The absence of such bands, as expected for a surface free of surface hydroxyl groups,[64] indicates no detectable amount of Os oxide was present.

The spectra under reaction conditions, shown in Figure 8, indicate an increase in intensity in the region associated with CH_x bands with increasing temperature and time on-stream. The adsorbed CO species, giving a broad band between 2030 and 1950 cm^{-1} at these temperatures, decreased in intensity with increasing temperature as anticipated for equilibrated surface coverage. Previous studies on Fe/SiO_2 and Ru/SiO_2 have investigated the 2700–3100-cm^{-1} range, and it has been routinely concluded that most of the species providing the observed CH_x bands are present on the support and not on the metal surface.[61,124,125] Furthermore, since only frequencies at 2930 and 2850 cm^{-1} were observed, CH_2 groups predominated and were attributed to higher molecular weight saturated hydrocarbon chains, in agreement with the known capability of Ru and Fe catalysts to form longer chain hydrocarbons.[126,127] In the present study on carbon-supported Os, approximately equal quantities of CH_2 and CH_3 species were present, as seen by a comparison of the 2927- and 2862-cm^{-1} doublet for CH_2 stretching frequencies, and the 2962- and 2872-cm^{-1} doublet for CH_3 stretching frequencies. This indicates a preponderance of short-chain hydrocarbons which exist possibly on the Os surface, but more likely on the carbon surface within the small pore structure. However, at a given temperature the CH_x intensities and the CO intensity seem to be inversely related, and since the CO is present only on the Os surface, this provides indirect evidence that at least a portion of the detected CH_2 and CH_3 species may have been present on the Os surface.

Summary

A carbon-supported metal catalyst has been characterized by IR spectroscopy for the first time, as DRIFTS, along with a modified controlled environment cell, was successfully applied to study carbon-supported Os clusters. The decarbonylation of $Os_3(CO)_{12}$ on oxygen-free carbon surfaces was followed quantitatively to obtain first-order rate constants and activation energies of decarbonylation of 27–29 kcal/mol in He and 30–33 kcal/mol in H_2. To the best of our knowledge, this is the first time that the kinetics of thermal decomposition of $Os_3(CO)_{12}$ has been determined. The activation energies are slightly lower than those reported for nucleophilic substitution reactions of $Os_3(CO)_{12}$ in solution; however, the assumption of rapid formation of Os–Os bonds to produce small metallic Os particles allowed an estimation of activation energies based on known Os–Os and Os–CO bond strengths that were consistent with the values measured. Decarbonylation in He proceeded to Os metal without the formation of stable intermediates, whereas decomposition in H_2 first produced $H_4Os_4(CO)_{12}$, which then decomposed to Os metal.

CO adsorption on the carbon-supported Os crystallites after decomposition in either H_2 or He yielded spectra in excellent agreement with literature values of 2035–2037 cm^{-1} for CO adsorbed on metallic Os surfaces. IR spectra under reaction conditions showed the presence of adsorbed CO as well as similar concentrations of CH_2 and CH_3 groups which indicated the presence of only short-chain hydrocarbons on the catalyst surface. The integral heat of adsorption of CO at 300 K on these metallic Os crystallites was determined calorimetrically to be 31.3 ± 1.1 kcal/mol, in good agreement with the value of 33 kcal/mol reported for CO adsorption on an Os(0001) single crystal. The chemisorption measurements showed that the Os particles were well-dispersed and resistant to sintering under reaction conditions. The turnover frequency for methanation, the only hydrocarbon product detected, was similar to that on well-reduced Os/SiO_2 catalysts, but much higher than TOF values reported for Os on Al_2O_3 and MgO where Os remains in a stabilized, positive-valent state. Regardless, even the best Os catalysts have low turnover frequencies for CO hydrogenation compared to the most active group VIII metals, such as Ru and Fe, which lie just above Os in the periodic table.

Acknowledgment. This study was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. $Os_3(CO)_{12}$, 15696-40-9; $H_4Os_4(CO)_{12}$, 12375-04-1; H_2, 1333-74-0; CO, 630-08-0.

---

(124) Ekerdt, J. G.; Bell, A. T. *J. Catal.* **1979**, *58*, 170.
(125) Ekerdt, J. G.; Bell, A. T. *J. Catal.* **1979**, *62*, 19.
(126) Vannice, M. A. *Catal. Rev. Sci. Technol.* **1976**, *14*, 153.
(127) Boudart, M.; McDonald, M. A. *J. Phys. Chem.* **1984**, *88*, 2185.

Gas-Phase Study of Fe^+–Benzyne with Alkanes

Yongqing Huang and Ben S. Freiser*

Contribution from the Department of Chemistry, Purdue University,
West Lafayette, Indiana 47907. *Received August 1, 1988*

Abstract: The unimolecular chemistry of Fe^+–benzyne and its reactivity with small alkanes in the gas phase are studied by Fourier transform mass spectrometry (FTMS). Collision-induced dissociation of Fe^+–benzyne yields benzyne loss exclusively. In contrast, photodissociation of Fe^+–benzyne yields not only cleavage of benzyne from Fe^+, but competitive loss of C_2H_2 and C_4H_2 as well. The Fe^+–benzyne is formed from chlorobenzene by loss of HCl. This dehydrochlorination of chlorobenzene also occurs in secondary reactions up to six times forming products of the type Fe^+–polyphenylene. Fe^+–benzyne reacts with alkanes larger than methane to form a wide variety of product ions by mechanisms including hydrogenation and methanation of the benzyne ligand. All of the product ions can be explained by mechanisms based on Fe^+ insertion into either C–C or C–H bonds as the reaction-initiating step, followed by either alkyl or H migration from Fe^+ onto the benzyne ligand or, alternatively, by the migratory insertion of benzyne into a metal–carbon or metal–hydrogen bond. Photodissociation and ion–molecule reaction studies yield a value for the metal–ligand bond energy of $D°(Fe^+\text{–benzyne}) = 76 \pm 10$ kcal/mol.

Recent studies on bare gas-phase transition metal cations M^+ have provided abundant information on their reactivities and mechanisms with a wide variety of organic compounds.[1] A logical extension of this work has been to compare the results obtained from studies on ML_n^+ (L = ligand, $n \geq 1$) with that of the bare metal species in order to gain an understanding of the intrinsic effect of the ligand on the reactivity of the metal center.[2,3] Studies thus far have included a wide variety of small ligands (e.g., H,

---

(1) For a recent review, see: Allison, J. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; Wiley-Interscience: New York, 1986; Vol. 34, p 628 and references therein.

