Carbocationic polymerization in the gas phase: polymerization of acetylene induced by BF_2^+

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Gas-phase measurements for the primary reaction of BF_2^+ with acetylene and the ensuing higher-order reactions with acetylene have been performed at 296 ± 2 K in helium at 0.35 torr using the Selected-Ion Flow Tube (SIFT) technique. The primary reaction was observed to be rapid and to produce two species which both initiated rapid polymerization of acetylene. The major primary product, C_2HBF^+, was observed to initiate the sequential addition of four molecules of acetylene, most likely by termolecular association reactions. The first few steps in this polymerization were also followed using *ab initio* molecular orbital theory. The calculations and measurements provide structural, energetic, and kinetic information and, in combination, reveal several intrinsic features of the initial steps of the cationic polymerization of acetylene initiated by BF_2^+.

Key words: polymerization, acetylene, aromaticity.

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Opérant à 296 ± 2 K, à une pression de 0,35 torr d'hélium et faisant appel à la technique du tube à écoulement ionique sélectif (SIFT), on a effectué des mesures en phase gazeuse sur la réaction primaire du BF_2^+ avec l'acétylène et sur les réactions subséquentes d'ordre plus élevées avec l'acétylène. On a observé que la réaction primaire est rapide et qu'elle conduit à deux espèces qui initient chacune une polymérisation rapide de l'acétylène. On a observé que le produit primaire majeur, le C_2HBF^+, initie une addition séquentielle de quatre molécules d'acétylène qui se produisent probablement par des réactions d'association termoléculaires. On a aussi suivi les premières étapes de cette polymérisation à l'aide de la théorie des orbitales moléculaires *ab initio*. Les calculs et les mesures fournissent des informations sur la structure, sur les énergies et sur le cinétique de la réaction et, lorsqu'on les combine, ils révèlent plusieurs caractéristiques intrinsèques des étapes initiales de la polymérisation cationique de l'acétylène initiée par le BF_2^+.

Mots clés : polymérisation, acétylène, aromaticité.

[Traduit par la revue]

Introduction

Our recent observations of the "clean" gas-phase polymerization of ethylene and other olefinic monomers initiated by BF_2^+ (1, 2) prompted us to study the related ion-induced gas-phase polymerization of acetylene. Acetylene has been polymerized in solution by Friedel–Crafts or Lewis acid catalysts such as $AlCl_3$ and BF_3 (3), but the mechanism of the initiation of polymerization remains a matter of speculation.

For the polymerization of olefins in solution, one theory attributes initiation to the ionized form of the initiator resulting from self-dissociation (4, 5). For example, in the polymerization of isobutene by $AlCl_3$, the $AlCl_2^+$ cation formed by self-dissociation could add to the double bond to give an equivalent concentration of propagating carbenium ions (4, 5). Indirect evidence for such a mechanism has been given (5, 6), but direct identification of the initiating and propagating species in solution is lacking. However, we have recently shown that the intrinsic nature and reactivity of these species can be revealed with measurements of the polymerization of isobutene induced by BF_2^+ in the gas phase (2). The gas-phase polymerization of several other olefinic monomers was also investigated (2).

It is reasonable to assume that a similar initiation mechanism can apply to the polymerization of alkynes by Lewis acids. To test this assumption we chose to investigate the polymerization of acetylene initiated by the BF_2^+ cation in the gas phase, both experimentally and theoretically. In our experimental study, mass-selected BF_2^+ ions were allowed to react with acetylene in a flowing helium buffer gas and the primary and higher-order ions evolving in the polymerization chemistry were monitored downstream with a second mass spectrometer. The first few steps of this polymerization also were followed theoretically using *ab initio* molecular orbital calculations. In combination, the measurements and the calculations reveal a number of the intrinsic features of this cationic polymerization by providing kinetic, energetic, and structural information. Such insight is not accessible to measurements made in solution.

Experimental

The selected-ion flow tube (SIFT) apparatus was used to perform the measurements. The apparatus and technique have been described in detail elsewhere (7). BF_2^+ was generated from a mixture of BF_3 (Matheson C.P. grade) and helium (about 30 mol%) by electron impact at 55–80 eV. BF_2^+ was then selected using a quadrupole mass filter and injected into a flow tube containing helium at ca. 0.33 torr. We have seen that $FBOH^+$ arises from the reaction of BF_2^+ with water vapour impurity in the carrier gas (2). All measurements were performed at a room temperature of 296 ± 2 K and a total pressure of ca. 0.33 torr. Helium (Matheson, high purity 99.995 mol%) was used as the carrier gas and acetylene (Matheson, prepurified 99.6 mol%) as the reactant gas.

Table 1 includes a summary of the measured rate coefficients. At least two measurements were made for each determination of a rate coefficient. Sources of uncertainty have been discussed previously (7). The rate coefficient for the reaction for BF_2^+, which was determined from 11 measurements, was derived from a fit to the semilogarithmic decay of this ion and has an estimated accuracy of less than ±30%. The rate coefficients for the secondary and higher-order reactions were derived from a double-exponential computer fit to the profile of the corresponding reactant ion and have an estimated accuracy of less than ±40%.

