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Gas phase ion molecule chemistry of tetracarbonyl (η^5-cyclopentadienyl) vanadium by Fourier transform ion cyclotron resonance

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Abstract

The kinetics of the reactions between the $CpV(CO)_4$ molecule and its fragment cations and anions have been examined using Fourier transform ion cyclotron resonance (FTICR) techniques. With 25 eV electron impact ionization the fragment cations V^+ and $CpV(CO)^+_{n=0-4}$ react principally by charge exchange or by condensation with the parent neutral molecule. Rate constants for these pathways have been determined along with kinetic evidence for the existence of excited state cations. Some of the product cations show unexpected stability despite their large formal electron deficiency. Exchange of carbonyl ligands was also observed. Under 2.5 eV electron impact, only two anions are produced: $CpV(CO)^-_{n=2,3}$, both of which are unreactive with the parent neutral. (Int J Mass Spectrom 182/183 (1999) 139–148) © 1999 Elsevier Science B.V.

Keywords: Carbonyl ligands; Fourier transform ion cyclotron resonance mass spectrometry; Gas phase ion chemistry

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1. Introduction

Tetracarbonyl (η^5-cyclopentadienyl) vanadium, $CpV(CO)_4$, is an orange-coloured crystalline, air-sensitive solid, melting at 139 °C and subliming at 90 °C (0.5 mm Hg). First prepared by Fischer and Hafner in 1954 [1], its molecular geometry resembles a "four-legged piano stool" consisting of a square pyramidal $V(CO)_4$ unit capped by a pinacoid pentagonal η^5-Cp unit. The crystal structure was first elucidated in 1967 [2].

Vanadium carbonyls and organo-vanadium carbonyls have been of marked interest since the synthesis in 1956 of the vanadium homologue of ferrocene; i.e. Cp_2V, or vanadocene by Wilkinson [3]. Some related organo-vanadium species, first synthesised in solution, were $Cp_2V_2(CO)_5$ in 1970 [4], the $Cp_2V(CO)_2^+$ cation [5], and vanadium carbonyls, $V(CO)_4$ and $V(CO)_5$ [6].

Gas phase reactions of bare and complexed vanadium ions have been examined since the positive ion mass spectral analyses on $CpV(CO)_4$ by Winters [7] and Müller [7] from 1965–1970. Under 70 eV electron impact, a series of fragment cations showing successive losses of CO and Cp ligands were observed. Energetics of bonds involving vanadium atoms in the gas phase have been analysed and collated [8–11]. Bond order, bond strength, and kinetics of gaseous V^+ when combined with hydrogen [12], alkane, alkene and alkyne units [13–16], and oxygen [17,18] have been measured and compiled.

Other mass spectral analyses have yielded evi-

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Dedicated to the fond memory of Professor Ben Freiser; a colleague, a friend, a creative and dedicated scientist.

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Table 1
Disappearance rate constants for vanadium cations

Ion	Electron deficiency per V atom	Pseudo-first order rate constant (k') d (s^{-1})[a]	Second order rate constant (k) ($\times 10^9$ mol^{-1} cm^3 s^{-1})[b]
V^+	14	0.604	2.61
CpV^+	9	0.382	1.65
$CpVCO^+$	7	0.227	0.98
$CpV(CO)_2^+$	5	0.120	0.52
$CpV(CO)_3^+$	3	0.0255	0.12
$CpV(CO)_4^+$	1	0.010	0.043
$(CpV)_2^+$	8.5	0.259	1.12
$(CpV)_2CO^+$	7.5	0.211	0.91
$(CpV)_2(CO)_2^+$	6.5	0.101	0.44
$(CpV)_2(CO)_3^+$	5.5	0.0394	0.17
$(CpV)_2(CO)_4^+$	4.5	<0.005	<0.02
$(CpV)_3(CO)_2^+$	7	<0.005	<0.02
$(CpV)_3(CO)_3^+$	6.3	0.0413	0.18
$(CpV)_3(CO)_4^+$	5.7	0.0749	0.32
$(CpV)_4(CO)_3^+$	6.8	<0.005	<0.02

[a] Calculated from initial slopes of semilog plots; all data ± 10%.
[b] All data ± 30%.

dence of gas phase cation–molecule condensations resulting in generation of bimetal clusters such as $Cp_2V_2(CO)_3^+$, first noted by Fischer and Schneider [19] and Müller [20] in 1970. In the latter study, $Cp_2V_2(CO)_{0-5}^+$ ions were seen in the mass spectra of $Cp_2V_2(CO)_5$. However, gas phase kinetic studies on these and related ions, and on other Cp-vanadium carbonyls have not yet been performed. The present study, involving $CpV(CO)_4$ positive and negative ion–molecule chemistry utilising Fourier transform ion cyclotron resonance (FTICR) provides further information regarding the behaviour of bare and ligated organo-vanadium ions in the gas phase.

