Gas-phase measurements of the kinetics of BF_2^+-induced polymerization of olefinic monomers

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The initial steps in the BF_2^+-induced polymerization of the monomers of ethylene, propylene, *cis*-2-butene, isobutene, and styrene have been observed in the gas phase at room temperature using the Selected-Ion Flow Tube (SIFT) technique. Rate constants and product distributions have been determined for the initiation of the polymerization in each case. All five initiation reactions were found to be rapid ($k \geq 5.0 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}). The primary product ions that propagate polymerization have been identified and sequential addition reactions have been followed in all five systems. For ethylene the energetics of the initial steps have been followed using *ab initio* molecular orbital theory. Reactions of BF_2^+ with the vapours of water and benzene have also been characterized.

Key words: ion-induced polymerization, alkenes, kinetics, gas phase ion chemistry.

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Opérant en phase gazeuse, à la température ambiante et faisant appel à la technique du tube à écoulement sélectif d'ion (SIFT), on a observé les étapes initiales de la polymérisation, induite par le BF_2^+, de monomères de l'éthylène, du propylène, du *cis*-but-2-ène, de l'isobutène et du styrène. Dans chacun des cas, on a déterminé les constantes de vitesse ainsi que les distributions des produits obtenus pour l'initiation de la polymérisation. On a trouvé que chacune de ces cinq initiations est rapide ($k < 5{,}0 \times 10^{-10}$ cm^3 molécule^{-1} s^{-1}). Dans chacun des cinq systèmes, on a identifié les ions des produits primaires qui propagent la polymérisation et on a suivi les réactions subséquentes d'addition. Dans le cas de l'éthylène, on a déterminé les énergies impliquées dans les étapes initiales en faisant appel à la théorie des orbitales moléculaires *ab initio*. On a aussi caractérisé les réactions du BF_2^+ avec les vapeurs d'eau et de benzène.

Mots clés : polymérisation induit par les ions, alkènes, cinétique, chimie des ions en phase gazeuse.

[Traduit par la revue]

Introduction

Friedel–Crafts or Lewis acid catalysts such as the halides BF_3, $AlCl_3$, and $TiCl_4$ are widely used to initiate carbocationic polymerization in solution (1). In industry, polymerizations designed to yield high-molecular-weight polymers invariably involve Friedel–Crafts catalysts in the presence of protogenic cocatalysts. At one time cocatalysts were thought to be essential for the initiation of cationic polymerization (2), but the number of systems in which cationic polymerization has been shown to occur without the purposeful addition of a cocatalyst has grown. Compilations of such systems have recently appeared in the literature (3, 4). We note here that the mechanism of direct initiation and the nature of the species involved in the initiation remain a matter of speculation (5–7). One theory attributes initiation to the ionized form of the initiator, which becomes available in solution by self-dissociation of the initiator (8). For example, in the polymerization of isobutene by $AlCl_3$, the $AlCl_2^+$ cation formed by self-dissociation would immediately add to the double bond to give an equivalent concentration of carbenium ions (8, 9). Indirect evidence for such a mechanism based on conductivity measurements has been given by Grattan and Plesch, but direct identification of the initiating and propagating species is lacking (9, 10). The initial steps are difficult to isolate for study in solution. We show here that this is not the case in the gas phase, as we address the intrinsic features of such a mechanism with gas-phase measurements designed to mimic the initiation of cation-induced polymerization in solution (11).

We have chosen to investigate the initiation of the polymerization of ethylene, propylene, *cis*-2-butene, isobutene, and styrene by the BF_2^+ cation in the gas phase. The experiments provide both the specific rate and the product distribution of the initial step, as well as insight into the ensuing steps that propagate the polymerization. For the reaction with ethylene, quantum-chemical calculations that follow the energetics of the initial steps of polymerization are also reported. Such a combined experimental and theoretical approach can provide a detailed understanding of the intrinsic features of the initial steps in cationic polymerization.

Experimental

The experiments were performed with the selected-ion flow tube/flowing afterglow apparatus in the Ion Chemistry Laboratory at York University. The apparatus and technique have been described in detail elsewhere (12, 13). The range of the downstream mass spectrometer was ca. 260 amu. The BF_2^+ cation was generated from either pure BF_3 (Matheson, C.P. grade) or mixtures of BF_3 in helium by electron impact at energies in the range 55–80 eV. The BF_2^+ was selected from the ionized gas using a quadrupole mass filter and injected into a flow tube containing helium at ca. 0.3 Torr (1 Torr = 133.3 Pa). A typical spectrum of BF_2^+ in helium, observed downstream using a second quadrupole mass filter, is shown in Fig. 1. The ion at m/z 47 ($FBOH^+$) arises from reaction with water impurity in the helium and the ion at m/z 30 (BF^+) arises from collisional dissociation of BF_2^+. Low ion injection energies (nominally 18–24 V) were used to minimize collisional dissociation.

Ethylene, isobutene, propylene (all Matheson, C.P. grade), and *cis*-2-butene (Phillips, research grade) were used as reagent gases while styrene and benzene (both Aldrich) were used as their vapours, diluted with helium as 5 mol% and 10 mol% mixtures, respectively.

All measurements were done at a room temperature of 296 ± 2 K and a total pressure of 0.34 Torr. Helium (Matheson, high purity 99.995%) was used as carrier gas.

