

VCD. These earlier models take into account electronic motion distinct from nuclear motion, but ignore ring currents, and for isolated bands the calculated anisotropy ratios $\Delta\epsilon/\epsilon$ lie well below the experimental values. Efforts are currently underway to provide a more quantitative description of the ring current mechanism and to carry out calculations using recently developed vibronic coupling formulations^{37,38} which implicitly include ring current effects.

As a basis for the qualitative interpretation of observed VCD spectra, the ring current model provides a new direct way to probe both solution conformation and intramolecular interactions. The conformations which we have postulated based on ring current enhancement of VCD are in agreement with those postulated from other evidence, when available, and have provided a consistent explanation of the OH and CH stretching VCD in a wide range

of molecules. The VCD spectra for bond-stretching motions considered here are easily recorded. Ring current enhancement can often be detected as a biased component superimposed on the VCD arising from coupled nuclear motion, allowing conformational information to be obtained without the precise vibrational analysis needed to interpret the nuclear coupling VCD. The role of ring currents generated by bending vibrations remains to be investigated, but may prove significant in the midinfrared where weak absorptions with large anisotropy ratios, and hence, significant magnetic dipole character, have been recorded.

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Registry No. (S)-(-)-1-Phenylethanol, 1445-91-6; (S)-(-)-1-phenylethanethiol, 33877-11-1; (S)-(-)-chloro-1-phenylethane, 3756-41-0; D- α -phenylglycine, 875-74-1; (S)-methyl mandelate, 21210-43-5; O-acetylmandelic acid, 5438-68-6; α -methoxyphenylacetic acid, 1701-77-5.

Heteronuclear Transition-Metal Cluster Ions in the Gas Phase. Photodissociation and Reactivity of VFe^+

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Abstract: The transition-metal cluster ion VFe^+ was synthesized in the gas phase by reaction of V^+ with $Fe(CO)_5$, followed by appropriate collisional activation pulses. Photodissociation of VFe^+ to generate V^+ exclusively reveals two peaks at 260 ± 10 and 340 ± 10 nm with a threshold dissociation at 380 ± 10 nm. A cross-section $\sigma(340 \text{ nm}) = 6 \pm 3 \times 10^{-18} \text{ cm}^2$ is determined for the photodissociation of VFe^+ . The threshold at 380 ± 10 nm yields $D^\circ(V^+-Fe) = 75 \pm 5 \text{ kcal/mol}$, which implies $D^\circ(Fe^+-V) = 101 \pm 5 \text{ kcal/mol}$, $\Delta H_f^\circ(VFe^+) = 302 \pm 5 \text{ kcal/mol}$, and $IP(VFe) = 5.4 \text{ eV}$. No reaction is observed between VFe^+ and linear or cyclic alkanes. VFe^+ is also unreactive with all linear alkenes through hexene but reacts with C_6 and C_7 cycloalkenes. The primary reaction between VFe^+ and cyclohexene (or benzene) produces $VFe(C_6H_6)^+$, which upon collisional activation readily eliminates C_6H_6 . Collisional activation of $VFe(C_6H_6)_2^+$, formed by a secondary reaction with cyclohexene, produces loss of Fe to yield $V(C_6H_6)_2^+$. VFe^+ abstracts a carbene from cycloheptatriene, indicating $D^\circ(VFe^+-CH_2) > 70 \text{ kcal/mol}$. The oxide chemistry of VFe^+ is also modified from that of V^+ or Fe^+ . VFe^+ reacts very slowly with O_2 to yield VO^+ and Fe^+ whereas $VFe(CO)_x^+$ ($x = 2-4$) reacts quickly with O_2 to produce $VFeO_2^+$, which then abstracts an oxygen from O_2 to form $VFeO_3^+$. VFe^+ will react sequentially with ethylene oxide to abstract up to three oxygens, producing $VFeO^+$, $VFeO_2^+$, and $VFeO_3^+$. No reaction is observed between VFe^+ and N_2O , although both V^+ and Fe^+ will abstract an oxygen from N_2O .

The production and examination of small metal clusters have become topics of considerable interest over the past decade.¹ Transition-metal clusters are particularly important in astronomy, homogeneous nucleation,² and surface science, specifically heterogeneous catalysis.³

Metal clusters are thought to mimic metal surfaces, particularly when the clusters are ligand free.⁴ Gas-phase techniques are well suited for studying bare transition-metal cluster ions. Most of the metal cluster ions examined thus far have been generated by electron impact⁵ or multiphoton ionization⁶ of metal carbonyls.

