Structures and Energetics of $V_n(C_6H_6)_m^+$ Clusters: Evidence for a Quintuple-Decker Sandwich

Patrick Weis, Paul R. Kemper, and Michael T. Bowers*

Department of Chemistry, University of California at Santa Barbara, Santa Barbara, California 93106-9510

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$V_n(C_6H_6)_m^+$ cluster ions were produced by laser vaporization/ionization of a vanadium rod into a mixture of helium and benzene. The clusters with $m = n + 1$ show strongly enhanced intensities. Ion mobility measurements and collision-induced dissociation experiments were used to determine the structure of the different species. Density functional theory calculations using the B-LYP parametrization were performed to provide candidate structures and energetics of these clusters. Comparison of experimental and theoretical model cross sections indicated these clusters have sandwich structures with an alternation of vanadium atoms and benzene molecules. We also found that mass-selected V_n^+ clusters ($n < 5$) react with benzene, sequentially adding benzene neutrals to form terminal ions of formula $V_n(C_6H_6)_{n+1}^+$. Mobility measurements on these ions strongly suggest they also have the sandwich structure, indicating major structural reorganization occurs when benzene interacts with the vanadium cluster.

I. Introduction

The study of complexes between aromatic molecules and transition metals is an old and well-established field of organometallic chemistry.[1] In many cases the metal atom is not bound to a single ligand atom but instead interacts with the rather delocalized π-electron system of the entire ligand molecule. This often leads to highly symmetrical sandwich compounds such as ferrocene[2] and bis(benzene)chromium[3] where the metal is completely symmetrically enclosed by the two ligand molecules. In some cases it is possible to produce triple-decker sandwich compounds, like $C_5H_5-V-C_6H_6-V-C_5H_5$,[4] using the standard methods of preparative chemistry. More recently, laser vaporization has been established by several groups as a completely different method to produce and investigate complexes of transition metals and aromatic molecules.[5−8] This method allows a much wider variety in the size and composition of these clusters than the conventional methods. Furthermore, it is possible to investigate the metal−ligand interaction in the gas phase without solvent effects. Armentrout and co-workers have used collision-induced dissociation (CID) to obtain binding energies for a wide variety of metal ion−ligand complexes including transition-metal benzene compounds.[9] Duncan and co-workers have investigated the photofragmentation of metal ion−benzene complexes.[7]

Recently, Kaya and co-workers were able to make mixed cobalt−benzene clusters with up to nine cobalt atoms and six benzene molecules.[5] Using reactivity studies with ammonia and ionization potential measurements of the neutral clusters, they concluded that the cobalt atoms formed metal clusters that were coated with benzene molecules. In a similar study they synthesized mixed vanadium−benzene clusters with up to six metal atoms and six benzene molecules and measured their ionization potentials and reactivity with carbon monoxide.[6] Under certain conditions they were able to produce almost exclusively clusters with the composition V_nBz_{n+1} ($Bz = C_6H_6$). On the basis of these magic numbers and the reactivity studies with CO, they proposed that these clusters have sandwich structures with an alternation of benzene molecules and metal atoms—in strong contrast to their findings on the cobalt—benzene system.

In this paper we report our investigations of complexes of vanadium and benzene. The goals of the study are 3-fold: first, to use ion mobility and collision-induced dissociation measurements to obtain structural information on these multimetal−multiligand clusters; second, to use theoretical calculations to obtain binding energies of the mixed clusters and compare them with the energetics of pure metal and benzene clusters; third, to study the reactivity of pure vanadium metal clusters with benzene as a function of cluster size.

II. Experiment

The experiments were performed with a differentially pumped high-vacuum apparatus comprised of a laser vaporization/ionization cluster source followed by a quadrupole mass filter, a movable detector, a high-pressure drift cell, a second quadrupole mass analyzer, and a second detector. Details of this MS/MS instrument are given elsewhere.[10] A schematic of the apparatus is shown in Figure 1.

The cluster ion source is a modified Smalley setup[11] with a rotating and translating vanadium rod ($^1/_4$ in. diameter) in a 1 cm long, 1 cm diameter cylindrical cavity (see Figure 2). Vaporization of the vanadium is effected with a pulsed 308 nm excimer laser (Lambda Physik, EMG 202 MSC) tightly focused onto the target rod and typically run at 10 Hz with powers of 50−100 mJ. The desorption plasma is cooled in a pulsed carrier gas jet timed by a home-built delay generator to coincide with the laser pulse. The gas pulses are generated by a pulsed solenoid valve (General Valve) with a typical pulse width of 100 μs and 5 bar backing pressure. When forming pure vanadium clusters, pure helium is used as a carrier gas. The mixed vanadium−benzene clusters are produced with 80 Torr of benzene (its vapor pressure at room temperature) mixed with 5 bar of helium. The clusters seeded in the carrier gas undergo a supersonic expansion through a 1.3 mm inner diameter nozzle into the source chamber. The cluster ions are mass selected by the first quadrupole mass filter, and a mass spectrum is obtained by moving the first detector into the beam path. Once the source has been tuned to yield the clusters of interest, the first detector is moved out of the ion path. A specific cluster is then mass selected and injected into the drift cell. The cell length is 40 mm with entrance and exit holes typically 0.5 mm in diameter.