Theory

Closed shell *ab initio* molecular orbital calculations were carried out with the MONSTERGAUSS program (14). Geometry optimization on the ions $C_2H_4BF_2^+$ and on all smaller species was performed at the 6-31G* level (15), while the 3-21G basis

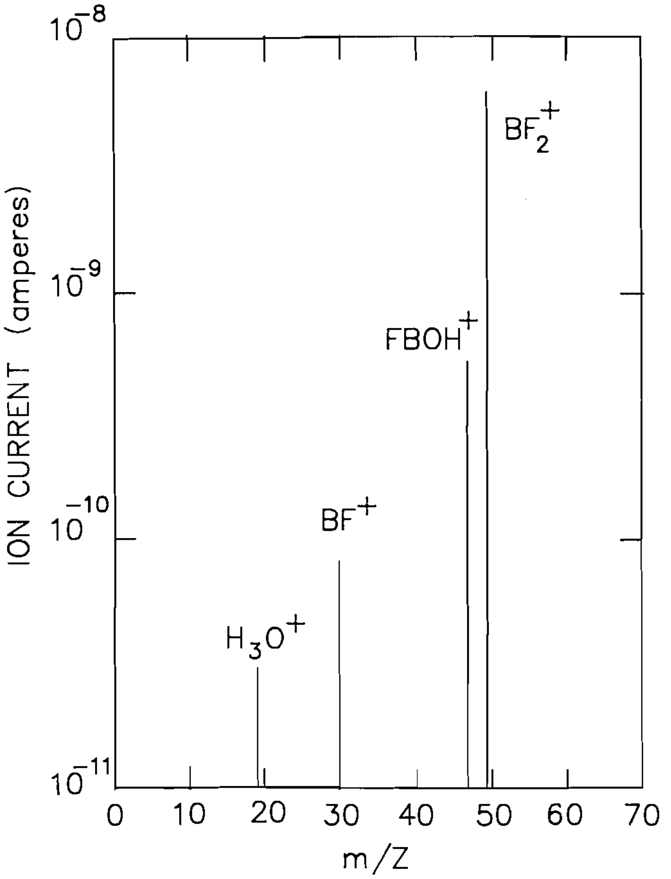


FIG. 1. Downstream SIFT spectrum for $BF_2{}^+$ derived from a mixture of BF_3 in He by electron ionization at 51 eV. The buffer gas is helium at 0.33 Torr and the ion injection energy is ca. 24 V. The background "chemical noise" arises from the collisional dissociation of $BF_2{}^+$ and from reactions with water vapour impurity in the buffer gas.

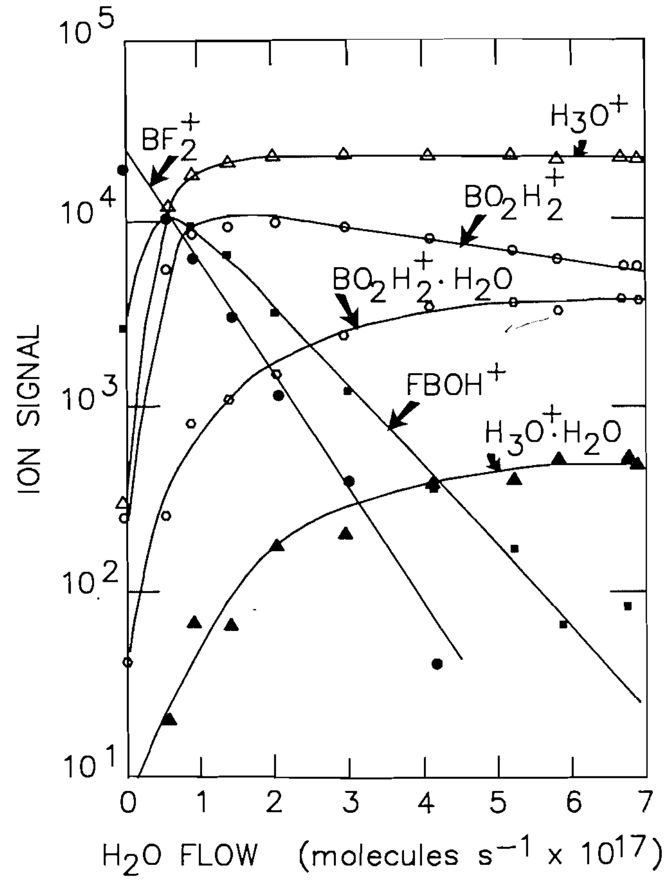


FIG. 2. The variation in ion signals observed for the addition of water vapour into the reaction region of the SIFT apparatus in which the $BF_2{}^+$ ion is initially established in helium buffer gas. P = 0.35 Torr, [He] = 1.1×10^{16} atoms cm^{-3}, $\bar{v} = 7.1 \times 10^3$ cm s^{-1}, L = 46 cm, and T = 296 K.

set (16) was used for preliminary work and for optimization of the ion $C_4H_7BF^+$. For the ion $C_4H_7BF^+$, single point 6-31G* calculations were performed at the 3-21G structure (these calculations are denoted as 6-31G*//3-21G).

Results and discussion

Table 1 provides a summary of the reaction rate constants and product distributions obtained in this study and a comparison with specific rates for collision. Standard enthalpy changes are also indicated for those reactions for which the required enthalpies of formation were available.

Water

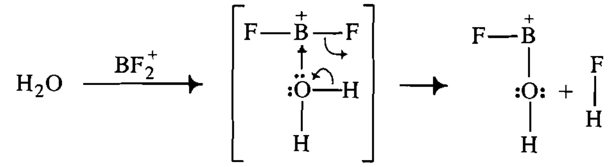
The reaction of $BF_2{}^+$ with water vapour was investigated in order to elucidate the contribution to the ion spectrum observed downstream of ion–molecule reactions with the water vapour impurities in the helium carrier gas. When water vapour was deliberately added into the reaction region in which $BF_2{}^+$ was established as a dominant ion, $FBOH^+$ was observed to be produced according to reaction [1].

$$[1] \quad BF_2{}^+ + H_2O \longrightarrow FBOH^+ + HF$$

The $FBOH^+$ ion reacted further with H_2O by proton transfer and condensation according to reaction [2]. Both H_3O^+ and $BO_2H_2{}^+$ were observed to react further by adding a water molecule in what are presumed to be termolecular reactions with He as the third molecule. The observed reaction sequence initiated by $BF_2{}^+$ in H_2O is shown in Fig. 2. The semilogarithmic decay of $BF_2{}^+$ provides a measure of the rate constant for reaction [1], which was found to be $(1.5 \pm 0.5) \times 10^{-9}$ cm^3 $molecule^{-1}$ s^{-1}. The rate constant for reaction [2] was determined to be 1.3×10^{-9} cm^3 $molecule^{-1}$ s^{-1} from a computer fit to the growth and decay of the $FBOH^+$ ion.

$$[2] \quad FBOH^+ + H_2O \xrightarrow{0.75} H_3O^+ + FBO$$
$$\xrightarrow{0.25} BO_2H_2{}^+ + HF$$

Mechanistic considerations suggest that the $FBOH^+$ ion produced in reaction [1] is FB=O protonated at the oxygen, F—B⁺—O—H, which may be formed directly by electrophilic attack on the oxygen of water with elimination of HF as shown in reaction [3]. The isomers F—B(H)—O⁺ and H—B⁺—O—F would require more bond redisposition for their formation. The secondary reaction of F—B⁺—O—H with H_2O can proceed similarly to eliminate HF and produce HO—B⁺—OH rather than, say, H—B⁺—OOH.

