from primary  $-CH_3$  groups is slow compared to abstraction from secondary  $-CH_2$ - groups, the rate constant data for the *n*-alkanes and cyclohexane allow a group rate constant of  $(9 \pm 2) \times 10^{-18}$ cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> to be derived for the reaction of NO<sub>3</sub> radicals with  $-CH_2$ - groups. The present data base is not sufficiently precise to allow any further differentiation into  $-CH_2$ - groups bonded to  $-CH_2$ - or  $-CH_3$  groups, as carried out recently by Atkinson et al.<sup>23</sup> for the reactions of OH radicals with a series of alkanes.

The rate constants for isobutane and 2,3-dimethylbutane allow >CH- group rate constants of  $k[CH(CH_3)_3] = 2.9 \times 10^{-17} \text{ cm}^3$ molecule<sup>-1</sup> s<sup>-1</sup> and  $k[CH(CH)(CH_3)_2] = 6.0 \times 10^{-17} \text{ cm}^3$  molecule<sup>-1</sup> s<sup>-1</sup> to be derived at room temperature (where  $k[CH(CH_3)_3]$ and  $k[CH(CH)(CH_3)_2]$  refer to the rate constants for NO<sub>3</sub> radicals reacting with a >CH- group bonded to three -CH<sub>3</sub> groups and one >CH- and two -CH<sub>3</sub> groups, respectively). That these >CH- group rate constants are higher than those for -CH<sub>2</sub>groups is expected by analogy with OH radical reactions<sup>23</sup> and with the fact that H atom abstraction from a >CH- group is 2.5 kcal mol<sup>-1</sup> more exothermic than is H atom abstraction from a -CH<sub>2</sub>- group.<sup>24</sup>

The rate constants obtained in this work show that for nighttime NO<sub>3</sub> radical concentrations of  $\sim 2 \times 10^9$  molecules cm<sup>-3</sup> (i.e.,  $\sim 100$  ppt, a value we have observed in urban and desert areas of California<sup>5,9,10</sup>) these nighttime reactions are an order of magnitude or more less effective as total loss processes for the alkanes compared to daytime reaction with the OH radical (assuming an average daytime OH radical concentration of  $\sim 1 \times 10^6$  molecules cm<sup>-3</sup>). However, these nighttime reactions of alkanes with NO<sub>3</sub> do lead directly to loss of NO<sub>x</sub> and concurrent formation of nitric acid, a key species involved in acid deposition.

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Thus, for example, in polluted urban atmospheres nighttime NO<sub>3</sub> radical and NO<sub>2</sub> concentrations are  $\sim 2 \times 10^9$  and (5-7)  $\times 10^{10}$  molecules cm<sup>-3</sup> (~100 ppt and 2-3 ppb) respectively,<sup>5</sup> leading<sup>17</sup> to an N<sub>2</sub>O<sub>5</sub> concentration of  $\sim 2 \times 10^9$  molecules cm<sup>-3</sup> (~80 ppt). For an alkane concentration of  $\sim 100$  ppb, this then results in a HNO<sub>3</sub> formation rate of  $\sim 0.04$  ppb h<sup>-1</sup> from the reaction of NO<sub>3</sub> radicals with *n*-alkanes. This rate can be compared to a HNO<sub>3</sub> formation rate of  $\sim 0.3$  ppb h<sup>-1</sup> from the hydrolysis of N<sub>2</sub>O<sub>5</sub> with H<sub>2</sub>O at  $\sim 50\%$  relative humidity by using the upper limit value for the homogeneous gas-phase rate constant of the reaction of N<sub>2</sub>O<sub>5</sub> with water vapor recently determined in these laboratories.<sup>18</sup>

For air masses typical of semiarid and desert areas,<sup>9,10</sup> NO<sub>3</sub> radical and NO<sub>2</sub> concentrations are  $\gtrsim 2 \times 10^8$  and  $\sim 2 \times 10^{10}$  molecules cm<sup>-3</sup>, respectively. For this situation, if one assumes an alkane concentration of  $\sim 50$  ppb, the HNO<sub>3</sub> formation rates from the reaction of NO<sub>3</sub> radicals with alkanes and from the N<sub>2</sub>O<sub>5</sub> hydrolysis reaction are both lower by a factor of  $\sim 20-30$  than those for the polluted atmosphere scenerio described above.