(2) Freas, R. B.; Ridge, D. P. *J. Am. Chem. Soc.* **1980**, *102*, 7129.

(3) Some examples are: Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 3891; **1985**, *107*, 67. Cassady, C. J.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 6176. Jackson, T. C.; Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*, 1252.

0002-7863/89/1511-2387$01.50/0

CH_2, CH_3, O, OH, NO, CO, C_2H_4, etc.) and have demonstrated dramatic changes in the reactivities due to the attachment of ligand species to the metal center. In this paper we report on the distinctive nature of benzyne as a ligand.

The high intrinsic reactivity of benzyne in solution not only renders it very useful for a large number of organic syntheses, but also makes it difficult to isolate and, therefore, it has to be prepared in situ for further synthesis.[4] However, the coordination of benzyne to a transition metal center can greatly increase its stability and lead to the isolation and crystallization of stable benzyne complexes. This permits an alternative way of characterizing the benzyne structure and achieving, in a sense, controlled reactivity of benzyne.[5-7] While benzyne is intrinsically very reactive, we are aware of only one documented example where benzyne is hydrogenated by an alkane, cyclohexane, although such hydrogenation is expected to be exothermic in general.[8-10] The chemistry observed in this study between Fe^+–benzyne and alkanes suggests the ability of the Fe^+ center to catalyze reactions between benzyne and simple alkanes.

Experimental Section

All experiments were performed on a prototype Nicolet FTMS-1000 Fourier transform mass spectrometer previously described in detail.[11] It is 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 utilizes two stainless steel screens of 80% transmittance as the transmitter plates, permitting the irradiation of the interior with various light sources. Fe^+ was generated by focusing the beam of a Quanta Ray Nd:YAG laser (operated either at the fundamental wavelength 1.064 μ or frequency doubled to 532 nm) onto a high-purity Fe target. Details of the laser desorption experiment have been described elsewhere.[12]

Chemicals were obtained in high purity from commercial sources and used as supplied except for multiple freeze–pump–thaw cycles to remove noncondensable gases from samples. Sample pressures were measured with an uncalibrated Bayard–Alpert ionization gauge and were typically $2-4 \times 10^{-6}$ Torr. For collision-induced dissociation (CID) experiments, Ar was added as the collision gas, yielding a total pressure of $\sim 4 \times 10^{-5}$ Torr.

The reactant ion, $FeC_6H_4^+$, was prepared by the previously reported reaction of Fe^+ with chlorobenzene[13] and isolated by swept double-resonance ejection pulses[14] before its reactions with a variety of different samples. The minor isotope peak $^{54}Fe^+$ was ejected prior to its reaction with chlorobenzene to avoid any interference. As discussed below, chlorobenzene reacts with Fe^+–benzyne to form a series of higher mass products.[13] To avoid this interference, chlorobenzene was pulsed in through a General Valve Corp. Series 9 pulsed solenoid valve, triggered simultaneously with the laser desorption of the Fe target, filling the cell to a maximum pressure of $\sim 10^{-5}$ Torr in about 150 ms and then being pumped away in about 300 ms by a 5-in. diffusion pump.[15]

The product ion distributions are reproducible to ±10% absolute. To ensure that the product branching ratios were collected primarily for ground-state $FeC_6H_4^+$, a high background pressure of argon was maintained during the experiment to allow cooling of the reactant ions. However, a minor population of nonthermal species cannot be completely ruled out.

The major primary product ion structures were investigated by collision-induced dissociation (CID). Details of the CID experiments have been discussed previously.[16] The translational energy of the parent ions in the laboratory frame can be varied typically between 0 and 100 eV. The spread in kinetic energy is approximately 35% at 1 eV, 10% at 10 eV, and 5% at 30 eV.[17]

$D°(Fe^+\text{–benzyne})$ was bracketed by photodissociation. The details of the photodissociation experiments are described elsewhere.[18] $FeC_6H_4^+$ was isolated by swept double resonance ejection pulses and trapped in a background pressure of argon for 5 s. During this time, the ion was irradiated with light from a 2.5-kW mercury-xenon arc lamp, used in conjugation with a series of cutoff filters.

Results and Discussion

Unimolecular Chemistry of Fe^+–Benzyne. Crystal structure studies of mononuclear transition metal benzyne complexes have indicated that the metal center is coplanar with the benzyne plane, with benzyne binding symmetrically with respect to the metal center and C–C triple bond.[5,6] This is also likely to be the structure for the gas-phase $FeC_6H_4^+$, which can be properly represented by the two resonance structures, Fe^+–benzyne and benzoironacyclopropene ion. No H/D exchange is observed between $FeC_6H_4^+$ and D_2 or C_6D_6. In addition, CID on the condensation product $Fe(C_6H_4)(C_6D_6)^+$ from perdeuterated benzene yields $FeC_6H_4^+$ and Fe^+ only, suggesting that the benzyne ligand is intact even under collisional activation. CID on $FeC_6H_4^+$ forms Fe^+ exclusively. However, photodissociation using white light from the arc lamp leads to fragmentation of the benzyne ligand in addition to loss of the entire ligand, as shown in reactions 1–3.

$$FeC_6H_4^+ \rightarrow Fe^+ + C_6H_4 \qquad 69\% \qquad (1)$$

$$\rightarrow FeC_2H_2^+ + C_4H_2 \qquad 5\% \qquad (2)$$

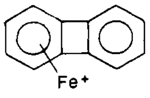
$$\rightarrow FeC_4H_2^+ + C_2H_2 \qquad 26\% \qquad (3)$$

Facile dehydrochlorination of chlorobenzene by Fe^+ indicates that $D°(Fe^+\text{–benzyne}) \geq 66$ kcal/mol.[13] While the low cross section made it very difficult to get an accurate threshold for reaction 1, photodissociation suggests that $D°(Fe^+\text{–benzyne}) \leq 86$ kcal/mol. Thus, the Fe^+–benzyne bond energy is assigned 76 ± 10 kcal/mol.