[3]


The assignment of F—B⁺—O—H is consistent with results of molecular orbital calculations. Calculations at the 6-31G*

TABLE 1. Summary of rate constants (in units of 10^9 cm^3 molecule^{-1} s^{-1}) and product distributions measured at 296 ± 2 K for reactions of BF_2^+ with selected olefinic monomers, with benzene, and with water vapour

Monomer	Products	Branching ratio[a]	k_{exp}[b]	k_{ADO}[c]	ΔH^0_{298}[d] (kJ mol^{-1})
$H_2C{=}CH_2$	$C_2H_3BF^+ + HF$	1.0	0.73 (0.66)	1.1	
$H_2C{=}CH(CH_3)$	$C_3H_5^+ + HBF_2$	0.80	0.50 (0.38)	1.3	−130 to −92
	$C_2H_2BF_2^+ + CH_4$	0.20			
$H_2C{=}C(CH_3)_2$	$C_2H_5^+ + C_2H_3BF_2$	0.35	0.81 (0.58)	1.4	−146
	$C_4H_7^+ + HBF_2$	0.25			−225
	$C_2H_4BF_2^+ + C_2H_4$	0.25			
	$C_3H_4BF_2^+ + CH_4$	0.15			
	$C_3H_5^+ + CH_3BF_2$				
	$C_4H_8{\cdot}BF_2^+$ (He)				
cis-2-C_4H_8	$C_2H_5^+ + C_2H_3BF_2$	0.20	0.78 (6.60)	1.3	−156
	$C_4H_7^+ + HBF_2$	0.40			−225
	$C_2H_4BF_2^+ + C_2H_4$	0.25			
	$C_3H_4BF_2^+ + CH_4$	0.15			
	$C_3H_5^+ + CH_3BF_2$				
	$C_4H_8{\cdot}BF_2^+$ (He)				
$C_6H_5CHCH_2$	$C_8H_8{\cdot}BF_2^+$ (He)	0.95	0.82 (0.43)	1.9	
	$C_8H_7BF^+ + HF$	0.05			
	$C_6H_7^+ + C_2HBF_2$				−74
C_6H_6 (benzene)	$C_6H_6{\cdot}BF_2^+$ (He)	0.80	0.74 (0.53)	1.4	
	$C_6H_5BF^+ + HF$	0.20			
H_2O	$FBOH^+ + HF$	1.0	1.5 (0.75)	2.0	

[a] Primary product ions that contribute 5% or more to the total product ions observed are listed. The branching ratio is rounded off to the nearest 5%.

[b] The apparent bimolecular rate constant is given in each case. All measurements were taken in helium buffer gas at a total pressure of 0.34 Torr and a number density of 1.1×10^{16} atoms cm^{-3}. The accuracy of the rate constants is estimated to be ±30%. The value given in parentheses represents the reaction efficiency, k_{exp}/k_{ADO}.

[c] Collision rate constants were derived with the combined variational transition-state theory/calculated trajectory approach of Su and Chesnavich (29).

[d] Enthalpies of formation were derived from ref. 30.

level indicated an energy for F—B═O 184 kcal mol^{-1} lower than that for B—O—F, compared to a difference of 146 kcal mol^{-1} based on calculations at the STO-4G* level reported previously (17). Protonation of FBO was also investigated at the 6-31G* level. The proton affinity of the oxygen site was found to be 90 kcal mol^{-1} higher than the proton affinity at the fluorine site. Protonation on the boron atom did not give rise to a minimum and gave rise to H-atom migration to the oxygen site in the structure optimization procedure.

Due to the presence of water vapour impurities in the helium buffer, $FBOH^+$ ions were always present in the reaction tube when BF_2^+ was selected upstream (in spite of the depletion of its precursor ion, BF_2^+, in the reaction region). The $FBOH^+$ was observed to react rapidly with benzene and with all of the olefins investigated in this study. The predominant channel in each case was proton transfer. In each case the observed decay of $FBOH^+$ was rate-limited by the depletion of its precurser ion, BF_2^+, so that only a lower limit of the rate constant equal to the rate constant for the reaction of BF_2^+ can be derived from these observations. The protonated ethylene was observed to react rapidly with ethylene to form $C_3H_5^+$ and the adduct ion, as reported previously (18). Protonated propylene produced only the adduct ion with propylene with a rate constant of 2.3×10^{-10} cm^3 molecule^{-1} s^{-1}. The two butenes, styrene, and benzene reacted only slowly with their protonated parent molecules to form adduct ions. Rate constants of 3×10^{-11}, 8×10^{-11}, $\leq 4 \times 10^{-11}$, and $\leq 1 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} were obtained for the reactions with *cis*-2-butene, isobutene, styrene, and benzene, respectively. In the case of the reaction with isobutene there is good agreement with a previous determination of 7×10^{-11} cm^3 molecule^{-1} s^{-1} using high-pressure mass spectrometry at 450 K (19).

Ethylene

BF_2^+ was found to react rapidly with ethylene in a bimolecular fashion with a rate constant of $(7.3 \pm 2.2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1} to form the $C_2H_3BF^+$ cation as shown in reaction [4].

$$[4] \qquad BF_2^+ + H_2C{=}CH_2 \longrightarrow C_2H_3BF^+ + HF$$

Figure 3 shows the further occurrence of several propagation steps. In total, the sequential addition of four molecules of ethylene was observed as expressed in reaction [5].