2. Experimental

Kinetic experiments were performed using an FTICR mass spectrometer equipped with a 1.9 Tesla electromagnet and Nicolet FTMS 1000 FTICR controller. A 16.4 cm^3 cubic cell [21,22] served as ion trap and reaction chamber.

Pseudo-first order rate constants for reactive ions were determined from intial slopes of log intensity versus time plots. Pressures were monitored with a Varian 971-0018 ion gauge that has an ion gauge sensitivity calibrated to read the correct pressure for N_2. Since ion gauge sensitivity varies with compound, the indicated pressure was converted to an actual organometallic pressure using the method of Bartmess [23] that corrects for relative gauge sensitivities. A molecular polarizability of 22.36 $(Å)^3$ [24] for $CpV(CO)_3$ was used in this sensitivity correction.

Operating parameters were as follows: electron beam energies: 10–70 eV [positive electron ionization (EI)], 1–5 eV (negative EI); trap voltages: ±1.0V; indicated gauge pressures: 10^{-6}–10^{-9} Torr; ion trapping time: 0–25 s. The kinetic data in Tables 1–5 were obtained at $T = 300$ K with $CpV(CO)_3$ pressure $= 6 \times 10^{-8}$ Torr. Pure $CpV(CO)_4$ was obtained from Alfa Products. After several freeze–pump–thaw cycles, no impurities were observed in the mass spectra.

3. Results and discussion

Ionization by 25 eV electrons on tetracarbonyl (η^5-cyclopentadienyl) vanadium, (**I**), generates frag-

Table 2
Relative electron transfer rate constants for vanadium cations reacting with neutral $CpV(CO)_4$ molecules

Ion	Second order rate constant (k) ($\times 10^9$ mol^{-1} cm^3 s^{-1})[a]	Relative rate[b]
V^+	2.61	100
CpV^+	0.541	21
$CpVCO^+$	0.372	14
$CpV(CO)_2^+$	0.238	9
$CpV(CO)_3^+$	0.06[c]	2
$(CpV)_2^+$	0.368	14
$(CpV)_2CO^+$	0.273	10
$(CpV)_2(CO)_2^+$	0.134	5
$(CpV)_2(CO)_3^+$	0.02	1
$(CpV)_3(CO)_3^+$	0.043	2
$(CpV)_3(CO)_4^+$	<0.02	<1

[a] All data ± 30%.
[b] Relative to V^+ rate taken as 100; all data ± 10%.
[c] May be due to carbonyl addition contribution as well.

ment ions as follows: CpV^+ (42%), $CpVCO^+$ (10%), $CpV(CO)_2^+$ (14%), $CpV(CO)_3^+$ (4%), $CpV(CO)_4^+$ (12%), V^+ (7%), and minor amounts of $C_3H_3V^+$ (5%). This distribution compares with that of Winters [7], using 70 eV electron ionisation: CpV^+ (41%), $CpVCO^+$ (2.5%), $CpV(CO)_2^+$ (4.3%), $CpV(CO)_3^+$ (1.5%), $CpV(CO)_4^+$ (3.3%), V^+ (24%), $C_3H_3V^+$ (13%).

Table 3
Relative clustering rates for vanadium cations reacting with neutral $CpV(CO)_4$ molecules

Ion	Second order rate constant (k) ($\times 10^9$ mol^{-1} cm^3 s^{-1})[a]	Relative rate[b]
CpV^+	1.02	100
$CpVCO^+$	.355	35
$CpV(CO)_2^+$	.199	20
$CpV(CO)_3^+$	.028	3
$CpV(CO)_4^+$	.017	2
$(CpV)_2^+$	.290	30
$(CpV)_2CO^+$	.411	40
$(CpV)_2(CO)_2^+$	.208	20
$(CpV)_2(CO)_3^+$	.100	10
$(CpV)_2(CO)_4^+$	<.02	<2
$(CpV)_3(CO)_2^+$	<.02	<2
$(CpV)_3(CO)_3^+$	.065	6
$(CpV)_3(CO)_4^+$	.260	26

[a] All data ± 30%.
[b] Relative to CpV^+ rate taken as 100; all data ± 10%.

Table 4
Relative CO ligand loss rates for vanadium cations reacting with neutral $CpV(CO)_4$ molecules

Ion	Rate constant (k) ($\times 10^9$ mol^{-1} cm^3 s^{-1})	Relative rate
$CpVCO^+$	<.010	<.2
$CpV(CO)_2^+$	.043	.7
$CpV(CO)_3^+$	.061	1.0
$CpV(CO)_4^+$	.018	.3
$(CpV)_2CO^+$	.048	.8
$(CpV)_2(CO)_2^+$	.052	.9
$(CpV)_2(CO)_3^+$	.026	.45
$(CpV)_2(CO)_4^+$	<.010	<.2
$(CpV)_3(CO)_2^+$	<.010	<.2
$(CpV)_3(CO)_3^+$	.048	.8
$(CpV)_3(CO)_4^+$	<.010	<.2

[a] All data ± 30%.
[b] Relative to $CpV(CO)_3^+$ rate taken as 1.0 all data ± 10%.