Smalley and others have recently developed novel beam expansion techniques for generating neutral clusters of various sizes for study in the gas phase.⁷

A convenient method of generating heteronuclear transition-metal cluster ions in the gas phase has allowed the reactivity of $CoFe^+$ to be examined in detail.⁸ In order to further probe the nature of these cluster ions, the VFe^+ ion was chosen since it combines both an early and a late transition metal. In this cluster, the electron density should be polarized and the resulting charge localization might greatly influence the reactivity of the cluster.

Photodissociation of VFe^+ provides an indirect measure of the absorption spectrum of the ion, as well as a thermodynamic threshold which provides bond energy information. In order to observe the photodissociation process, $AB^+ + h\nu \rightarrow A^+ + B$, the

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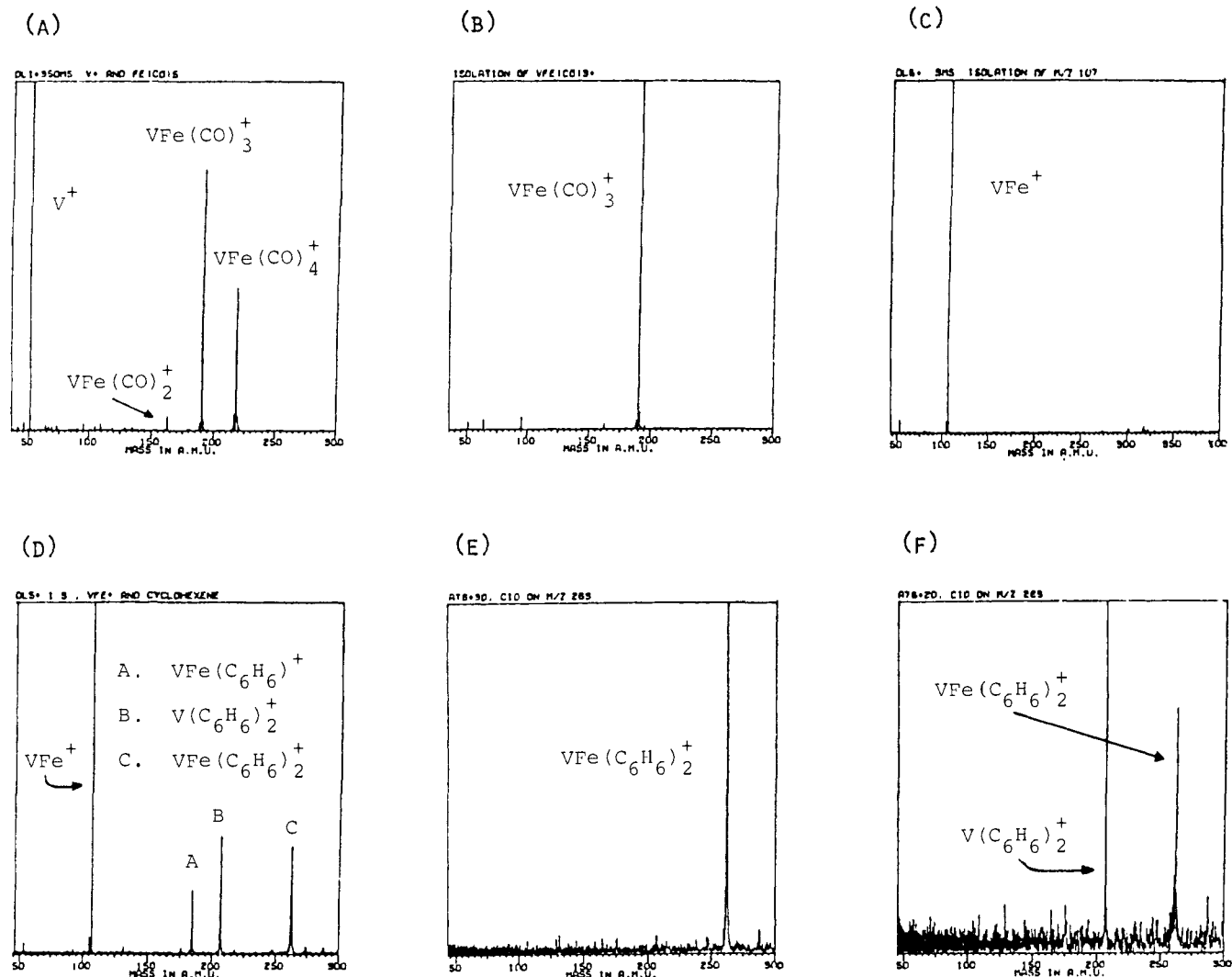


