}$. Assuming this to be the case, $D°(\mathrm{NbFe^+–benzene}) > 30$ kcal/mol and $D°(\mathrm{NbFe^+–(c\text{-}C_6H_8)}) > 36$ kcal/mol are implied from the formation reactions. Formation of the other products in reactions 26, 27, 29, and 30, with 1-hexene, which are not formed in the reaction with cyclohexene, may be due to the lower reaction exothermicity of the 1-hexene reaction.





3,3-Dimethyl-1-butene is the only molecule to react with NbFe$^+$ via C–C cleavage, reaction 31. This is reasonable, however, since this is the only molecule with an allylic C–C bond and no allylic C–H bonds to insert into. This reaction was observed to be slow, which is possibly due to the difficult C–C insertion process. Surprisingly, $\mathrm{NbFeC_5H_6^+}$, generated in reaction 31, reacts with 3,3-dimethyl-1-butene to produce $\mathrm{NbFeC_{11}H_{12}^+}$, reaction 32. This secondary product requires a 1,3-hydride abstraction to occur. This behavior is, however, similar to Nb$^+$, which multiply dehydrogenates molecules with no β-hydrogens.[13]

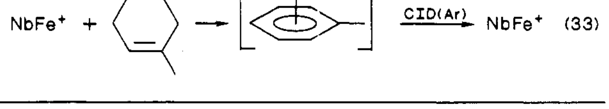


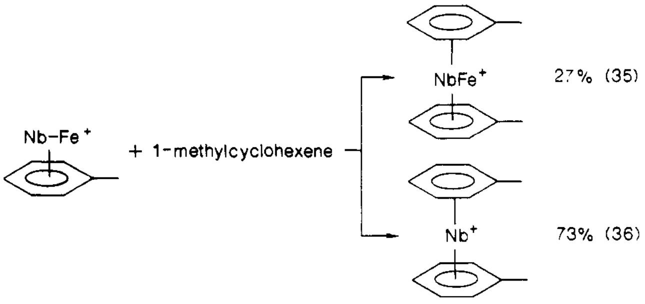


1-Methylcyclohexene reacts with NbFe$^+$ to form NbFe$^+$–toluene, which, upon collisional activation, regenerates NbFe$^+$, exclusively. The CID results yield IP(NbFe) < IP(toluene) = 8.8 eV, which is consistent with a value of IP(NbFe) = 6.5 eV previously reported.[25] From reaction 34 a value of $D°(\mathrm{Nb^+\text{-}toluene}) > 49$ kcal/mol is implied.

$$\mathrm{Nb^+} + \text{methylcyclohexane} \rightarrow \mathrm{Nb^+\text{–}toluene} + 3\mathrm{H_2} \qquad (34)$$

The NbFe$^+$–toluene CID results indicate $D°(\mathrm{Nb^+–toluene}) < 68 \pm 5$ kcal/mol. Combining these results indicates $D°(\mathrm{Nb^+–toluene}) = 61 \pm 12$ kcal/mol. NbFe(toluene)$^+$ reacts with 1-methylcyclohexene to produce NbFe(bis(toluene))$^+$ and Nb(bis(toluene))$^+$, reactions 35 and 36. It is interesting that in this case a bis(cycloalkene) cluster ion is observed, whereas it was not observed for the secondary reaction of cyclohexene with NbFe$^+$.





Cycloheptatriene reacts with NbFe$^+$ to eliminate Fe

$$\mathrm{NbFe^+} + \text{cycloheptatriene} \rightarrow \mathrm{NbC_7H_8^+} + \mathrm{Fe} \qquad (37)$$

indicating $D°(\mathrm{Nb^+–(c\text{-}C_7H_8)}) > 68 \pm 5$ kcal/mol and $\mathrm{IP(Nb\text{-}C_7H_8)} < \mathrm{IP(Fe)} = 7.87$ eV.

Cycloheptene reacts with NbFe$^+$ as in reactions 38 and 39.