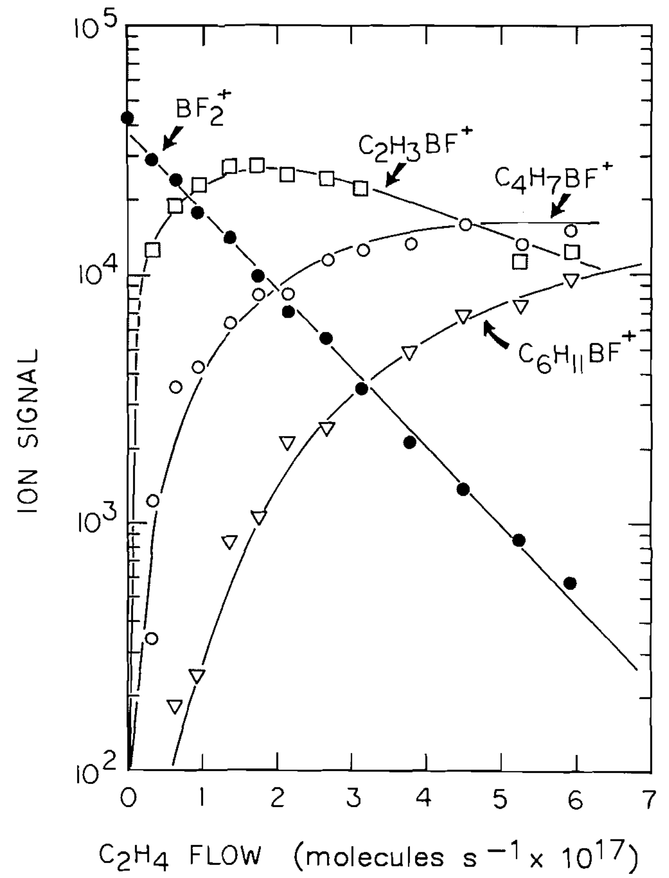


FIG. 3. SIFT measurements of the sequential ion chemistry initiated by BF_2^+ in ethylene and helium buffer gas. P = 0.349 Torr, [He] = 1.15×10^{16} atoms cm^{-3}, $\bar{v} = 6.5 \times 10^3$ cm s^{-1}, L = 46 cm, and T = 294 K. The solid lines represent a computer fit by the method of least squares.

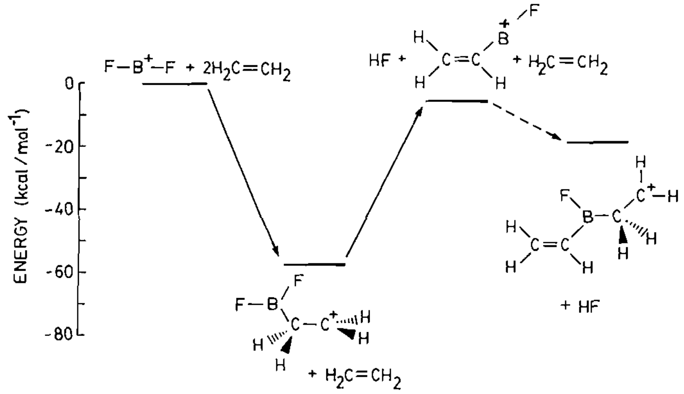


FIG. 4. Relative energies (in kcal mol^{-1}) computed at the 6-31G*//6-31G* level (4 is at the 6-31G*//3-21G level) for combinations of BF_2^+ and two ethylene molecules.

$$[5] \quad C_2H_3BF^+ \xrightarrow{C_2H_4} C_4H_7BF^+ \xrightarrow{C_2H_4} C_6H_{11}BF^+ \xrightarrow{C_2H_4} C_8H_{15}BF^+ \xrightarrow{C_2H_4} C_{10}H_{19}BF^+$$

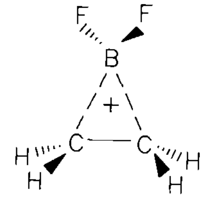
The sequential additions of ethylene proceed with slightly decreasing specific rates. Rate constants were determined with a computer fit to the ion profiles using the method of least squares. One such fit is shown in Fig. 3 and it provides effective bimolecular rate constants for the first three steps in reaction [4] of 1.6, 1.3, and 1.3×10^{-10} cm^{-3} $molecule^{-1}$ s^{-1}. The individual steps are likely to be termolecular with helium acting as the stabilizing third body.

TABLE 2. Total energies (in hartrees) computed for the open and cyclic isomers of the adduct formed from BF_2^+ and ethylene[a]

Structure	3-21G	6-31G*	MP2/6-31G*
Cyclic	−299.78534 (10.6)	−301.43044 (2.4)	−302.08957 (0)
Open	−299.80229 (0)	−301.43424 (0)	−302.07991 (6.1)

[a] Numbers in parentheses indicate relative energies (in kcal mol^{-1}).

The reaction profile for the addition of BF_2^+ to ethylene was examined using molecular orbital theory and is shown schematically in Fig. 4. At the level of theory indicated in Fig. 4 (HF 6-31G*), the most stable form of the intermediate adduct ion $BF_2^+.C_2H_4$ has an open structure, but the cyclic structure is more stable when correlation energy is included. Preliminary calculations at the 3-21G//3-21G level of theory showed the cyclic ion with structure **1** to be 10.6 kcal mol^{-1} higher in energy than the open ion with structure **2**. At the 6-31G* level of theory the energy of the cyclic ion was found to be only 2.4 kcal mol^{-1} higher, but at the MP2/6-31G* level of theory it became lower by 6.1 kcal mol^{-1}. Table 2 summarizes the energies obtained for the cyclic and open $C_2H_4BF_2^+$ isomers at the different levels of theory. Structural parameters for the 6-31G* optimized structures of the cyclic and open ions shown as **1** and **2** are given in Table 3. One structural feature is worthy of note. In **1** the C—B distance of 1.967 Å is extremely long and compares with a formal single-bond distance of 1.533 Å in borirane (20). The 6-31G* calculated charge distribution for **1** has a charge of +0.45 on the BF_2 group and +0.55 on the ethylene fragment. The bonding between ethylene and BF_2^+ then is best described as π donation from $H_2C{=}CH_2$ to the vacant p orbital on BF_2^+ with little or no back-donation from BF_2^+ to the π* orbital on ethylene, i.e., only two electrons are formally involved in the bonding and **1** should be considered to be a π complex and not a three-membered ring.



