

AD-A281 950



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June 28, 1994

Reprint

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PE 61102F  
PR 2303  
TA GJ  
WU 01

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PL-TR-94-2185

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Reprinted from J. Chem. Phys. 100 (10) 15 May 1994

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Rate coefficients and product branching fractions have been determined for 31 ion-molecule reactions involving PF<sub>3</sub> or PF<sub>5</sub><sup>-</sup>. About half of the reactions studied show an ion-molecule association channel. NH<sub>2</sub><sup>-</sup> and OH<sup>-</sup> reaction with PF<sub>5</sub> yields HF product. F<sup>-</sup> and electron transfer channels are also observed in many of the reactions studied. Consideration of the efficiency of the electron transfer channel in these reactions leads to the conclusion that the adiabatic electron affinity of PF<sub>5</sub> is 0.75±0.15 eV.

DTIC QUALITY INSPECTED 3

14. SUBJECT TERMS Rate constant, Electronaffinity, Phosphorous Pentafluoride			15. NUMBER OF PAGES 6
			15. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT SAR

# Negative ion reactions with PF<sub>5</sub> and the electron affinity of PF<sub>5</sub>

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(Received 7 December 1993; accepted 31 January 1994)

Rate coefficients and product branching fractions have been determined for 31 ion-molecule reactions involving PF<sub>5</sub> or PF<sub>5</sub><sup>-</sup>. About half of the reactions studied show an ion-molecule association channel. NH<sub>2</sub><sup>-</sup> and OH<sup>-</sup> reaction with PF<sub>5</sub> yields HF product. F<sup>-</sup> and electron transfer channels are also observed in many of the reactions studied. Consideration of the efficiency of the electron transfer channel in these reactions leads to the conclusion that the adiabatic electron affinity of PF<sub>5</sub> is 0.75±0.15 eV.

## I. INTRODUCTION

In recent experiments we have determined<sup>1,2</sup> (nondissociative) electron attachment rate coefficients for a number of perfluorinated compounds, including PF<sub>5</sub>, SF<sub>6</sub>, and SF<sub>4</sub>. The room-temperature rate coefficient for electron attachment to PF<sub>5</sub> is rather small ( $3.2 \times 10^{-10}$  cm<sup>3</sup> s<sup>-1</sup>) corresponding to electron attachment in about 1 in every 1000 collisions, and the rate coefficient shows little variation with temperature in the range studied (300–550 K). The attachment rate constants for PF<sub>5</sub> are orders of magnitude below those for attachment to SF<sub>6</sub> (which are nearly collisional and show little temperature dependence) and SF<sub>4</sub> (which is about 1/10th collisional and also shows little temperature dependence), despite the structural and electronic similarity of these three molecules. In order to understand the energetics of the electron attachment, and possibly provide some information on the dynamics of the process, we have determined the electron affinity of PF<sub>5</sub>.

Gutsev<sup>3</sup> has recently given the results of calculations on the structure and energetics of the complete series of PF<sub>n</sub> neutrals and PF<sub>n</sub><sup>-</sup> ions ( $n=1-6$ ). His calculations utilized a Hartree-Fock-Slater approach, with a local spin density approximation (LSDA) for the exchange and correlation contributions to the neutrals and anions, and a higher level of theory which included a nonlocal gradient correction to the exchange potential (LSDA/NL). He calculated the adiabatic electron affinity (EA) of PF<sub>5</sub> to be 0.97 eV at the LSDA level of theory and 1.82 eV at the LSDA/NL level. Both of these values lie above Gutsev *et al.*'s earlier estimate of 0.7 eV,<sup>4</sup> obtained using the discrete variational  $X_\alpha$  method. Gutsev found<sup>3</sup> that PF and PF<sub>2</sub> have low adiabatic EAs (0.64 and 0.77 eV, respectively). PF<sub>3</sub> was found to have a negative EA, and the electron affinities of PF<sub>4</sub> and PF<sub>6</sub> were found to be quite high, 3.56 and 7.33 eV, respectively. All these values are at the LSDA/NL level, and are uncorrected for differences in zero-point vibrational energy. Little experimental

data exists with which to compare the calculated EAs: the relatively low EAs for PF and PF<sub>2</sub> and the high EAs for PF<sub>4</sub> and PF<sub>6</sub> are in qualitative agreement with the experimental evidence based on their reactive stabilities, and the negative EA for PF<sub>3</sub> is consistent with the fact that PF<sub>3</sub><sup>-</sup> has never been observed. No data have been reported on the EA of PF<sub>5</sub>.<sup>5</sup>