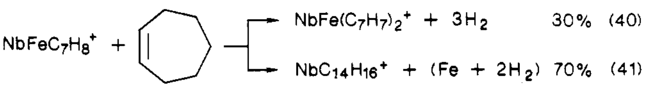
$$\mathrm{NbFe^+} + \text{cycloheptene} \rightarrow \begin{cases} \mathrm{NbFeC_7H_8^+} + 2\mathrm{H_2} & 60\%\ (38) \\ \mathrm{NbC_7H_8^+} + (\mathrm{Fe} + 2\mathrm{H_2}) & 40\%\ (39) \end{cases}$$

CID of $\mathrm{NbFeC_7H_8^+}$ generates $\mathrm{NbC_7H_8^+}$ at low and high energies, in contrast to the CID results for $\mathrm{NbFeC_7H_8^+}$ generated from 1-methylcyclohexene, reaction 33. This indicates $\mathrm{NbFeC_7H_8^+}$ has at least two different isomeric structures with the hydrocarbon backbone of the reactant most likely retained. Reaction 38 implies $D°(\mathrm{NbFe^+–(c\text{-}C_7H_8)}) > 48$ kcal/mol.

$\mathrm{NbFeC_7H_8^+}$ generated in reaction 38 reacts with cycloheptene to form $\mathrm{NbFeC_{14}H_{14}^+}$ and $\mathrm{NbC_{14}H_{16}^+}$, reactions 40 and 41. CID of $\mathrm{NbFe(C_7H_7)_2^+}$ yields loss of benzene, reaction 42. Although

$$\mathrm{NbFe(C_7H_7)_2^+} \xrightarrow[\substack{45\ \mathrm{eV} \\ \mathrm{(lab)}}]{\mathrm{CID(Ar)}} \mathrm{NbFe(C_7H_7)CH^+} + \mathrm{C_6H_6} \qquad (42)$$

it is clearly speculative, the $\mathrm{NbFeC_{14}H_{14}^+}$ species is believed to be a bis(tropylium) structure as written.



Oxide Chemistry. Recently there have been several studies related to the oxide chemistry of small cluster ions.[27-29] These studies have shown the cluster ion chemistry to differ significantly from the atomic ion reactivity. For example, $\mathrm{Mn_2^+}$[28] and CoFe$^+$[29] react with $\mathrm{O_2}$ by abstraction of oxygen, as in reactions 43 and 46, indicating $D°(\mathrm{Mn_2^+–O}) > 119$ kcal/mol and $D°(\mathrm{CoFe^+–O}) > 119$ kcal/mol, almost twice the values for the atomic species, $D°(\mathrm{Mn^+–O}) \sim 70$ kcal/mol,[28] $D°(\mathrm{Fe^+–O}) = 68 \pm 3$ kcal/mol, and $D°(\mathrm{Co^+–O}) = 65 \pm 3$ kcal/mol.[30] Cluster ions containing

$$\mathrm{Mn_2^+} + \mathrm{O_2} \rightarrow \begin{cases} \mathrm{Mn_2O^+} + \mathrm{O} & (43) \\ \mathrm{Mn^+} + \mathrm{MnO_2} & (44) \\ \mathrm{MnO^+} + \mathrm{MnO} & (45) \end{cases}$$

$$\mathrm{CoFe^+} + \mathrm{O_2} \rightarrow \begin{cases} \mathrm{CoFeO^+} + \mathrm{O} & (46) \\ \mathrm{Co^+} + \mathrm{FeO_2} & (47) \end{cases}$$

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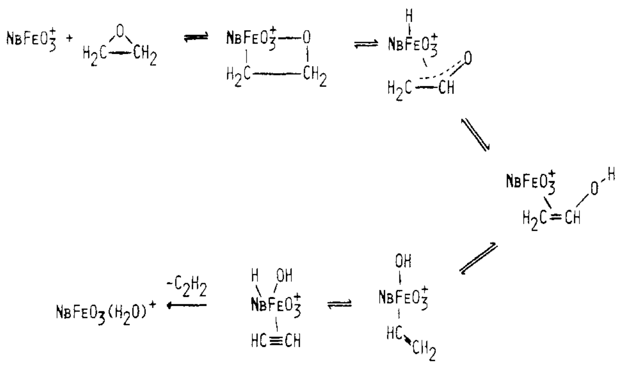
SCHEME II

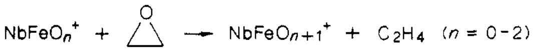


early transition metals have been observed to react with O_2 with splitting of the cluster ion as the only pathway.[2d] This is due to very high oxide bond strengths for early-transition-metal cations. For example, VFe^+ reacts with O_2 as in reactions 48 and 49.[2d]

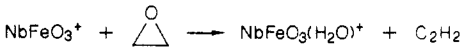
$$VFe^+ + O_2 \rightarrow VO^+ + FeO \quad (48)$$
$$ \rightarrow Fe^+ + VO_2 \quad (49)$$