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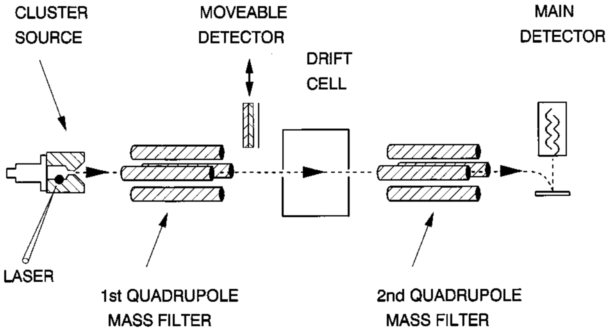

Figure 1. Schematic of the instrument. The apparatus consists of a laser vaporization cluster source, a quadrupole mass filter, an intermediate movable detector, a high-pressure drift cell, a second quadrupole mass analyzer, and a second detector. The cell is filled with up to 7 Torr of helium or a mixture of benzene and helium and allows studies of reactivity, collision-induced dissociation, and mobility of the mass-selected cluster ions. See text for details.

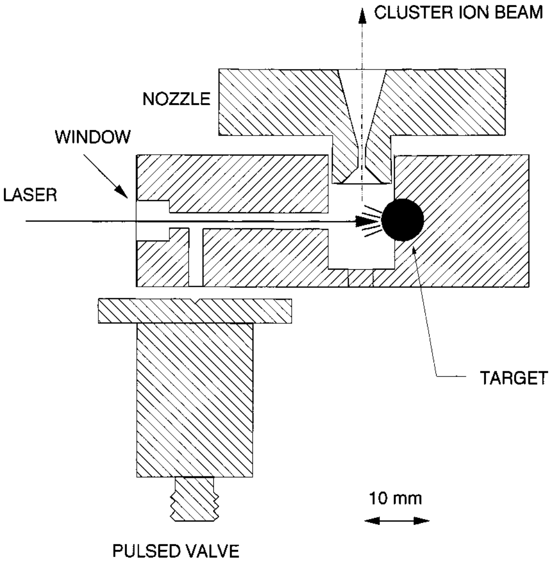

Figure 2. Schematic of the cluster source. The carrier gas pulse is collinear to the laser beam to prevent the deposition of sputtered material on the entrance window. The target is a translating and rotating vanadium rod ($^1/_4$ in. diameter). The conical nozzle has an inner diameter of 1.3 mm. Vaporization and ionization are performed in a single step with a focused XeCl excimer laser (308 nm).

For mobility and CID experiments on the mixed vanadium−benzene clusters the cell is filled with pure helium at a pressure of typically 7 Torr. For reactivity studies of the pure vanadium clusters, the cell is filled with a variable amount of benzene (40−300 mTorr) diluted in up to 7 Torr of helium. In all experiments reported here the cell temperature was 300 K. The ions leaving the drift cell are mass-analyzed by scanning the second quadrupole mass filter and detected with an electron multiplier/multichannel scaler.

III. Vanadium−Benzene Clusters

Figure 3 shows a typical cluster ion distribution measured at the movable detector by scanning the first quadrupole mass spectrometer. In agreement with the findings of Kaya and co-workers,[6] clusters of the composition $V_nBz_{n+1}^+$ show clearly enhanced intensities. With our current source setup we can produce VBz_2^+, $V_2Bz_3^+$, and $V_3Bz_4^+$ in intensities high enough for mobility and CID experiments. The composition of the ion beam is very sensitive to the time delay between the pulsed valve and laser. At slightly different source conditions, significant amounts of benzene-depleted clusters, like $V_2Bz_2^+$, are also obtainable—albeit at lower intensities than the clusters with the composition $V_nBz_{n+1}^+$.

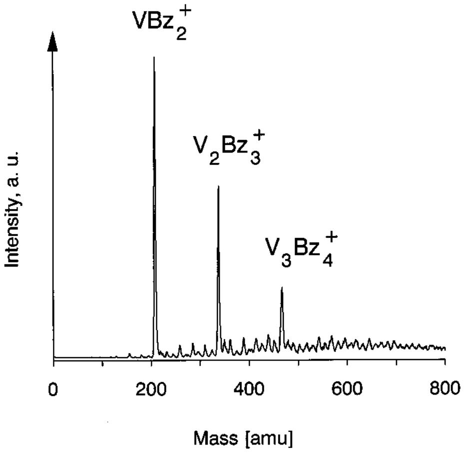

Figure 3. Typical mass spectrum of vanadium−benzene cluster ions. The spectrum is obtained by scanning the first quadrupole mass analyzer and using the movable detector prior to the drift cell. The laser power is 100 mJ/pulse, and the carrier gas is composed of 80 Torr of benzene in 5 bar of helium.

A. Collision-Induced Dissociation (CID). Collision-induced dissociation allows us to obtain structural information by fragmenting a cluster ion in collisions with neutral bath gas atoms and monitoring the fragmentation pattern as a function of the collision energy. In our experiment this can be done by varying the translational energy with which the ions enter the high-pressure drift cell. Figure 4a shows the CID patterns of VBz_2^+ for two different collision energies. As expected, the complex loses first one and at a higher collision energy also the second benzene molecule. Note that the collision energies are given in the lab frame coordinate system. We did not attempt to obtain the threshold energy for fragmentation since the internal energy of the complex, which has a strong influence on the fragmentation rate, is not well-known in a pulsed laser vaporization source.