Figure 1. (A) Mass spectrum obtained when laser desorbed V^+ reacts with $Fe(CO)_5$ at 2×10^{-7} torr in the presence of 4×10^{-6} torr argon for 350 ms. (B) Same as part A except all ions other than $VFe(CO)_3^+$ have been ejected from the cell by swept double resonance ejection pulses. (C) Same as part B except following isolation, $VFe(CO)_3^+$ is accelerated to 88 eV and allowed to undergo collision-induced dissociation for 35 ms followed by isolation of the resulting VFe^+ ion. (D) Same as part C except an additional 1-s trap allows VFe^+ to react with cyclohexene. (E) Same as part D except $VFe(C_6H_6)_2^+$ has been isolated. (F) Same as part E except $VFe(C_6H_6)_2^+$ is accelerated to 21 eV kinetic energy with the fragmentation detected. Each individual spectrum has been normalized to the most intense peak.

energy of the photon absorbed must exceed the bond dissociation energy, $D^0(A^+-B)$. This method of determining bond energies has been used in our laboratory to obtain, for example, $D^0(Fe^+-OH) = 73 \pm 3$ kcal/mol, which is in excellent agreement with other experimentally determined values.⁹

The absorption spectra for these bare diatomic heteronuclear cluster ions have not been obtained. Several homonuclear cluster neutrals have been examined. For example, Mn_2 , Fe_2 , and Ni_2 show broad absorption bands in the visible spectral region.¹⁰

Experimental Section

The theory and instrumentation of Fourier transform mass spectrometry (FTMS) have been discussed elsewhere.¹¹ All experiments were performed on a Nicolet prototype FTMS-1000 Fourier transform mass spectrometer previously described in detail¹² 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 in this study utilized two 80% transmittance stainless steel screens as the transmitter plates which permit irradiation with a 2.5 kW Hg-Xe arc lamp. Metal ions were generated by focusing the beam of

a Quanta Ray Nd:YAG laser (frequency doubled to 530 nm) into the center-drilled hole (1 mm) of a high-purity iron or vanadium rod supported on the transmitter plate nearest to the laser. Details of the laser ionization technique have been described elsewhere.¹³

Chemicals were obtained commercially in high purity and were used as supplied except for multiple freeze-pump-thaw cycles to remove non-condensable gases. $Fe(CO)_5$ was introduced into the vacuum chamber at a static pressure of $\sim 3 \times 10^{-7}$ torr. The hydrocarbon reagents were added to bring the total pressure to $\sim 1 \times 10^{-6}$ torr. Argon was used as the collision gas for collision-induced dissociation (CID) at a total pressure of $\sim 4 \times 10^{-6}$ torr. A Bayard-Alpert ionization gauge was used to monitor the pressure.

Details of the CID experiments have previously been outlined.¹⁴ The collision energy of the ions can be varied (typically between 0 and 100 eV) from which plots of CID product ion intensities vs. ion kinetic energy can be made. The spread in ion kinetic energy is dependent on the total average kinetic energy and is approximately 35% at 1 eV, 10% at 10 eV, and 5% at 30 eV.¹⁵

VFe^+ was generated and examined by the following procedure in exact analogy to an earlier study on $CoFe^+$.⁸ Laser desorbed vanadium ions react with $Fe(CO)_5$ to displace one or more carbonyls, shown in reactions

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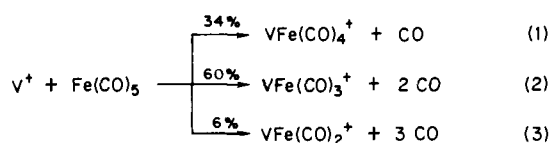
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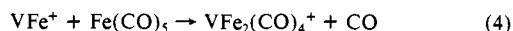
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1-3. The products of reactions 1 and 2 were isolated and accelerated



to ~78 and ~88 eV kinetic energy, respectively, causing inelastic collisions with the argon target gas which resulted in sequential loss of carbonyls for each ion to produce VFe^+ . The VFe^+ was then isolated by using swept double resonance ejection pulses and allowed to react with other reagent gases. Figure 1 illustrates the generation and reaction of VFe^+ with cyclohexene.

$\text{VFe}(\text{CO})_3^+$ and $\text{VFe}(\text{CO})_4^+$ both react rapidly with $\text{Fe}(\text{CO})_5$ to eliminate two carbonyls to form $\text{VFe}_2(\text{CO})_6^+$ and $\text{VFe}_2(\text{CO})_7^+$, respectively, while VFe^+ reacts very slowly with $\text{Fe}(\text{CO})_5$ by displacing exclusively one carbonyl, reaction 4. Because this reaction is slow, it does not

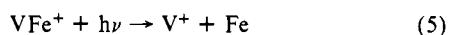


cause difficulties in the study of VFe^+ with the organic substrates. The relatively high pressure of argon is believed to allow any excess energy of the cluster to be dissipated by thermalizing collisions.