General temporal behaviour patterns for each fragment ion were determined by the single resonance technique [25], in which the ions were generated by EI, allowed to react with the neutral precursor over measured time periods, then analyzed by FTICR. During reaction periods of up to 25 s, the polynuclear ion clusters $Cp_2V_2(CO)_{n=0-4}^+$, $Cp_3V_3(CO)_{n=2-4}^+$, and $Cp_4V_4(CO)_{n=3,4}^+$ were generated.

Typical formation and disappearance behaviour of

Table 5
Relative rates of CO ligand addition for vanadium cations reacting with neutral $CpV(CO)_4$ molecules

Ion	Second order rate constant (k) ($\times 10^9$ mol^{-1} cm^3 s^{-1})[a]	Relative rate[b]
CpV^+	.100	1.0
$CpVCO^+$	.216	2.2
$CpV(CO)_2^+$	.043	0.4
$CpV(CO)_3^+$	.013[c]	0.1
$(CpV)_2^+$	.494	5.0
$(CpV)_2CO^+$	.173	1.7
$(CpV)_2(CO)_2^+$	.048	0.5
$(CpV)_2(CO)_3^+$	.026	0.3
$(CpV)_2(CO)_4^+$	<.020	<0.2
$(CpV)_3(CO)_2^+$	<.020	<.2
$(CpV)_3(CO)_3^+$	.048	0.5
$(CpV)_3(CO)_4^+$	<.020	<.2

[a] All data ± 30%.
[b] Relative to CpV^+ rate taken as 1.0 all data ± 10%.
[c] May be via electron transfer process only.

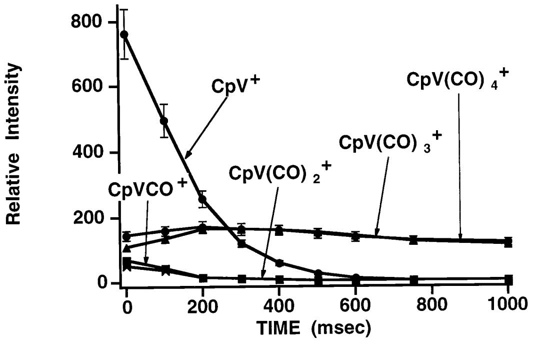

Fig. 1. Temporal behaviour of primary fragment cations of $CpV(CO)_4$.

primary $(CpV)_1(CO)^+_{0-4}$ ions are illustrated in Fig. 1. Figs. 2 and 3 show analogous temporal behaviour patterns of some of the more prominent binuclear cluster cations: $(CpV)_2(CO)^+_{2-4}$, and trinuclear cluster cations: $(CpV)_3(CO)^+_{3,4}$.

FTICR multiple resonance techniques developed earlier [25,26] permitted identification of reaction products of each fragment ion. Two sequential frequency sweeps were performed to retain selected ions and eject all others. For example, one frequency sweep ejected all ion masses below that of CpV^+ and this sweep was immediately followed by a second sweep to eject all ions of higher mass. CpV^+, the only remaining ion in the system, was then allowed to react with neutral compounds. A plot of the temporal behaviour of CpV^+ and its products is illustrated in Fig. 4. Analogous temporal behavioral plots for a representative secondary cation cluster, $(CpV)_2(CO)^+$, and its reaction products, are shown in Fig. 5.

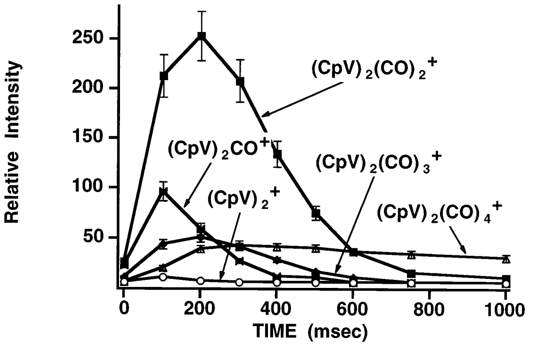

Fig. 2. Temporal behaviour of binuclear cluster cations of $CpV(CO)_4$.