Benzene loss is also the major fragmentation pathway for $V_2Bz_3^+$ at low energies (see Figure 4b). At 50 eV collision energy $V_2Bz_2^+$ is the only fragmentation product. At 100 eV further loss of a benzene molecule and of a vanadium atom leads to VBz_2^+ and V_2Bz^+ as well as VBz^+. In very high-energy collisions (200 eV and above) we also find V^+, V_2^+, Bz_2^+, and a plethora of V−hydrocarbon clusters—indications of severe rearrangement reactions in the collision event.

The fragmentation of $V_3Bz_4^+$ is also dominated by benzene loss and to a somewhat smaller extent by the loss of a vanadium atom. $V_3Bz_3^+$, $V_3Bz_2^+$, and $V_2Bz_2^+$ are essentially the only products at 50 eV collision energy (Figure 4c). All these findings are fully consistent with the sandwich structures proposed by Kaya and co-workers[6]—but cannot be considered a proof of their hypothesis.

B. Ion Mobilities: Experimental Method. To get more direct structural information, we measured the mobilities of VBz_2^+, $V_2Bz_3^+$, $V_3Bz_4^+$, and some of the CID fragmentation products. For mobility measurements the second quadrupole is set at a specific mass, and the transit time of those ions through the drift cell is measured as a function of the voltage applied across the cell and the bath gas pressure. As long as the voltage is small enough that the drifting ions are in thermal equilibrium with the bath gas,[12] the ion transit time through the drift cell is proportional to the ratio of the voltage and bath gas pressure. With our experimental setup we cannot directly obtain the ion drift time through the cell but must measure the total time for the passage through the cell, through the second

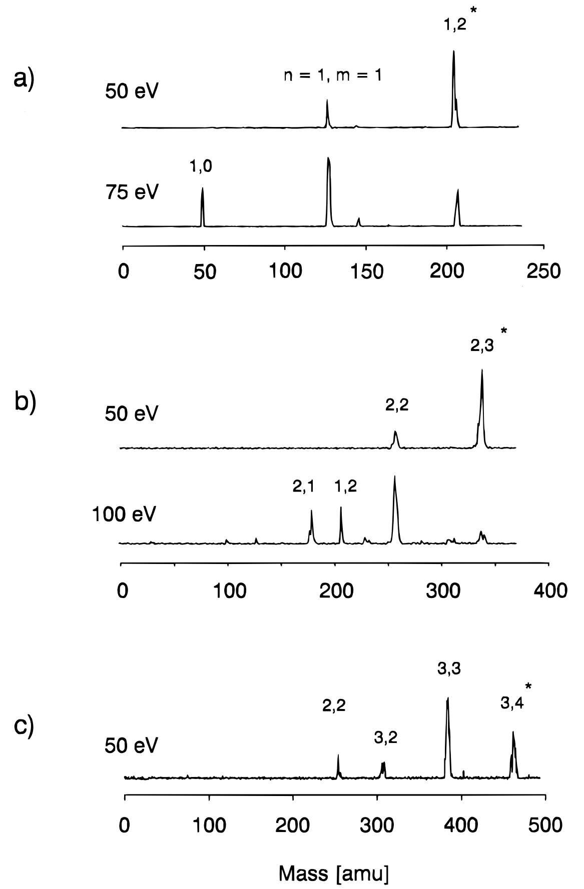

Figure 4. Collision-induced dissociation of $V_nBz_m^+$. The spectra are obtained by injecting the cluster ions with a specific kinetic energy into the drift cell filled with helium at 7 Torr. The parent ions are marked by a star (*). (a) VBz_2^+, collision energy 50 and 75 eV, respectively; the key features are the loss of one and two benzene molecules. (b) $V_2Bz_3^+$ and (c) $V_3Bz_4^+$.

quadrupole, and to the detector. An arrival time distribution (ATD) is recorded on a multichannel scaler (EG&G, MCS-plus) with a resolution of 2 μs/channel. To compensate for the unknown time offset due to the flight time from the drift cell to the detector, we measured the arrival time at several pressure/voltage ratios. This relation shows an excellent linearity. From the slope of a plot of arrival time versus p/V the reduced mobility is directly obtainable from eq 1:[12]

$$K_0 = \frac{273.15z^2}{760T}\frac{p/V}{t_d} \qquad (1)$$

where z is the cell length, t_d the arrival time, p the pressure in Torr, and V the voltage. Unfortunately, the relationship between the mobility of an ion and its structure is not unique. While a given structure leads to a unique mobility, a measured mobility can sometimes be related to several different structures. Therefore, we have to rely on theoretical calculations to provide reasonable candidate structures. From these structures it is fairly straightforward to obtain calculated mobilities via a Monte Carlo integration scheme.[13] Comparison of calculated and measured mobilities then allows us to verify or rule out a proposed theoretical structure.

C. Theoretical Method. The candidate structures were obtained from the density functional[14,15] method using a nonlocal functional, Becke's "BLYP" parametrization.[16,17] All calculations were performed on an IBM RISC 6000 workstation with the TURBOMOLE program package.[18,19] For carbon and vanadium we used TURBOMOLE's split-valence "SV" basis set,[20] augmented by a d-function for carbon atoms (exponent = 0.8) and a p-function for vanadium atoms (exponent = 0.111) as polarization functions resulting in a (7s4p1d)[3s2p1d] basis for C and a (14s9p5d)[5s3p2d] basis for V. Since the hydrogen atoms are not directly involved in the metal−benzene interaction, we restricted ourselves to a (4s)[2s] "SV" basis for H, without a polarization function. This comparatively small basis set allowed us to perform geometry optimizations without any symmetry restrictions for clusters as big as $V_3Bz_4^+$. In addition to pure structural information, these calculations also provided spin states and binding energies, thus allowing us to rule out some candidate structures from an energetic point of view.