Figure 1 shows that BF_2^+ reacts rapidly with acetylene to produce two primary products according to reaction [1]. The semilogarithmic

$$[1]\quad BF_2^+ + HC\equiv CH \xrightarrow{0.95} C_2HBF^+ + HF$$

$$\xrightarrow{0.05} C_2H_2\cdot BF_2^+$$

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TABLE 1. Effective bimolecular rate coefficients (in units of 10^{-10} cm^3 molecule^{-1} s^{-1}) for initiating and propagating reactions in the BF_2^+-induced gas-phase polymerization of acetylene at 296 ± 2 K in helium buffer gas at 0.35 torr

Reactant ion	k_{exp}[a]	k_c[b]	k_{exp}/k_c
BF_2^+	4.5	11.0	0.41
C_2HBF^+	3.8	10.8	0.35
$C_4H_3BF^+$	5.5	10.2	0.54
$C_6H_5BF^+$	3.2	9.9	0.32
$C_8H_7BF^+$	0.92	9.7	0.09
$C_2H_2 \cdot BF_2^+$	8.4	10.3	0.82
$C_4H_4 \cdot BF_2^+$	0.57	10.0	0.06

[a] Deduced from data of the type shown in Fig. 1 with computer-fitting techniques using single (for BF_2^+) or double exponentials (for the remaining ions). The estimated accuracies are less than ±30% for the reaction of BF_2^+ and less than ±40% for the remaining reactions.

[b] Collision-rate coefficients were derived using the Average Quadrupole Orientation theory (8) with $\alpha(C_2H_2) = 3.3$ Å^3 (9) and $Q = 3.6 \times 10^{-26}$ esu cm^2 (10).

decay of BF_2^+ provides a rate coefficient of $(4.1 \pm 1.6) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. The adduct ion presumably is formed in a termolecular reaction with helium as the stabilizing third body. The C_2HBF^+ product ion was seen to undergo a rapid sequential addition of four acetylene molecules as shown in reaction [2], again presumably in a termolecular fashion.

$$[2]\quad C_2HBF^+ \xrightarrow[k_2]{C_2H_2} C_4H_3BF^+ \xrightarrow[k_3]{C_2H_2} C_6H_5BF^+ \xrightarrow[k_4]{C_2H_2} C_8H_7BF^+ \xrightarrow[k_5]{C_2H_2} C_{10}H_9BF^+$$

Figure 1 also shows clearly the occurrence of the first three propagation steps indicated by reaction [2]. The fourth was observed in a separate experiment.

Table 1 shows that the acetylene additions in reaction [2] proceed with a slight overall decrease in efficiency, where efficiency is defined as the ratio of the experimental reaction rate coefficient, k_{exp}, to the computed collision rate coefficient, k_c. Collision rate coefficients were computed with the Average Quadrupole Orientation theory (8) taking the polarizability and rotation-averaged quadrupole moment (one-half of the static quadrupole moment) to be 3.33 Å^3 (9) and 3.6×10^{-26} esu cm^2 (10)), respectively. The effective bimolecular rate coefficients for the addition reactions were found to be 3.8, 5.5, 3.2, and 0.92×10^{-10} cm^3 molecule^{-1} s^{-1}. It is interesting to note that the rate coefficient and efficiency maximize for the addition of the second molecule of acetylene.

The adduct ion, $C_2H_2 \cdot BF_2^+$, also reacted further with two sequential additions of acetylene being observed, as shown in Fig. 1 and reaction [3], with helium presumably acting as the stabilizing third body.

$$[3]\quad C_2H_2BF_2^+ \xrightarrow[k_2']{C_2H_2} C_4H_4BF_2^+ \xrightarrow[k_3']{C_2H_2} \text{products}$$

The effective bimolecular rate coefficients for reaction [3] were found to be 8.4 and 0.57×10^{-10} cm^3 molecule^{-1} s^{-1} (Table 1). Here we note a sharp decrease in rate coefficient for the addition of a second molecule of acetylene.

Theory

The reaction sequences for the first three reactions with acetylene were examined using *ab initio* molecular orbital calculations at the HF 3-21G level of theory (11) and for the smaller ions also at the HF 6-31G* level (12). All Hartree–Fock calculations were performed with the MONSTERGAUSS program (13) and single-point MP2 calculations (14) were performed with the Gaussian 82 program (15).

