

EXPERIMENTAL AND THEORETICAL STUDIES OF THE PROTON AFFINITY OF FLUOROBOROXINE*

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ABSTRACT

The proton affinity of fluoroboroxine, FBO, is explored both experimentally and theoretically. Results of selected-ion flow tube measurements are reported for proton transfer reactions which place the proton affinity (PA) of FBO between those of ethylene and acetylene, $PA(C_2H_4) > PA(FBO) > PA(C_2H_2)$, with $PA(FBO)$ equal to $158 \pm 6 \text{ kcal mol}^{-1}$. $FBOH^+$ is produced from the reaction of BF_2^+ with H_2O and is observed to rapidly transfer a proton to H_2O , ethylene, propylene, benzene, *cis*-2-butene, iso-butene and styrene but only to add to acetylene to form $FBOH^+ \cdot C_2H_2$ at $296 \pm 2 \text{ K}$. The results of ab initio molecular orbital calculations on FBO and on isomers of $FBOH^+$ are reported for the Hartree–Fock and the full second-order Moeller–Plesset levels of theory with the 6-31G** basis set. Structure optimizations were performed at both levels of theory using gradient techniques in the GAUSSIAN 82 program. The proton affinity, corrected for zero-point and thermal energies, and including correlation energy, is computed to be $163.8 \text{ kcal mol}^{-1}$.

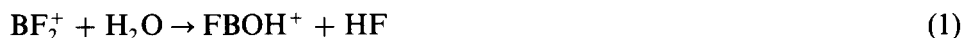
INTRODUCTION

Recent studies of the gas phase kinetics of BF_2^+ -induced polymerization of olefinic monomers [1,2] have indicated a co-catalytic role for water vapour with protonated FBO as an ionic co-initiator. The reaction of BF_2^+ with water vapour efficiently produces $FBOH^+$ which in turn efficiently protonates water, and together with H_3O^+ , olefinic monomers. Neutral fluoroboroxine, FBO, is a known molecule in the gas phase. It has been identified in transpiration and mass spectrometric studies of reactions between BF_3 , or MgF_2 , and B_2O_3 at elevated temperatures [3,4]. Matrix isolation experiments have provided its infrared spectrum [5]. However, nothing is known about the proton

* Dedicated to Dr Fred P. Lossing on the occasion of his 75th birthday and in honour of his outstanding achievements in mass spectrometry and ion processes. The authors especially wish to recognize his important and guiding contributions to the early blossoming of this field in Canada.

affinity of FBO. The proton affinity determines the ability of FBOH^+ to protonate water vapour and olefinic monomers in the gas phase and so to initiate gas-phase polymerization. Here we present results of an experimental and theoretical investigation directed at establishing this affinity.

Selected-ion flow tube (SIFT) experiments performed in our laboratory have shown that FBOH^+ is produced from BF_2^+ according to



with a rate constant of $(1.5 \pm 0.5) \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and an efficiency of 0.75 ± 0.23 [2]. The secondary reaction of FBOH^+ with water vapour proceeds with a rate constant of $(1.3 \pm 0.4) \times 10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and produces two products according to



in the proportions indicated. Mechanistic considerations suggest that the FBOH^+ produced in reaction (1) is $\text{FB}=\text{O}$ protonated at the oxygen, $\text{F}-\text{B}=\text{O}^+\text{H}$, which may be formed directly by electrophilic attack of the oxygen atom of H_2O with elimination of HF [2]. The isomers $\text{F}-\text{B}(\text{H})-\text{O}^+$ and $\text{HF}^+-\text{B}=\text{O}$ would require more bond redistribution for their formation.

In this study we present SIFT measurements of proton-transfer reactions directed to the experimental bracketing of the proton affinity of FBO with molecules spanning a range of proton affinities from 144 to 202 kcal mol^{-1} . All three atoms in FBO were considered as possible sites for protonation in the theoretical study. Ab initio molecular orbital calculations were performed on FBO and on isomers of FBOH^+ at two levels of theory, the Hartree-Fock level with the 6-31G** basis set [6] (denoted HF/6-31G**) and the full second-order Moeller-Plesset level [7,8], again with the 6-31G** basis set (denoted MP2/6-31G**), to ascertain the proton affinity of FBO and to obtain structural information on the isomers of FBOH^+ .

EXPERIMENTAL

The measurements 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 [9,10]. The reactions of FBOH^+ were investigated concomitantly with a study of the chemistry of BF_2^+ . FBOH^+ was invariably present in the SIFT spectrum of BF_2^+ because of the reaction of this ion with water vapour impurities in the helium buffer gas [2].