Thus, for both polluted and relatively unpolluted atmospheres the rate of formation of  $HNO_3$  from the reaction of  $NO_3$  radicals with alkanes can be a significant fraction of the total nighttime  $HNO_3$  formation rate. Clearly, the reactions of  $NO_3$  radicals with alkanes should be included in chemical models of regional air pollution for the assessment of the impacts of acid deposition.

Acknowledgment. We gratefully acknowledge the financial support of the U.S. Environmental Protection Agency Grant No. R807739-02 and wish to thank Sara M. Aschmann for carrying out the gas chromatographic analyses and W. D. Long for assistance in conducting the chamber experiments. Although the research described in this article has been funded by the Environmental Protection Agency, it has not been subjected to Agency review and therefore does not necessarily reflect the views of the Agency, and no official endorsement should be inferred.

## A Photoelectron Spectroscopic Study of the Ground States of $CH_2F^+$ and $CD_2F^+$

## Lester Andrews,\* John M. Dyke, Neville Jonathan, Noureddine Keddar, Alan Morris, and Abed Ridha

Department of Chemistry, The University, Southampton, S09 5NH, U.K. (Received: July 14, 1983)

The fluorine atom/methyl fluoride reaction has been studied by photoelectron spectroscopy. A new product band with vibrational components at  $9.04 \pm 0.01$  eV adiabatic and  $9.22 \pm 0.01$  eV vertical ionization energies is assigned to the CH<sub>2</sub>F free radical. The v' = 0-1 vibronic separation measured as  $1450 \pm 30$  cm<sup>-1</sup> is due to the C-F stretching fundamental of the ground state of CH<sub>2</sub>F<sup>+</sup>; this vibronic interval was  $1530 \pm 30$  cm<sup>-1</sup> for CD<sub>2</sub>F<sup>+</sup>. The positive deuterium shift for CH<sub>2</sub>F<sup>+</sup> is due to interaction with the H-C-H bending mode, which shifts below the C-F stretching mode on deuteration. The substantial increase in the C-F stretching modes for CH<sub>2</sub>F<sup>+</sup> and CD<sub>2</sub>F<sup>+</sup>, as compared to 1163- and 1193-cm<sup>-1</sup> values for the CH<sub>2</sub>F and CD<sub>2</sub>F free radicals in solid argon, respectively, is due to increased net C-F bonding in the cations.

### Introduction

The application of photoelectron spectroscopy to the study of transient species has increased in recent years as methods for producing free radicals, high-temperature molecules, and hydrogen-bonded complexes have been developed.<sup>1-5</sup> Recently, the unstable diatomic fluorides BF, CF, NF, and OF have been prepared for photoelectron spectroscopic studies of the ground-state cations using evaporative methods and fluorine atom reactions.<sup>6-9</sup> The larger fluoromethyl cations have been studied to date only by mass spectroscopic and infrared absorption matrix methods.<sup>10-12</sup> In particular, the most intense infrared absorptions of CF<sub>3</sub><sup>+</sup>,

 $CF_2Cl^+$ , and  $CHFCl^+$  have been recorded in solid argon matrices.<sup>13-15</sup> These cations exhibited unusually high C-F stretching

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<sup>\*</sup>To whom correspondence should be addressed at the Chemistry Department, University of Virginia, Charlottesville, VA 22901.

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Figure 1. He I photoelectron spectrum in the 9.0-10.0-eV ionization energy region of the products of the  $F + CH_3F$  reaction at short (0.2 cm) mixing distance with use of relatively low F atom and relatively high CH<sub>3</sub>F partial pressures. The inset dashed spectrum of the CF radical (ref 7) is included for comparison.

fundamentals, and this effect was ascribed to increased  $(C_{2p}-F_{2p})$  $\pi$  bonding in the cation as compared to that in the free-radical species.