For the photodissociation studies, VFe^+ was isolated and trapped for 4 s in the presence of $\text{Fe}(\text{CO})_5$. It was determined that $\text{Fe}(\text{CO})_5$ could be used at a pressure of $\sim 2 \times 10^{-6}$ torr as both the reagent and the collision gas, thereby eliminating the need for argon. The efficiency of CID for $\text{Fe}(\text{CO})_5$ at this pressure appeared comparable to using argon at the elevated pressure. During the 4-s trapping time, the ions were irradiated with light from a 2.5-kW mercury-xenon arc lamp, used in conjunction with a 0.25 m monochromator set for 10-nm resolution. A photoappearance curve was obtained by plotting the log of one plus the ratio of V^+ intensity to the VFe^+ intensity, correcting for the blank and normalizing for the light intensity, as a function of wavelength. Poor reproducibility of the VFe^+ signal (due to laser shot-to-shot variations) made monitoring the photodissociation of VFe^+ impractical. The photodissociation threshold was confirmed by using cutoff filters.

Results and Discussion

Photodissociation and Bonding of VFe^+ . VFe^+ photodissociates readily to give V^+ as the only product, reaction 5, as might be expected from the relative IP's of V and Fe.



The photodissociation spectrum of VFe^+ is shown in Figure 2. Two absorption bands, centered at 260 ± 10 and 340 ± 10 nm, are observed along with a threshold at 380 ± 10 nm, which is independent of neutral gas pressure in the cell. To obtain a value for the cross section for reaction 5, the relative photodissociation of toluene parent ion (C_7H_8^+) was determined under similar conditions as those given in the Experimental Section. The ratio of C_7H_8^+ photodissociation at 410 nm/ VFe^+ photodissociation at 340 nm was found to be 0.80. This ratio, along with $\sigma(410 \text{ nm}) = 5 \times 10^{-18} \text{ cm}^2$ for C_7H_8^+ ,¹⁶ yields a value of $\sigma(340 \text{ nm}) = 6 \pm 3 \times 10^{-18} \text{ cm}^2$ as the absolute cross section for reaction 5.

Assuming the cutoff at 380 ± 10 nm is a thermodynamic threshold, an absolute bond energy $D^\circ(\text{V}^+-\text{Fe}) = 75 \pm 5 \text{ kcal/mol}$ is determined. This value yields $D^\circ(\text{Fe}^+-\text{V}) = 101 \pm 5 \text{ kcal/mol}$ and $\Delta H_f^\circ(\text{VFe}^+) = 302 \pm 5 \text{ kcal/mol}$. For comparison, $D^\circ(\text{Fe}^+-\text{Fe}) = 63.5 \pm 6 \text{ kcal/mol}$ and $D^\circ(\text{Co}^+-\text{Fe}) = 66 \pm 7 \text{ kcal/mol}$.¹⁷ A theoretical V-Fe bond energy of 44 kcal/mol has been reported.¹⁸ Using these values in equation 6 yields $\text{IP}(\text{VFe}) = 5.40 \text{ eV}$. For comparison, $\text{IP}(\text{Fe}_2) = 5.90 \text{ eV}$ and $\text{IP}(\text{CoFe}) = 6.34 \text{ eV}$.¹⁹

$$\text{IP}(\text{VFe}) = D^\circ(\text{V}-\text{Fe}) + \text{IP}(\text{V}) - D^\circ(\text{V}^+-\text{Fe}) \quad (6)$$

The low IP of VFe , along with the strong bond energy of VFe^+ , implies that the d electrons might participate in the bonding process. Since the d orbitals are the largest for the early transition

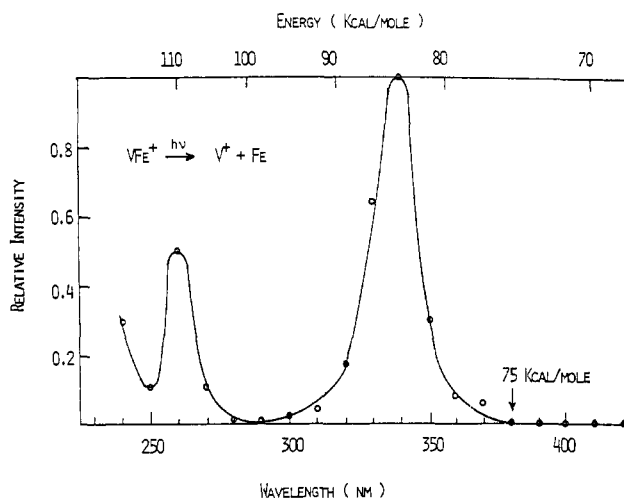


Figure 2. Photodissociation spectrum of VFe^+ obtained by monitoring reaction 5 as a function of wavelength at 10-nm resolution.

