face away from it. With all electrons facing inward, inserted spheres of diameters that range from about 3.4 to about 5.2 Å fill the cavity, depending on the aryl–aryl dihedral angles. The diameter of Cs^+ is about 3.4 Å. A molecular model of chair cyclohexane can be inserted into the cavity. Host **5** crystallizes with 1 mol of cyclohexane to give **5**$\cdot C_6H_{12}$.[11] With all methyl groups turned inward, the cavity shrinks to a cylinder of about 2.7–3.0-Å diameter and a length of about 7.7 Å. This cylinder is lined with methyl hydrogens and neatly accommodates a model of diacetylene. Thus, depending on which and how many methyl groups or electron pairs are turned inward, the cavity can assume a variety of shapes, sizes, and distributions on its surface of hydrophilic or lipophilic sites. The 10 oxygens in molecular models of spherand **6** possess an arrangement complementary to that of the 10 hydrogens of ferrocene. With all methyl groups turned outward, a model of ferrocene beautifully fills the minimum sized cavity, with each hydrogen of the guest touching an oxygen of the host. The dimensions of the cavity of this conformation range from about 6 × 8 Å to about 7.2 × 8.4 Å. With all of the methyl groups turned inward, the cylindrical cavity is about 4.8 Å in diameter and about 7.2 Å in length. A model of chair cyclohexane nicely fills this cavity.

A comparison of these spherands with the cyclodextrins is instructive. Both sets of hosts are cyclic oligomers composed of rigid, chiral support units arranged in the form of a torus whose diameter increases with the number of monomer units. Both sets of hosts contain attached functional groups which possess some degrees of conformational freedom, but which cannot fill the cavity of the torus in any of their conformations. Thus the host *cavities are enforced.* The cavity sizes of the spherands can be designed to be smaller than that of the smallest cyclodextrin or comparable to those of α-, β-, or γ-cyclodextrin. The spherands reported thus far are highly lipophilic on the outside and somewhat hydrophilic on the inside. The cyclodextrins are very hydrophilic on their rims but lipophilic on the remainder of their inner and outer surfaces. Since the spherands are totally synthetic, they are more subject to structural design than the cyclodextrins.

On the Structure of $C_4H_4^+$ Produced in the Unimolecular Fragmentation of $C_6H_6^+$ and $C_5H_5N^+$

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Received February 9, 1981

The $C_4H_4^+$ ion is one of the major primary fragment ions produced in the unimolecular decomposition of excited $C_6H_6^+$ isomers:

$$C_6H_6^+ \rightarrow C_4H_4^+ + C_2H_2 \qquad (1)$$

Appearance potential measurements indicate that at *threshold*, the $C_4H_4^+$ ion originating from C_6H_6, as well as from pyridine, may have the methylenecyclopropene structure.[1-4] Furthermore, $C_6H_6^+$ ions from all precursors dissociate, when their total energy (heat of formation plus excitation energy) is in the range 15–15.6 eV, to give $C_3H_3^+$ and $C_4H_4^+$ in a ratio which does not depend on the structure of the precursor. This implies the existence of a common structure for the $C_6H_6^+$ ions of this energy and also common structures for the $C_3H_3^+$ and $C_4H_4^+$ fragments. At total internal energies above 15.6 eV, there is a sudden increase of the $C_4H_4^+/C_3H_3^+$ branching ratio, in apparent contradiction to RRKM calculations which predict a monotonic decrease of this ratio with increasing energy, assuming a cyclic structure for both $C_3H_3^+$ and $C_4H_4^+$ throughout the energy range. As pointed out by Baer et al., this result suggests the accessibility of a different, probably linear, $C_4H_4^+$ isomer.

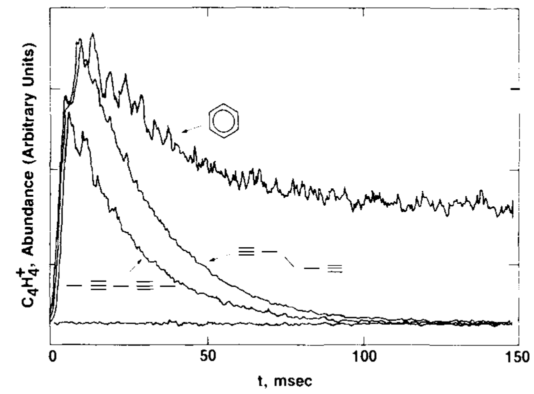

Figure 1. Abundance of $C_4H_4^+$ ions in benzene, 1,5-hexadiyne, and 2,4-hexadiyne as a function of time. Nominal electron energy, 30 eV; pressure, 1.4 × 10^{-6} torr. In benzene, no further decay of the $C_4H_4^+$ abundance was observed from 150 to 400 ms.