Gutsev,<sup>6</sup> and Ziegler and Gutsev,<sup>7</sup> used the LSDA/NL method to calculate the properties of SF<sub>n</sub> and SF<sub>n</sub><sup>-</sup> ( $n=1-6$ ) including electron affinities. The EAs of SF, SF<sub>4</sub>, and SF<sub>6</sub> are now well-established experimentally, as EA(SF)=2.285±0.006 eV,<sup>8</sup> EA(SF<sub>4</sub>)=1.5±0.2 eV,<sup>9</sup> and EA(SF<sub>6</sub>)=1.05±0.10.<sup>10</sup> By comparison, the calculated values are 2.19,<sup>7</sup> 2.56,<sup>7</sup> and 3.44 eV,<sup>6</sup> respectively. The EAs of SF<sub>3</sub> and SF<sub>5</sub> have not been directly measured, but may be deduced from appearance potentials and measured bond energies; EA(SF<sub>3</sub>)~3.8 eV<sup>11</sup> and EA(SF<sub>5</sub>)~4.2 eV.<sup>11,12</sup> These experimental estimates may be compared to the calculated<sup>7</sup> values 1.84 and 4.79 eV, respectively. There is no experimental value for EA(SF<sub>2</sub>). Although calculated and experimental EAs are in quite good agreement for SF, the calculated values for SF<sub>n>1</sub> are rather different. We thus conclude that the LSDA/NL method should not be expected to give EA(PF<sub>5</sub>) to better than 1–2 eV.

PF<sub>5</sub> is trigonal bipyramidal ( $D_{3h}$ ),<sup>13</sup> while ESR work<sup>14</sup> and the calculations of Gutsev<sup>3</sup> give the ground configuration of PF<sub>5</sub><sup>-</sup> to be square pyramidal ( $C_{4v}$  symmetry), with the PF bonds longer than in the neutral. The vertical electron affinity will be substantially greater than the adiabatic electron affinity as a consequence of the large geometry change between ion and neutral. For this reason, as with the related molecules SF<sub>4</sub> and SF<sub>6</sub>, it is unlikely—perhaps impossible—for inherently more accurate photodetachment techniques to be used to measure EA(PF<sub>5</sub>). In the SF<sub>4</sub> and SF<sub>6</sub> cases, however, the electron affinities have been reliably determined by charge-transfer reactions (or charge transfer equilibrium).<sup>9,10</sup> In the present experimental work, we have utilized charge-transfer reactions (or lack thereof) to establish EA(PF<sub>5</sub>)=0.75±0.15 eV.

PF<sub>5</sub> gas finds applications in ion implantation and molecular implantation doping of silicon with phosphorous<sup>15</sup> and in intercalation chemistry.<sup>16</sup> PF<sub>5</sub> is an interesting molecule in itself; NMR spectra<sup>17</sup> show five equivalent fluorine

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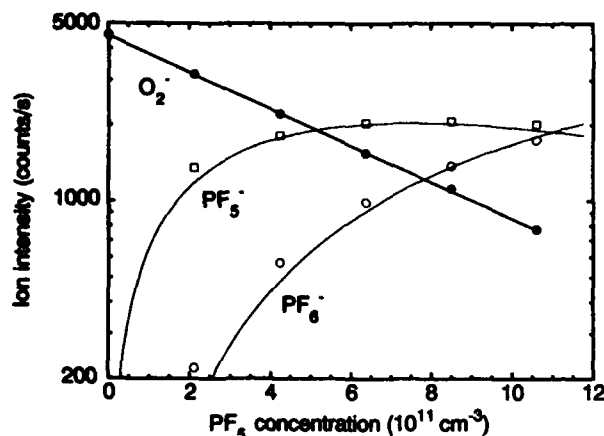


FIG. 1. Analysis of data for  $O_2^-$  reaction with  $PF_5$  and the secondary reaction  $PF_5^-$  with  $PF_5$  at 300 K. The solid lines were calculated from Eq. (3) with  $k_1 = 9.7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ,  $k_2 = 6.2 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , and a reaction time of 1.7 ms.