D. Mobilities, Structures, and Energetics. *VBz^+.* The electronic ground state for the unligated vanadium cation has four unpaired electrons ($3d^4$ ^5D). Experimentally, the lowest triplet excited state ($3d^4$ ^3F) is 25.5 kcal/mol higher in energy than the quintet ground state,[21] while our calculation predicts an energy difference of 18.3 kcal/mol. In VBz^+, the binding of the metal ion to the benzene can be interpreted as an interaction between the strongly π-donating ligand benzene and the empty 4s-acceptor orbital of V^+. This interaction, however, depends strongly on a close approach between the ligand and metal cation and is enhanced if the π-electron cloud of the benzene molecule points toward empty metal d-orbitals. This latter condition suggests a spin change in the V^+ cation may occur, leading to triplet or even singlet spin multiplicities. To take this possible spin change into account, the VBz^+ geometries were optimized without any symmetry restrictions for singlet, triplet, and quintet states. We found the triplet to be lowest in energy; however, the lowest quintet state is only 2.1 kcal/mol higher in energy. This difference is within the expected uncertainty at this level of theory, and therefore we cannot rule out the quintet as the electronic ground state for VBz^+. The lowest energy singlet is far higher in energy, 9.7 kcal/mol above the triplet. The optimized structure of triplet VBz^+ consists of a V atom centered 1.67 Å above a slightly deformed benzene ring (see Figure 5). This structure yields a reduced mobility (K_0) of 10.3 cm^2/(V s). In the quintet state the vanadium−benzene distance is increased to 1.92 Å, reflecting the repulsive effect of the singly occupied d_{z^2} orbital. The larger distance leads to a somewhat smaller mobility: 10.0 cm^2/(V s). Our experimental value of 10.1 ±0.2 cm^2/(V s) (see Table 1) falls between the triplet and quintet values. Therefore, from the experimental point of view we cannot distinguish between the two structures. The calculated V^+−benzene binding energy (for the triplet) is 53.2 kcal/mol, in somewhat better agreement with the experimental value of 55.8 kcal/mol[9] than the quintet value of 51.1 kcal/mol. At this point it is uncertain whether the VBz^+ ground state is a triplet or quintet.

VBz_2^+. The minimum geometry for VBz_2^+ is a sandwich structure with the vanadium atom equally spaced between the centers of the benzene rings at a distance of 1.81 Å (see Figure 5). Again the geometry was optimized without any symmetry restriction. In this structure the benzene rings are essentially free to rotate with an energy difference between the eclipsed and the staggered structures of only 0.1 kcal/mol. The calculated mobility for the minimum energy structure is 7.4 cm^2/(V s), and our experimental value is 7.5 ± 0.2 cm^2/(V s). In this case there is no question about the electronic ground state since the addition of a second benzene molecule further stabilizes the triplet spin state. The lowest energy singlet state is 7.0 kcal/mol above the triplet ground state, and the lowest energy quintet is 31 kcal/mol above the triplet. The calculated binding energy (with respect to V^+ and two benzene molecules) is 120.7 kcal/mol, again in good agreement with experiment (114.6 kcal/