Acetylene, ethylene, propylene, isobutenc (all Matheson, C.P. grade), and

TABLE 1

Summary of rate constants (in units of $10^{-9} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and products obtained for reactions of FBOH^+ with molecules, M, at $296 \pm 2 \text{ K}$

M	PA ^a	Products ^b	$k_{\text{exp}}^{\text{c}}$	k_{c}^{d}
C_8H_8 (styrene)	202.0	$\text{C}_8\text{H}_9^+ + \text{FBO}$ ($\text{C}_8\text{H}_7\text{BF}^+ + \text{H}_2\text{O}$)	> 0.82	1.9
iso- C_4H_8	195.9	$\text{C}_4\text{H}_9^+ + \text{FBO}$	> 0.81	1.5
cis-2- C_4H_8	179.4	$\text{C}_4\text{H}_9^+ + \text{FBO}$	> 0.78	1.4
C_6H_6	181.3	$\text{C}_6\text{H}_7^+ + \text{FBO}$	> 0.74	1.4
C_3H_6	179.5	$\text{C}_3\text{H}_7^+ + \text{FBO}$ ($\text{C}_3\text{H}_5\text{BF}^+ + \text{H}_2\text{O}$)	> 0.50	1.3
H_2O	166.5	$\text{H}_3\text{O}^+ + \text{FBO}$ $\text{BO}_2\text{H}_2^+ + \text{HF}$	1.3	2.4
C_2H_4	162.6	$\text{C}_2\text{H}_5^+ + \text{FBO}$	> 0.74	1.1
C_2H_2	153.3	$(\text{C}_2\text{H}_2\text{FBOH})^+$	0.19	1.0

^a Proton affinity in kcal mol^{-1} taken from ref. 15. Uncertainties in the absolute value are less than 2 kcal mol^{-1} for proton affinities equal to or greater than that of H_2O and less than 1 kcal mol^{-1} for C_2H_2 and C_2H_4 .

^b When proton transfer is observed, it predominates. With water, proton transfer is favoured by 3:1.

^c Rate constants are lower limits because the disappearance of FBOH^+ is rate-limited by the disappearance of the precursor ion BF_2^+ .

^d Collision rate constant determined with the combined variational transition-state theory—calculated trajectory approach of T. Su and W.J. Chesnavich, *J. Chem. Phys.*, 76 (1982) 183.

cis-2-butene (Phillips, research grade) were used as reagent gases while benzene and styrene (both Aldrich) were used as vapours diluted with helium as 10 and 5 mol% mixtures, respectively.

All measurements were made at a room temperature of $296 \pm 2 \text{ K}$ and a total pressure of 0.34 Torr. Helium (Matheson, 99.995% purity) was used as the carrier gas.

Rapid reactions in which proton transfer was the dominant reaction channel were observed with all of the reactants except acetylene. With styrene and propylene a minor channel (< 10%) leading to elimination of H_2O could not be excluded but the source of the corresponding product ions could not be unequivocally associated with FBOH^+ . The experimental results are summarized in Table 1. The rate constants are reported as lower limits because of an unknown contribution to the observed decay by depletion of the precursor ion BF_2^+ in the reaction region. The reaction with H_2O leads to both proton transfer and the elimination of HF, and in this case an absolute value of the rate constant could be derived from a two-exponential computer fit to the observed FBOH^+ profile.

Acetylene was observed not to react by proton transfer but instead simply

TABLE 2

Parameters obtained from optimization of structures with the 6-31G** basis set

Parameter ^a	FBO		FBOH ⁺ ^a		HFBO ⁺ ^b
	HF	MP2	HF	MP2	HF
Bond length (Å)					
B-F	1.273	1.296	1.229	1.250	1.397
B-O	1.190	1.221	1.226	1.245	1.164
O-H			0.953	0.970	
F-H					0.950
Bond angle (°)					
< FBO	180.0	180.0	176.4	174.7	177.9
< BOH			147.0	143.3	
< HFB					126.5

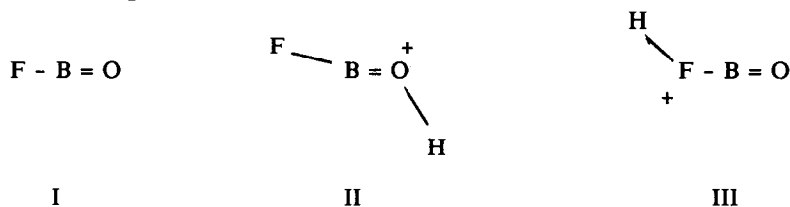
^a *trans* bent.^b *cis* bent.

to add to FBOH⁺ with an effective bimolecular rate constant of $1.9 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ at 0.346 Torr and a helium density of $1.13 \times 10^{16} \text{ atoms cm}^{-3}$.

THEORY

In a previous *ab initio* molecular orbital study at the HF/STO-4G level, FBO (linear) was found to be 148 kcal mol⁻¹ lower in energy than the bent isomer BOF [11]. Our preliminary calculations at the HF/6-31G* level confirmed that linear FBO is the global minimum with BOF 184 kcal mol⁻¹ higher in energy. Consequently we did not consider isomer BOF at higher levels of theory.