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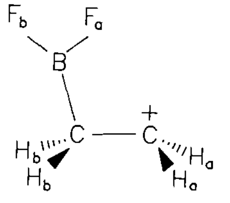


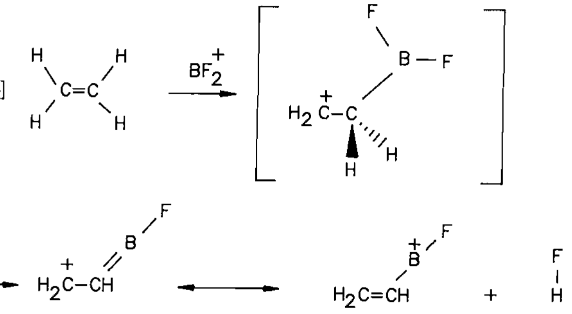
2

The addition of ethylene to BF_2^+, which is shown mechanistically in eq. [6], is computed to be exothermic by 58 kcal mol^{-1} at the 6-31G*//6-31G* level of theory and so provides sufficient energy to eliminate HF, leaving the observed ion $C_2H_3BF^+$, which can be drawn in the two resonance forms 3*a* and 3*b*. A Mulliken population analysis showed the boron atom to carry most of the positive charge. Nucleophilic attack by another ethylene molecule may then occur, in principle, at either the terminal carbon or the boron atom, with the latter being indicated by the charge distribution. Calculations at the STO-3G level (21) showed the product of attack at boron (structure **4**) to be lower in energy (by 38 kcal mol^{-1}) than that formed by attack on carbon (structure **5**). The primary carbenium ions **4** and **5** are both at local minima in C_s symmetry. However, the barrier to rearrangement of primary carbenium ions to secondary ions by 1,2-hydride shifts is, in general, very low and it is likely that these ions will rearrange prior to reacting further with another

TABLE 3. Structural parameters optimized at 6-31G* for the cyclic (I) and open (II) isomers of the adduct formed from BF_2^+ and ethylene. Bond lengths are in angstroms and angles in degrees

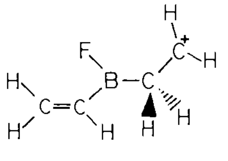
Parameter	I(C_{2v})	II(C_s)
r(CC)	1.356	1.410
r(CH)	1.078	
r(CH$_a$)		1.078
r(CH$_b$)		1.086
r(CB)	1.967	1.667
r(BF)	1.270	
r(BF$_a$)		1.292
r(BF$_b$)		1.279
∠CCH	120.9	
∠CCH$_a$		121.7
∠CCH$_b$		114.5
∠CCB		105.6
∠FBF	129.4	
∠CBF$_a$		120.4
∠CBF$_b$		115.5
∠HCCB	92.8	
∠H$_a$CCB		87.9
∠H$_b$CCB		113.7

[6]



3*a* **3***b*

ethylene molecule. Therefore it is uncertain whether polymerization occurs by repeated ethylene addition at the end of the newly formed primary carbenium ion, or whether ethylene adds at secondary carbenium sites to form polymers with ($CHCH_3$) repeating units.



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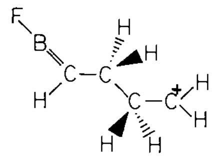

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Propylene

A rapid reaction was observed between BF_2^+ and propylene, $k = (5.0 \pm 1.6) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}. The following primary products were identified:

[7*a*] $BF_2 + C_3H_6 \xrightarrow{0.80} C_3H_5^+ + HBF_2$

[7*b*] $\xrightarrow{0.20} C_2H_2BF_2^+ + CH_4$

The preferred channel [7*a*] corresponds to hydride abstraction, which results in the formation of the $C_3H_5^+$ ion. This latter ion has several possible structures including the allyl, propenyl, and cyclopropyl structures, which decrease in thermodynamic stability in the order presented. The formation of all three isomers is exothermic. Channel [7*b*], which corresponds to the elimination of methane, proceeds in one of every five reactive collisions of BF_2^+ with propylene. The occurrence of a minor (≃5%) channel corresponding to the elimination of HF could not be excluded. The ion $C_3H_5BF^+$ was observed as a product but could not be attributed unambiguously to the reaction of BF_2^+. An alternative or additional source for this ion at the operating conditions of the experiment was the reaction of the impurity ion $FBOH^+$ with propylene.

Secondary and higher-order reactions were also observed. The $C_3H_5^+$ was seen to react rapidly with propylene according to reaction [8] in approximately the following proportions:

[8*a*] $C_3H_5^+ + C_3H_6 \xrightarrow{0.6} C_4H_7^+ + C_2H_4$

[8*b*] $\xrightarrow{0.4} C_6H_{11}^+$

A fit to the rise and decay of the $C_3H_5^+$ signal led to a rate constant of 5.0×10^{-10} cm^3 molecule^{-1} s^{-1} for the overall reaction. Both $C_4H_7^+$ and $C_6H_{11}^+$ were observed to add one molecule of propylene to form the adduct ions $C_7H_{13}^+$ and $C_9H_{17}^+$, respectively, presumably in a termolecular fashion by collisional stabilization. The addition reaction with $C_4H_7^+$ was rapid, $k \geq 10^{-10}$ cm^3 molecule^{-1} s^{-1}, while that with $C_6H_{11}^+$ was much slower, $k \leq 3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The propylene adduct of $C_7H_{13}^+$, $C_{10}H_{19}^+$, was also observed but was formed again in a slow reaction, $k \leq 2 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. In the absence of further work the mechanisms of reactions [8*a*] and [8*b*] are necessarily a matter of conjecture, but it is interesting to note that the $2\pi_s + 2\pi_s$ cycloaddition of allyl cations and alkenes is thermally forbidden by the Woodward–Hoffman orbital symmetry rules, so that the rapid addition of propene to the allyl cation may best be viewed as electrophilic attack by a terminal carbon of the cation on the double bond of propene, forming a secondary cation that may ring-close to the methylcyclopentyl cation. This latter ion can eliminate ethylene to form a methylcyclopropyl cation, which will ring-open without barrier to form the 1-methylallyl cation, $C_4H_7^+$. Alternatively the adduct $C_6H_{11}^+$ may be stabilized by collision. The further reaction of the methylcyclopentyl cation, $C_6H_{11}^+$, with propene is likely to be slower than the further reaction of the 1-methylallyl cation, $C_4H_7^+$, with propene as the latter can be expected to proceed with a similar mechanism and probably similar rate as the initial allyl cation.