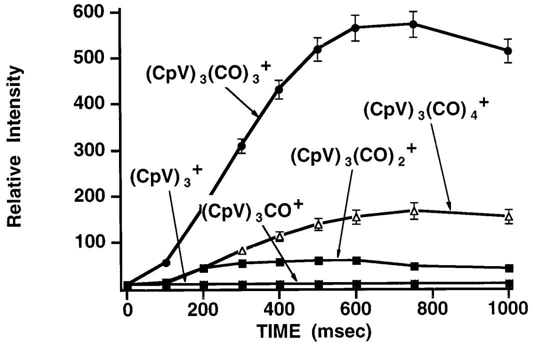

Fig. 3. Temporal behaviour of trinuclear cluster cations of $CpV(CO)_4$.

Kinetic data obtained from such temporal ion monitoring were used to calculate rate constants of formation and decay of each ion product. Table 1 lists rate constants for the disappearance of the principal reactive ions. Monitoring the temporal history of each ion product revealed an interrelated series of reaction pathways that are summarized in the following section.

4. Principal reaction pathways in the $CpV(CO)_4$ system

4.1. Primary (EI) fragmentation of the neutral parent $CpV(CO)_4$ molecule

Electron impact on the parent neutral molecule generates its characteristic fragment ions

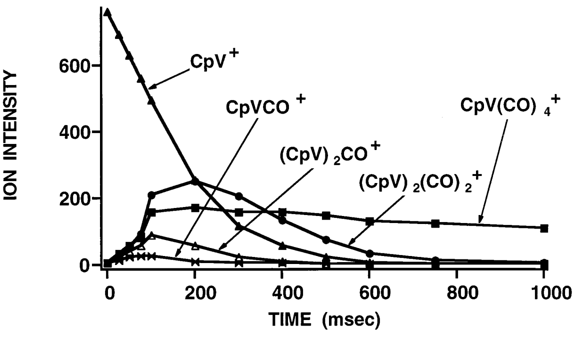

Fig. 4. Temporal behaviour of CpV^+ and cation products.

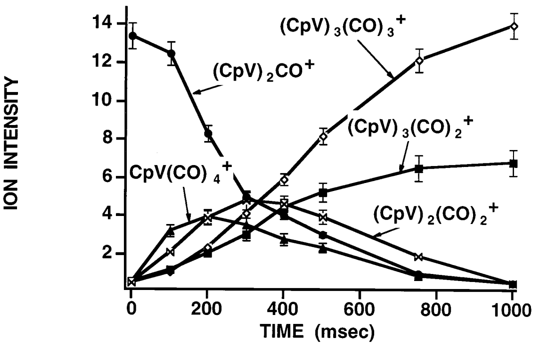

Fig. 5. Temporal behaviour of $(CpV)_2CO^+$ and cation products.

$$CpV(CO)_4 + e^- \rightarrow CpV(CO)^+_{n=0\text{–}4},$$

$$V^+ \text{ (minor } C_3H_3V^+) + 2e$$

4.2. Ion–molecule reactions: (positive ion + $CpV(CO)_4$ → products)

The reactions of the $CpV(CO)_4$ fragment ions with the parent neutral can be classified according to the type of ion–molecule reaction.

4.2.1. Type 1. Charge transfer

$$(CpV)(CO)^+_{n=0\text{–}3} + CpV(CO)_4$$

$$\rightarrow CpV(CO)_4^+ + \ldots$$

$$(CpV)_2(CO)^+_{n=0\text{–}4} + CpV(CO)_4$$

$$\rightarrow CpV(CO)_4 + \ldots$$

$$(CpV)_3(CO)^+_{n=2\text{–}4} + CpV(CO)_4$$

$$\rightarrow CpV(CO)_4 + \ldots$$

$$(CpV)_4(CO)^+_{n=3,4} + CpV(CO)_4$$

$$\rightarrow CpV(CO)_4 + \ldots$$

$$V^+ + CpV(CO)_4 \rightarrow CpV(CO)_4 + \ldots$$

The relative rates of these electron transfer processes are listed in Table 2. Ions with very large formal electron-deficient vanadium cores, such as in CpV^+ or $CpVCO^+$, react rapidly in this mode. For example, CpV^+ (with nine electrons per vanadium atom) reacts approximately 2.3 times faster than $CpV(CO)_2^+$ (13 electrons per V atom), and $CpVCO^+$ (11 electrons per V atom) reacts 1.6 times faster, in producing $CpV(CO)_4^+$. Furthermore, $(CpV)_2^+$ reacts approximately 2.8 times faster, and $(CpV)_2CO^+$ reacts 2.0 times faster, than does $(CpV)_2(CO)_2^+$.

Apparently all ionic species produced, including all polynuclear ionic cluster fragments such as $(CpV)_3(CO)_3^+$, $(CpV)_3(CO)_4^+$, and $(CpV)_4^+$ clusters, eventually absorb an electron from the parent molecule that is ever present in large excess. Consequently, $CpV(CO)_4^+$ becomes the predominant ionic species present after 25 s.

4.2.2. Type 2. Ion–molecule condensation reactions with simultaneous ejection of up to seven CO ligands

Principal reaction paths for each fragment ion are summarised in the following equations.