The present paper describes a photoelectron spectroscopic study of the F + CH<sub>3</sub>F reaction, which produced HF and the CH<sub>2</sub>F free radical. Although this reaction has been studied extensively, earlier work monitored the reaction in competition with other reactions<sup>16</sup> or used HF chemiluminescence<sup>17</sup> and HF laser emission to investigate the energetics and dynamics of the fluorine atom abstraction process.<sup>18,19</sup> More recent investigations have employed this reaction to focus on the CH<sub>2</sub>F radical product; laser magnetic resonance, microwave, and diode laser spectra of CH<sub>2</sub>F have been recorded in the gas phase,<sup>20-22</sup> and the infrared spectrum of CH<sub>2</sub>F has been observed in solid argon.<sup>23</sup> The CH<sub>2</sub>F radical was first identified from ESR spectra recorded for the radical trapped in solid argon; the observed hyperfine coupling constants were interpreted to indicate a nearly planar radical.<sup>24</sup> Subsequent infrared work recorded the C-F stretching mode at 1163 cm<sup>-1</sup> in solid argon.<sup>23,25-27</sup> However, no out-of-plane bending mode was observed for CH<sub>2</sub>F as seen for the planar CH<sub>2</sub>Cl radical;<sup>28</sup> this comparison supported a nearly planar equilibrium structure for  $CH_2F^{26}$  The microwave spectrum also suggests that  $CH_2F$  is essentially planar.<sup>21</sup>

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Figure 2. He I photoelectron spectrum in the 9-12-eV ionization energy region of the products of the  $F + CH_3F$  reaction at long (5 cm) mixing distance with use of relatively high F atom and relatively low CH<sub>3</sub>F partial pressures.

## **Experimental Section**

Helium I $\alpha$  (21.22 eV) photoelectron spectra (PES) were recorded on a new minicomputer-controlled transient spectrometer equipped with a channel plate/phosphor/SIT camera detector for rapid data collection.<sup>29</sup> Radicals were prepared by reaction of fluorine atoms, from microwave discharge of 5% F<sub>2</sub> in helium (B.O.C. special gases), with methyl fluoride (Columbia Organic Chemicals) in a flow reactor using approximately 1-torr total pressures and reagent mixing 0.2-7 cm above the photon beam. Spectra were calibrated with methyl iodide<sup>30</sup> added to the sample chamber; reported ionization energies are accurate to within  $\pm 0.01$ eV. A sample of CD<sub>3</sub>F was prepared by reacting CD<sub>3</sub>Br (Merck and Co., 99.5% D) with HgF<sub>2</sub> at 200 °C for 3 h;<sup>27</sup> CD<sub>3</sub>F was distilled from the reaction mixture at -132 °C. Photoelectron spectra of reaction products were studied in 225 spectra as a function of reagent partial pressure and mixing distance above the ionizing photon beam.

#### Results

The He I $\alpha$  PES of CH<sub>3</sub>F contained a structured first band at 13.10-eV vertical ionization energy in agreement with reported spectra,<sup>31</sup> and the F<sub>2</sub>/He mixture revealed the first band of molecular fluorine at 15.83-eV vertical ionization potential (vip).<sup>32</sup> Microwave discharge of the  $F_2$ /He mixture virtually destroyed the F<sub>2</sub> signal and produced a strong, sharp F atom band at 17.42-eV vip.<sup>33</sup> The initial reaction conditions employed a relatively high CH<sub>3</sub>F partial pressure, a short mixing distance (0.2 cm) above the photon beam, and just enough fluorine to observe the structured 9.0-10.0-eV ionization energy product band shown in Figure 1. The first bands of fluoroacetylene at 11.26-eV vip<sup>31</sup> and HF at 16.06-eV vip with a 16.41-eV vibrational component<sup>34</sup>

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Figure 3. He I photoelectron spectrum in the 9-10-eV ionization energy region for the  $F + CD_3F$  reaction products with use of relatively low F atom and relatively high CD<sub>3</sub>F partial pressures and a short mixing distance. CH<sub>3</sub>I was added for calibration during the run.

were also observed under these conditions. The first band of CF from this and earlier work<sup>7</sup> is also shown (dashed) in Figure 1; a new species with 9.04  $\pm$  0.01 eV adiabatic and 9.22  $\pm$  0.01 eV vertical ionization energies and  $1450 \pm 30 \text{ cm}^{-1} v' = 0-1$  vibrational spacing is produced by the  $F + CH_3F$  reaction in addition to the CF radical. Increasing the F atom partial pressure at this short mixing distance decreased the 9.04-eV product band relative to the CF first band and increased the fluoroacetylene and HF band intensities.