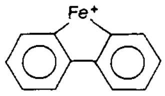
Primary and Secondary Reactions of Fe^+ with Chlorobenzene. In their original study, Ridge and co-workers reported the dehydrohalogenation and polymerization of phenyl halides in the gas phase by Fe^+ up to triphenylene.[13] Detection of product ions of higher order polyphenylenes was unsuccessful because of instrumental limitations. In this study, the polymerization was observed to occur up to the sixth step, as shown in reaction 4. The last

$$FeC_{6n}H_{4n}^+ + C_6H_5Cl \rightarrow FeC_{6(n+1)}H_{4(n+1)}^+ + HCl \qquad n = 0\text{–}5 \quad (4)$$

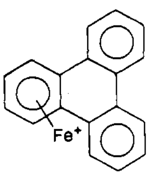
step is somewhat slower than the earlier steps, and no reaction beyond that was observed at extended reaction time. In addition, several polyphenylene cations without the Fe center were also observed as products. Ridge and co-workers proposed metal ion–polyphenylene, structures I and III, or alternatively the Fe^+ C–C inserted polyphenylene, structures II and IV, for the product



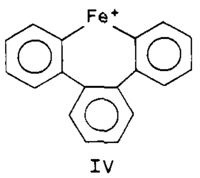
I



II



III



IV

---

[4] Hoffmann, R. W. *Dehydrobenzene and Cycloalkynes*, Academic Press: New York, 1967.

[5] Bennett, M. A.; Hambley, T. W.; Roberts, N. K.; Robertson, G. B. *Organometallics* **1985**, *4*, 1992.

[6] McLain, S. J.; Schrock, R. R.; Sharp, P. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 263. Churchill, M. R.; Youngs, W. J. *Inorg. Chem.* **1979**, *18*, 1697.

[7] Gomez-Sal, M. P.; Johnson, B. F. G.; Lewis, J.; Raithby, P. R.; Wright, A. H. *J. Chem. Soc., Chem. Commun.* **1985**, 1682.

[8] Rosenstock, H. M.; Draxl, D.; Steiner, R. W.; Herron, J. T. *J. Chem. Phys. Ref. Data* **1977**, *6*.

[9] Moini, M.; Leroi, G. F. *J. Phys. Chem.* **1986**, *90*, 4002.

[10] Wittig, G.; Ebel, H. F. *Justus Liebigs Ann. Chem.* **1961**, *20*, 650.

[11] Cody, R. B.; Burnier, R. C.; Freiser, B. S. *Anal. Chem.* **1982**, *54*, 96.

[12] Burnier, R. C.; Byrd, G. D.; Freiser, B. S. *J. Am. Chem. Soc.* **1981**, *103*, 4360.

[13] Dietz, T. G.; Chatellier, D. S.; Ridge, D. P. *J. Am. Chem. Soc.* **1978**, *100*, 4905.

[14] Comisarow, M. B.; Grassi, V.; Parisod, G. *Chem. Phys. Lett.* **1978**, *57*, 413.

[15] Carlin, T. J.; Freiser, B. S. *Anal. Chem.* **1983**, *55*, 571.

[16] Burnier, R. C.; Cody, R. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1982**, *104*, 7436.

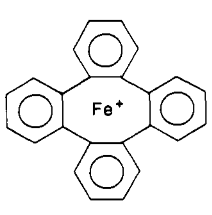
[17] Huntress, W. T.; Mosesman, M. M.; Elleman, D. D. *J. Chem. Phys.* **1971**, *54*, 843.

[18] Hettich, R. L.; Jackson, T. C.; Stanko, E. M.; Freiser, B. S. *J. Am. Chem. Soc.* **1986**, *108*, 5086.

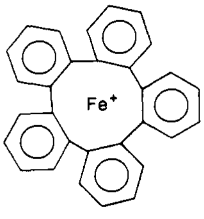
Table I. Reactions of Fe$^+$-Benzyne with Alkanes

	methane	ethane	propane	*n*-butane	*n*-pentane	*n*-hexane	isobutane	neopentane
$FeC_6H_6^+$			16	22	26	33	77	
$FeC_7H_8^+$			16	6	15	10	10	89
$FeC_8H_8^+$		100	47	2	41	17		
$FeC_8H_{10}^+$				21	5	15		
$FeC_9H_{10}^+$			21	9	4	17	11	
$FeC_9H_{12}^+$					2	1		
$FeC_{10}H_{10}^+$				17	3			
$FeC_{10}H_{12}^+$				23	1	3	2	11
$FeC_{10}H_{14}^+$						1		
$FeC_{11}H_{12}^+$					2			
$FeC_{11}H_{14}^+$					1			
$FeC_{12}H_{14}^+$						2		
$FeC_{12}H_{16}^+$						1		

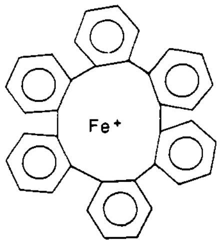
ions with *n* equal 1 and 2, respectively. Using the same consideration, structures V–VII can be proposed for the product ions



V



VI



VII

with *n* of 3–5. Without knowing the exact way by which the metal center coordinates with the polyphenylene ligand, Fe$^+$ is simply positioned in the middle of the ligand, as shown in the structures. These structures are reasonable considering that the C–C single bonds in the polyphenylenes are the only weak sites susceptible to further chemical reactions, and products of higher orders can be obtained simply by building the ring system along the C–C single bonds. Upon CID, $Fe(C_6H_4)_n^+$ ($n = 2$–4) all readily lose neutral Fe to form $(C_6H_4)_n^+$, suggesting $IP((C_6H_4)_n) < IP(Fe) = 7.870$ eV.[8] This is consistent with the literature ionization potential value of 7.56 eV for bisphenylene.[8] CID results for VI and VII were not obtained because at the higher masses the ions are more susceptible to ejection from the cell before enough kinetic energy is obtained for CID and because of the difficulty of isolating VII owing to the slow reaction. During the course of the preparation of this paper, the results from a similar study on the polymerization reactions of Fe$^+$ with phenyl halides were presented at the 36th ASMS meeting, which are in agreement with our results.[19]

Reactions of $FeC_5H_4^+$ with Alkanes. The product ions and their branching ratios from the reactions of $FeC_6H_4^+$ with alkanes are listed in Table I. With the exception of methane, all of the other alkanes studied react readily to give a wide variety of product ions. The fact that Fe$^+$–benzyne reacts with ethane, while Fe$^+$ itself does not, suggests that the attachment of the highly unsaturated benzyne provides an energetically favorable elimination pathway after the initial Fe$^+$ insertion into the C–H bond, thereby enhancing Fe$^+$ reactivity.[20] It is interesting to note that the dehydrogenation of alkanes by benzyne is estimated to be highly exothermic. For example, reaction 5 is exothermic by 51

$$C_6H_4 + C_3H_8 \rightarrow C_6H_6 + C_3H_6 \qquad (5)$$

kcal/mol.[8,9] The lack of reported reactivity between the otherwise very reactive benzyne and propane, reaction 5, probably suggests the presence of a high kinetic barrier, or the lack of a proper reaction initiation mechanism. In addition, no reaction is observed between *n*-butane and $C_6H_4^+$ generated from benzonitrile by electron impact. Taken together, these results indicate that the reactions in Table I are initiated by the metal ion center, suggesting the catalytic role played by Fe$^+$ through its ability to oxidatively add into C–C and C–H bonds. It should also be mentioned that the universally present ion-induced dipole interaction in gas-phase ion–molecule reactions also contributes to the lowering of activation barriers.