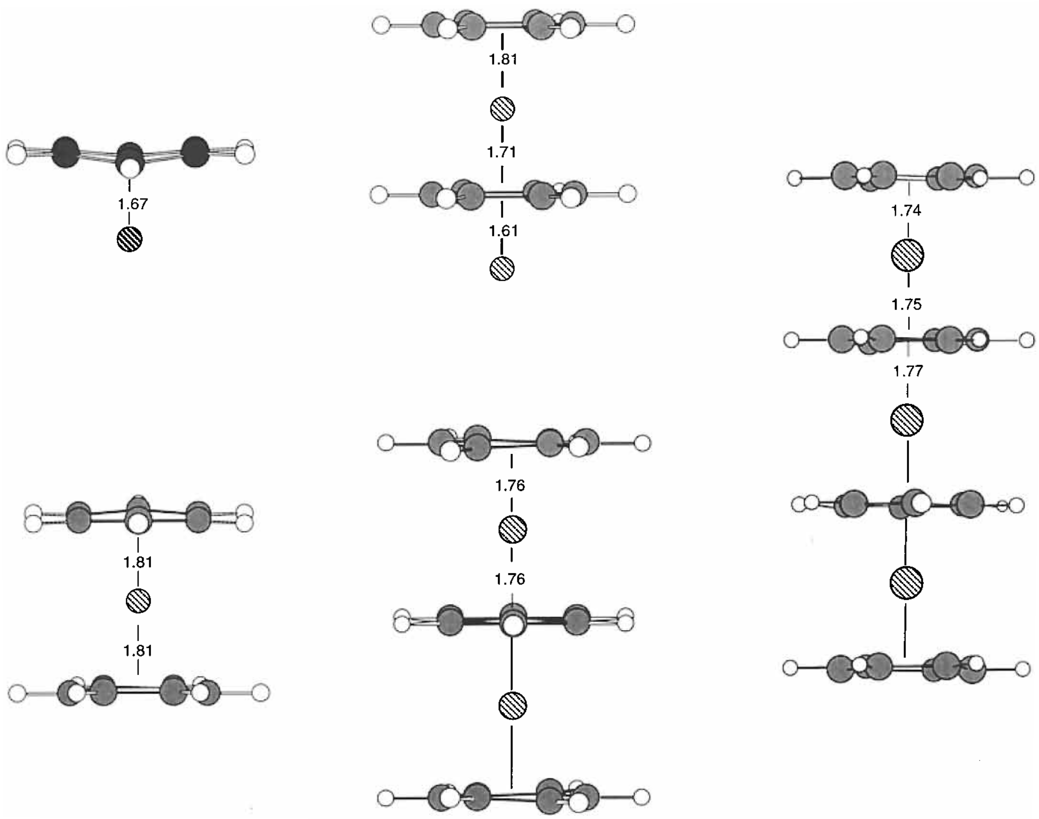

Figure 5. Calculated sandwich structures for different vanadium−benzene clusters. The geometries are optimized without any symmetry restrictions with the DFT- BLYP method. See text for details of the computation and basis set used. Distances in Å.

TABLE 1: Experimental and Calculated Mobilities ($cm^2/(V\ s)$)

	exptl mobility		calcd mobility	
molecule	source[a]	cell[b]	sandwich	other
VBz^+		10.1 ± 0.2[c]	10.3 (triplet), 10.0 (quintet)	
VBz_2^+	7.5 ± 0.2	7.6 ± 0.2[d]	7.4	
$V_2Bz_2^+$	7.3 ± 0.2	7.3 ± 0.2[e]	7.0	6.4[g]
$V_2Bz_3^+$	5.6 ± 0.2	5.6 ± 0.2[f]	5.5	5.2[g]
$V_3Bz_4^+$	4.9 ± 0.4		4.5	

[a] Formed in the laser desorption source. [b] Formed in the mobility/reaction cell either by CID or by injection of V_n^+ and reaction with benzene. [c] Formed by CID of VBz_2^+. [d] Formed by injection of V^+ into the mobility cell. [e] Formed by CID of $V_2Bz_3^+$. [f] Formed by injection of V_2^+ into the mobility cell. [g] These structures have the V_2^+ unit intact. See Figure 6.

mol).[9] This result gives us confidence in the method and basis set used, and we expect to obtain reasonable binding energies for the bigger clusters (for which no experimental data are available).

$V_2Bz_2^+$. For $V_2Bz_2^+$ we found two different isomers with comparable binding energies: the sandwich structure (V−Bz−V−Bz, Figure 5) with a binding energy of 152 kcal/mol and the complex of a V_2 unit and two benzene molecules (Bz−V−V−Bz, Figure 6) which has a slightly higher binding energy of 160 kcal/mol. In both cases the binding energy is calculated with respect to separated V, V^+ and two benzene molecules. The calculated mobilities of the two isomers are quite different, however. The sandwich has a calculated mobility of 7.0 $cm^2/(V\ s)$ and the V−V-bound isomer of 6.4 $cm^2/(V\ s)$. This difference is large enough that we are able to distinguish between the two structures experimentally. Mobility measurements on $V_2Bz_2^+$ were performed in two different ways. First, $V_2Bz_2^+$ was formed directly in the laser vaporization event in the cluster source, and second, $V_2Bz_2^+$ was formed by collision-induced dissociation of $V_2Bz_3^+$ injected at 50 eV into the drift cell. In both experiments the second quadrupole was tuned to the mass of $V_2Bz_2^+$. In both cases we obtained the same mobility of 7.3 ± 0.2 $cm^2/(V\ s)$. This number agrees within the experimental and theoretical errors with the sandwich structure (V−Bz−V−Bz) and clearly rules out the Bz−V−V−Bz isomer (Table 1).

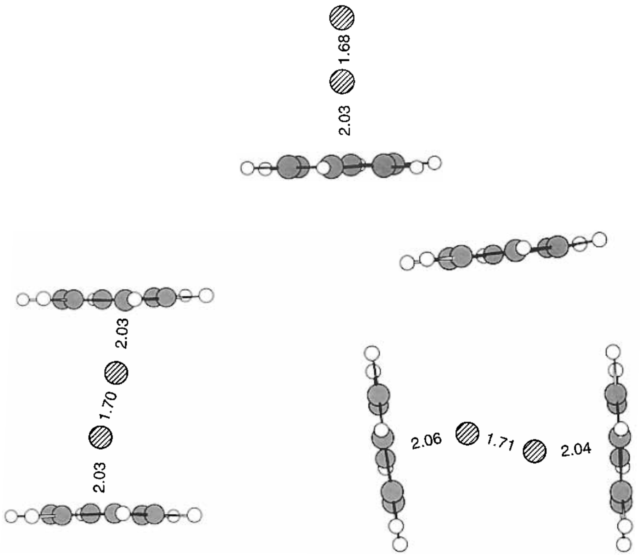

Figure 6. Calculated structures for V_2^+−benzene complexes. The geometries are fully optimized. The geometries are optimized without any symmetry restrictions with the DFT- BLYP method. See text for details of the computation and basis set used. Distances in Å.