Primary fragment ion condensations:

$$CpV^+ + CpV(CO)_4$$

$$\rightarrow (CpV)_2(CO)^+_{n=0\text{–}2} + mCO$$

$$CpVCO^+ + CpV(CO)_4$$

$$\rightarrow (CpV)_2(CO)^+_{n=0\text{–}3} + mCO$$

$$CpV(CO)_2^+ + CpV(CO)_4$$

$$\rightarrow (CpV)_2(CO)^+_{n=0\text{–}3,4*} + mCO$$

$$CpV(CO)_3^+ + CpV(CO)_4$$

$$\rightarrow (CpV)_2(CO^+_{n=0*,1\text{–}4} + mCO$$

$$CpV(CO)_4^+ + CpV(CO)_4$$

$$\rightarrow (CpV)_2(CO)^+_{n=1\text{–}4} + mCO$$

Binuclear ionic cluster condensations:

$$(CpV)_2^+ + CpV(CO)_4$$

$$\rightarrow (CpV)_3(CO)^+_{n=1*,2,3} + mCO$$

$$(CpV)_2(CO)^+_{n=1\text{–}3} + CpV(CO)_4 \rightarrow (CpV)_3(CO)^+_{n=2\text{–}4} + mCO$$

$$(CpV)_2(CO)^+_4 + CpV(CO)_4 \rightarrow (CpV)_3(CO)^+_{n=3,4} + mCO$$

Trinuclear ionic cluster condensations:

$$(CpV)_3(CO)^+_{n=2\text{–}4} + CpV(CO)_4 \rightarrow (CpV)_4(CO)^+_{n=2*,3,4} + mCO$$

(The asterisk represents ion intensities that are less than 5%.)

Overall relative clustering rates for the more abundant cations are listed in Table 3. Rates generally decrease with cluster size and with number of carbonyl ligands present in the reacting cation. Condensation with the parent neutral molecule, with simultaneous loss of one or more CO ligands, is commonly observed in many other aryl transition-metal carbonyl systems recently investigated by several authors such as Fredeen [27,28], Foster [29], Meckstroth [30,31], Parisod [30,31], and Mullen [20].

In the present system, generation of larger cluster ions containing Cp_5V_5, Cp_6V_6, or larger cores has not been detected. If the process of condensation with the parent molecule must compete with electron transfer, then the highly electron-deficient ions in this system may generate a cluster during one collision with the parent neutral, but later gain an electron from the neutral molecule in a subsequent collision, losing the positive charge and becoming invisible to the detector. In each polynuclear series, clustering rates apparently are largest for reactive ions with less than three CO ligands; rates are small when the number of CO units present in the ion is larger (i.e. > 3), indicating that coordination sites are less available.

4.2.3. Type 3. Carbonyl loss by some reacting cations, possibly during electron transfer

Here y = number of CO ligands lost subsequently by the following reacting ions:

$(CpV)(CO)^+_2 (y = 1, 2)$;

$(CpV)(CO)^+_3 (y = 1, -3)$;

$(CpV)(CO)^+_4 (y = 1\text{–}4)$;

$(CpV)_2(CO)^+ (y = 1)$;

$(CpV)_2(CO)^+_2 (y = 1, 2)$;

$(CpV)_2(CO)^+_3 (y = 1\text{–}3)$;

$(CpV)_2(CO)^+_4 (y = 1)$;

$(CpV)_3(CO)^+_{3,4} (y = 1)$

Table 4 lists relative rates of CO loss for some of these ions. Cations that are relatively rich in CO [e.g. $CpV(CO)^+_4$, $Cp_2V_2(CO)^+_4$, or $Cp_3V_3(CO)^+_4$] and which also may be excited (possess excess kinetic energy after electron ionization or rebound from collisions with neutrals) react by ejecting one or more CO ligands. Measured CO loss rates reflect this to some degree: for instance relative rates of CO ejection by ions $CpV(CO)^+_3$, $CpV(CO)^+_2$; and $CpVCO^+$ are in the ratios 10:7: < 2, as shown in Table 4.

Addition of CO ligands by some reactive cations (z = number of CO ligands abstracted from the neutral parent molecule by the following reacting ions):

$CpV^+ (z = 1\text{–}3)$; $CpVCO^+ (z = 1, 2)$;

$CpV(CO)^+_2 (z = 1)$; $(CpV)^+_2 (z = 1, 2)$;

$(CpV)_2CO^+ (z = 1, 2)$;

$(CpV)_2(CO)^+_2 (z = 1)$;

$(CpV)_2(CO)^+_3 (z = 1)$;

$(CpV)_3(CO)^+_2 (z = 1, 2)$;