atoms while electron diffraction<sup>13</sup> and IR spectroscopy<sup>18</sup> give axial fluorine bond lengths about 3% longer than equatorial bond lengths. The explanation lies in Berry pseudorotation,<sup>19</sup> large amplitude motions of the F atoms which exchanges F atoms over a time short compared to the NMR time scale. The most recent calculation of the barrier to pseudorotation in  $PF_5$  is that of Marsden,<sup>20</sup> who estimated a barrier height of  $3.8 \pm 0.5 \text{ kcal mol}^{-1}$ . Raman scattering indicates a barrier height between 2.84 and  $3.26 \text{ kcal mol}^{-1}$ .<sup>21</sup>

## II. EXPERIMENT

The measurements were carried out using a selected ion flow tube (SIFT) apparatus. This type of apparatus and associated techniques have been reviewed in detail.<sup>22,23</sup> Figure 1 shows a sample of the data, for the attenuation of  $O_2^-$  intensity as the  $PF_5$  concentration is changed. The logarithmic slope gives a reaction rate coefficient  $k = 9.7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  for this reaction at 300 K.

Anions were produced in an electron-impact ion source as in our work<sup>9</sup> on  $SF_4$ , supplemented here by  $C_6F_5COCH_3^-$  made by electron bombardment from 2',3',4',5',6'-pentafluoroacetophenone vapor;  $CF_3C_6H_4CN^-$  from  $\alpha, \alpha$ -trifluorotolunitrile vapor;  $C_6F_6^-$  from perfluorobenzene vapor;  $C_6F_5Cl^-$  from chloropentafluorobenzene vapor;  $Br^-$ ,  $C_6F_5^-$ , and  $C_6F_5Br^-$  from bromopentafluorobenzene vapor;  $I^-$  from iodopentafluorobenzene vapor ( $C_6F_5I^-$  could not be made—it dissociated mainly into  $C_6F_5^-$  inside the ion source);  $C_6F_5CN^-$  from perfluorobenzonitrile vapor;  $C_6F_5CF_3^-$  from octafluorotoluene vapor;  $C_6F_{11}CF_3^-$  from perfluoromethylcyclohexane vapor;  $F^-$  from  $PF_3$  gas;  $OH^-$  from water vapor; and  $NH_2^-$  from  $NH_3$  gas. The  $PF_5$  gas (Ozark-Mahoning) either contains a small amount of oxide impurity or reacts with oxides deposited on feedline surfaces, as  $POF_4^-$  was observed in the mass spectra on both the electron attachment<sup>12</sup> and SIFT apparatuses when  $PF_5$  was the source gas. For use as a reactant neutral,  $PF_5$  was introduced into the flow tube in the form of a 10% mixture in helium gas, pri-

marily because neat  $PF_5$  had a sluggish effect on the flowmeter, but also to allow the flowmeter to be operated closer to full scale (for better control and more accurate flow measurement). The calibration of the reactant flowmeter was checked by timing the pressure drop in a reservoir of known volume connected to the flowmeter inlet.

We were unable to produce  $PF_5^-$  in our high-pressure ion source from either  $PF_5$  or  $PF_3$ . Use of a dilute mixture of  $PF_5/He$  (<2%) in the ion source led to no significant anion production, while stronger mixtures gave only  $PF_6^-$ . Thermal electron attachment to  $PF_5$  is inefficient, but is known<sup>1</sup> to produce  $PF_5^-$ , which then fluoride transfers to  $PF_5$  giving the highly stable  $PF_6^-$ . Therefore, we were unable to study reverse reactions (i.e.,  $PF_5^-$  as the reactant) using the standard SIFT technique. Instead,  $O_2^-$  was injected into the flow tube, and  $PF_5^-$  was generated by efficient charge transfer via reaction (1):



and  $PF_5^-$  was then reacted with various neutrals. The secondary reaction



was studied by fitting the  $PF_5^-$  and  $PF_6^-$  intensities vs  $PF_5$  concentration to solutions of the appropriate rate equations<sup>24</sup> as illustrated in Fig. 1. The solid curves in Fig. 1 are given by<sup>24</sup>