The secondary reaction of $C_2H_2BF_2^+$ with propylene was seen to be fast, $k = 8.0 \times 10^{-11}$ cm^3 molecule^{-1} s^{-1}. While the propylene adduct ion was observed in small amounts, the main product appeared to be $C_5H_7^+$:

[9] $C_2H_2BF_2^+ + C_3H_6 \longrightarrow C_5H_7^+ + HBF_2$

The $C_5H_7^+$ did not react further, $k \leq 3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}.

Isomeric butenes

The reaction of BF_2^+ with the isomeric butenes, *cis*-2-butene and isobutene, proved to be more complex than the others. Both reactions were equally rapid, $k = (7.8 \pm 2.4) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, and led to product ions with identical m/z as indicated by reaction [10].

[10*a*] $BF_2^+ + C_4H_8 \longrightarrow C_4H_7^+ + HBF_2$

[10*b*] $\longrightarrow C_2H_4BF_2^+ + C_2H_4$

[10*c*] $\longrightarrow C_2H_5^+ + C_2H_3BF_2$

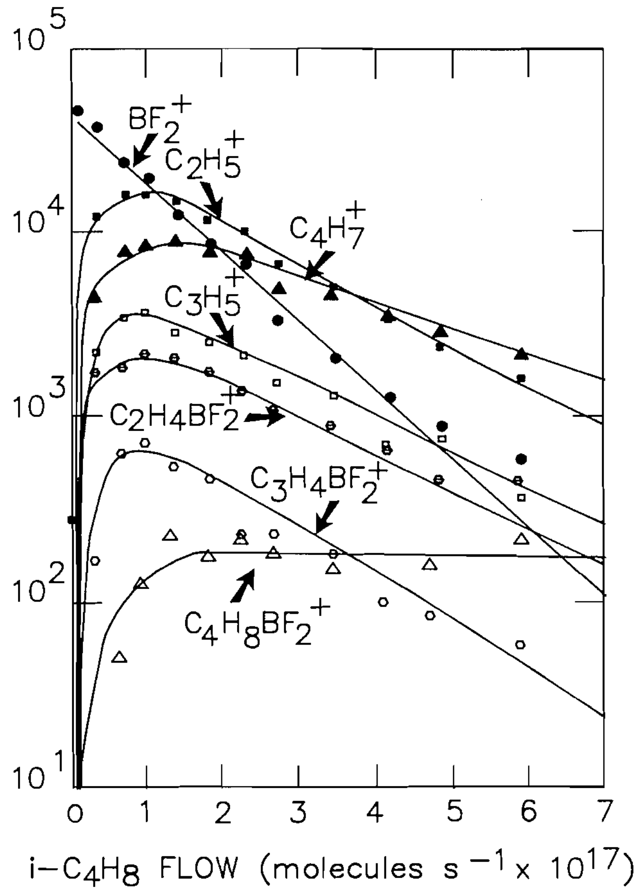


FIG. 5. The variation in ion signals observed for the addition of isobutene into the reaction region of the SIFT apparatus in which BF_2^+ is initially established in helium buffer gas. $P = 0.35$ Torr, [He] $= 1.1 \times 10^{16}$ atoms cm^{-3}, $\bar{v} = 6.9 \times 10^3$ cm s^{-1}, $L = 46$ cm, and $T = 294$ K. Only primary products are indicated.

[10*d*] $\longrightarrow C_3H_5^+ + CH_3BF_2$

[10*e*] $\longrightarrow C_3H_4BF_2^+ + CH_4$

[10*f*] $\longrightarrow C_4H_8BF_2^+$

Channel [10*a*] corresponds to H^- abstraction. Channel [10*b*] leads to elimination of C_2H_4 and will be preempted by channel [10*c*] if a proton is transferred before the products separate. Channel [10*d*] corresponds to CH_3^- abstraction, which may leave the allyl cation $C_3H_5^+$. Channel [10*e*] leads to elimination of methane while [10*f*] corresponds to adduct formation.

Figure 5 shows the semilogarithmic decay of BF_2^+ upon addition of isobutene, and the appearance of the product ions indicated in reaction [10]. All of the primary product ions in reaction [10], with the exception of the adduct, were observed to react further with isobutene. Several of the primary product ions were active in propagating additions of isobutene molecules, which presumably occur in a termolecular fashion. For example, the $C_4H_7^+$ cation formed primarily by H-abstraction from the isobutene, and, to some extent, by secondary reactions of $C_2H_5^+$ and $C_3H_5^+$ with isobutene, was observed to add two molecules of isobutene in sequential reactions. Other isobutene adducts observed were those of $C_3H_4BF_2^+$, $C_4H_9^+$, which is a derivative of the chemistry initiated by $C_2H_5^+$, and $C_5H_{11}^+$, which is a derivative of $C_4H_9^+$ (22). $C_4H_9^+$ is also produced by proton transfer from the impurity $FBOH^+$ to the isobutene.

Slightly different product distributions were observed for the two butene isomers. Channels [10*a*]–[10*c*] account for about 85% of the total reaction in both cases. Formation of $C_4H_7^+$ by hydride abstraction constitutes a larger channel than does formation of $C_2H_5^+$ in the case of *cis*-2-butene. The reverse is true in the case of isobutene. This may reflect differences in stabilities of the two isomeric $C_4H_7^+$ ions. Hydride abstraction from *cis*-2-butene forms the 1-methylallyl cation, whereas abstraction from isobutene yields the 2-methylallyl cation. Allyl cations are stabilized by π-electron-donating substituents on a terminal carbon, but substitution at the central carbon has little effect. The methyl group is a weak π donor and *ab initio* molecular orbitals at the HF 6-31G*//3-21G level indicate the 1-methylallyl cation to be 11.3 kcal mol^{-1} lower in energy than the 2-methylallyl cation (23). Thus when the 1-methylallyl cation is the product, hydride abstraction competes more effectively with other channels.