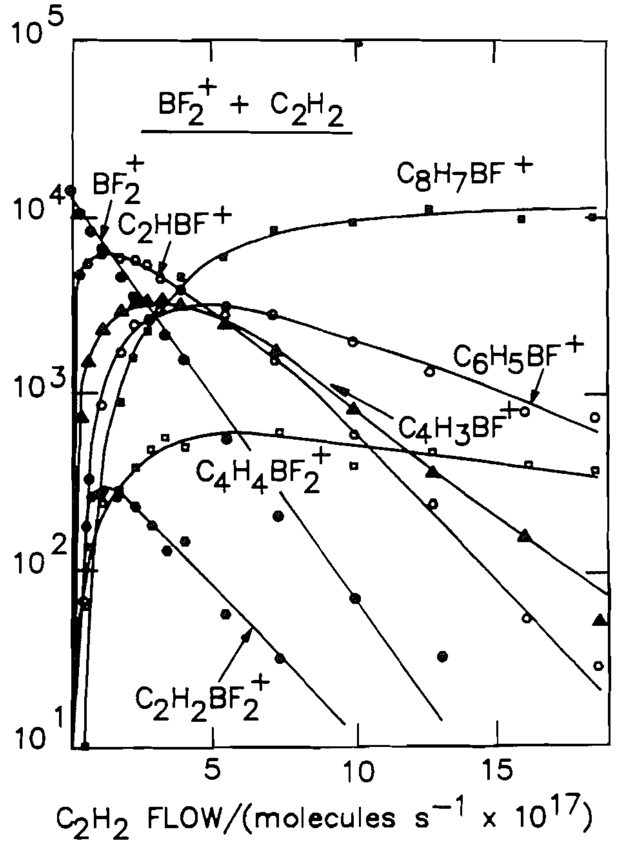


FIG. 1. Observed variation in ion signals upon addition of C_2H_2 into the reaction region in which the reacting ion BF_2^+ has been established with the SIFT technique. $P = 0.35$ torr, $T = 295$ K, [He] $= 1.13 \times 10^{16}$ atoms cm^{-3}, $\bar{v} = 6.6 \times 10^3$ cm s^{-1}, $L = 46$ cm.

The energy differences as calculated at the HF 3-21G level for the first three reactions of BF_2^+ with acetylene are shown in Fig. 2. Structures for the small ions, **1**, **3**, **5**, **6**, **7**, **8**, and **9** were optimized at both the HF 3-21G and HF 6-31G* levels of theory and the results of the higher level calculations are given in Fig. 3. For the larger ions, **4**, **10**, **11**, **12**, and **13**, several conformers were optimized at the HF 3-21G level and for each ion the main structural features of the lowest energy conformer are given in Fig. 4. The total energies as calculated at the HF 3-21G//3-21G and HF 6-31G*//6-31G* levels are recorded in Tables 2 and 3.

Reaction profile at the 3-21G level of theory

(a) The major channel

The gas-phase addition of BF_2^+ to acetylene has a large exothermicity, and in the dominant channel, much of this excess energy is used to fragment the initial complex into HF and C_2HBF^+ (**1**). The calculated ΔE for this reaction is -9.9 kcal mol^{-1}. Ion **1** can be represented by two valence tautomers, **1***a* and **1***b*. At the 3-21G level the C—C bond is 1.199 Å

$$\underset{\mathbf{1}a}{F\text{—}B^+\text{—}C\equiv C\text{—}H} \leftrightarrow \underset{\mathbf{1}b}{F\text{—}B\text{=}C\text{=}C^+\text{—}H}$$