$$I(O_2^-) = I_0 \exp(-k_1 nt), \quad (3a)$$

$$I(PF_5^-) = I_0 [k_1 / (k_2 - k_1)] [\exp(-k_1 nt) - \exp(-k_2 nt)], \quad (3b)$$

$$I(PF_6^-) = I_0 - I(O_2^-) - I(PF_5^-), \quad (3c)$$

where  $I(A^-)$  is the detected intensity of ion  $A^-$ ,  $I_0$  is the initial intensity of  $O_2^-$ ,  $k_1$  and  $k_2$  are the reaction rate coefficients for reactions (1) and (2), respectively,  $n$  is the concentration of  $PF_5$  vapor, and  $t$  is the reaction time (reaction distance divided by ion velocity). In fitting Eq. (3) to the data of Fig. 1, it is important that there is little overall loss of ion flux. The reaction was studied with low mass resolution to minimize mass discrimination error; the sum of the  $O_2^-$ ,  $PF_5^-$ , and  $PF_6^-$  ion signals was constant to within 3% as  $n$  was varied.

Other reactions with  $PF_5^-$  reactant proved more difficult to study because yet another neutral reactant must be added. For these other reactions,  $PF_5$  was introduced into the flow tube at an inlet 25 cm ahead of the usual reactant inlets, at a concentration ( $4 \times 10^{12} \text{ cm}^{-3}$  at 300 K) sufficient to reduce the  $O_2^-$  intensity to less than 1% of the injected current, in a distance of 25 cm. Reactant gases were then added at the usual reactant inlets, and reaction rates were determined from the  $PF_5^-$  attenuation. Identification of ionic products was more problematic, however, because of the presence of a large concentration of  $PF_5$  in the flow tube, coupled with secondary processes and the low rate coefficients for several of the reactants studied. Mass spectra were obtained with different concentrations of both  $PF_5$  and the reactant gas (e.g.,  $O_2$ ). In each case it was clear what the major ionic product was, but in some cases it was difficult to say with

TABLE I. Rate coefficients and product branching fractions for reaction of various ions with PF<sub>5</sub> at 300 K. The reactant ions are listed in order of electron binding energy.