The reactivity of $NbFe^+$ and $NbFeL^+$ (L = CO, O) with O_2 was investigated. As is the case for VFe^+, the reactivity of $NbFe^+$ is strongly influenced by the high bond strength of Nb^+ to oxygen. The gas-phase oxide chemistry of Nb^+ has not been studied extensively, but values of $D°(NbO^+–O) = 123 \pm 4$ and 151 kcal/mol $< D°(Nb^+–O) <$ 257 kcal/mol have been obtained by bracketing methods.[13,31]

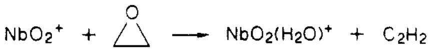
$NbFe^+$ sequentially abstracts three oxygen atoms from ethylene oxide, reaction 50, implying $D°(NbFeO_n^+–O) >$ 85 kcal/mol (n = 0–2). Interestingly, $NbFeO_3^+$ reacts with ethylene oxide by abstraction of H_2O, reaction 51. This is unusual, considering that bare atomic metal ions and metal cluster ions have previously been observed to react with ethylene oxide only by abstraction of an oxygen atom or a carbene unit. These latter reaction pathways, however, require ~85 and ~93 kcal/mol, respectively, whereas abstraction of H_2O from ethylene oxide only requires ~9 kcal/mol and, thus, reaction 51 indicates $D°(NbFeO_3^+–H_2O) >$ 9 kcal/mol. NbO_2^+ also reacts with ethylene oxide via abstraction of H_2O, reaction 52, whereas Nb^+ and NbO^+ only react with ethylene oxide via oxygen abstraction, reaction 53. This could imply that the metal center in NbO_2^+ has a formal oxidation state of +5 and that further oxidation of Nb by ethylene oxide is not possible, making abstraction of H_2O the only available reaction pathway. A similar restriction may apply to $NbFeO_3^+$, with the cluster ion in a formal oxidation state of +7.



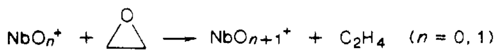
$$NbFeO_n^+ + \overset{O}{\triangle} \rightarrow NbFeO_{n+1}^+ + C_2H_4 \quad (n = 0-2) \quad (50)$$



$$NbFeO_3^+ + \overset{O}{\triangle} \rightarrow NbFeO_3(H_2O)^+ + C_2H_2 \quad (51)$$



$$NbO_2^+ + \overset{O}{\triangle} \rightarrow NbO_2(H_2O)^+ + C_2H_2 \quad (52)$$



$$NbO_n^+ + \overset{O}{\triangle} \rightarrow NbO_{n+1}^+ + C_2H_4 \quad (n = 0, 1) \quad (53)$$

A mechanism consistent with reaction 51 is shown in Scheme II. Collisional activation of $NbFeO_3(H_2O)^+$ produces efficient loss of H_2O even at low energies, reaction 54.

$$NbFeO_3(H_2O)^+ \xrightarrow{Ar} NbFeO_3^+ + H_2O \qquad (4\text{ eV (lab)}) \quad (54)$$

$NbFe^+$ reacts with O_2 to break up the cluster, reactions 55–57.

$$NbFe^+ + O_2 \rightarrow NbO^+ + FeO \quad (55)$$
$$ \rightarrow NbO_2^+ + Fe \quad (56)$$
$$ \rightarrow Fe^+ + NbO_2 \quad (57)$$

NbO^+ reacts rapidly with O_2 to form NbO_2^+. The formation of NbO_2^+ in reaction 56 and not from a subsequent reaction of NbO^+ with O_2 was confirmed by double resonance ejection of NbO^+. Using thermochemical limits for $\Delta H_f(NbO_2^+)$ and $\Delta H_f(NbO^+)$,[13,31] reactions 55–57 were determined to be exothermic. The observation of both NbO_2^+ and Fe^+ indicates IP(NbO_2) ~ IP(Fe) = 7.87 eV. Using eq 58 and previously determined values

$$D°(NbO^+–O) = -IP(NbO_2) + D°(NbO–O) + IP(NbO) \quad (58)$$

of $D°(NbO–O) = 6.7$ eV[32] and $D°(NbO^+–O) = 5.3$ eV indicates IP(NbO_2) – IP(NbO) = 1.4 eV, which yields IP(NbO) ~ 6.5 eV. Since NbO^+ is formed in reaction 55, IP(FeO) = 8 eV > IP(NbO) is implied, which agrees with these results. Using (59)

$$D°(Nb^+–O) = IP(Nb) + D°(Nb–O) - IP(NbO) \quad (59)$$

and $D°(Nb–O) = 8.0$ eV,[32] a value of $D°(Nb^+–O)$ ~ 194 kcal/mol is obtained which is in agreement with the result obtained from bracketing measurements described above.