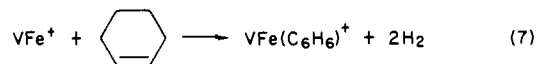
metals, d-d overlap between V^+ and Fe would be more dominant than between Co^+ and Fe. For CoFe^+ , the bond is postulated to be a single bond almost entirely due to the $4s$ molecular orbitals.⁸ The bonding in VFe and VFe^+ awaits detailed theoretical consideration, but if the bonding is due to both s and d orbital overlap, then VFe^+ could have all 12 valence electrons in bonding orbitals. The last electron in VFe would occupy an antibonding orbital, which is consistent with the low IP of VFe and its reduced bond energy relative to the ion.

Formation of VFe^+ . VFe^+ can be produced not only by the reaction of V^+ with $\text{Fe}(\text{CO})_5$ as described above but also by the reaction of Fe^+ with $\text{V}(\text{CO})_6$. The VFe^+ produced by either route reveals identical reactivity. Collision-induced dissociation of VFe^+ yields V^+ only, in accordance with Stevenson's rule.²⁰

Reactions with Alkanes. VFe^+ does not react with either linear (C_1-C_6) or cyclic (C_3-C_6) alkanes. Other metal dimers, such as Co_2^+ and CoFe^+ , have also been reported to be unreactive with alkanes.⁸ These results are in contrast to the corresponding atomic ions. Fe^+ and Co^+ react readily with alkanes by C-H and C-C bond insertion,^{21a} whereas V^+ reacts mainly by C-H bond insertion.^{21b} Table I summarizes the reactions of CoFe^+ and VFe^+ with hydrocarbons.

Reactions with Alkenes. VFe^+ is completely unreactive with linear (C_1-C_6) alkenes compared to CoFe^+ , which is unreactive with ethene, propene, and isobutene, but reacts extensively to dehydrogenate C_4-C_6 alkenes.⁸ The inertness of VFe^+ is surprising since both V^+ and Fe^+ readily react with C_4-C_6 alkenes to form predominantly dehydrogenation products.²² $D^\circ(\text{VFe}^+-\text{C}_4\text{H}_6)$ probably exceeds the 26 kcal/mol required to dehydrogenate 1-butene to butadiene, thus, there is evidently a barrier to the allylic C-H bond insertion required for the dehydrogenation process.

No reaction is observed between cyclopentene and VFe^+ . However, cyclic C_6 and C_7 alkenes do react with VFe^+ . For example, VFe^+ reacts rapidly with cyclohexene to eliminate 2H_2 , reaction 7. CID of $\text{VFeC}_6\text{H}_6^+$ formed in reaction 7 results in facile



elimination of C_6H_6 to yield VFe^+ . This result indicates that $D^\circ(\text{Fe}^+-\text{V}) > D^\circ(\text{Fe}^+-\text{C}_6\text{H}_6) = 59 \pm 5 \text{ kcal/mol}$ ²³ and

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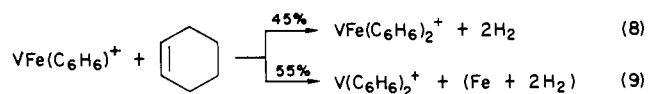
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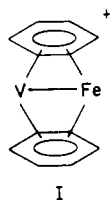
(19) (a) IP for Fe_2 : Lin, S.-S.; Kant, A. J. *Phys. Chem.* **1969**, 73, 2450.

(b) IP for CoFe : ref 17.