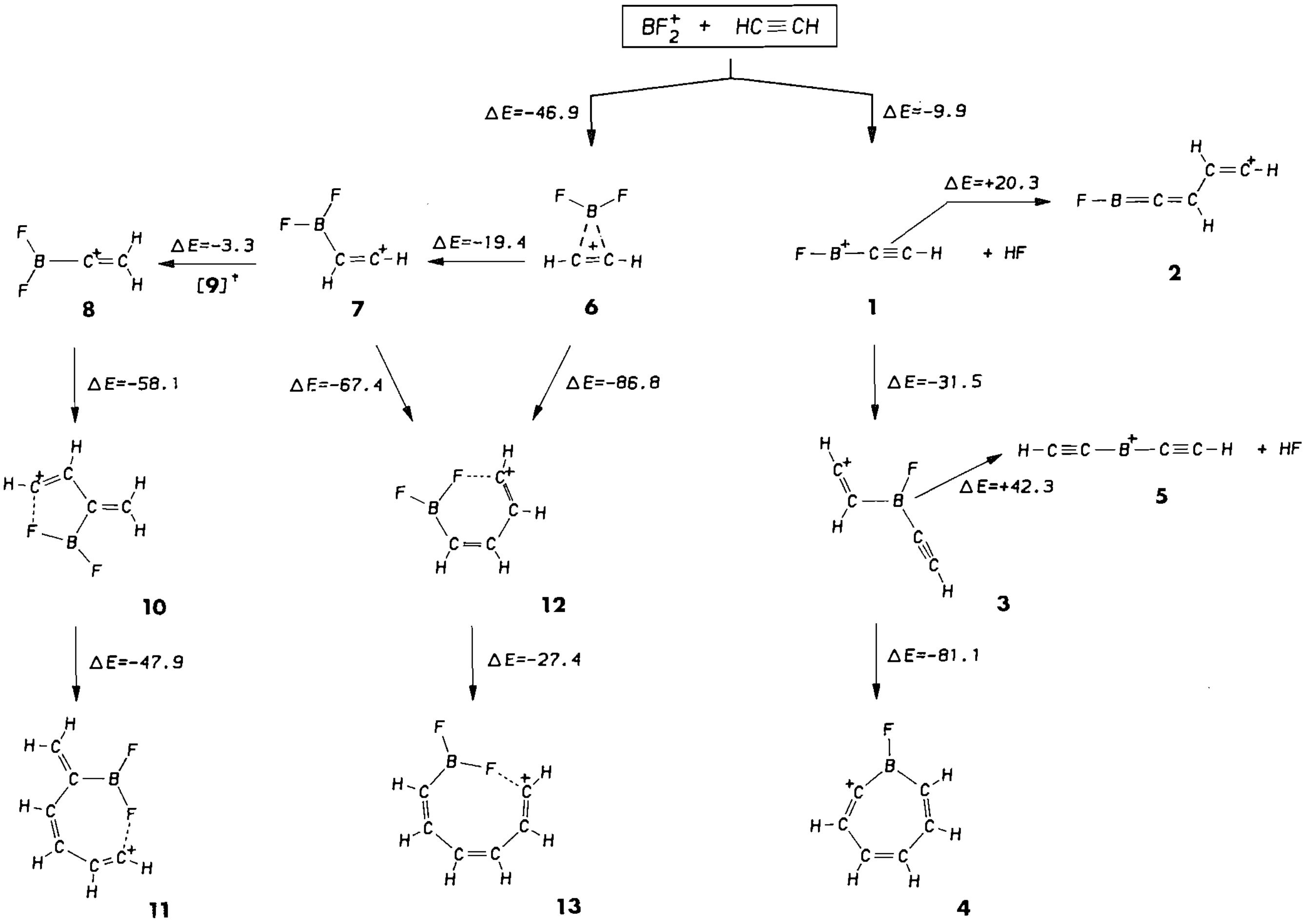
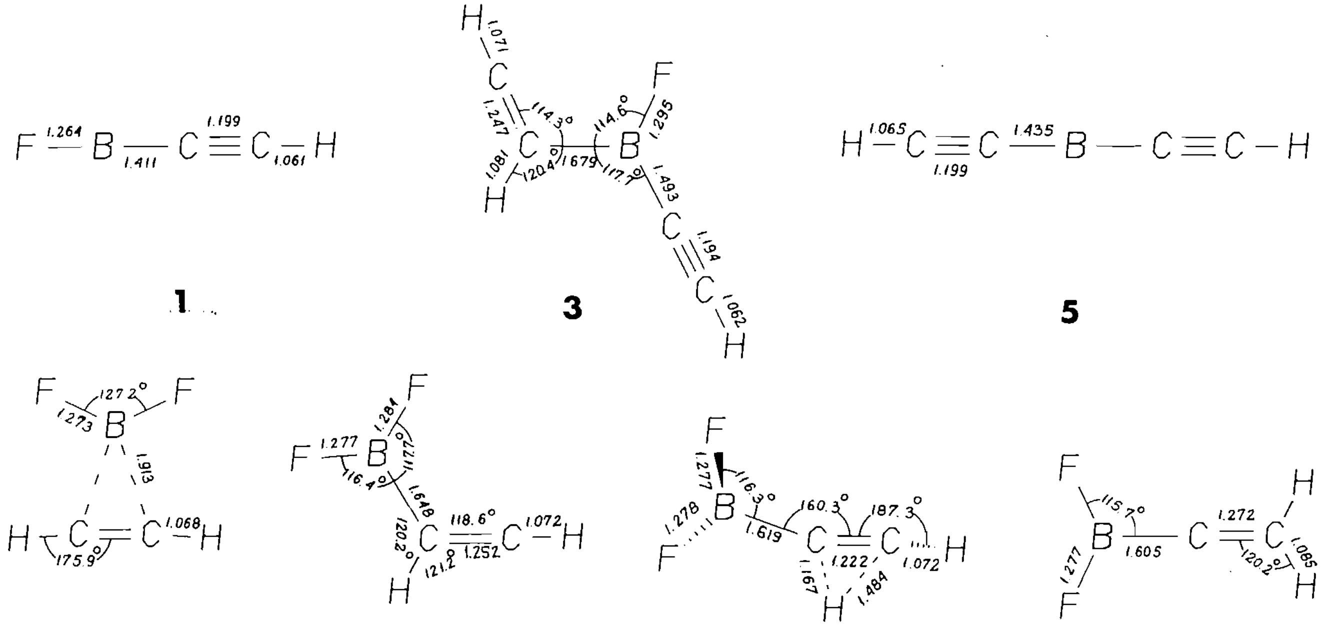


FIG. 2. Differences in total energy, ΔE (in kcal mol^{-1}), computed at 3-21G, for the first three steps in the reaction of $BF_2{}^+$ with C_2H_2.



1 **3** **5**

6 **7** **9** **8**

FIG. 3. Structures from HF 6-31G* optimization studies on ions **1**, **3**, **5**, **6**, **7**, **8**, and **9**. Bond lengths are in Ångstroms and bond angles in degrees. Based on the results of optimizations at the HF 3-21G level, ions **1** and **5** were assumed to be linear ($C_{\infty v}$ and $D_{\infty h}$), **6** and **8** were taken to have C_{2v} symmetry, and angles in acetylenes and at cationic carbons in vinyl cations were assumed to be 180°. In transition structure **9** both fluorines and both hydrogens are out of the plane defined by BCC, but all dihedral angles are less than 2°.