Structure and Mechanistic Studies. Determination of the structures of the product ions in Table I is the key to gaining insight into the simplest mechanistic aspects of these reactions. As shown in Table I, most of the alkanes react with $FeC_6H_4^+$ to form $FeC_6H_6^+$ and $FeC_7H_8^+$ ions, which are presumably Fe$^+$–benzene and Fe$^+$–toluene, respectively. Characteristically, these ions undergo CID by the loss of the entire ligand to form Fe$^+$ exclusively. The lack of the hydrogenation product ion, $FeC_6H_6^+$, from neopentane in comparison with the other alkanes, with the exception of ethane, suggests that hydrogenation of the benzyne ligand only occurs for alkanes with hydrogen atoms on neighboring carbon positions. To provide further mechanistic information, the reaction with propane-*2,2-d*$_2$ was studied. The majority of the hydrogenation product ion is $FeC_6H_5D^+$. Surprisingly, $FeC_6H_6^+$ also accounts for 24% of the hydrogenation product ion intensity, as shown in Figure 1. While this seems contradictory to the lack of hydrogenation from neopentane, it can be explained by invoking a reversible step in the reaction mechanism as shown in Scheme I. In this mechanism, the reaction occurs via initial Fe$^+$ insertion into a C–H bond, followed by H migration onto the benzyne ligand. Alternatively, the latter step could also proceed by the migratory insertion of the benzyne ligand into the Fe$^+$–H bond across the carbon–carbon triple bond. Unfortunately, our experiments do not provide any evidence as to which mechanism is operating here. Similarly, Scheme II is proposed to explain the formation of Fe$^+$–toluene from propane, except in this case insertion into a carbon–carbon bond might be involved. As expected, $FeC_7H_8^+$ accounts for the majority of the methanation product ion from the reaction with propane-*2,2-d*$_2$ with only minor amounts of H/D scrambling, as shown in Figure 1. It should be pointed out that repeated experiments show $FeC_7H_8^+$ as the major product ion for reaction with propane-*2,2-d*$_2$, as shown in Figure 1, while the reaction with undeuterated propane repeatedly gives $FeC_8H_8^+$ as the product ion of highest intensity, as shown in Table I. This is certainly due to the isotope effect involved in the reaction. Detailed study of this phenomenon and its mechanistic implications are under further investigation.

---

(19) Bjarnason, A.; Taylor, J. W. *An FTMS Study of Metal Catalyzed Oligomer Formation in the Gas Phase.* Oral presentation at the 36th American Society for Mass Spectrometry (ASMS) Meeting, June 1988.

(20) Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1983**, *105*, 5197.

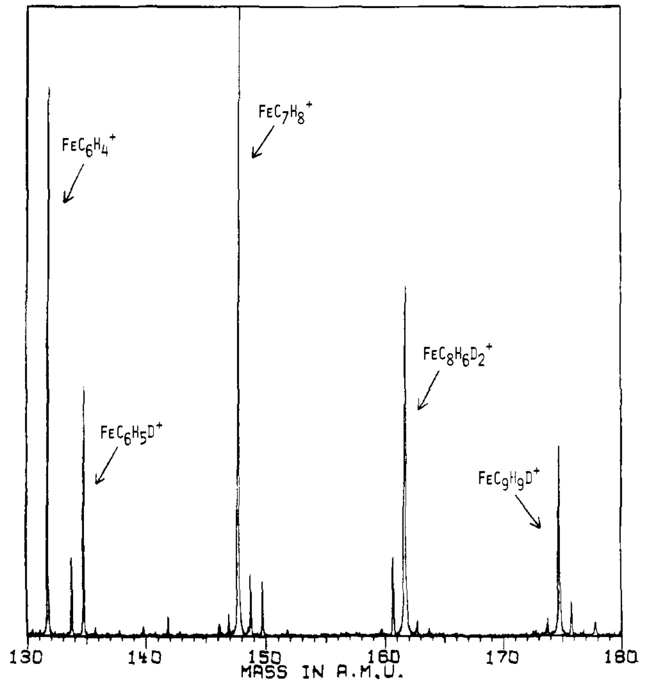
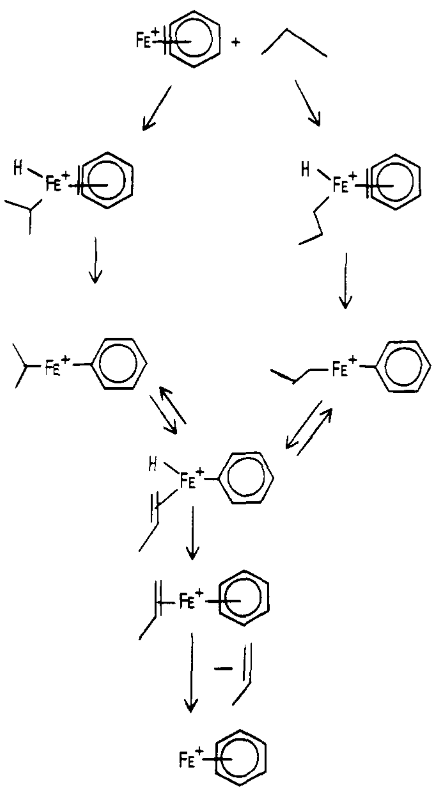


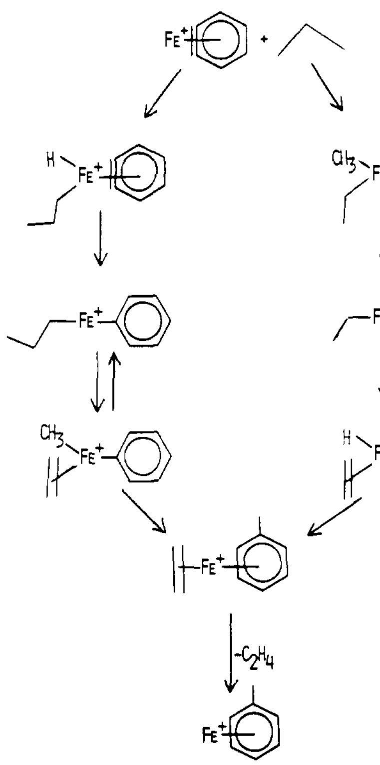
Figure 1. $FeC_6H_4^+$ reaction with propane-*2,2-d*$_2$.