Reactant ion	Electron binding energy <sup>a</sup> (eV)	Reaction rate coefficient (10 <sup>-10</sup> cm <sup>3</sup> s <sup>-1</sup> )	Calculated reaction efficiency <sup>b</sup>	Ionic products (%)
Fe <sup>-</sup>	0.151 ±0.003	5.7	0.62	PF <sub>4</sub> <sup>-</sup> (65) FeF <sub>2</sub> (20) FeF <sub>3</sub> (15) PF <sub>5</sub> (100)
O <sub>2</sub> <sup>-</sup>	0.451 ±0.007	9.7	0.85	PF <sub>4</sub> <sup>-</sup> (90) PF <sub>5</sub> (10)
C <sub>6</sub> F <sub>6</sub> <sup>-</sup>	0.52 ±0.10	2.5	0.36	PF <sub>4</sub> <sup>-</sup> (90) PF <sub>5</sub> (10)
<i>m</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CN <sup>-</sup>	0.67 ±0.10	4.1	0.61	PF <sub>5</sub> ·CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CN <sup>-</sup> (75) PF <sub>5</sub> (25) PF <sub>6</sub> <sup>-</sup> (<2) PF <sub>4</sub> <sup>-</sup> (80)
C <sub>3</sub> F <sub>3</sub> N <sup>-</sup>	0.68 ±0.11	2.5 <sup>c</sup>	0.36	PF <sub>5</sub> (20) PF <sub>4</sub> <sup>-</sup> (80)
<i>o</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CN <sup>-</sup>	0.70 ±0.10	4.0	0.60	PF <sub>5</sub> ·CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CN <sup>-</sup> (80) PF <sub>5</sub> (20) PF <sub>6</sub> <sup>-</sup> (<2) PF <sub>4</sub> <sup>-</sup> (100)
PF <sub>5</sub> <sup>-</sup>	0.75 ±0.15	6.2	0.85	PF <sub>6</sub> <sup>-</sup> (100)
<i>p</i> -CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CN <sup>-</sup>	0.76 ±0.10	3.5	0.52	PF <sub>5</sub> ·CF <sub>3</sub> C <sub>6</sub> H <sub>4</sub> CN <sup>-</sup> (85) PF <sub>5</sub> (15) PF <sub>6</sub> <sup>-</sup> (<2) NPF <sub>3</sub> <sup>-</sup> (70) HNPF <sub>4</sub> <sup>-</sup> (25) HNPF <sub>2</sub> <sup>-</sup> (5) PF <sub>3</sub> Cl <sup>-</sup> (100)
NH <sub>2</sub> <sup>-</sup>	0.771 ±0.005	18.0 <sup>d</sup>	1.2	PF <sub>4</sub> <sup>-</sup> (90) PF <sub>5</sub> ·C <sub>6</sub> F <sub>5</sub> CF <sub>3</sub> (5) PF <sub>5</sub> (5)
C <sub>6</sub> F <sub>5</sub> Cl <sup>-</sup>	0.82 ±0.11	4.2	0.64	PF <sub>4</sub> <sup>-</sup> (90) PF <sub>5</sub> ·C <sub>6</sub> F <sub>5</sub> CF <sub>3</sub> (5) PF <sub>5</sub> (5)
C <sub>6</sub> F <sub>5</sub> CF <sub>3</sub> <sup>-</sup>	0.86 ±0.11	1.4	0.22	PF <sub>4</sub> <sup>-</sup> (90) PF <sub>5</sub> ·C <sub>6</sub> F <sub>5</sub> CF <sub>3</sub> (5) PF <sub>5</sub> (5)
C <sub>6</sub> F <sub>5</sub> COCH <sub>3</sub> <sup>-</sup>	0.88 ±0.11	4.4 <sup>e</sup>	0.67	PF <sub>5</sub> ·C <sub>6</sub> F <sub>5</sub> COCH <sub>3</sub> (100)
SF <sub>6</sub> <sup>-</sup>	1.05 ±0.10	3.7	0.52	PF <sub>6</sub> <sup>-</sup> (100)
C <sub>6</sub> F <sub>11</sub> CF <sub>3</sub> <sup>-</sup>	1.06 ±0.10	5.6	0.93	PF <sub>6</sub> <sup>-</sup> (100) <sup>f</sup>
SO <sub>2</sub> <sup>-</sup>	1.107 ±0.008	5.4 <sup>e</sup>	0.61	PF <sub>5</sub> ·SO <sub>2</sub> (100)
C <sub>6</sub> F <sub>5</sub> CN <sup>-</sup>	1.11 ±0.11	1.6	0.25	PF <sub>5</sub> ·C <sub>6</sub> F <sub>5</sub> CN <sup>-</sup> (55) PF <sub>6</sub> <sup>-</sup> (45)
C <sub>6</sub> F <sub>5</sub> Br <sup>-</sup>	1.15 ±0.11	<0.1	<0.015	PF <sub>5</sub> Br <sup>-</sup> (100)
FeCO <sup>-</sup>	1.157 ±0.005	4.9	0.60	FeF <sub>2</sub> (75) <sup>g</sup> PF <sub>4</sub> <sup>-</sup> (25)
OH <sup>-</sup>	1.827 670 ±0.000 021	13.4	0.90	OPF <sub>4</sub> <sup>-</sup> (100)
C <sub>6</sub> F <sub>5</sub> <sup>-</sup>	2.7 ±0.2	5.6	0.83	PF <sub>5</sub> ·C <sub>6</sub> F <sub>5</sub> (100)
I <sup>-</sup>	3.059 038 ±0.000 010	<0.05	<0.007	PF <sub>3</sub> I <sup>-</sup> (100)
Br <sup>-</sup>	3.363 590 ±0.000 003	0.86	0.10	PF <sub>3</sub> Br <sup>-</sup> (100)
F <sup>-</sup>	3.401 190 ±0.000 004	15.0 <sup>e</sup>	1.1	PF <sub>6</sub> <sup>-</sup> (100)
Cl <sup>-</sup>	3.612 69 ±0.000 06	2.5 <sup>e</sup>	0.23	PF <sub>3</sub> Cl <sup>-</sup> (100)
SF <sub>5</sub> <sup>-</sup>	3.8 ±0.14	4.7	0.65	PF <sub>6</sub> <sup>-</sup> (100)

<sup>a</sup>Electron binding energies (electron affinities of the corresponding neutrals) were taken from Ref. 25, except for PF<sub>5</sub><sup>-</sup> (this work), SF<sub>5</sub><sup>-</sup> (Refs. 11 and 12), CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CN<sup>-</sup> (Ref. 26), FeCO<sup>-</sup> (Ref. 27), C<sub>6</sub>F<sub>5</sub><sup>-</sup> (Ref. 28), and C<sub>6</sub>F<sub>11</sub>CF<sub>3</sub><sup>-</sup> (Ref. 29).