At intermediate mixing distances (2-4 cm) the high CH<sub>3</sub>F/low F reaction mixture revealed a decrease in the 9.04-eV product band, an increase in fluoroacetylene and HF signal intensities, and a new structured band with components at 10.37, 10.56, and 10.73 eV due to vinyl fluoride.<sup>35</sup> Using the same reaction distance and fluorine partial pressure, but reducing the CH<sub>3</sub>F reagent, resulted in an increase in the first bands of CF and fluoroacetylene at the expense of the first band of vinyl fluoride and the new product band. At long mixing distances (5-7 cm), the high CH<sub>3</sub>F/low F reaction mixture revealed a weak signal due to the CF first band and practically no 9.04-eV product band but increased vinyl fluoride and fluoroacetylene signal intensities. With long mixing distances, increased fluorine and decreased CH<sub>3</sub>F partial pressures produced the spectrum shown in Figure 2 containing the structured CF first band at  $9.11 \pm 0.01 \text{ eV}$  (adiabatic) and 9.55  $\pm$  0.01 eV (vertical) ionization energies<sup>7</sup> and the fluoroacetylene first band with vibrational components at 11.26, 11.53, 11.80, and 12.07 eV and, of course, HF which is not illustrated.

The photoelectron spectrum of the products of high  $CD_3F/low$ F conditions at short mixing distance is shown in Figure 3 with added CH<sub>3</sub>I calibrant; DF was observed at 16.07-eV vip with a  $16.33 \pm 0.01$  eV vibrational component.<sup>34</sup> The deuterated product band exhibited 9.04 and 9.23  $\pm$  0.01 eV adiabatic and vertical ionization energies, respectively, and the second vibronic component of CF was observed at  $9.33 \pm 0.01$  eV in agreement with this band position in  $CH_3F$  reactions. For the new deuterated product band, the v' = 0-1 and 1-2 vibrational intervals were measured as  $1530 \pm 30$  and  $1490 \pm 30$  cm<sup>-1</sup>, respectively. If one takes this vibrational mode to be the  $\nu_3$ (C-F) stretching mode, these intervals yield  $\omega_3 = 1570 \pm 30 \text{ cm}^{-1}$  and  $\omega_3 x_3 = 20 \pm 10$ cm<sup>-1</sup>.

Similar experiments performed with CH<sub>2</sub>F<sub>2</sub> at short and medium mixing distances ( $\leq 4$  cm) and low to medium F atom partial pressures produced a strong HF first band, comparable in intensity to that observed with CH<sub>3</sub>F, but no new product bands were detected in the spectrum. An experiment with CHF<sub>3</sub> required

TABLE I: Computed Vertical Ionization Energies (eV) of  $CH_2F(X^2B_2)^a$ 

c ie	orbital onized	ionic state	ΔSCF	ΔSCF plus correlation correcn	
	2b <sub>2</sub>	$X^1A_1$	8.87	10.17	
	$2b_1$	${}^{3}A_{2}$	13.37	14.70	
	2b <sub>1</sub>	$^{1}A_{2}^{-}$	13.58	15.09	
	1b <sub>2</sub>	$^{3}A_{1}$	14.36	15.93	
	1b <sub>2</sub>	${}^{1}A_{1}$	14.52	16.09	

<sup>a</sup>The planar geometry of ref 37 is used in these calculations. The electronic configuration of  $CH_2F(X^2B_2)$  is<sup>37</sup> ...  $(5a_1)^2(1b_2)^2(2b_1)^2$ - $(2b_2)^1$ .

long mixing distances to produce a weak HF signal; no new product bands were found. Several experiments with CF<sub>3</sub>I and F atoms at short mixing distances consumed the CF<sub>3</sub>I and produced strong He I $\alpha$  IF signals at 10.62 and 11.32 eV<sup>36</sup> and weak He I $\beta$  IF bands 8.75 and 9.45 eV, but no new product bands were observed.