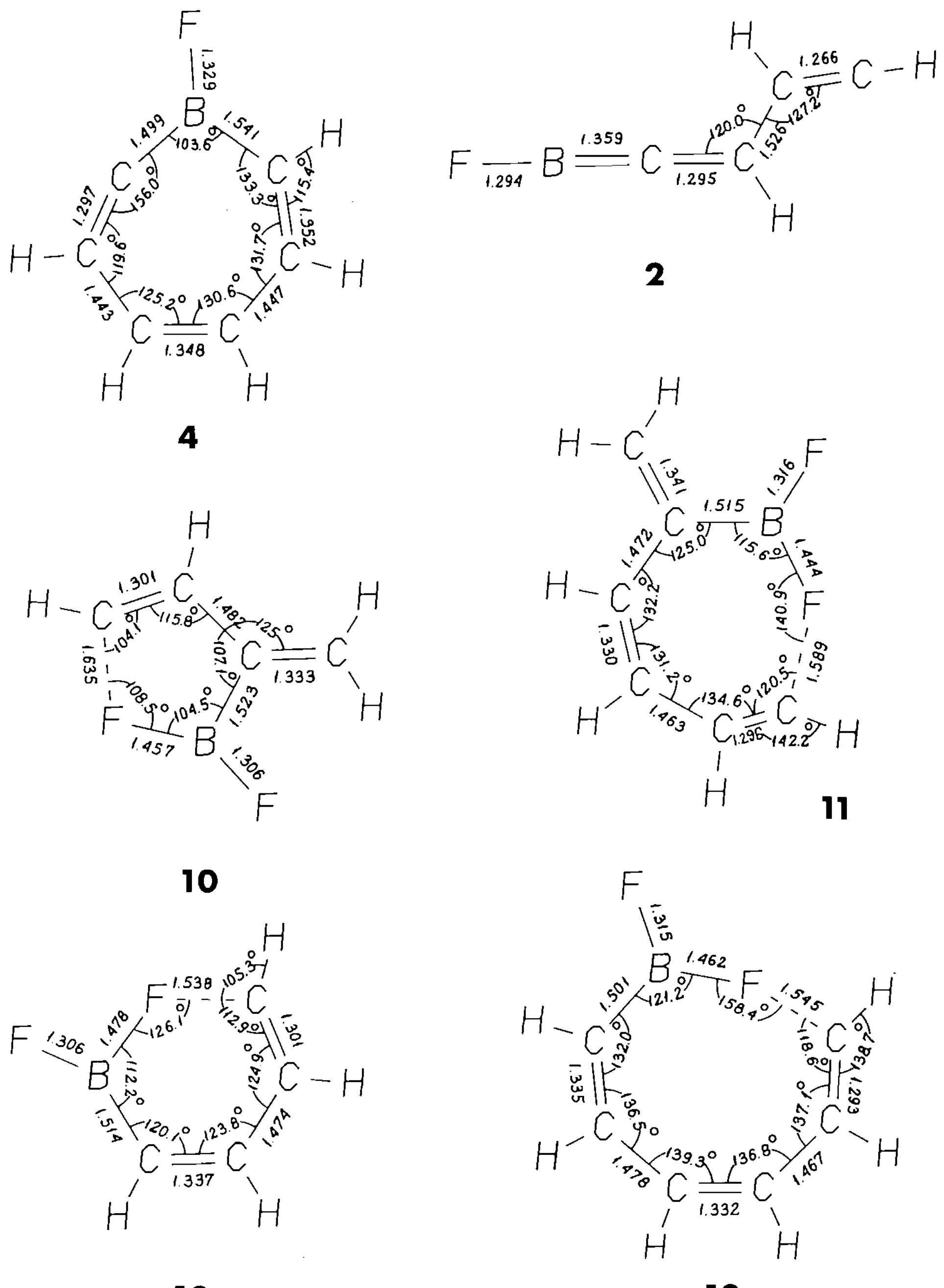


FIG. 4. Structural parameters for planar ions **2**, **4**, **10**, **11**, **12**, and **13** as obtained from HF 3-21G level calculations. Bond lengths are in Ångstroms and bond angles in degrees.

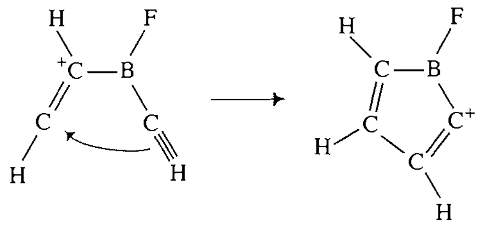
and C—B bond is 1.411 Å, indicating that structure 1*a* is the better representation. Structures 1*a* and 1*b* formally localize the positive charge on boron and the terminal carbon, respectively, and, in principle, nucleophilic attack by acetylene could occur at either of these atoms. However, addition at the carbon leads to ion **2** which is higher in energy than the initial reactants and the only energetically allowed pathway results in formation of **3**, a vinyl cation with a substituent on the β-carbon atom. We studied the profile to rotation about the C—B bond and found the conformation with the fluorine eclipsing the double bond (Figs. 2 and 3) to have the lowest energy. In this structure the positive charge is localized on the cationic carbon, with little participation from the substituent. Rotation by 180° about the C—B bond results in the triple bond eclipsing the double bond, a structure which might be expected to be stabilized by through-space π-donation from the triple bond to the cationic carbon (3*a*). However, the product formed by collapsing this internal complex is a five-membered ring, 3*b*, which has anti-aromatic character (4π electrons in the ring) and is a vinyl cation with badly distorted geometry at the cationic carbon (bending at the α carbon of vinyl cations is a high energy process (16)). These destabilising interactions result in the structure with fluorine eclipsing the double bond being 2 kcal mol^{-1} lower in energy than 3*a*.