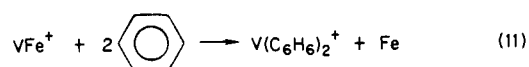
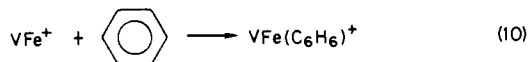
$D^{\circ}(V^+-Fe) > D^{\circ}(V^+-C_6H_6) = 62 \pm 7$ kcal/mol,²⁴ both of which are consistent with the photodissociation results. Secondary reaction of $VFeC_6H_6^+$ with cyclohexene yields two products, reactions 8 and 9. The product of reaction 8 probably has the



bis-benzene structure I. Binuclear palladium complexes containing two benzene rings sandwiching the Pd-Pd unit have been prepared and characterized.²⁵ Also, bridging arene-metal clusters of

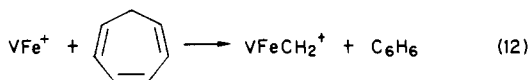


$M'M(\text{arene})_2$ (where $M'M = Cr, V$) have been observed in a frozen matrix by Ozin, et al.²⁶ With use of $\Delta H_f^{\circ}(V(C_6H_6)_2^+) = 163.5$ kcal/mol²⁷ and $\Delta H_f^{\circ}(VFe^+) = 302$ kcal/mol, the formation of $V(C_6H_6)_2^+$ from VFe^+ and cyclohexene is found to be exothermic by approximately 37 kcal/mol. It is even more exothermic if FeH_2 is lost as the neutral instead of Fe and H_2 .²⁸ Isolation and collision-induced dissociation of $VFe(C_6H_6)_2^+$ formed in reaction 8 produces $V(C_6H_6)_2^+$ exclusively (see Figure 1), indicating that the presence of the second benzene changes the bonding in the cluster dramatically. CID of $CoFe(C_6H_6)_2^+$ also revealed Fe loss resulting in $Co(C_6H_6)_2^+$.⁸ Reaction of VFe^+ with benzene, reactions 10 and 11, yields similar results to cyclohexene.



When the heats of formation mentioned above for reaction 9 are used, reaction 11 is determined to be exothermic by 79 kcal/mol.

VFe^+ will dehydrogenate cycloheptene slowly to form $VFe(C_7H_8)^+$. Unfortunately, this reaction was too slow to permit the isolation and CID of $VFe(C_7H_8)^+$. Carbene abstraction results from the reaction of VFe^+ with cycloheptatriene, reaction 12. In order for this reaction to occur, $D^{\circ}(VFe^+-CH_2) > 70$ kcal/mol.²⁹



For comparison, $D^{\circ}(Fe^+-CH_2) = 96 \pm 5$ kcal/mol³⁰ and

(23) Ligand displacement bracketing methods indicate that $D^{\circ}(Fe^+-C_6H_6) \sim D^{\circ}(Fe^+-H) = 59 \pm 5$ kcal/mol, see ref 17.

(24) Photodissociation measurements indicate a threshold at 460 ± 20 nm for $V-C_6H_6^+$, which implies a $D^{\circ}(V^+-C_6H_6) = 62 \pm 7$ kcal/mol: Jackson, T. C.; Freiser, B. S., in preparation.

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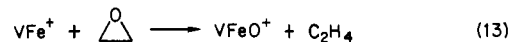
(27) Heat of formation of (bis-benzene)vanadium taken from Fischer and Reckziegel (Fischer, E. O.; Reckziegel, A. *Chem. Ber.* **1961**, *94*, 2204) and the ionization potential of (bis-benzene)vanadium obtained from Rosenstock et al. (Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data, Suppl. 1*, **1977**, *6*, I-494).

(28) $\Delta H_f^{\circ}(FeH_2) < 77.5$ kcal/mol: Halle, L. F.; Klein, F. S.; Beauchamp, J. L. *J. Am. Chem. Soc.* **1984**, *106*, 2543.

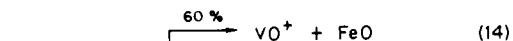
(29) Heats of formation of cycloheptatriene, carbene, and benzene taken from Rosenstock et al. (Rosenstock, H. M.; Draxl, K.; Steiner, B. W.; Herron, J. T. *J. Phys. Chem. Ref. Data, Suppl. 1* **1977**, *6*).

$D^{\circ}(V^+-CH_2) = 75 \pm 8$ kcal/mol.³¹ Isolation and CID of $VFeCH_2^+$ yields mainly ejection of $VFeCH_2^+$, with a small amount of $VFeC^+$ formed. H_2 loss was also observed for the low-energy CID of $FeCo_2CH_2^+$.³²