$(CpV)_3(CO)^+_3 (z = 1)$

Table 5 lists comparative CO addition rates for some of these ions. The preceding ions, which are ligand unsaturated and “carbonyl poor” (e.g. CpV^+, $Cp_2V_2CO^+$, or $Cp_3V_3(CO)^+_2$), abstract one or more CO ligands from the parent neutral $CpV(CO)_4$. During any specific ion–molecule interaction, the strong σ basicity of CO ligands in the neutral $CpV(CO)_4$

molecule should favor their addition to cations of greater ligand unsaturation (i.e. CO transfer to CpV^+, $Cp_2V_2^+$, $Cp_3V_3(CO)_2^+$) rather than their remaining attached to a neutral, electron-saturated "CO-rich" $CpV(CO)_4$ parent molecule. Experimental rates of carbonyl abstraction generally exhibit this: for example, the relative rate of single CO absorption by $CpVCO^+$ and $CpV(CO)_2^+$ are in the approximate ratios 5:1; and by $(CpV)_2(CO)^+$ and $(CpV)_2(CO)_2^+$ in the ratios 3:1, as shown in Table 5.

4.2.4. Type 4. Hydrogen exchange reactions

The appearance of protonated molecules, $CpV(CO)_{3,4}H^+$, indicates that one of two processes must occur: either the molecular cation donates a proton to a neutral molecule, i.e.

$$C_5H_5V(CO)_4^+ + CpV^*(CO)_4 \rightarrow CpV^*(CO)_{3,4}(H)^+ + C_5H_4V(CO)_4 + \ldots$$

or else the neutral molecule donates a hydrogen atom to the molecular ion, i.e.

$$CpV(CO)_4^+ + C_5H_5V^*(CO)_4 \rightarrow CpV(CO)_{3,4}(H)^+ + C_5H_4V^*(CO)_4 + \ldots$$

Without discriminatory isotopic experiments, these processes are indistinguishable. Initial rates of these reactions are similar to those of clustering and CO loss processes, but after 25 s, the abundance of $CpV(CO)_4H^+$ (which possesses an 18-electron metal centre) slowly increases with respect to that of the molecular ion, $CpV(CO)_4^+$ (a 17-electron metal centre).

4.3. Negative ion chemistry

Electron impact (2.5 eV) on $CpV(CO)_4$ produces two unreactive anions, $CpV(CO)_2^-$ (60%) and $CpV(CO)_3^-$ (30%). This distribution compares with that of Müller [20] using 70 eV EI: $CpV(CO)_2^-$ (33%), $CpV(CO)_3^-$ (67%). Further reaction, such as clustering of these products, was not observed for up to 1000 ms. These anions are not highly electron deficient compared to their parent molecule, and consequently are relatively slow to interact with it.

5. Conclusions: general features of the $CpV(CO)_4$ system

(1) All of the principal cations initially formed by electron impact on (**I**), i.e. V^+, $CpV(CO)_{0-4}^+$, are chemically reactive with parent neutral, whereas both fragment anions, $CpV(CO)_{2,3}^-$, are unreactive. Second order decay rate constants (Table 1) decline with coordination unsaturation, varying from 2.6–.02 ($\times 10^{-9}$ mol^{-1} cm^3 s^{-1}), within approximate Langevin ranges for ion-nonpolarised molecule reactions.

(2) Electron transfer, which is essentially a competition with the parent molecule for an electron, appears to be one of the two most important reaction pathways for all the cationic species in this system. Rate constants for electron transfer are listed in Table 2. For the bare metal cation V^+, electron transfer rather than condensation is the sole mode of interaction with the parent molecule. This behaviour contrasts with that of bare metal cations in the η^6-benzene chromium tricarbonyl, η^5-Cp-manganese tricarbonyl, and other systems [33], in which clustering channels are also important.

(3) Cluster formation is the second dominant reaction pathway for all the cations in this $CpV(CO)_4$ system except for that of the bare metal cation (V^+). Several new cation clusters containing three and four vanadium atoms were seen here for the first time: $(CpV)_3(CO)_{1-4}^+$ and $(CpV)_4(CO)_{2-4}^+$. Larger cations containing five vanadium atoms, for example, $(CpV)_5(CO)_4^+$ were also observed in small quantities. The integrity of the Cp–V bond within the vanadium clusters tends to be maintained throughout successive condensation hierarchies; i.e. in $(CpV)_2$, $(CpV)_3$, $(CpV)_4$, etc., cationic cluster fragments. This behaviour has been noted in several other analogous metal systems [33]. Metal–aryl bond integrity is apparently a reflection of the powerful multiple d-π, metal-aryl electronic interaction that exists in this type of complex.