## **Computational Details**

The electronic ground-state configuration of  $CH_2F(X^2B_2)$  is

... 
$$(5a_1)^2(1b_2)^2(2b_1)^2(2b_2)^1$$

where the half-filled  $2b_2$  level is an antibonding  $\pi$  orbital composed essentially of carbon and fluorine 2p contributions.<sup>37</sup> Vertical ionization potentials have been predicted by performing SCF calculations for the  $CH_2F X^2B_2$  state and the  $CH_2F^+$  states,  ${}^{1}A_1$ ,  ${}^{1,3}A_2$  and  ${}^{1,3}A_1$ , arising from the  $(2b_2)^{-1}$ ,  $(2b_1)^{-1}$ , and  $(1b_2)^{-1}$ ionizations using the ATOML 3 suite of programs.<sup>38</sup> All calculations were performed with the planar geometry estimated by Konishi and Morokuma.<sup>37</sup> The basis set used in these ab initio calculations was a double-5 STO basis taken from the atomic basis sets of Clementi<sup>39</sup> with added polarization functions (the exponents used were C3d (2.27), F3d (2.01), and H2p (1.08)). The method of Liu and Verhaegen<sup>40</sup> was used to estimate the correlation energy difference between  $CH_2F(X^2B_2)$  and the ionic state under consideration. The computed  $\Delta$ SCF vertical ionization potentials for  $CH_2F$  are shown in Table I.

#### Discussion

The new product band observed from the  $F + CH_3F$  reaction and shown in Figure 1 will be assigned to the  $CH_2F(X^2B_2)$  radical. The structure and bonding in this radical and probable mechanism of the  $F + CH_3F$  reaction will now be discussed.

Assignments. The new band observed at 9.04 eV is assigned to the CH<sub>2</sub>F radical product of reaction 1. Reaction 1 is fast,

$$F + CH_3F \rightarrow HF + CH_2F \tag{1}$$

with a rate constant at room temperature comparable to that of the  $F + CH_4$  reaction,<sup>16</sup> which is known to give a large yield of CH<sub>3</sub> radicals for PES observation.<sup>41</sup> The 9.04-eV band behaved as a primary product transient species when reagent partial pressures and mixing distance were changed. Reaction conditions of high CH<sub>3</sub>F/low F and short mixing distances favored the 9.04-eV band; however, increasing the mixing distance for this same reagent ratio decreased the intensity of the 9.04-eV band and produced vinyl fluoride. This can be rationalized by reaction

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2. Reaction conditions of high  $CH_3F$  and medium F resulted

$$CH_2F + CH_2F \rightarrow [CH_2FCH_2F]' \rightarrow HF + CH_2CHF$$
 (2)

in a decrease in the 9.04-eV band relative to the CF product band. The CF radical is produced by the further reactions 3 and 4.

$$F + CH_2F \rightarrow HF + CHF$$
 (3)

$$F + CHF \rightarrow HF + CF$$
 (4)

Unfortunately, the CHF intermediate was not detected in this reaction mixture (expected VIP = 10-11 eV)<sup>42,43</sup> although the fluoroacetylene product of reaction 5 was observed in substantial

$$CHF + CHF \rightarrow [CHFCHF]^{\dagger} \rightarrow HF + HCCF \qquad (5)$$

yield. Apparently, reactions 4 and 5 are sufficiently rapid to consume CHF under the relatively high pressure (approximately 1-torr total pressure)<sup>44</sup> conditions in the flow reactor before the product stream reaches the ionizing radiation. It is, however, noteworthy that the CHF product has been trapped in recent matrix-isolation studies of the atomic fluorine-methyl fluoride reaction.<sup>23</sup> Studies in this laboratory have found that the CF radical product of reaction 4 gives an identical first PES band within experimental error to that observed from the F + CH<sub>3</sub>CHO and the F + CH<sub>3</sub>Br reactions,<sup>7,45</sup> confirming assignment of this band to CF ionization.

The adiabatic ionization energy of  $CH_2F$  of 9.04 eV determined in this PES study is intermediate between an electron-impact value of 8.90  $\pm$  0.05 eV determined directly for  $CH_2F$  produced by pyrolysis<sup>10</sup> and a value of 9.16  $\pm$  0.02 eV deduced indirectly from a photoionization-mass spectrometric study of 1,1-difluoroethylene using 9.24 eV for the CF ionization energy.<sup>11</sup> This latter study measured a 0.08  $\pm$  0.04 eV difference between the appearance potentials of CF<sup>+</sup> and CH<sub>2</sub>F<sup>+</sup>, which was ascribed to different ionization energies of CF and CH<sub>2</sub>F. This difference and the more accurate PES adiabatic ionization energy of CF (9.11  $\pm$  0.01 eV)<sup>7</sup> yield 9.03  $\pm$  0.05 eV for the adiabatic ionization energy of CH<sub>2</sub>F, in excellent agreement with the present 9.04  $\pm$  0.01 eV PES value.