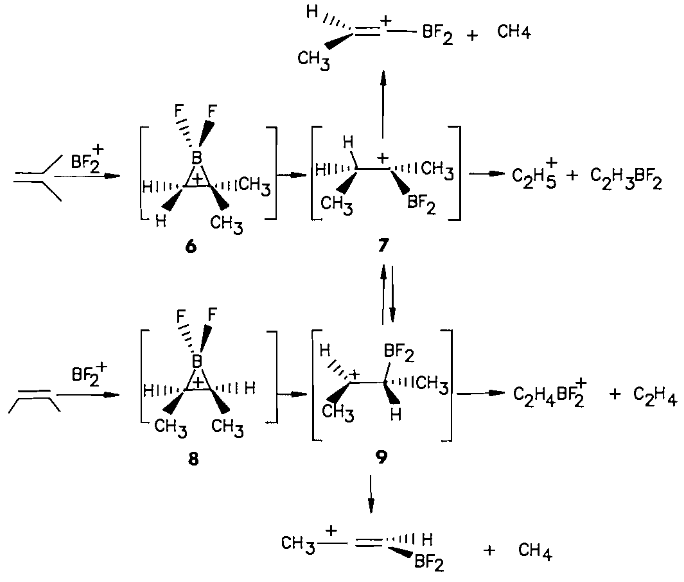
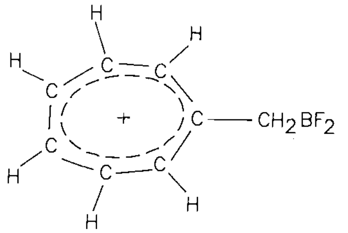


FIG. 6. Possible mechanism for the formation of the primary product ions $C_2H_5^+$, $C_2H_4BF_2^+$, and $C_3H_4BF_2^+$ from the reaction of BF_2^+ with *cis*-2-butene and isobutene.

A mechanism for the formation of the primary products $C_2H_5^+$, $C_2H_4BF_2^+$, and $C_3H_4BF_2^+$ is proposed in Fig. 6. The reactions of the two isomeric butenes are likely to involve similar intermediates since their observed products are the same and the product distributions are not radically different. BF_2^+ and isobutene are likely to form the cyclic π complex indicated by structure **6**. Rearrangements of the type shown in Fig. 6 may then lead to structure **9**. These rearrangements involve the migration of the BF_2 group with a concomitant transfer of CH_3^- to leave structure **7**, which may undergo a 1,2 hydride transfer to leave structure **9**. Addition of BF_2^+ to *cis*-2-butene should give the cyclic π complex indicated by structure **8**, which can open to yield structure **9**. Structures **7** and **9** may decompose by 1,2 CH_4 elimination to form the vinyl cations shown in Fig. 6 or by C—C bond scission as indicated.

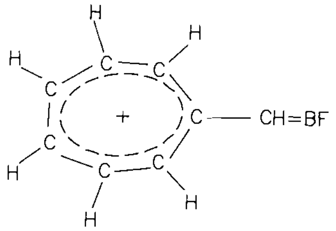
Styrene

The major primary product ion observed in the reaction of BF_2^+ with styrene was the adduct ion, possibly a termolecular product at our operating pressure. The observed effective bimolecular rate constant is quite large so that chemical bonding in the adduct ion is indicated. One could assume the structure of the adduct to be benzylic ($C_6H_5C^+HCH_2BF_2$) in which the positive charge is delocalized onto the phenyl group. However, other experimental evidence indicates that benzylic-type ions can rearrange to form tropylium-type ions (24, 25). It is therefore possible that the structure of the adduct ion observed in this case is that of the tropylium-like ion shown in **10**. The other



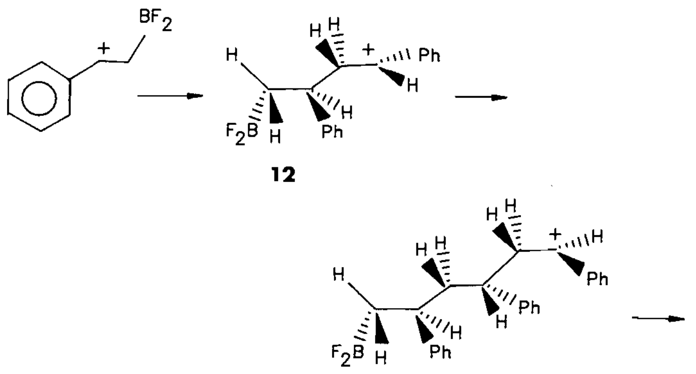
10

minor primary product ions that were observed may arise from the elimination of HF or C_2HBF_2 from the intermediate adduct ion, which is likely to leave an ion with structure **11** or protonated benzene, respectively. The identification of the source for the $C_8H_7BF^+$ ion observed at *m*/*e* 133 as the reaction of BF_2^+ with styrene and the elimination of HF was not unequivocal. Another possible source for this ion was the reaction of $FBOH^+$ with styrene and the elimination of H_2O.



11

One other styrene molecule was observed to add to the primary adduct ion. The specific rate for this addition was one half that for the primary addition, having an effective bimolecular value of 4.7 × 10^{-10} cm^3 molecule^{-1} s^{-1} at our operating conditions. Further additions could not be observed due to the low vapour pressure of styrene that permitted the introduction of only a limited flow of styrene molecules into the reaction region. The high specific rate of addition of the second styrene molecule is suggestive of further chemical bonding. Such bonding seems more probable if the primary adduct ion has a benzylic rather than tropylium-like structure. In the former case the second addition of styrene could occur on the benzylic carbon to yield the structure indicated in reaction [11] as **12**. Reaction [11] shows how polymerization would then be achieved by repeated styrene addition to the cationic carbon of the benzyl cations.



12

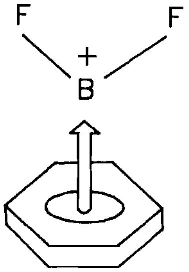
Benzene

For the reaction of BF_2^+ with styrene the question arose as to whether BF_2^+ could be adding to the benzene ring of styrene. Thus we decided to carry out the reaction of BF_2^+ with benzene. It was found to be rapid, $k = (7.4 \pm 2.2) \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, and to produce two primary species according to reaction [12].