Scheme I

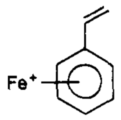


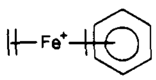
As the size of the ligand in the product ion increases, the number of reasonable structures also increases. The strategy used in this study was to prepare a series of reference ions of "known" structures of the possible product ion isomeric forms. The matchup of the CID results of a product ion of unknown structure with that of a known structure suggests the identity of its structure. Reference ions are best prepared by the ligand displacement reaction of the parent ligand of known structure with Fe$^+$–benzene. The reaction exothermicity is low, minimizing the possibility of rearrangment of the displacing ligand. In cases where the parent ligand of a certain structure is not available and the reference ion cannot be prepared, the results are rationalized in terms of proposed CID processes.

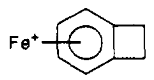
Scheme II



$FeC_8H_8^+$ Ions. There are three reasonable structures for ions of this composition generated from the reaction of $FeC_6H_4^+$ with alkanes, VIII–X. The ion with structure VIII was synthesized


VIII


IX


X

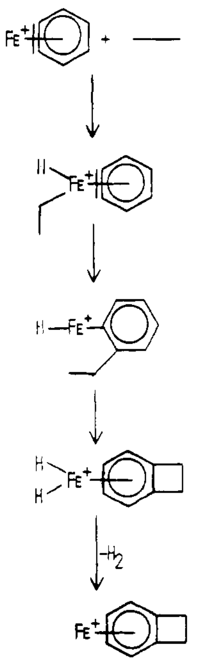
readily by reacting Fe$^+$–benzene with styrene. CID of VIII yields loss of the entire ligand exclusively over the energy range studied (10–49 eV). Unfortunately, structure X could not be synthesized owing to the commercial unavailability of benzocyclobutene. CID on $FeC_8H_8^+$ generated from ethane yields both $FeC_6H_4^+$ and Fe$^+$, with the former being the predominant fragment over the energy range studied (10–49 eV) and with Fe$^+$ intensity increasing with energy. These results are consistent with those expected for structure IX. The absence of $FeC_2H_4^+$ fragment ion could be due to the much lower Fe^+–C_2H_4 bond energy (~35 kcal/mol[18]) relative to the Fe$^+$–benzyne bond energy (~76 kcal/mol). However, the same fragmentation pattern could also be rationalized from structure X, because it is possible that cleavage of the cyclobutene ring could be facile. Additional ion–molecule reaction studies were performed to assist in structure determination. If structure IX is correct, displacement of the ethene ligand by another alkene ligand should be possible. For structure X, however, displacement might not occur unless the cleavage of the cyclobutene ring occurs. When the $FeC_8H_8^+$ ion is reacted with propene, reactions 6 and 7 occur. Reaction 7 tends to suggest

$$FeC_8H_8^+ + C_3H_6 \rightarrow FeC_9H_{10}^+ + C_2H_4 \qquad 23\% \qquad (6)$$

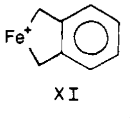
$$\rightarrow FeC_{11}H_{14}^+ \qquad 77\% \qquad (7)$$

that the ion consists primarily of structure X. However, reactions 6 and 7 do not provide conclusive structural evidence. For example, the possibility of the simple attachment of propene to structure IX cannot be completely ruled out, and reaction 6 could be explained by the cleavage of the cyclobutene ring due to the incoming propene ligand. More convincing evidence to support structure X, however, comes from the CID results on the product ion in reaction 7, in which propene loss to form $FeC_8H_8^+$ is the

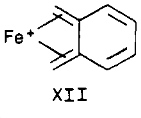
Scheme III



exclusive process observed at a collision energy of 12 eV. This rules out the possibility of propene attachment to structure IX because, in that case, loss of ethylene should be competitive with loss of propene, with the former loss being favored. At higher energies, Fe$^+$ and $FeC_9H_{10}^+$ are also observed, with the latter always a minor peak within the energy range studied (24–60 eV). Scheme III is thus proposed to explain the reaction between Fe$^+$–benzyne and ethane to form Fe$^+$–benzocyclobutene. In Scheme III the reaction is initiated by Fe$^+$ insertion into a C–H bond. Fe$^+$–ethylbenzene is apparently never formed as an intermediate in Scheme III since otherwise it would lead to the formation of Fe$^+$–styrene, which is formed from Fe$^+$ reaction with ethylbenzene and by CID on Fe$^+$–ethylbenzene (vide infra). It is interesting to note that ethane is the only alkane in Table I that has 1,2-hydrogen atoms, but does not hydrogenate the benzyne ligand. Thermochemical calculation indicates that this hydrogenation should be exothermic by 26 ± 15 kcal/mol.[8,9,17] Thus, the lack of hydrogenation can only be due to kinetic factors. The complete lack of hydrogenation at least in this case might lead to the surprising conclusion that ethyl migration to the benzyne carbon position is very much favored over the lighter H migration. Alternatively, it might suggest that benzyne migratory insertion into the Fe$^+$–ethyl bond is favored over that of the Fe$^+$–H bond here. As discussed above for the Fe$^+$–polyphenylene ions, structures with both intact polyphenylene or Fe$^+$ C–C bond inserted polyphenylene have been proposed.[12] The same is possible for the complex Fe$^+$–benzocyclobutene. Alternative structures for X could be, for example, the C–C bond inserted structure XI, or its mesomeric form XII. Complexes with structures XI and XII have been characterized.[21,22] However, the facile cleavage of the ligand to form Fe$^+$–benzyne and ethene seems to indicate that the contribution of such structures is not important here.