Clustering dwindles with formation of trimetallic

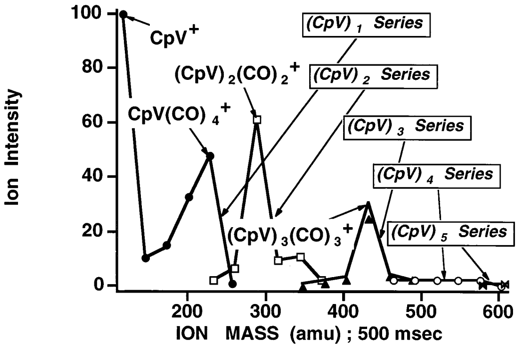

Fig. 6. Relative abundances of cation clusters of $CpV(CO)_4$ at 500 ms.

$(CpV)_3^+$, or larger cores at pressures presently used (10^{-6}–10^{-9} Torr); $(CpV)_{4,5}^+$ cation cluster fragments were observed in very low yields only in the higher pressure ranges or after long reaction times. Relative clustering rates, listed in Table 3, depend inversely upon cation mass and carbonyl coordination number. Cluster termination may be a consequence of ligand crowding around the central metal–metal core of each ion–molecule cluster. Also, excess vibrational energies in the transition state complex formed by collisions between any specific cation and the neutral molecule may not favour formation of larger [i.e. $(CpV)_5$, etc.] cation clusters. This may also explain the mobility of CO units seen in some of the primary cations.

(4) The cations CpV^+, $CpV(CO)_4^+$, $(CpV)_2(CO)_2^+$, and $(CpV)_3(CO)_3^+$ appear kinetically stable compared to other ions in the same $(CpV)_n$ series. For example, Fig. 6 shows ion abundances at 500 ms versus ionic mass. Relatively large intensities of ions $(CpV)_2(CO)_2^+$ and $(CpV)_3(CO)_3^+$ appear here as peaks on the intensity plot, whereas other ions in each series, such as $(CpV)_2CO^+$ and $(CpV)_3(CO)_2^+$, are of relatively low intensity. As suggested earlier, the anomalously large abundance of certain ions like these may be the consequence of increased metal–metal bond order, or of enhanced CO ligand hapticity [30,32–34] within some cluster ions.

The large intensity of $CpV(CO)_4^+$, illustrated in Fig. 6 is not surprising, since it is the molecular ion and expectedly abundant immediately after 25 eV electron ionization. Subsequently, this ion dominates the entire reaction regime, because of its relative electronic stability and also because it is the principal product of all the electron transfer reactions.

However, the large and persistent intensities of the ions CpV^+, $CpV(CO)_3^+$, $(CpV)_2(CO)_2^+$, and $(CpV)_3(CO)_3^+$ are unexpected, especially because all possess large formal electron deficiencies. Some degree of multiple metal–metal bonding within the latter two ions, $(CpV)_2(CO)_2^+$ and $(CpV)_3(CO)_3^+$, may contribute to their unusual abundances. This behaviour resembles that seen in some cationic Cr_2 complexes, noted elsewhere [30,31,33,34].

CpV^+, possessing nine electrons and a very strong Cp-vanadium linkage [11], may possess enhanced electronic (i.e. half-full metal orbital) stability. However, apparent anomalous abundances, as shown by CpV^+, $CpVCO^+$, and $CpV(CO)_4^+$, are possibly unrelated to bonding phenomena, but may be related to the presence of highly reactive, excited states of some of these ion reactants.

(5) Fig. 8 illustrates the relationship between pseudo-first order decay rate constants for each reacting cation (summarised in Table 1) and formal electron deficiencies for several of the more abundant cations of this system. Such plots have proved useful for predicting unusual bonding patterns within ion clusters [31,33]. The relationship between rate and electron deficiency is fairly well behaved here. More electron-rich ions such as $(CpV)_2(CO)_3^+$ may possess stabilising multiple- or partial multiple-bonded vanadium–vanadium cores, surrounded by a protective sheath of ligands.

(6) In accounting for kinetic behaviour of the primary vanadium fragment cations, participation by excited states must be considered. The energy difference between ground and first excited state bare vanadium cations is only 0.33 eV [10]; therefore it is possible that many of the smaller daughter fragment cations possess excited electronic configurations after ionisation by 25 eV electrons. There are several lines of evidence for the existence of such excited states in this $CpV(CO)_4$ system: (1) nonlinear pseudo-first order decay behaviour shown by some of the smaller cation cluster fragments, e.g. V^+ and CpV^+, illus-

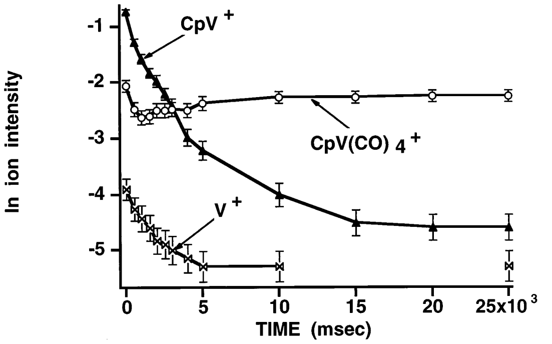

Fig. 7. Deviations from pseudo-first order decay behaviour in the $CpV(CO)_4$ system.