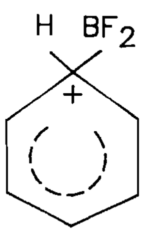
$$[12] \quad BF_2^+ + C_6H_6 \xrightarrow{0.80} BF_2^+.C_6H_6$$

$$\xrightarrow{0.20} C_6H_5BF^+ + HF$$

Adduct formation was the major channel observed. The high efficiency of this channel is again suggestive of chemical bonding. Several structures can be envisaged for a chemically bonded adduct, including a complex in which BF_2 sits on top of the benzene π cloud (structure **13***a*) as well as the σ complex **13***b*.



13*a*



13*b*

Conclusions

The results of the experiments reported in this study characterize the intrinsic chemistry that the BF_2^+ ion initiates by reacting with the olefinic monomers of ethylene, propylene, isobutene, *cis*-2-butene, and styrene, and with benzene and H_2O. They provide values for the specific rates and product distributions of the initiation steps and the early propagating steps that lead to the build-up or polymerization of the ions.

All of the initiation reactions of BF_2^+ are rapid, $k \geq 5.0 \times 10^{-10}$ cm^3 molecule^{-1} s^{-1}, and efficient, and they show an interesting range in the nature of their reaction products. The major reaction pathways for the monomers selected for study are elimination of HF, CH_4, C_2H_4, or $C_2H_3BF_2$, hydride transfer, and adduct formation. HF elimination is unique to the reaction with ethylene. It is not observed with the butenes and constitutes only a very small channel with styrene and possibly propylene. Hydride transfer is an important channel in the reactions with monomers containing an allylic hydrogen. For instance, hydride transfer was observed to compete effectively with other channels in the reactions of BF_2^+ with propylene and the butenes from which stable allylic cations can be formed. Styrene and ethylene do not contain an allylic hydrogen and were not observed to react with BF_2^+ by hydride transfer. The implication of these results is that other monomers having an allylic hydrogen such as, for example, α-methylstyrene and cyclopentadiene, can also be expected to react with BF_2^+ by hydride transfer to form allylic cations that may propagate polymerization.

The results indicate that ethylene, styrene, *cis*-2-butene, and isobutene can all be polymerized in the gas phase by propagating species formed in reactions with BF_2^+. The BF or BF_2 group may or may not be retained in the propagating ion. The former (e.g., $C_2H_3BF^+$, $C_8H_8BF_2^+$) appear more reactive in propagating monomer additions and are predominant in the polymerization observed with ethylene and styrene. Carbocations are the main propagating ions produced in the initiation reactions of BF_2^+ with the two butenes.

Propylene appears to be an exception in that propagation is terminated early in the reaction sequence. A possible explanation is illustrated in Fig. 7. If an allylic structure is assumed for $C_3H_5^+$, addition of propylene should lead to the 1-methylallyl

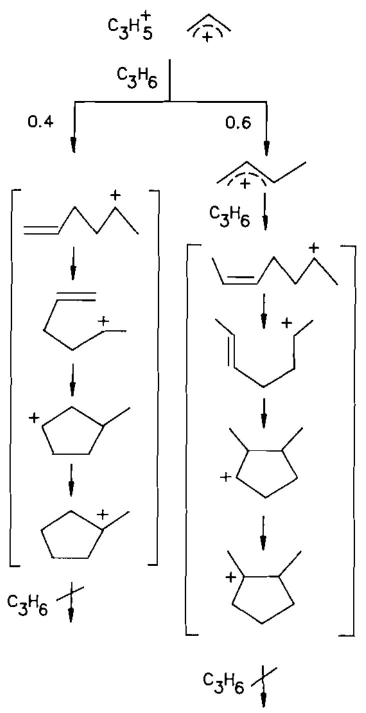


FIG. 7. Possible mechanism for the termination of the polymerization of propylene initiated by allylic $C_3H_5{}^+$ in the gas phase.

cation and a secondary methylcyclopentyl cation, which might undergo a 1,3 hydride shift to form the thermodynamically more stable tertiary methylcyclopentyl cation. If the further reaction of the 1-methylallyl cation with propene proceeds with a mechanism and rate similar to the initial allyl cation, we can expect the intramolecular cyclization to produce the tertiary 1,2-methylcyclooentyl cation shown in Fig. 7. Both of the methyl-substituted tertiary cyclopentyl cations should be less reactive because the attack by another propylene molecule is hindered. This is consistent with our experimental observations, which indicate further propylene additions to the tertiary cyclic cations, which proceed with rate constants that are much smaller, $k \leq 3 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}, than those for the addition of propylene to the acyclic precursor cations, $k \geq 10^{-10}$ cm^3 molecule^{-1} s^{-1}. The polymerization of propylene therefore appears to be impeded in the gas phase by intramolecular cyclization. In contrast, if solvent molecules act to hinder the cyclization, we can expect the analogous polymerization to be allowed in solution.

It is interesting to compare the cocatalytic role of water in the gas phase and solution. Water is known to act as a coinitiator in many polymerization systems in solution, including BF_3/isobutene (26), BCl_3/isobutene (27), and $TiCl_4$/diphenylethylene (28). Our gas-phase measurements indicate that water vapour acts in a cocatalytic fashion by leading to the protonated monomers $C_2H_4{}^+$, $C_3H_7{}^+$, $C_4H_9{}^+$, and $C_8H_9{}^+$ via the $FBOH^+$ ion formed by reaction of $BF_2{}^+$ with water vapour. $FBOH^+$ was observed to transfer a proton to all of the monomers investigated and also to water vapour. The latter implies that H_3O^+ may be an intermediate when $FBOH^+$ is formed in solution in the presence of water.

The interaction between other Lewis acid cations and olefinic monomers remains to be examined in the gas phase. Of special interest is the reaction of olefinic monomers with $AlCl_2{}^+$ derived from $AlCl_3$, perhaps the best known and most popular initiator. Gas-phase measurements of the reaction of $AlCl_2{}^+$ with isobutene may allow some insight into one of the oldest and most studied cationic polymerizations.

Acknowledgment

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