The first band in the photoelectron spectrum of CD<sub>2</sub>F provides isotopic vibronic data in support of assignment of the observed band in the F + CH<sub>3</sub>F reaction to CH<sub>2</sub>F. The 1450  $\pm$  30 cm<sup>-1</sup> interval v' = 0-1 in the first PES band of CH<sub>2</sub>F is assigned to the C-F stretching mode  $v_3$  in the ground-state cation which has recently been observed at 1170 cm<sup>-1</sup> for the neutral gaseous radical.<sup>22</sup> The small deuterium shift for the v' = 0-1 interval to  $1530 \pm 30 \text{ cm}^{-1}$  in the first PES band of CD<sub>2</sub>F further characterizes  $\nu_3$  as a C-F stretching mode, and the shift to higher energy can be explained by using the neutral radicals as a model.<sup>23,26</sup> Although the H–C–H valence angle bending mode  $v_2$  was not observed for CH<sub>2</sub>F, a 1440  $\pm$  40 cm<sup>-1</sup> estimate for  $\nu_2$  of CH<sub>2</sub>F can be made by extrapolating the 1391-, 1356-, and 1332-cm<sup>-1</sup> values for CH2Cl, CH2Br, and CH2I in solid argon.28,46 Corresponding  $v_2$  and  $v_3$  values have been observed for CD<sub>2</sub>F at 1013 and 1191 cm<sup>-1</sup>, respectively, in solid argon.<sup>23,26</sup> These symmetric vibrational modes interact, and the C-F stretching mode in the  $CD_2F$  radical increased on deuteration due to interaction with  $\nu_2$ , which is displaced below  $v_3$  in the CD<sub>2</sub>F species. Since the in-plane H-C-Cl bending mode of CHCl<sub>2</sub> at 1226 cm<sup>-1</sup> increased<sup>47</sup> to 1292 cm<sup>-1</sup> for CHCl<sub>2</sub><sup>+</sup>,  $\nu_2$  of CH<sub>2</sub>F<sup>+</sup> is estimated to be 1520 ± 40 cm<sup>-1</sup> before interaction with the C-F stretching mode. The deuterium shift expected for this mode allows  $\nu_2$  for CD<sub>2</sub>F<sup>+</sup> to be estimated at 1130 ± 40 cm<sup>-1</sup>, which is the value measured for  $\nu_2$  of CD<sub>2</sub>Br<sup>+</sup> in the first PES band of the CD<sub>2</sub>Br radical.<sup>45</sup> The central point here is that  $\nu_2$  and  $\nu_3$  are mixed modes for the cations as found for the radicals, but more mixing is expected for CH<sub>2</sub>F<sup>+</sup> since  $\nu_2$ and  $\nu_3$  are closer than for CD<sub>2</sub>F<sup>+</sup>. Hence, the 1530  $\pm$  30 cm<sup>-1</sup> C-F fundamental for CD<sub>2</sub>F<sup>+</sup> closely approximates the simple C-F vibration for carbocations, and the positive deuterium shift for the C-F fundamental in CH<sub>2</sub>F<sup>+</sup> is due to interaction with the  $\nu_2$ mode which shifts below the C-F mode on deuteration.

Comparison of the first vertical ionization energy of  $CH_2F$ measured in this work, 9.22 eV, with that obtained via  $\Delta SCF$ calculations shows reasonably good agreement (Table I). The  $\Delta SCF$  value, 8.87 eV, is slightly low whereas approximate allowance for the correlation correction gives a value which is too high, a result which is typical for calculations of this type on small molecules using basis sets of the double- $\zeta$  plus polarization function quality. As can be seen from Table I, four other bands of  $CH_2F$ are expected in the 13.0–16.5-eV range, but these were not observed because of overlapping band problems in this region.