Structure optimization for FBO, FBOH⁺ and HFBO⁺, at the HF/6-31G** level of theory and for the first two at the MP2/6-31G** level, were carried out using gradient techniques in the GAUSSIAN 82 program [12]. Parameters obtained from optimization calculations of structures I, II and III



are summarized in Table 2. Previously it has been noted that structures optimized at the MP2 level have slightly longer bond lengths than those from Hartree-Fock level calculations [13] and the same trend is found here for

TABLE 3

Total energies (hartree)

	HF/6-31G** ^a	HF/6-31G*** ^b	MP2/6-31G*** ^b	ZPE ^c
F-B=O	-199.07650	-199.07651	-199.51135	5.7
B-O-F	-198.78274			
FBOH ⁺	-199.34962	-199.35734	-199.77968	11.1
HFBO ⁺	-199.20671	-199.21591		10.8

^a Calculations with the Monstergauss program.^b Calculations with the GAUSSIAN 82 program.^c Zero-point energies calculated with theoretical frequencies scaled by 0.89 [14,15].

structures I and II (see Table 2). At both levels of theory FBO is calculated to be linear. At the MP2 level the B-F distance (1.296 Å) is slightly shorter than the experimental single bond in BF₃ (1.307 Å) [13] and the B-O distance (1.221 Å) is much shorter than the experimental single bond in F₂BOH (1.344 Å) [13], but slightly longer than the experimental double bond in BO (1.205 Å) [13]. Clearly then, FBO is best represented by the valence bond structure I.

All three atoms in FBO were considered as possible sites for protonation, but attempts to attach the proton to the boron atom resulted in migration to the oxygen atom (structure II). The fluorine-protonated isomer, III, is at a high minimum (88.7 kcal mol⁻¹ above II at the HF/6-31G** level) and was not considered further. Structural optimization at the MP2/6-31G** level showed the oxygen-protonated isomer II to be planar and slightly bent at boron (\angle FBO = 174.7°). The preferred conformation has the proton *trans* to fluorine with \angle BOH = 143.3°. Protonation of FBO at oxygen then results in a slight lengthening of the B-O distance (by 0.024 Å) and a shortening of the B-F distance (by 0.046 Å).

Proton affinities corrected for zero-point energy contributions (calculated at the HF/6-31G** level and scaled by a factor of 0.89 [14,15]) and for thermal energies [16] are 171.6 kcal mol⁻¹ at the HF/6-31G** level and 163.8 kcal mol⁻¹ at the MP2/6-31G** level. Inclusion of correlation energy then results in a decrease of 7.8 kcal mol⁻¹ in the calculated proton affinity. Total energies from all our calculations are given in Table 3.

DISCUSSION

The combined approach of experiment and theory has provided previously unavailable information on the proton affinity of fluoroboroxine, its site of protonation and the structure of the protonated molecule. Theory predicts that protonation results in a slight bending of the FBO molecule and that it occurs preferentially at the oxygen site. The best value for the proton affinity

of FBO predicted by theory, $163.8 \text{ kcal mol}^{-1}$, is confirmed, within experimental error, by experiment.

The proton-transfer bracketing measurements summarized in Table 1 place PA(FBO) between PA(C₂H₂) and PA(C₂H₄), assuming that the FBOH⁺ ions are thermalized and that the failure to observe proton transfer is an indication of endothermicity. Previously established values for PA(C₂H₂) of $153.3 \pm 1 \text{ kcal mol}^{-1}$ and PA(C₂H₄) of $162.6 \pm 1 \text{ kcal mol}^{-1}$ [17] then provide an experimental value for PA(FBO) of $158 \pm 6 \text{ kcal mol}^{-1}$. The proton transfer reactions with C₂H₄ and with H₂O, propylene, benzene, *cis*-2-butene, iso-butene and styrene, molecules with proton affinities greater than C₂H₄, are all rapid, ($k > 5.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$), and efficient. The collision rate constants provided in Table 1 indicate efficiencies, k_{exp}/k_c , > 0.4 .

The experimental proton affinity together with established values for the enthalpies of formation of FBO, $143 \pm 3 \text{ kcal mol}^{-1}$ [3], and H⁺, $365.7 \text{ kcal mol}^{-1}$ [18], provide a value for the enthalpy of formation for FBOH⁺ of $65 \pm 9 \text{ kcal mol}^{-1}$. This means that reaction of BF₂⁺ with H₂O, which is the source of FBOH⁺, will dispose $19 \pm 9 \text{ kcal mol}^{-1}$ between FBOH⁺ and HF. At the helium densities used in our experiments any internal energy which may appear in FBOH⁺ is expected to be dissipated to the helium buffer gas by collisional deactivation so that the FBOH⁺ ions should be thermalized at $296 \pm 2 \text{ K}$ prior to reaction.

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