$V_2Bz_3^+$. We performed geometry optimizations for different arrangements of the vanadium atoms and benzene molecules, with and without V−V bonds. These calculations show that the most stable structure for $V_2Bz_3^+$ is clearly the sandwich

with vanadium atoms and benzene molecules alternating. It is bound by 224 kcal/mol (with respect to separated V, V^+ and benzene units). The two vanadium atoms are centered between benzene molecules at a distance of 1.76 Å (Figure 5). The spin state is a quartet, with the lowest doublet 3.8 kcal/mol higher in energy. The calculated mobility for this structure is 5.5 $cm^2/(V\ s)$, which is in very good agreement with our experimental value of 5.6 $cm^2/(V\ s)$ (Table 1).

For comparison, we also calculated the geometry and binding energy of the isomer consisting of a V_2^+ unit bound to three benzene molecules. The lowest energy structure (Figure 6) has two benzene molecules strongly bound to the V_2^+ unit while the third (at an angle of almost 90°) is only very weakly bound. This arrangement is 60.5 kcal/mol less stable than the sandwich structure. Its calculated mobility is 5.2 $cm^2/(V\ s)$, significantly lower than our experimental value of 5.6 $cm^2/(V\ s)$, and therefore this structure can be clearly ruled out.

$V_3Bz_4^+$. $V_3Bz_4^+$ is the biggest cluster we investigated in detail experimentally and theoretically. The geometry optimization was performed from a sandwich start geometry but without restrictions on the symmetry during the minimization. The optimized structure is a linear "quadruple-decker" sandwich with all V−benzene distances close to 1.75 Å (Figure 5). The calculated binding energy is 316 kcal/mol (with respect to separated benzene molecules, V atoms, and V^+), and the calculated mobility is 4.5 $cm^2/(V\ s)$. The experimental mobility is 4.9 ± 0.4 $cm^2/(V\ s)$. The difference between experimental and theoretical mobility is somewhat bigger than for the other clusters. This can at least partially be attributed to experimental uncertainties due to small signal intensities. On the other hand, the calculations seem to underestimate the mobilities by a few percent relative to experiment for VBz_2^+, $V_2Bz_2^+$, and $V_2Bz_3^+$. For VBz^+ the situation is not clear due to the small energy difference between triplet (for which the calculated mobility is higher than the experimental) and quintet structures (with a mobility lower than the experimental value). Therefore, our mobility data on $V_3Bz_4^+$ are consistent with the sandwich structure—which is further supported by the CID pattern of $V_3Bz_4^+$ (Figure 4).

We conclude that the $V_nB_{n+1}^+$ clusters that we obtained by laser vaporization of vanadium atoms and ions into a He/benzene gas pulse possess the sandwich structures proposed by Kaya and co-workers.[6]

IV. Reactions of Pure Vanadium Clusters with Benzene

Gas-phase vanadium clusters have been made before by several other groups,[22−24] yet so far little is known of either their chemical behavior as a function of the cluster size or their electronic structure.[24] In the previous section we have shown that a coexpansion of vanadium atoms and benzene molecules leads to the formation of very stable sandwich structures. A possible growth mechanism is via sequential addition of vanadium atoms and benzene molecules. On the other hand, the formation of pure metal clusters and subsequent reaction with benzene cannot be ruled out. To get some more information on (meta) stable compounds of vanadium and benzene, we also investigated the reaction of mass-selected, pure V_n^+ clusters with benzene vapor. To study the reactivity of these clusters, we selected a specific ion V_n^+ ($1 \leqslant n \leqslant 4$) with the first quadrupole and injected it into the drift cell filled with either benzene vapor or a mixture of benzene and helium. The second quadrupole mass filter was scanned to obtain the mass spectrum of the different reaction products. We could also measure the arrival time distribution and mobility of these products when the reaction was significantly faster than the drift time through the cell.

V^+. V^+ adds up to two benzene molecules under our experimental conditions (benzene partial pressure 50−200 mTorr, helium partial pressure 0−7 Torr, drift times through the cell 100−1000 μs). We do not see any trace of VBz_3^+ or higher clusters—which is consistent with VBz_2^+ sandwich formation. From the absence of VBz_3^+ we can estimate a lower limit on the equilibrium constant and a resulting upper limit for the binding energy of the third benzene molecule of 10 kcal/mol.

Although we had little doubt about the sandwich structure of the VBz_2^+ formed in the reaction of mass-selected V^+ with benzene in the drift cell, we confirmed the structure by a mobility measurement. These experiments are performed in a mixture of 7 Torr of helium and 65 mTorr of benzene. Generally, two possible complications must be taken into account in mobility measurements made in a mixture of two different gases:

(1) Since the product ion investigated is formed in the drift cell during the mobility measurement and spends some time in the cell as one or more reactant ions, the measured mobility is a weighted average of the respective mobilities of reactants and product. The experimental ATD peak shape is a very good indication of the reaction rates. Fast reactions have a quasi-Gaussian, narrow arrival time distribution very close to the "true" distribution of the product (i.e., the distribution obtainable if the product were injected intact into the mobility cell). Slower reactions feature a shoulder to shorter times, and if the reaction is very slow, then the ATD is broad, non-Gaussian and extends from the "true" ATD of the reactant(s) to the "true" ATD of the product. In our analysis of VBz_2^+ we find no indication of a shoulder toward shorter times. [The two precursors of VBz_2^+ have higher mobilities: VBz^+, 10.1 $cm^2/(V\ s)$; V^+ (ground state), 16.7 $cm^2/(V\ s)$.[25]] From a fit of the diffusion equation[12] to the data we conclude that the addition of the two benzene molecules to V^+ must be completed within the first 1−2 μs. Since average drift times are hundreds of microseconds, the reaction time has a negligible effect on the mobility.