Bonding and Structure. The increased C-F stretching fundamentals for  $CH_2F^+$  and  $CD_2F^+$  at 1450 and 1530 ± 30 cm<sup>-1</sup> respectively, relative to these modes for  $CH_2F$  and  $CD_2F$  measured at 1163 and 1191 cm<sup>-1</sup> in solid argon<sup>25,26</sup> demonstrate a substantial increase in C-F bond strength for the cations. Ab initio calculations performed in this study indicate that the outermost half-filled  $2b_2$  level in CH<sub>2</sub>F(X<sup>2</sup>B<sub>2</sub>) is essentially an antibonding (C2p-F2p)  $\pi$  orbital, and an increase in the C-F stretching mode is expected upon ionization from this orbital. Furthermore, the total electron density difference between the CH<sub>2</sub>F radical and cation ground states, from Mulliken analysis of the converged SCF wave functions, for the atomic centers (C, 0.51; H, 0.16; F, 0.17) shows that, although the  $2b_2$  MO in the neutral radical is mainly localized on carbon, upon ionization the electron density change on C, H, and F centers is significant. This arises because of electronic reorganization in the cation, which leads to a significant increase in the C-F bond strength in the cation. Similar conclusions have been reached from INDO calculations on the CH<sub>2</sub>F<sup>+</sup> cation.49

Although the C-F stretching fundamental for substituted carbocations is subject to mixing with other modes, the C-F fundamental for  $CH_2F^+$  measured from the photoelectron spectrum (1450 ± 30 cm<sup>-1</sup>) is near the 1436- and 1352-cm<sup>-1</sup> values for C-F stretching modes of CHFCl<sup>+</sup> and CFCl<sub>2</sub><sup>+</sup> in solid argon.<sup>13-15</sup> This demonstrates general agreement between the matrix infrared and vibronic PES methods of measuring C-F stretching fundamentals in carbocations.

The observation of a vibronic progression involving only the C-F stretching fundamental in the first PES band of  $CH_2F$  implies a structural change in only the C-F bond length in the cation compared with the case of the radical, which is consistent with ionization from an essentially planar radical to a planar cation.

Reaction Mechanisms. The overall mechanism of the fluorine atom/methyl fluoride reaction consistent with the observation of the  $CH_2F$  and CF free-radical products and the stable vinyl fluoride and fluoroacetylene products has been given in reactions 1–5. The failure to observe the CHF intermediate in a system where it must be produced points to the rapid reactivity of CHF under these conditions.

The fluorine atom/methylene fluoride reaction (rate constant  $0.2k_1$  at 25 °C)<sup>16</sup> was also studied by PES, and only the HF product was observed. Since the CHF<sub>2</sub> radical departs significantly from planarity,<sup>24</sup> it is suggested that secondary reactions rapidly consume the CHF<sub>2</sub> radical and prevent its detection. The fluorine atom/fluoroform reaction is 2 orders of magnitude slower<sup>16</sup> than reaction 1; hence, long mixing distances were required to detect HF. However, the fluorine atom/trifluoromethyl iodide reaction is very rapid<sup>48</sup> as evidenced by complete precursor reaction at short mixing distances. Nevertheless, CF<sub>3</sub> radicals could not be detected by PES in these studies; this negative ev-

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idence suggests that the pyramidal CF<sub>3</sub> radical is extremely reactive under these high-pressure conditions.

## Conclusions

The fluorine atom/methyl fluoride reaction provides sufficient CH<sub>2</sub>F radicals for observation of its first photoelectron band at  $9.04 \pm 0.01$  eV adiabatic and  $9.22 \pm 0.01$  eV vertical ionization energies. The measured v' = 0-1 vibronic separation of 1450 ± 30 cm<sup>-1</sup> is due to the C-F stretching fundamental of the  $CH_2F^+$ ground state; this vibronic interval shifts to  $1530 \pm 30 \text{ cm}^{-1}$  for  $CD_2F^+$  due to interaction with the scissor bending mode. Considerable increases in the C-F stretching fundamentals of the cation as compared to the case of the neutral radicals are explained by increased net C-F bonding in the cations. Vinyl fluoride, fluoroacetylene, and the CF radical were also observed in this

reaction system; although the CHF intermediate was not detected directly, its production is indicated by the observation of HCCF and CF. This study demonstrates the usefulness of a multidetector photoelectron spectrometer to characterize the reactive and stable products of a reaction system; this method, in principle, can identify all species with sufficient lifetime to reach the ionization region.