The cluster carbonyls, $NbFe(CO)_2^+$ and $NbFe(CO)_3^+$, react with O_2 as in reactions 60–64. Reaction pathways where splitting of the cluster ion occurs are indicative of formation of an activated cluster oxide ion with subsequent fragmentation. Both cluster carbonyls form $NbFeO_2^+$ with loss of all CO ligands. $NbFeO_2^+$ can then undergo dissociation to form NbO_2^+ (vide infra, reaction 67). The cluster oxides formed in reactions 60, 62, and 63 react with O_2 further to abstract oxygen, reaction 65. The reaction to form $NbFeO_4^+$ is much slower than the reactions forming $NbFeO_n^+$ (n = 2, 3) and may be endothermic. Reaction 65 indicates $D°(NbFeO_n^+–O) >$ 119 kcal/mol (n = 1,2).

$$NbFe(CO)_3^+ + O_2 \rightarrow NbFeO_2^+ + 3CO \quad (60)$$
$$ \rightarrow NbO_2^+ + Fe + 3CO \quad (61)$$

$$NbFe(CO)_2^+ + O_2 \rightarrow NbFeO_2^+ + 2CO \quad (62)$$
$$ \rightarrow NbFeO^+ + (O + 2CO) \quad (63)$$
$$ \rightarrow NbO_2^+ + Fe + 2CO \quad (64)$$

$$NbFeO_n^+ + O_2 \rightarrow NbFeO_{n+1}^+ + O \qquad (n = 1–3) \quad (65)$$

The cluster oxides undergo collision-induced dissociation as in reactions 66–68. Approximate energies where dissociation is first observed are shown in parentheses. There have been numerous ion beam studies which have utilized energy thresholds for various reaction channels to determine ion thermochemistry.[33] However, in an ICR spectrometer the dynamic range is relatively low (~10^4) so reaction channels with low cross sections will not exhibit thresholds which are thermodynamic,[16,34] as is the case here. In particle-counting experiments with high sensitivities, like ion beams, this problem is not encountered. Cluster oxide ions have previously been shown to be very stable toward dissociation, with low efficiency dissociation only at high energy.[29]

$$NbFeO^+ \xrightarrow{CID(Ar)} NbO^+ + Fe \qquad (29\text{ eV (lab)}) \quad (66)$$

$$NbFeO_2^+ \xrightarrow{CID(Ar)} NbO_2^+ + Fe \qquad (41\text{ eV (lab)}) \quad (67)$$

$$NbFeO_3^+ \xrightarrow{CID(Ar)} NbO_2^+ + FeO \qquad (60\text{ eV (lab)}) \quad (68)$$

Conclusion

$NbFe^+$ is much more reactive than its first-row analogue, VFe^+, toward activation of hydrocarbons. This trend is similar to that observed for other dimers containing a second- or third-row metal bound to a first-row metal. However, the reactivity $NbFe^+$ is less

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than that of Fe^+ and considerably less than that of Nb^+. This is consistent with the behavior of other heterodinuclear cluster ions studied to date. An alkene ligand attached to the cluster greatly enhances the reactivity of the cluster, as expected from previous results on the reactivity of Co_2CO^+. Preliminary results from our laboratory show heteronuclear cluster carbonyl ions, $MM'CO^+$, also to be very reactive toward alkanes in cases where the bare cluster ion is unreactive toward alkanes. Thermochemical values from the reactions with alkenes indicate $D°(Nb^+\text{–}Fe) >$ 60 kcal/mol and $IP(NbFe) < 8.8$ eV, in agreement with previous photodissociation results. The oxide chemistry of $NbFe^+$ indicates $D°(NbFe^+\text{–}O) > 85$ kcal/mol, $D°(NbFeO_3{}^+\text{–}H_2O) > 9$ kcal/mol, and $D°(NbFeO_n{}^+\text{–}O) > 119$ kcal/mol ($n = 1, 2$).

Acknowledgment. Acknowledgment is made to the Division of Chemical Sciences in the Office of Basic Energy Sciences in the U.S. Department of Energy (DE-FG02-87ER13776) for supporting the transition-metal-ion research and to the National Science Foundation (CHE-8612234) for continued support of the Fourier transform mass spectrometry instrumentation. S.W.B. gratefully acknowledges the Purdue Research Foundation for providing fellowship support.