TABLE 2. Total energies of ions and relative energies of products shown in Fig. 2

Products	Total energy of ion[a]	Relative energy[b]
1 + HF	−199.03755	−9.9
2 + HF	−275.40120	+10.4
3 + HF	−275.48363	−41.4
4 + HF	−352.00849	−122.2
5 + 2HF	−175.95598	+0.9
6	−298.55678	−46.9
7	−298.58772	−66.4
8	−298.59292	−69.6
9	−298.55944	−48.6
10	−375.08150	−127.7
11	−451.55376	−175.6
12	−375.09107	−133.7
13	−451.53074	−161.1

[a] Total energy in hartrees computed at the HF/3-21G//HF/3-21G level.

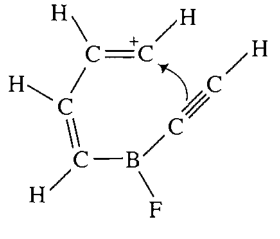
[b] Energy (in kcal mol^{-1}) relative to the reactants BF_2^+ + nC_2H_2. Total energies for BF_2^+, C_2H_2, and HF are −222.08601, −76.39596, and −99.46022 hartrees, respectively.

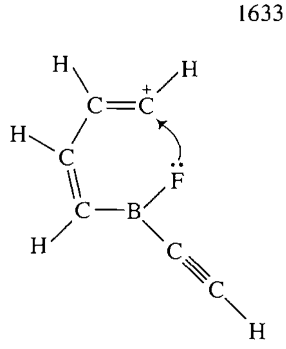

3*a* 3*b*

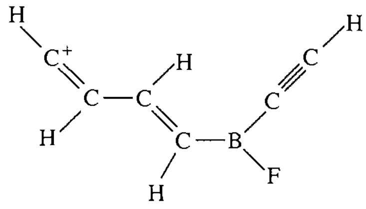
Addition of a further acetylene molecule to the cationic carbon of **3** results in the vinyl cation

$$HC^+{=}CH{-}CH{=}CH{-}B(F){-}C{\equiv}C{-}H$$

Assuming that this ion is planar, then rotation about the HC—B, HC═CH, and HC—CH bonds lead to eight possible structures. Two of these structures permit formation of cyclic ions both with 6π electrons and these two aromatic ions have the lowest energies. The *trans,cis,cis* arrangement, **4***a*, permits stabilization of the cationic carbon by through-space π-donation


4*a*


4*b*


4*c*

from the alkynyl group. This structure, which is the lowest energy conformer, has a distance of 1.443 Å between the terminal carbon atoms, and is best regarded as a seven-membered ring with alternating single and double C—C bonds (Fig. 4, structure **4**). The bond angle of 156° at the α-carbon is far from ideal, but is similar to that calculated for the 1-cyclohexenyl cation (16).

The *cis,cis,cis* structure **4***b* permits through-space donation from fluorine to the cationic carbon. The $^+$C—F distance is 1.506 Å and the ∠C—C—H at the cationic carbon is 139.7°, showing considerable $^+$C—F interaction. This structure is 16 kcal mol^{-1} higher in energy than **4***a*. All other structures are higher in energy and the *trans,trans,trans* structure **4***c*, where the positive charge is further from the unsaturated bonds and lone pairs, is 47 kcal mol^{-1} above **4***a*. Addition of acetylene to **3** gives the aromatic ion **4** in the most exothermic reaction in the major pathway (ΔE is −80.8 kcal mol^{-1}). Elimination of HF from **3** to form **5**, an analogous reaction to the major pathway

TABLE 3. Total and relative energies for structures shown in Fig. 3

	HF/6-31G*//HF/6-31G*		HF/MP2/6-31G*//HF/6-31G*	
Ion[a]	Total energy of ion[b]	Relative energy[c]	Total energy of ion[b]	Relative energy[c]
1 ($C_{\infty v}$) + HF	−200.12709	−0.8	−200.59836	−2.2
3 (C_s) + HF	−276.98776	−27.7		
5 ($D_{\infty h}$) + 2HF	−176.92115	+12.3		
6 (C_{2v})	−300.20554	−48.2	−300.85686	−50.4
7 (C_s)	−300.21451	−53.8	−300.84870	−45.3
8 (C_{2v})	−300.22232	−58.7	−300.84823	−45.0
9 (C_s)	−300.20596	−48.5	−300.84819	−45.0

[a] Molecular point group used in calculations is given in parentheses.