Acknowledgment. We gratefully acknowledge financial support for this research from the S.E.R.C. (U.K.). L.A. acknowledges a Sesquicentennial Associateship from the University of Virginia, a Visiting Fellowship from the S.E.R.C., and a Fulbright Senior Research Fellowship.

Registry No. F, 14762-94-8; CH<sub>3</sub>F, 593-53-3; CH<sub>2</sub>F, 3744-29-4; CD<sub>2</sub>F, 89578-59-6.

# Effects of Quaternary Ammonium Salts on Reactions of Aromatic Radical Anions Formed in Tetrahydrofuran by Pulse Radiolysis

Yukio Yamamoto,\* Shoichi Nishida, Katsuyoshi Yabe, Koichiro Hayashi, Seishi Takeda, and Kunihiko Tsumori

The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567, Japan (Received: August 22, 1983)

Pulse radiolysis of biphenyl (BP) and pyrene (Py) in tetrahydrofuran (THF) solution was carried out in the presence of various kinds of quaternary ammonium salts, such as Bu<sub>4</sub>NPF<sub>6</sub>, Bu<sub>4</sub>NBF<sub>4</sub>, Bu<sub>4</sub>NI, BzMe<sub>3</sub>NPF<sub>6</sub>, and PhMe<sub>3</sub>NPF<sub>6</sub> (Bu, butyl; Me, methyl; Bz, benzyl; and Ph, phenyl). The decay behaviors of the radical anions, BP- and Py-, are significantly affected by the addition of the salts. The anions of the salts,  $PF_6^-$ ,  $BF_4^-$ , and  $I^-$ , are considered to form ion pairs with the solvent counterions,  $THF(H^+)$ , resulting in a retardation of the neutralization reactions. The rate constants for the neutralization reactions have been determined in the absence and presence of  $Bu_4NPF_6$ . The addition of  $BzMe_3NPF_6$  (or PhMe\_3NPF<sub>6</sub>) accelerates the decay of BP- and retards the decay of Py-, depending on the rates of reactions of the radical anions with  $BzMe_3N^+$  (or PhMe\_3N^+). The reactivity of BP- in the electron transfer to Py seems to be reduced in the presence of  $Bu_4NPF_6$ . The effect of  $Bu_4N^+$  on the reactions of the radical anions is discussed.

## Introduction

Numerous studies have been reported for the salt effects on ionic reactions in radiation chemistry. According to the Bronsted-Bjerrum theory the rates of reactions between charged species depend on the ionic strength if other ions are present in the solution.<sup>1</sup> Such an effect has been studied on the reactions of solvated electrons with various kinds of inorganic ions in water<sup>2-4</sup> and methanol.<sup>5</sup> On the other hand, in solvents of low polarity where ion-pair formation is important the reactivities of charged species are affected by the addition of salts through ion-pair formation with the counterions from the salts. The salt effect has been studied on reactions of negatively charged species such as solvated electrons, aromatic radical anions, and carbanions in tetrahydrofuran (THF) by pulse radiolysis methods.<sup>6-13</sup> The salts

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used in these studies are tetrahydroaluminate and tetraphenylborate salts of alkali metals, whose addition to the THF solutions results in ion pairs of the negatively charged species, generated by pulse radiolysis, with the alkali metal cations. The rate constants for several types of reactions have been determined for the free and paired states. The values are smaller for the paired states than for the free states except for those of proton transfer reactions of benzyl anions from water and alcohols.<sup>9</sup> This subject has also been studied by flash photolysis of aromatic radical anions in THF, demonstrating that the reactivities of the solvated electrons and aromatic radical anions are reduced upon ion-pair formation with the alkali metal cations from the added salts.<sup>14-16</sup>

We have recently reported that the lifetime of the biphenyl radical cations formed in dichloromethane by pulse radiolysis is extended by the addition of salts having complex metal halide anions, such as diphenyliodonium, triphenylsulfonium, and tetrabutylammonium hexafluorophosphates.<sup>17</sup> This effect has been attributed to the stabilization of the radical cations through ion-pair formation with the nonnucleophilic anions from the salts. It was also found that the stabilization of the monomer and dimer

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