In this work, we present proof that, indeed, at least two distinct $C_4H_4^+$ structures are produced in the fragmentation of $C_6H_6^+$ and $C_5H_5N^+$. The relative abundances of these two isomeric ions are dependent on the internal energy of the parent ion.

A pulsed ion cyclotron resonance spectrometer (ICR) was utilized in this work. The technique for determining the abundance and identities of the various structurally distinct ion populations based on their kinetic properties has been described before.[5,6] A similar procedure has been used by Gross et al.[7]

Figure 1 shows decay tracings of $C_4H_4^+$ isomers produced in a 3-ms pulse of 30-eV electrons. The time-dependent behavior of $C_4H_4^+$ ions in benzene indicates that there are at least two different $C_4H_4^+$ isomers present in benzene, one which reacts with benzene and one which does not. The $C_4H_4^+$ population which shows a fast decay as a function of time (Figure 1) reacts mainly by charge transfer to benzene:

$$C_4H_4^+ + C_6H_6(B) \rightarrow C_4H_4 + C_6H_6^+ \qquad (2)$$

About 10% of these ions undergo condensation reactions to give $C_{10}H_8^+$ and $C_9H_7^+$ products. These two reaction channels have been reported before,[8-10] and the branching ratio found in this study is in good agreement with that obtained in a tandem ion cyclotron resonance study of ionic reactions in benzene.[10]

The total decay rate constant of the reactive $C_4H_4^+$ population is $(6 \pm 1)10^{-10}$ cm^3/(molecule s), independent of electron energy (15–30 eV) and benzene pressure (3 × 10^{-7}–5 × 10^{-6} torr). The upper limit of the corresponding rate constant for loss of the unreactive $C_4H_4^+$ ions in benzene is 5 × 10^{-13} cm^3/(molecule s). The $C_4H_4^+$ fragment ions formed in 1,5-hexadiyne, 2,4-hexadiyne, and pyridine decay by reaction with the parent compounds with rate constants of 7.9, 12.9, and 22 × 10^{-10} cm^3/(molecule s), respectively. However, when the total pressure of these precursor compounds is kept low enough (5 × 10^{-8} torr) that reaction of $C_4H_4^+$ with the precursor compound is unimportant on the time scale (150–300 ms) of the experiments, the rate of reaction with various added reagents (benzene-d_6, NO, c-C_6H_{12}, *n*-C_5H_{12}, etc.) can be determined (precursor–additive = 1:10–1:50). Results

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obtained in this way demonstrate that the rate constants cited above are composite values for the reaction of two or more $C_4H_4^+$ isomers. In both hexadiynes and pyridine, there is present a $C_4H_4^+$ species which reacts with benzene-d_6 with the same rate constant as that measured for the reactive $C_4H_4^+$ component produced in pure benzene and a $C_4H_4^+$ population which is unreactive with benzene-d_6. With a nominal electron energy of 15 eV, the fraction of reactive $C_4H_4^+$ ions in benzene, 1,5-hexadiyne, 2,4-hexadiyne, and pyridine was, respectively, 60 ± 5%, 65 ± 5%, 60 ± 10%, and 50 ± 10%.

In order to assess the effect of internal energy on the relative abundance of the two $C_4H_4^+$ populations in benzene, $C_6H_6^+$ ions were produced by charge transfer from CO^+ (CO ionization energy = 14.0 eV), N_2^+ (N_2 ionization energy = 15.58 eV), and Ar^+ (Ar ionization energy = 15.75 eV) so that the range of energy content of the $C_6H_6^+$ ions formed in these experiments was 14.8–16.6 eV. The dissociative charge transfer involving CO^+, whose recombination energy is close to the appearance potential of $C_4H_4^+$ in benzene (13.7 ± 0.2 eV), yielded mainly unreactive $C_4H_4^+$ (>95%). In sharp contrast, 82 ± 3% of the $C_4H_4^+$ ions formed in the dissociative charge transfer

$$Ar^+ + C_6H_6(B) \rightarrow Ar + C_4H_4^+ + C_2H_2 \qquad (3)$$

react with benzene with the same rate constant as the reactive $C_4H_4^+$ ions formed in pure benzene [$k_{Rn} = (6 \pm 1)10^{-10}$ cm^3/(molecule s)]. An average value of 80 ± 2% was found for the abundance of the reactive isomer in similar experiments involving N_2^+ as charge donor. The relative abundances of the reactive and unreactive populations of $C_4H_4^+$ formed in the experiments with Ar^+ and N_2^+ as charge donors was independent of the Ar–C_6H_6 or N_2–C_6H_6 ratio from 5:1 to 40:1. Analogous charge-transfer experiments with the hexadiynes and pyridine could not be carried out because of the reactivity of the $C_4H_4^+$ ions with these compounds.