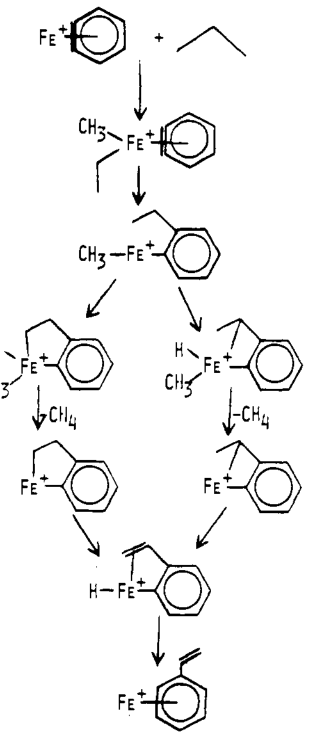
XI



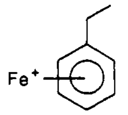
XII

Surprisingly, CID on $FeC_8H_8^+$ ions formed from reactions with propane, *n*-pentane, and *n*-hexane all lose the ligand exclusively, yielding Fe$^+$ over the energy range studied (10–49 eV), suggesting that their structure is Fe$^+$–styrene. Scheme IV is proposed to explain the formation of Fe$^+$–styrene from propane. It is interesting to note that intermediates of both metallacyclobutene and metallacyclopentene are possibly involved. As shown in Figure 1, $FeC_8H_6D_2^+$ accounts for the majority of the C_8 product ion in the reaction with propane-*2,2-d$_2$*. Examination of the mechanism suggests that this product ion is formed through the ironacyclopentene intermediate ion, while the minor amount of $FeC_8H_7D^+$ is formed through the ironacyclobutene intermediate ion. The large difference in their relative intensity suggests that the five-membered intermediate is considerably more favored over the four-membered counterpart, probably because of the ring strain involved.

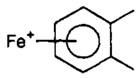
Scheme IV



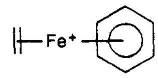
$FeC_8H_{10}^+$ Ions. The conceivable structures for an ion of this formulation from the reactions of Fe$^+$–benzyne with alkanes are XIII–XV. Structure XIII is easily prepared by reacting Fe$^+$ with ethylbenzene. Fe$^+$ dehydrogenates ethylbenzene to form Fe$^+$–styrene, which undergoes a secondary reaction by displacement of styrene with ethylbenzene. CID on XIII forms Fe$^+$–styrene and Fe$^+$ within the energy range studied (10–48 eV), with the latter increasing with energy. Structure XIV is easily prepared from the displacement reaction of *o*-xylene with Fe$^+$–benzene. Its CID yields the exclusive loss of the ligand to form Fe$^+$ over the energy range studied (10–48 eV). CID on XV is expected to yield predominantly Fe$^+$–benzene, with Fe$^+$–ethylene and Fe$^+$ increasing at higher energies. The smallest alkane to form $FeC_8H_{10}^+$ is *n*-butane. CID on this ion yields $FeC_8H_8^+$ predominantly with Fe$^+$ increasing with CID energy, suggesting that the structure is Fe$^+$–ethylbenzene (XIII). CID on $FeC_8H_{10}^+$ from *n*-hexane also indicates the Fe$^+$–ethylbenzene structure. Scheme V is proposed to explain the formation of Fe$^+$–ethylbenzene from *n*-butane.



XIII



XIV



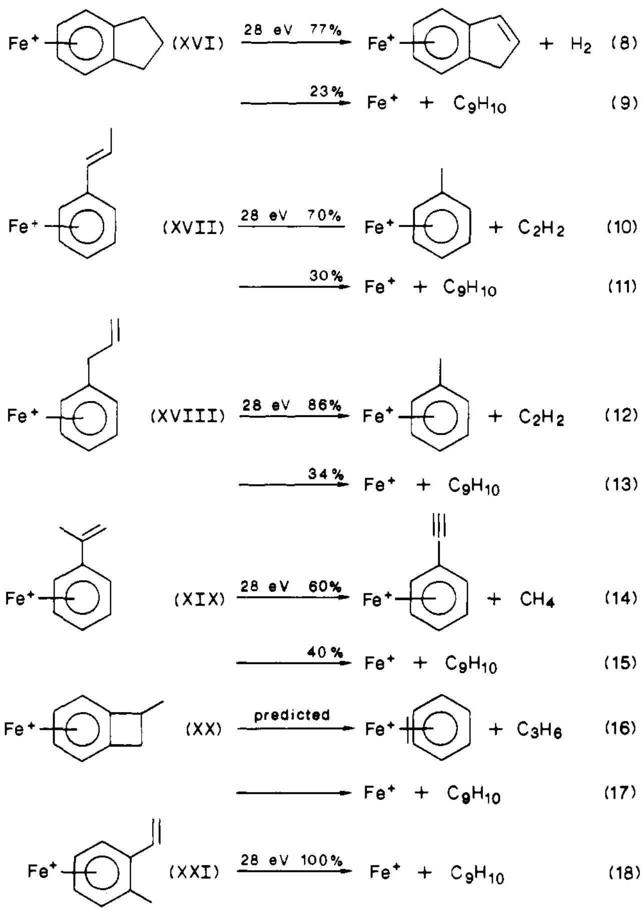
XV

$FeC_9H_{10}^+$ Ions. There are several conceivable structures for $FeC_9H_{10}^+$ ions formed from the reactions of Fe$^+$–benzyne with alkanes. Their structures and CID reactions are shown in structures XVI–XXI and reactions 8–18. Again, because the

---

(21) Lappert, M. F.; Raston, C. L.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1985**, 485.

(22) Chappell, S. D.; Cole-Hamilton, D. J. *J. Chem. Soc., Chem. Commun.* **1981**, 319. Chappell, S. D.; Cole-Hamilton, D. J.; Galas, A. M. R.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1982**, 1867.