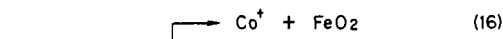
Reactions with Oxygenated Compounds. Since vanadium ion easily abstracts oxygen from many compounds ($D^{\circ}(V^+-O) = 131 \pm 5$ kcal/mol)³¹ while iron ion does not ($D^{\circ}(Fe^+-O) = 68 \pm 3$ kcal/mol),³³ the reactivity of the VFe^+ cluster ion was examined with several oxygenated compounds. VFe^+ will abstract an oxygen from ethylene oxide, reaction 13. VFe^+ will not abstract an



oxygen from O_2 to form $VFeO^+$ but does react very slowly to give two products, reactions 14 and 15. For reaction 14, FeO must



be the neutral lost for the reaction to be exothermic. This eliminates the possibility that $VFeO^+$ might be initially formed with enough excess internal energy to fragment to $Fe + VO^+$. Reaction 15 implies $\Delta H_f^{\circ}(VO_2) < 23$ kcal/mol, $D^{\circ}(V-2O) > 219$ kcal/mol, and $IP(VO_2) > IP(Fe) = 7.87$ eV.²⁹ Observation of reaction 13 combined with the absence of $VFeO^+$ formation from $VFe^+ + O_2$ indicates 85 kcal/mol $< D^{\circ}(VFe^+-O) < 119$ kcal/mol. $CoFe^+$ also abstracts an oxygen from ethylene oxide and will react with O_2 to yield two products, reactions 16 and 17.³⁴ Reaction 17 implies $D^{\circ}(CoFe^+-O) > 119$ kcal/mol.



CID of $VFeO^+$ formed in reaction 13 produces VO^+ exclusively, as would be expected from the strong V^+-O bond strength. $VFeO^+$ can also be produced by reaction of VO^+ with $Fe(CO)_5$, followed by the appropriate collisional activation pulses. CID of the $VFeO^+$ formed in this reaction gives identical results to the ion formed in reaction 13.

$VFeO^+$ reacts sequentially with ethylene oxide to abstract two additional oxygen atoms, giving first $VFeO_2^+$ and then $VFeO_3^+$. No further reaction is observed. For comparison, $CoFe^+$ will react with ethylene oxide to abstract up to two oxygens, producing $CoFeO_2^+$, whereas $FeCo_2^+$ and Co_3^+ abstract up to three oxygens from ethylene oxide.³⁴ CID of $VFeO_2^+$ produces two products, VFe^+ and at higher collisional energies Fe^+ . VO^+ is not observed in the CID of $VFeO_2^+$, in contrast to the results of reaction 14. This is surprising since less energy is required to form VO^+ and FeO than to form VFe^+ and O_2 ($\Delta H_f^{\circ}(VFe^+ + O_2) = 302$ kcal/mol while $\Delta H_f^{\circ}(VO^+ + FeO) = 274$ kcal/mol).³⁵ Apparently once the oxygens are bound to the cluster, there is a barrier to formation of VO^+ and FeO even though it is energetically favorable. $VFeO_3^+$ could not be collisionally dissociated even at energies up to 100 eV, implying that this is a tightly bound unit.

$VFe(CO)_4^+$ reacts with O_2 by displacing all the carbonyls to form $VFeO_2^+$, which then readily abstracts an oxygen from O_2

(30) $D^{\circ}(Fe^+-CH_2) = 96 \pm 5$ kcal/mol has been assigned by Halle et al. (Halle, L. F.; Armentrout, P. B.; Beauchamp, J. L. *Organometallics* **1982**, *1*, 963) but a lower $D^{\circ}(Fe^+-CH_2) = 83 \pm 4$ kcal/mol has been suggested by Jacobson and Freiser (Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1985**, *107*, 2605).

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(35) Heat of formation of VO^+ obtained from ref 31 and the heat of formation of FeO calculated from Murad (Murad, E. J. *Chem. Phys.* **1980**, *73*, 1381) along with ref 28.

Table I. Distribution of Neutral(s) Lost for the Primary Reactions of CoFe^+ and VFe^+ with Hydrocarbons^a

	CoFe^+ ^b			VFe^+		
	neutral(s)	ion	rel %	neutral(s)	ion	rel %
linear alkanes		no reaction			no reaction	
cyclic alkanes		no reaction			no reaction	
ethene		no reaction			no reaction	
propene		no reaction			no reaction	
2-methylpropene		no reaction			no reaction	
1-butene	H_2	$\text{CoFeC}_4\text{H}_6^+$	100		no reaction	
1-pentene	H_2	$\text{CoFeC}_5\text{H}_8^+$	100		no reaction	
1-hexene	H_2	$\text{CoFeC}_6\text{H}_{10}^+$	58		no reaction	
	2H_2	$\text{CoFeC}_6\text{H}_8^+$	42			
cyclopentene	H_2	$\text{CoFeC}_5\text{H}_6^+$	100		no reaction	
cyclohexene	2H_2	$\text{CoFeC}_6\text{H}_6^+$	88	2H_2	$\text{VFeC}_6\text{H}_6^+$	100
	$(\text{Fe} + 2\text{H}_2)$	CoC_6H_6^+	12			
benzene	Fe	CoC_6H_6^+	100		$\text{VFeC}_6\text{H}_6^+$	100
cycloheptene ^c	2H_2	$\text{CoFeC}_7\text{H}_8^+$	66	2H_2	$\text{VFeC}_7\text{H}_8^+$	100
	$(\text{Fe} + 2\text{H}_2)$	CoC_7H_8^+	34			
cycloheptatriene	(CoH)	FeC_7H_7^+	23	C_6H_6	VFeCH_2^+	100
	Co	FeC_7H_8^+	13			
	Fe	CoC_7H_8^+	64			