Because 3-buten-1-yne is the only $C_4H_4^+$ isomer known,[1,11] to have an ionization potential (9.58 eV) higher than that of benzene (9.24 eV), the observation of reaction 2 leads to the conclusion that the reactive $C_4H_4^+$ population consists entirely of ions having the 3-buten-1-yne structure. For information obtainment about the structure(s) of the $C_4H_4^+$ ions which are unreactive toward benzene, various aromatic molecules with ionization potentials[12] below that of benzene were added to a CO–benzene (30:1) mixture. *p*-Difluorobenzene (IP = 9.14 eV), bromobenzene (IP = 8.98 eV), and *p*-dichlorobenzene (IP = 8.89 eV) were found to be unreactive [$k_{Rn} < 10^{-12}$ cm^3/(molecule s)], while electron transfer to $C_4H_4^+$ was found to occur from the following compounds: toluene [IP = 8.82 eV; $k_{Rn} = (1.1 \pm 0.3)10^{-10}$ cm^3/(molecule s)], *p*-fluorotoluene [IP = 8.79 eV; $k_{Rn} = (2.6 \pm 0.3)10^{-10}$ cm^3/(molecule s)], ethylbenzene [IP = 8.77 eV; $k_{Rn} = (8 \pm 0.5)10^{-10}$ cm^3/(molecule s)], and 1,3,5-trimethylbenzene [IP = 8.41 eV; $k_{Rn} = 10 \pm 1$ cm^3/(molecule s)].

The rapid rise in k_{Rn} with an increase in the exothermicity of reaction is typical for near-thermoneutral charge-transfer reactions.[13] On the basis of these rate constant data, a value of 8.8 ± 0.05 eV is suggested for the "apparent" recombination energy of the "unreactive" $C_4H_4^+$ ions in benzene. This value is substantially below the known ionization energy of butatriene (9.20 ± 0.05 eV) and is nearly 1 eV higher than that estimated for methylenecyclopropene (7.96 ± 0.1 eV).[14] However, the apparent recombination energy can be reconciled with what is known about the ionization energies of C_4H_4 isomers if the charge-transfer reaction is written as follows:

$$[\text{c-}C_3H_2({=}CH_2)]^+ + \text{aromatic} \rightarrow \text{aromatic}^+ + CH{\equiv}CCH{=}CH_2 \qquad (4)$$

This is the only reaction which can be written for which the charge transfer to toluene would be near thermoneutral. It has been shown before that isomerization to produce thermodynamically favored configurations can occur in the course of electron-transfer reactions[15] or as the outcome of ion–molecule collisions.[16]

The appearance of a new reaction channel producing linear rather than cyclic $C_4H_4^+$ ions at higher energies is consistent with the pronounced increase in formation of $C_4H_4^+$ relative to other fragment ions in C_6H_6 isomers, which occurs at total energies above 15.6 eV.[4,17]

Apparently, $C_4H_4^+$ is not the only fragment ion from $C_6H_6^+$ which exhibits more than one structure. The $C_6H_4^+$ ion produced in the 30-eV mass spectrum of benzene shows a reactive component [$k_{Rn} = 4.6 \times 10^{-10}$ cm^3/(molecule s)] and an unreactive component [$k_{Rn} < 5 \times 10^{-13}$ cm^3/(molecule s)].

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(14) This value is based on the assumption that the value of 7.7 ± 0.1 eV obtained for $\Delta H_f(C_4H_4^+)$ from appearance potential measurements[1-4] does indeed correspond to the heat of formation of the cyclic $C_4H_4^+$ ion. A value for the heat of formation of methylenecyclopropene of 4.18 eV was taken from ab initio calculations of Hehre and Pople W. J.; Pople, J. A. *J. Am. Chem. Soc.* **1975**, *97*, 6441.

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Metathesis of Acetylenes by Tungsten(VI)-Alkylidyne Complexes[1]

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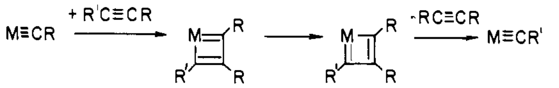
Received February 23, 1981
Revised Manuscript Received April 30, 1981

The few reports of homogeneously catalyzed[2] alkyne metathesis in the literature[3] provide no clues as to what the mechanism of this reaction might be, but since olefins are metathesized by alkylidene complexes,[4,5] one might propose that acetylenes are metathesized by alkylidyne complexes via (according to one proposal[6]) the metallacyclobutadiene intermediates shown in eq 1. Recently we prepared some oxoalkylidene complexes of tungsten(VI) (counting the alkylidene ligand as a dianion) which metathesize olefins at 25 °C.[5] Therefore if an alkylidyne complex



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