[b] Total energy in hartrees.

[c] Energy (in kcal mol^{-1}) relative to reactants BF_2^+ + nC_2H_2. Total energies for BF_2^+, C_2H_2, and HF are −223.31088, −76.81783, and −100.00291 hartrees, respectively, at the HF/6-31G*//HF/6-31G* level and −223.71188, −77.06463, and −100.181583 hartrees, respectively, at the MP2/6-31G*//HF/6-31G* level.

in the initial step, requires 10.8 kcal mol^{-1} more energy than the maximum available in the formation of **3** from **1**, and does not occur.

(b) The minor channel

Adduct $C_2H_2BF_2^+$ is a minor product in the gas-phase addition of BF_2^+ to acetylene. As BF_2^+ and acetylene approach, the initial long-range interaction is expected to be π-donation from the triple bond to the empty *p*-orbital on the boron atom. Similar π-complexes are believed to be intermediates in electrophilic addition to alkynes in solution (17). π-Complexes are stabilized by two interactions, π-donation from the alkyne to a vacant orbital on X^+ and back-donation usually from a lone pair on the electrophile to π* of the alkyne. In the reaction between BF_2^+ and acetylene, the electrophile is a good acceptor but back-donation is minimal and the C—B bonds are effectively one-electron bonds. The π-complex, **6**, has the anti Van't Hoff planar structure and is 19.5 kcal mol^{-1} higher in energy than the β-substituted vinyl cation, **7**. By analogy with profiles to interconversion between the open and cyclic $C_2H_2X^+$ ions (18), there is likely to be little or no barrier to interconversion of **6** and **7**. The planar α-substituted ion, **8**, has the lowest energy 3.2 kcal mol^{-1} below **7** and the barrier to interconversion of **7** and **8** via transition structure **9** is 17.8 kcal mol^{-1} above **7** (Table 1). Structure **8** is 69.6 kcal mol^{-1} below the reactants, C_2H_2 and BF_2^+, and structures **6** to **9** are all easily accessible on this reaction path.

We have calculated structures for the polymerization of acetylene starting with structures **6**, **7**, and **8**. For the larger ions where a multiple carbon–carbon bond or a fluorine atom is at one end of the molecule and the other terminus is a vinyl cation, there is a through-space interaction between the terminal groups and the ion is cyclic. Addition reactions which produce cyclic ions formally containing π electrons in the ring (ions **11** and **12**) are highly exothermic, a fact which we attribute to the aromaticity of the product.

Addition of acetylene to **8** occurs at the cationic carbon and gives ion **10**. This is formally a vinyl cation but there is considerable through-space interaction with the fluorine atom, as shown by the C…F distance of 1.635 Å, the long B—F bond and the bending at the cationic carbon (Fig. 4). Further addition yields the cyclic ion, **11**, in which the C—F distance of 1.589 Å is approximately 0.2 Å longer than a normal C—F bond. Formally there are six π electrons in the cross-conjugated ring in structure **11** and this ion is 14.4 kcal mol^{-1} lower in energy than the isomeric eight-membered ring, **12**, which formally contains eight π electrons in the ring.

Addition of acetylene to **6** and **7** is highly exothermic and leads to structure **12**, a six-membered ring which formally contains six π electrons. Ion **12** is 6.0 kcal mol^{-1} lower in energy than the isomeric ion, **10**. The aromaticity of **12** is destroyed by addition of a further acetylene molecule and ΔE for formation of **13**, which is an eight-membered ring formally carrying eight π electrons in the ring, is small.

Higher level calculations

Ab initio calculations with small gaussian basis sets favour classical structures like **7** and **8** over bridged structures like **6** and transition states like **9**. These ions are sufficiently small that inclusion of polarisation functions in the basis set used in structure optimisation is feasible. We have used the HF/6-31G* level of theory to reoptimize some of the smaller structures and have then used these structures to test the effect of inclusion of correlation energy on the calculated ΔE for the initial step of the reaction sequence. The results of these calculations are included in Table 3 and Fig. 3.

For the major channel, addition followed by elimination of HF, ΔE is −0.8 kcal mol^{-1} at the HF/6-31G* level and −2.2 kcal mol^{-1} at the MP2/6-31G*//HF/6-31G* level. These are much closer to thermoneutral than ΔE calculated at the HF/3-21G level (−9.9 kcal mol^{-1}). The subsequent addition reaction of acetylene to form the adduct **3** is calculated to have ΔE = −26.9 kcal mol^{-1} at the HF/6-31G* level, i.e. it is slightly less exothermic than at the HF/3-21G level. Formation of $B(C{\equiv}CH)_2^+$ by loss of HF from **3** is calculated to require 12.3 kcal mol^{-1} more energy than is available in the initial reactants. To summarise, then, for the major reaction pathway, increasing the basis set size has the effect of decreasing the relative energies of the products but does not change the overall mechanistic conclusions.