^a Product distribution reproducible to $\pm 10\%$. ^b Taken from ref 8. ^c This study.

to produce VFeO_3^+ , indicating $D^\circ(\text{VFeO}_2^+-\text{O}) > 119$ kcal/mol. $\text{VFe}(\text{CO})_3^+$ reacts more rapidly than $\text{VFe}(\text{CO})_4^+$ with O_2 to form VFeO_2^+ . In addition, VFe^+ and Fe^+ are also observed in minor abundance. The appearance of VFe^+ from $\text{VFe}(\text{CO})_3^+$ and O_2 requires that the neutral products formed be 2CO_2 and CO in order for the process to be exothermic. This indicates that once the oxygen atoms are bound to the metal, they can couple with the carbonyl ligands to eliminate CO_2 . $\text{VFe}(\text{CO})_2^+$ also reacts quickly with O_2 to yield predominantly VFe^+ and Fe^+ with a minor amount of VFeO_2^+ . Once again, exothermic formation of VFe^+ requires the loss of 2CO_2 as the corresponding neutral products. In all these cases, VFeO_2^+ , once formed, reacts quickly with O_2 to produce VFeO_3^+ . $\text{CoFe}(\text{CO})_3^+$ reacts readily with O_2 to produce CoFeO_2^+ exclusively, whereas $\text{Co}_2(\text{CO})_4^+$ reacts slowly to yield $\text{Co}_2\text{O}_2(\text{CO})^+$, and $\text{Co}_2(\text{CO})_3^+$ reacts quickly to produce Co_2O_2^+ .³⁴ Each of these reactions suggests that the added oxygen goes on as two oxygen atoms rather than as an O_2 molecule since multiple carbonyl loss is observed. Therefore, species with a greater number of carbonyls tend to react more slowly since there are fewer coordination sites available.

VFe^+ will not react with N_2O even though both V^+ and Fe^+ will abstract an oxygen. Fe_2^+ , Co_2^+ , and CoFe^+ are also found to be unreactive with N_2O .³⁴ Even though oxygen abstraction from N_2O should be energetically favorable, absence of reaction may imply a similar kinetic barrier due to spin multiplicity differences as was assigned by Beauchamp and co-workers for atomic transition-metal ions.³³

Conclusions

The photodissociation of VFe^+ shows absorption maxima in the ultraviolet region at 260 ± 10 and 340 ± 10 nm. The threshold

at 380 ± 10 nm is assigned to be thermodynamic and not spectroscopic since many of the metal complexes are observed to have low intensity "tails" that continue well out into the visible region.³⁶

The dimer VFe^+ is more strongly bound than other known heteronuclear cluster ions.^{8,37} This strong bond energy and the low ionization potential of VFe indicate that the d electrons are most likely involved in the bonding and are not localized on the metal atoms. Whereas V^+ and Fe^+ react with alkanes by C-H and C-C bond insertions, VFe^+ is unreactive with linear and cyclic alkanes. The gas-phase chemistry of VFe^+ is similar to CoFe^+ for alkanes but differs significantly in reactivity toward alkenes, where VFe^+ is observed to be considerably less reactive.

The bracketed value 85 kcal/mol $< D^\circ(\text{VFe}^+-\text{O}) < 119$ kcal/mol is intermediate to $D^\circ(\text{Fe}^+-\text{O}) = 68$ kcal/mol and $D^\circ(\text{V}^+-\text{O}) = 131$ kcal/mol and less than $D^\circ(\text{CoFe}^+-\text{O})$, which is determined to be greater than 119 kcal/mol. VFe^+ is considerably less reactive with O_2 than $\text{VFe}(\text{CO})_x^+$ ($x = 2-4$). VFe^+ does abstract up to three oxygens from ethylene oxide; in contrast to CoFe^+ , which will abstract only two oxygens.³²

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