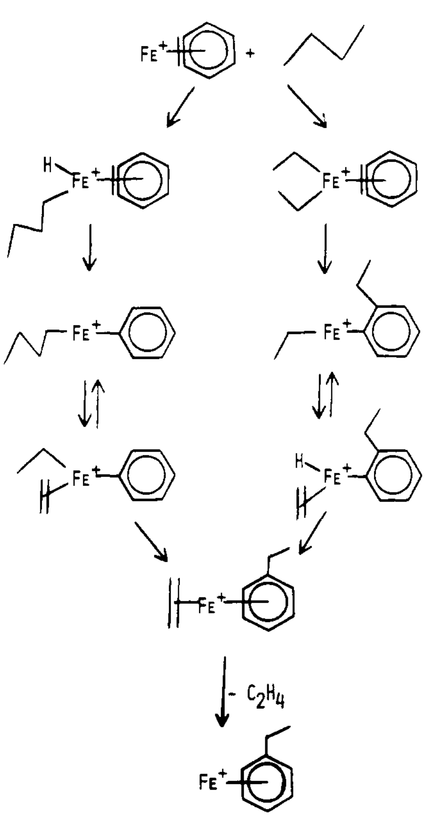


neutral parent for structure XX was unavailable, its CID spectra could not be collected directly. However, the results obtained in the study of $FeC_8H_8^+$ suggest the easy cleavage of the ring, and reactions 16 and 17 are thus expected. When $FeC_9H_{10}^+$ formed from propane and isobutane is subjected to CID at a collision energy of 28 eV, reactions 19–21 are observed. Comparison of

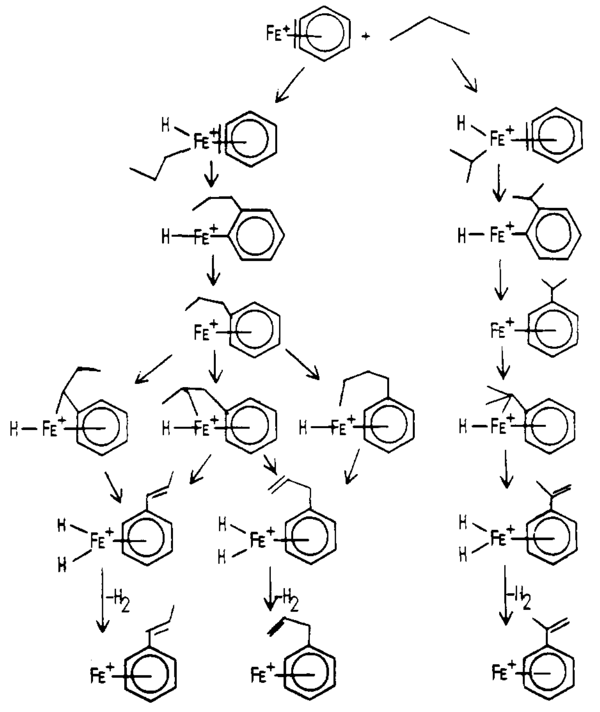
	propane	isobutane	
$FeC_9H_{10}^+ \xrightarrow{28\ eV} Fe^+ + C_9H_{10}$	33%	15%	(19)
$\longrightarrow FeC_7H_8^+ + C_2H_2$	25%	65%	(20)
$\longrightarrow FeC_8H_6^+ + CH_4$	42%	20%	(21)

this with reactions 8–18 clearly indicates the presence of more than one isomer in these product ions. Reaction 20 suggests the presence of structure XVII and/or XVIII. While the CID experiment cannot distinguish between these two structures, the former should be slightly more stable than the latter, because in XVII the double bond is conjugated with the benzene ring. However, their identical CID results suggest that, upon activation, they can isomerize and fragment through a common intermediate. Reaction 21 indicates the presence of structure XIX. Thus, Scheme VI can be proposed to explain the formation of these product ions from propane reacting with Fe⁺–benzyne. Scheme VI is partially supported from the reaction of Fe⁺ with *n*-propylbenzene, which yields 74% Fe⁺–toluene and 26% of the dehydrogenation product $FeC_9H_{10}^+$. This latter reaction probably proceeds by dehydrogenation, and the reaction energetics is such that the majority of the dehydrogenation product dissociates further to give Fe⁺–toluene, as in reactions 10 and 12. The different relative abundances of the different fragments in reactions 19–21 between propane and isobutane suggest their parent ions consist of mixed isomers with different abundances. In theory, it should be possible to estimate the relative contribution of the different isomers in the parent ion mixture from the data in reactions 19–21. However, the large number of variables involved, such as the collision energy, pressure, dissociation cross section of the different ions, and so forth, make such an estimation unreliable and, therefore, no values are given. Finally, it should be pointed out that the above CID results do not support or exclude the presence of structure XXI. From the above proposed mechanism, formation of such an isomer should be feasible.

Scheme V



Scheme VI



CID on $FeC_9H_{10}^+$ formed from *n*-butane at 28 eV yields 58% Fe⁺–toluene and 42% Fe⁺, indicating the presence of structure XVII and/or XVIII. The absence of any $FeC_8H_6^+$ is consistent with the mechanism in Scheme VI because, in this case, no isopropyl group can be present on the metal ion center to migrate onto benzyne.

As the ligand size increases, the CID results become more complicated. For example, CID on $FeC_{10}H_{10}^+$ from *n*-butane at

26 eV yields reactions 22-25. As is expected from the above

$$FeC_{10}H_{10}^{+} \xrightarrow{26\text{ eV}} Fe^{+} + C_{10}H_{10} \qquad 38\% \quad (22)$$

$$\longrightarrow C_{10}H_{8}^{+} + FeH_{2}\ (\text{or } Fe + H_{2}) \qquad 12\% \quad (23)$$

$$\longrightarrow FeC_{8}H_{8}^{+} + C_{2}H_{2} \qquad 11\% \quad (24)$$

$$\longrightarrow FeC_{10}H_{8}^{+} + H_{2} \qquad 39\% \quad (25)$$

discussion of the mechanism, a wide variety of isomeric product ions should be possible. While the large numbers of possible isomers make the study of the CID reactions for each one of them more difficult, the general mechanisms outlined above should be useful in predicting the most likely isomers present.

Conclusion

Interesting reactivity is observed for Fe^{+}–benzyne. Fe^{+} can induce polymerization of chlorobenzene to form Fe^{+}–polyphenylene or C–C inserted polyphenylene via dehydrochlorination up to the sixth step. The reaction to form Fe^{+}–hexaphenylene is significantly slower than the earlier steps. Collision-induced dissociation on Fe^{+}–polyphenylene suggests that bisphenylene, trisphenylene, and tetraphenylene all have ionization potentials lower than that of Fe at 7.870 eV.