(2) Adding benzene to the He bath gas changes (lowers) the mobility of every ion, independent of any clustering reactions. According to Blancs law,[26] the mobility of an ion in a mixture of two neutral gases is given to a good approximation by

$$\frac{1}{K_{\text{mix}}} = \frac{x_1}{K_1} + \frac{x_2}{K_2} \tag{2}$$

with x_1 and x_2 the mole fractions of the different gases in the mixture and K_1 and K_2 the mobilities of the ion in the pure gases. An obvious way to circumvent this difficulty is to keep the benzene partial pressure as low as possible (as long as it is still high enough that the clustering reaction is much faster than the overall drift time).

In the case of VBz_2^+ formed by injection of V^+ into the cell, the clustering reactions appear to be sufficiently fast even at a benzene partial pressure of only 65 mTorr, i.e., at a mole fraction of less than 1%. This mole fraction is low enough that it has no significant influence, and we obtain a mobility of 7.6 ± 0.2 $cm^2/(V\ s)$, essentially the same as for the VBz_2^+ produced in the source. We therefore conclude that the VBz_2^+ made (a) by clustering in the hot laser vaporization plasma in the source and (b) in a more controlled way by reaction of a mass-selected vanadium cation with benzene in the reaction cell have the same (sandwich) structure.

V_2^+. Injecting mass-selected V_2^+ at near 0 eV into the drift cell with 50−300 Torr of benzene leads to the formation of predominantly $V_2Bz_3^+$, with small amounts of $V_2Bz_2^+$ and

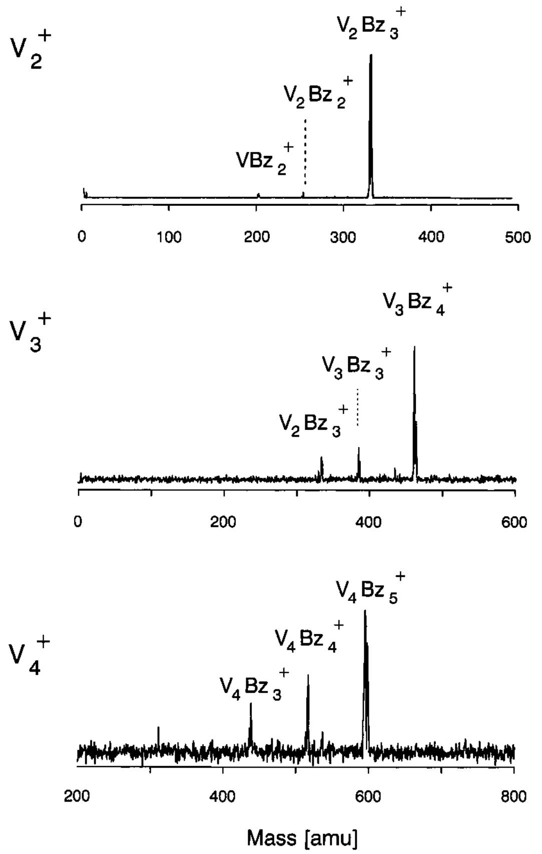

Figure 7. Clustering reactions of V_n^+ with benzene. The spectra are obtained by injecting the different mass-selected pure vanadium cluster ions into the drift cell filled with 80 mTorr of benzene in 7 Torr of helium and by scanning the second mass spectrometer. Note that in all three spectra the terminal cluster is V_nBz_{n+1}, a composition characteristic for closed sandwich molecules (see text for details).

TABLE 2: Experimental and Calculated Bond/Reaction Energies

	$\Delta H°_{0,rxn}$, kcal/mol	
	calcd	exptl
sandwich clusters		
$V^+ + Bz \rightarrow V{-}Bz^+$	53.2	55.8[a]
$V^+ + 2Bz \rightarrow Bz{-}V{-}Bz^+$	120.5	114.6[a]
$V^+ + V + 2Bz \rightarrow V{-}Bz{-}V{-}Bz^+$	151.9	
$V^+ + V + 3Bz \rightarrow Bz{-}V{-}Bz{-}V{-}Bz^+$	223.6	
$V^+ + 2V + 4Bz \rightarrow Bz{-}V{-}Bz{-}V{-}Bz{-}V{-}Bz^+$	316	
V_2^+−benzene clusters		
$V^+ + V \rightarrow V_2^+$	90.3	72.4[b]
$V^+ + V + Bz \rightarrow V_2^+{-}Bz$	121.5	
$V^+ + V + 2Bz \rightarrow V_2^+{-}Bz_2$	160.4	
$V^+ + V + 3Bz \rightarrow V_2^+{-}Bz_3$	163.1	

[a] From ref 9. [b] From ref 22.

VBz_2^+ (see Figure 7). Under these conditions (room temperature, up to 300 mTorr of benzene, 0−7 Torr of helium), we are not able to observe any $V_2Bz_4^+$ or higher clusters, which puts an upper limit of 10 kcal/mol on the binding energy of the fourth benzene ligand.

The predominance of $V_2Bz_3^+$ is rather surprising. According to the calculations, the binding energy of benzene to $V_2^+{-}Bz_2$ is only 2.7 kcal/mol (cf. Table 2) and is much smaller than the binding energy of Bz to $V_2^+{-}Bz$ (38.8 kJ/mol). Hence, if the $V^+{-}V$ bond remains intact, we would expect a $V_2^+{-}Bz_2$ cluster to have a significantly enhanced intensity over a $V_2^+{-}Bz_3$ cluster, at least at low benzene pressures.