Registry No. $NbFe^+$, 107474-41-9; $NbFeO_2{}^+$, 117605-08-0; NbO^+, 23625-94-7; $NbO_2{}^+$, 26317-75-9; $NbFeO_3{}^+$, 117605-09-1; $NbO_2(H_2O)$, 117526-57-5; $NbFeO^+$, 117605-07-9; $Fe(CO)_5$, 13463-40-6; Nb^+, 18587-63-8; O_2, 7782-44-7; ethene, 74-85-1; propene, 115-07-1; 1,3-butadiene, 106-99-0; 1-butene, 106-98-9; isobutene, 115-11-7; *cis*-2-butene, 590-18-1; *trans*-2-butene, 624-64-6; 1-pentene, 109-67-1; 1-hexene, 592-41-6; 3,3-dimethyl-1-butene, 558-37-2; cyclopentene, 142-29-0; benzene, 71-43-2; cyclohexene, 110-83-8; toluene, 108-88-3; 1-methylcyclohexene, 591-49-1; cycloheptene, 628-92-2; cycloheptatriene, 544-25-2; ethylene oxide, 75-21-8.

Characterization of the Interaction between a Nonionic Polymer and a Cationic Surfactant by the Fourier Transform NMR Self-Diffusion Technique

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Self-diffusion measurements have been performed on dodecyltrimethylammonium ions ($DoTA^+$) in aqueous solutions of ethyl(hydroxyethyl)cellulose (EHEC) by the Fourier transform NMR self-diffusion technique. The experimental data were analyzed by means of a simple two-site model, and a deduction of the amounts of free and bound $DoTA^+$ in the polymer solution was achieved. The approach was shown to be a convenient tool of characterizing polymer–surfactant interactions, and it was demonstrated that either the addition of salt or an increase in temperature promotes the binding of $DoTA^+$ to EHEC. The striking finding of an increased attraction between surfactant and EHEC at elevated temperatures demonstrates that the polymer molecules become increasingly more hydrophobic with increasing temperature, which is referred to as temperature-induced conformational changes in the polymer.

Introduction

The interaction between water-soluble nonionic polymers and ionic surfactants has become a field of intense research in recent years (cf. recent review articles[1–3]). Such studies mainly deal with the action of anionic surfactants, while it is often inferred that cationic species interact comparatively weakly with nonionic polymers. Thus, there are only a limited number of investigations performed on cationic surfactant–neutral polymer systems, where any considerable interaction effects are reported. However, if a rather hydrophobic polymer is used, a more pronounced interaction effect is observed, e.g., for ethyl(hydroxyethyl)cellulose[4] and poly(vinyl alcohol) containing 10–12% acetate groups.[5,6] This has been revealed both by measurements that probe changes in macroscopic behavior, e.g, cloud point[4,5] and viscosity measurements,[5] and by measurements of the surfactant cation activity.[6]

The Fourier transform NMR pulsed gradient spin-echo (FT-NMR-PGSE) technique is well-established in self-diffusion studies of surfactant solutions in order to characterize, inter alia, surfactant self-association equilibria, counterion binding, solubilization, and hydration.[7] In this work we apply this technique for monitoring the self-diffusion of the surfactant ion in aqueous solutions of ethyl(hydroxyethyl)cellulose (EHEC) and dodecyltrimethylammonium bromide (DoTAB). Particularly the temperature dependence of the surfactant ion self-diffusion was studied, but also the influence of small amounts of NaCl has been investigated, especially at low DoTAB concentrations. The DoTAB–water system was used as a reference system. By using a two-site model to interpret the observed self-diffusion coefficients, it was possible to deduce the amount of cationic surfactant bound to EHEC.

Experimental Section

Materials. EHEC (Bermocoll E 351 X) was manufactured by Berol Kemi AB, Stenungsund, Sweden (from the same batch previously used[4]). The viscosity-average molecular weight for this sample was 146 000. The degree of substitution of ethyl groups was 0.9 per anhydroglucose unit, and the molar substitution of ethylene oxide groups was 2.1 per anhydroglucose unit. DoTAB was obtained from Sigma and was always stored in a desiccator. The critical micelle concentration (cmc) of DoTAB in H_2O at 25 °C is 0.015 *m*.[8] D_2O (99.8 atom % D) was obtained from Norsk Hydro, Oslo, Norway. Hexadecane, used as a reference in the calibration procedure of the self-diffusion experiment, and

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