The observed reactions between Fe^{+}–benzyne and alkanes suggest that Fe^{+} acts as the reaction initiation center in Fe^{+}–benzyne. All reactions between Fe^{+}–benzyne and alkanes can be explained by initial Fe^{+} insertion into a C–H or C–C bond, followed by migration of an alkyl or H onto the benzyne ligand or, alternatively, by benzyne migratory insertion into a Fe^{+}–H or Fe^{+}–alkyl bond. Fe^{+}–benzyne reacts with all of the alkanes studied, with the exception of methane. With the exception of ethane, all of the alkanes studied having 1,2-hydrogen atoms hydrogenate benzyne to form Fe^{+}–benzene. CID study suggests formation of Fe^{+}–benzocyclobutene from ethane, which is favored over the hydrogenation product ion. However, the isomeric ion Fe^{+}–styrene is formed from reactions with propane, *n*-pentane, and *n*-hexane. The ion with the formulation of $FeC_{9}H_{10}^{+}$ produced from propane and isobutane consists of at least two isomeric forms, Fe^{+}–α-methylstyrene, Fe^{+}–3-phenylpropene, and/or Fe^{+}–β-methylstyrene. However, for the ion of the same formulation generated from *n*-butane, the CID results clearly indicate the absence of Fe^{+}–α-methylstyrene. All of these results can be explained by a series of mechanisms based on Fe^{+} acting as the reaction center.

Acknowledgment is made to the Division of Chemical Sciences in the Office of Basic Energy Sciences in the U.S. Department of Energy (DE-FG02-87ER13766) for supporting this research and to the National Science Foundation (CHE-8612234) for continued support of the FTMS.

Registry No. VIII, 119208-10-5; XIII, 119208-11-6; $FeC_{6}H_{4}^{+}$, 119208-09-2; $FeC_{6}H_{6}^{+}$, 102307-51-7; chlorobenzene, 108-90-7; methane, 74-82-8; ethane, 74-84-0; propane, 74-98-6; *n*-butane, 106-97-8; *n*-pentane, 109-66-0; *n*-hexane, 110-54-3; isobutane, 75-28-5; neopentane, 463-82-1; styrene, 100-42-5; ethylbenzene, 100-41-4; *o*-xylene, 95-47-6.

Investigations of Small Carbon Cluster Ion Structures by Reactions with HCN

Denise C. Parent* and Stephen W. McElvany

Contribution from the Chemistry Division/Code 6110, Naval Research Laboratory, Washington, D.C. 20375-5000. Received September 12, 1988

Abstract: The results of a detailed study of the primary and secondary reactions of carbon cluster ions, C_n^{+} ($3 \leq n \leq 20$), with HCN are used as a probe of the structures of small carbon cluster ions. The experiments were performed in a Fourier transform ICR mass spectrometer (FTMS), using direct laser vaporization of graphite to form the carbon cluster ions. The only ionic products observed for the HCN reactions were C_nX^{+} (primary reaction product) and C_nXY^{+} (secondary reaction product) where X and Y = H, CN, or HCN. Radiative association is an important reaction channel. Products resulting from fragmentation of the reactant carbon cluster ion were not observed. Evidence for two structural forms of the $n = 7$–9 cluster ions is presented. The anomalous behavior of C_7^{+} is interpreted by an isomerization mechanism. Low-energy collision-induced dissociation studies of the primary product ions support a mechanism of carbene insertion into the H–CN bond and formation of covalently bonded products. In contrast, the HCN associates weakly with most primary product ions.

The emphasis of experimental and theoretical research on semiconductor and metal clusters in the last few years has been on the elucidation of their structures. A variety of experimental techniques has been applied in pursuit of this goal. With carbon cluster studies used as an example, these include: laser vaporization of thin foils or solid samples (which may be followed by a supersonic expansion) to generate and study the distribution of neutral and ionized clusters;[1-8] a fast-flow gas-phase reactor to study the reactivity of neutral clusters;[2] photodissociation of mass-selected positive cluster ions;[3] Fourier transform mass spectrometry (FTMS) to study the reactions of cluster ions;[4-6] metastable dissociation of positive cluster ions;[7] ultraviolet pho-

---

(1) Fürstenau, N.; Hillenkamp, F. *Int. J. Mass Spectrom. Ion Phys.* **1981**, *37*, 135–51. Rohlfing, E. A.; Cox, D. M.; Kaldor, A. *J. Chem. Phys.* **1984**, *81*, 3322–30. Bloomfield, L. A.; Geusic, M. E.; Feeman, R. R.; Brown, W. L. *Chem. Phys. Lett.* **1985**, *121*, 33–7.

(2) Zhang, Q. L.; O'Brien, S. C.; Heath, J. R.; Liu, Y.; Curl, R. F.; Kroto, H. W.; Smalley, R. E. *J. Phys. Chem.* **1986**, *90*, 525–8. Heath, J. R.; Zhang, Q.; O'Brien, S. C.; Curl, R. F.; Kroto, H. W.; Smalley, R. E. *J. Am. Chem. Soc.* **1987**, *109*, 359–63.

(3) Geusic, M. E.; Jarrold, M. F.; McIlrath, T. J.; Freeman, R. R.; Brown, W. L. *J. Chem. Phys.* **1987**, *86*, 3862–9. O'Brien, S. C.; Heath, J. R.; Curl, R. F.; Smalley, R. E. *J. Chem. Phys.* **1988**, *88*, 220–30.

(4) McElvany, S. W.; Creasy, W. R.; O'Keefe, A. *J. Chem. Phys.* **1986**, *85*, 632–3.

(5) McElvany, S. W.; Dunlap, B. I.; O'Keefe, A. *J. Chem. Phys.* **1987**, *86*, 715–25.

(6) McElvany, S. W. *J. Chem. Phys.* **1988**, *89*, 2063–75.

(7) Radi, P. P.; Bunn, T. L.; Kemper, P. R.; Molchan, M. E.; Bowers, M. T. *J. Chem. Phys.* **1988**, *88*, 2809–14.

(8) Yang, S. H.; Pettiette, C. L.; Conceicao, J.; Cheshnovsky, O.; Smalley, R. E. *Chem. Phys. Lett.* **1987**, *139*, 233–8. Yang, S.; Taylor, K. J.; Craycraft, M. J.; Conceicao, J.; Pettiette, C. L.; Cheshnovsky, O; Smalley, R. E. *Chem. Phys. Lett.* **1988**, *144*, 431–6.