The ATD of $V_2Bz_3^+$ formed by injection of V_2^+ into the drift cell containing a small amount of benzene in 7 Torr of He is not Gaussian but rather has a shoulder to shorter drift times. A fit of the diffusion equation to the experimental data indicates a reaction time of 5−10 μs for formation of the cluster and a mobility of 5.6 ± 0.2 cm²/(V s)—the same value we obtained for the "sandwich" $V_2Bz_3^+$. The experimental data are clearly NOT in agreement with our best theoretical $V_2^+{-}(Bz)_3$ structure (Figure 6), which has a calculated mobility of 5.2 ± 0.2 cm²/(V s). This is a very surprising result and strongly suggests that, in the reaction with benzene, the metal−metal bond in the divanadium cation is cleaved and a benzene molecule inserted to form the sandwich structure.

Further (indirect) support for such a rearrangement arises from the fact that, by injecting V_2^+ into the drift cell filled with benzene, we see formation of VBz_2^+ as a product even under conditions where we do not expect CID (at near 0 eV injection energy, i.e., the V_2^+ ions enter the cell with only the velocity acquired in the coexpansion with the He carrier gas in the source). These results imply the reaction

$$V_2^+ + 2Bz \rightarrow VBz_2^+ + V \tag{3}$$

occurs at low energy. According to the experimental data in Table 2, this reaction is exoergic by 30.2 kcal/mol. The mechanism probably involves the following steps, where possible stabilizing collisions by He bath gas are not included for simplicity:

$$V_2^+ + Bz \rightarrow V_2^+{-}Bz \tag{4a}$$

$$V_2^+{-}Bz + Bz \rightarrow V^+Bz_2 + V \tag{4b}$$

$$\rightarrow V_2Bz_2^+ \tag{4c}$$

$$\rightarrow V_2^+{-}Bz_2 \tag{4d}$$

$$V_2Bz_2^+ + Bz \rightarrow V_2Bz_3^+ \tag{4e}$$

According to the data in Figure 7, it appears reaction 4c is favored over reactions 4b and 4d by approximately 20 to 1. Clearly for reactions 4b and 4c to proceed, a benzene ligand must insert into the $V^+{-}V$ bond. This process leads to a chemically activated $V{-}Bz{-}V{-}Bz^+$ species that either eliminates a vanadium atom or encounters a third benzene ligand and proceeds to the final $V_2Bz_3^+$ product, which has the sandwich structure. While other mechanisms are possible, this is the most likely since addition of the first benzene ligand does not provide enough energy to break the $V^+{-}V$ bond and addition of a third benzene ligand to $V_2^+{-}Bz_2$ leads to an awkward, weakly bond structure that is unlikely to lead to insertion. Consequently, the small signal at a mass of two vanadium atoms and two benzene molecules is presumably due to $V_2^+{-}Bz_2$ that does not react further with benzene under our experimental conditions.

V_3^+ and V_4^+. Injecting V_3^+ into the drift cell filled with benzene (partial pressure range 20−80 mTorr in 7 Torr of helium) leads to the formation of predominantly $V_3Bz_4^+$ and, with lower intensity, clusters with smaller benzene content (see Figure 7), but no reaction products containing more than four benzene molecules. Under the same conditions injection of V_4^+ forms $V_4Bz_5^+$ as the terminal ion and smaller intensities of $V_4Bz_4^+$ and $V_4Bz_3^+$, indicating that clustering has not yet gone to completion. These results very strongly suggest that extensive rearrangement is occurring in both systems, and the terminal $V_3Bz_4^+$ and $V_4Bz_5^+$ ions have the sandwich structure. Unfor-

tunately, low signal-to-noise prevented us from doing ion mobility experiments.

V. Conclusions

1. We have synthesized $V_nBz_m^+$ clusters by reaction of laser-vaporized vanadium atoms (and ions) with benzene vapor for $1 \leqslant n \leqslant 4$ and $1 \leqslant m \leqslant 5$. As terminal ions we find the same magic numbers $V_nBz_{n+1}^+$ as Kaya and co-workers.[6] From the measurement of the mobility of these clusters in helium gas, we were able to unambiguously determine that these clusters had structures with an alternation of vanadium atoms and benzene molecules, i.e., sandwich structures.

2. Collision-induced dissociation (CID) measurements on $V_nBz_m^+$ clusters formed in the ion source are fully consistent with the proposed sandwich structures.

3. In a slight variation of the source setup, we were also able to produce mass-selected beams of unligated vanadium cluster ions, V_n^+, and react them with benzene in the drift cell. The mobility of the predominant reaction product of V_2^+ and benzene, $V_2Bz_3^+$, agrees well with a sandwich structure but not with a complex consisting of a central V_2^+ unit surrounded by three benzene molecules. We therefore have to conclude that in the reaction with benzene V_2^+ undergoes a rearrangement that involves the breaking of the V−V bond and finally leads to the sandwich structure.

4. The reaction of mass-selected V_3^+ and V_4^+ with benzene leads to terminal ions $V_3Bz_4^+$ and $V_4Bz_5^+$, strongly suggesting that sequential addition of benzene to these metal clusters leads to massive rearrangement and formation of clusters with sandwich structures.

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