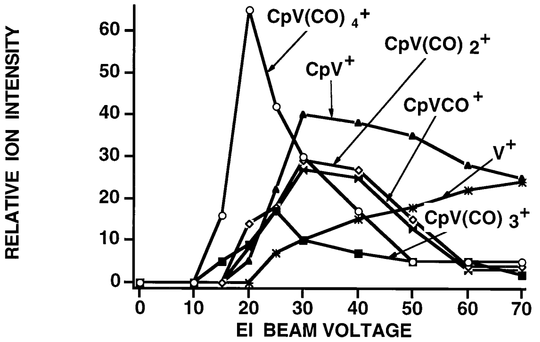

Fig. 9. Fragment cation abundances from $CpV(CO)_4$ vs. ionizing energy.

trated in Fig. 7; (2) marked mobility of CO ligands, especially in smaller cation cluster fragments; (3) lack of parallel anomalous behaviour in the anion regime, where reacting ions are generated at much lower energies; and (4) reappearance of the molecular ion $CpV(CO)_4^+$ after its initial disappearance (note Fig. 7), suggesting that the initial species of $CpV(CO)_4^+$ may be excited and reactive, whereas the final ionic species is in the ground state and kinetically stable.

Intercepts of the semilog rate plots allowed some estimation of the proportions of excited and ground state ions. For the bare vanadium cation (V^+) the proportion of excited state ions was thus calculated to be approximately 45%; for CpV^+, 80%; and for the molecular cation, $CpV(CO)_4^+$, 30%. Greater opportunity for relaxation should exist for larger cations (larger size, more vibrational modes) than for smaller ones such as monatomic V^+, so that residual energy would be expected to be retained longer in the smaller ion species; however, these data indicate that initial proportions of excited state ions was large for all three cations. As Russell has noted [35], bare metal cations such as Fe^+ in the $Fe(CO)_5$ system, are apparently able to retain excess excitation energy even after many collisions, and the reactivity of such excited state ions may differ widely from that of the corresponding ground state ions. Excited state reactivity differences between ground and excited state metal ions have been measured for small cations in the $Cr(CO)_6$ [36], $Fe(CO)_5$ [35], Co_2NO^+ [37], and $Mn_2(CO)_{10}$ [38,39] systems as well.

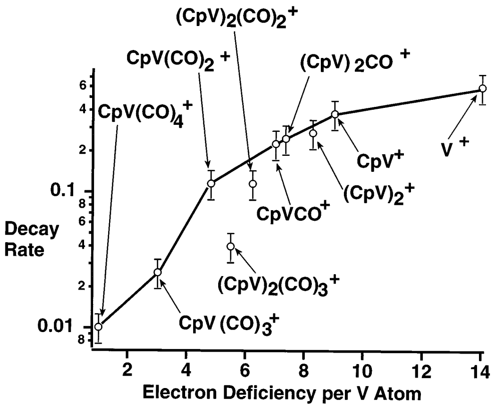

Fig. 8. Relationship between reactivity and electron deficiency for V and V_2 cations in the $CpV(CO)_4$ system.

For the other, larger vanadium cations in this system, semilog rate plots are linear, indicating ground state reactive behaviour.

(7) Threshold energies for the appearance of positive ions and their abundance with varying electron energy of ionisation in the $CpV(CO)_4$ system are shown in Fig. 9. These data for appearance of cations with ionising voltage are generally in accord with earlier results obtained by other mass spectrometric methods [7,40].

The structural geometries of the new binuclear and trinuclear cluster cations generated in this system are not yet characterised. Several possibilities for arrangement of multiple vanadium-Cp groups exist, either as intimately bound metal–metal cores, or as Cp–metal–Cp–metal alternating chains, or as some combination of both models. Most probably, these multinuclear cluster ions resemble the V-V central single-bonded core structure in $(\eta^5\text{-CpV})_2\text{-}(\eta^1\text{-CO})_3\text{-}(\mu_2\text{-CO})_2$ [4]. Only a few other multivanadium carbonyl clusters, prepared with difficulty in solution, such as $Cp_3V_3(CO)_9$ and $Cp_4V_4(CO)_4$ [41] have been studied.

Further detailed FTICR studies into long-term clustering processes of these and other vanadium complexes may provide information regarding these interesting complex ions. Multiple resonance tandem mass spectra experiments with small molecular addition agents such as H_2, O_2, N_2, and laser photodissociation to induce rupture of secondary and tertiary polynuclear ion clusters, will help elucidate structural geometry and yield a clearer conformational picture. Moreover, collisional relaxation techniques with higher pressure inert gases may enable resolution of excited and ground state reactivities [35].

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