For the initial ions in the minor channel, extension of the basis set and inclusion of correlation energy both result in significant stabilisation of the cyclic ions **6** and **9**. At the HF/6-31G* level the non-classical bridged ion, **6**, has the highest energy but is only 5.6 kcal mol^{-1} above the open ion **7**, and the transition structure **9** is only 5.3 kcal above **7**. Inclusion of correlation energy at the MP2 level (valence electrons only) has the dramatic effect of making the bridged ion **6** the lowest energy isomer, with structures **7**, **8**, and **9** all having similar energies 5 kcal mol^{-1} higher than **6**. The highest level calculations then show that, although BF_2^+ is ineffective as a back-donor, nevertheless $C_2H_2BF_2^+$ is a symmetrically bridged ion. Previous theoretical studies have found that the parent vinyl cation to have the open $H_2C{=}C^+H$ structure at the Hartree–Fock level but to have the symmetrically bridged structure when correlation is included (19, 20). A recent experimental study has shown the vinyl cation to be symmetrically bridged (21).

Discussion and conclusions

We have characterized the intrinsic chemistry of the initial steps in the polymerization of acetylene by BF_2^+ in the gas phase experimentally using the SIFT technique. The measurements provide a quantitative measure of the intrinsic reaction kinetics. The initiation reaction is quite rapid (k = 4.1×10^{-10} cm^3 $molecule^{-1}$ s^{-1}) with the major channel being the formation of C_2HBF^+ ion and the elimination of HF. Some addition product is also formed, most likely in a termolecular reaction at our operating pressures. Polymerization occurs mainly via the C_2HBF^+ ion followed by four additions of acetylene. The rate coefficient exhibits a maximum early in the reaction sequence. Two sequential addition reactions were observed with the addition product, $C_2H_2{\cdot}BF_2^+$.

The *ab initio* molecular orbital calculations provide insight into the structures and energetics of several of the intermediates in the polymerization chemistry. The energetics of the first few steps in the polymerization reaction involving the major initial product ion, C_2HBF^+, are of interest. Formation of C_2HBF^+ is fast, but the reaction of this ion to form **3** is somewhat slower and is less exothermic than most of the addition reactions in Fig. 2. Ion **3** is unusual in that, unlike other vinyl cations containing unsaturated linkages, it does not adopt the s-*cis* conformation which permits delocalization of the charge through space onto the triple bond. This may be attributed to the antiaromatic character of such a five-membered ring containing four π electrons. The reaction of **3** to form **4** is the fastest reaction in this channel and the product is a seven-membered ring with six π electrons (excluding the lone pair on fluorine). It therefore appears that the rates and energetics of reactions in the gas-phase polymerization are dictated by the aromaticity of the product ion.

In solution the major reaction pathway might be addition rather than elimination of HF since solvation of BF_2^+ would make it less reactive. Assuming that the solvent does not act to prevent ring formation, then structure **13** and probably **11** are likely to be major intermediates in the solution-phase polymerization. The highest level calculations show the adduct $C_2H_2BF_2^+$ to have the planar bridged structure **6**. Reaction of ion **6** with acetylene produces cyclic ion **12** which has six π electrons in the ring. This reaction has the largest calculated exothermicity in the two reaction schemes in Fig. 2 and the observed rate constant is the largest in Table 1. Further reaction of **12** with acetylene produces an eight-membered ring with eight π electrons. ΔE for this last step is small (-27.4 kcal mol^{-1}) and the experimental rate coefficient (5.7×10^{-11} cm^3 molecule^{-1} s^{-1}) is the smallest in Table 1. Here again the rates of formation and reaction of the aromatic ion **12** correlate with their calculated exothermicities.

The π-bonds of acetylene are stronger than that of ethylene (the ionization energies are 11.4 and 10.5 eV, respectively) (22). In general then, in reactions in which π-donation is dominant (e.g. electrophilic addition and formation of π-complexes with metals) alkenes react faster than alkynes. Previous results have been for solution reactions, but now we find that the gas-phase reaction of BF_2^+ with ethylene has a larger rate coefficient (7.3×10^{-10} cm^3 molecule^{-1} s^{-1}) than that for the reaction of BF_2^+ with acetylene (4.5×10^{-10} cm^3 molecule^{-1} s^{-1}). In both gas-phase reactions the major pathway is elimination of HF to produce the propagating species $C_2H_3BF^+$ in the ethylene reaction and C_2HBF^+ in the acetylene reaction. In the reaction with ethylene, loss of HF is the only reaction channel. In the reaction with acetylene some addition product is observed (5%) but the dominant pathway is loss of HF. The observation of an addition product in the reaction with acetylene and non-observation in the reaction with ethylene may be explained by the difference in the exothermicity of HF elimination. Elimination of HF in the ethylene reaction is more exothermic (5 kcal mol^{-1} at HF/6-31G*) than elimination in the acetylene reaction (1 kcal mol^{-1} at HF/6-31G*). Thus the initial acetylene adduct can persist for a longer time and can be more easily deactivated by collision with helium buffer atoms before HF is eliminated.

With the SIFT experiments in combination with theoretical calculations we have characterized the intrinsic features of the initial steps of the BF_2^+ ion induced polymerization of acetylene in the gas phase. Such a combined approach should have general applications in the elucidation of intrinsic features of cationic polymerization in the gas phase.

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