<sup>b</sup>Experimental rate coefficient divided by the calculated collisional rate. The calculation uses the classical trajectory parameterization of Ref. 30 with a PF<sub>5</sub> polarizability of 6.10×10<sup>-24</sup> cm<sup>3</sup> from Ref. 25, and a dipole moment of zero. An efficiency >1 simply reflects uncertainties in the measured and calculated rate coefficients.

<sup>c</sup>Also, 1.7×10<sup>-10</sup> cm<sup>3</sup> s<sup>-1</sup> at 385 K. The product branching fractions were unchanged.

<sup>d</sup>Carried out at a center-of-mass kinetic energy of 0.040 eV to enhance signal strengths. The 300 K reaction rate coefficient is likely unaffected by the weak electric field applied.

<sup>e</sup>Effective binary rate coefficient measured in a helium buffer at 0.39 Torr (number density 1.25×10<sup>16</sup> cm<sup>-3</sup>). The pressure dependence of the rate coefficient was not studied.

<sup>f</sup>FeF<sub>4</sub><sup>-</sup> also generated, but apparently in a secondary reaction between FeF<sub>2</sub><sup>-</sup> and PF<sub>5</sub>.

<sup>g</sup>It was not possible to inject only C<sub>6</sub>F<sub>11</sub>CF<sub>3</sub><sup>-</sup> because the ion source mass spectrometer would not reach 350 amu. Instead, all ions produced above about 300 amu were injected; C<sub>6</sub>F<sub>11</sub>CF<sub>3</sub><sup>-</sup> comprised 90% of the four ions injected. The balance of primary ion loss against ion production implies that PF<sub>6</sub><sup>-</sup> is the only product from C<sub>6</sub>F<sub>11</sub>CF<sub>3</sub><sup>-</sup>+PF<sub>5</sub>, but this cannot be stated with certainty.

certainly that the product was a direct product of the PF<sub>5</sub><sup>-</sup> reaction, or to rule out minor products or a PF<sub>6</sub><sup>-</sup> product. In presenting the results we will refer to these product ions as "terminal" ions. For the PF<sub>5</sub><sup>-</sup> reaction with O<sub>2</sub>, a low (but fixed) PF<sub>5</sub> concentration resulted in residual O<sub>2</sub><sup>-</sup> surviving the entire length of the flow tube, but, significantly, no increase in the O<sub>2</sub><sup>-</sup> signal was observed as the concentration of O<sub>2</sub> was increased; only the O<sub>2</sub>·PF<sub>5</sub><sup>-</sup> ion was created in the reaction zone. Only five reactions with PF<sub>5</sub><sup>-</sup> were studied because of the expense of the PF<sub>5</sub> and the difficulty in pinning down the products; except for the O<sub>2</sub> reaction, these reactions with PF<sub>5</sub><sup>-</sup> were of no use in bracketing EA(PF<sub>5</sub>). Certain reactions that might be of interest (e.g., PF<sub>5</sub><sup>-</sup> + CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CN) from the point of view of determining EA(PF<sub>5</sub>), were not studied because of the low vapor pressures of the reactants.

The reaction rate coefficients reported here are estimated to be accurate to ±30%. When more than one product ion is observed in a reaction, the branching ratios are considered to be accurate to within ten percentage points. Neutral products were not detected, but may usually be inferred from the energetics of the reactions.

### III. DISCUSSION OF RESULTS

Results of the present measurements for PF<sub>5</sub> reactant are given in Table I. Also given are electron binding energies<sup>11,12,25-29</sup> of the reference anions and the reaction efficiency (measured rate constant divided by the collisional rate constant). The collisional rate constant was calculated using the method of Su<sup>30</sup> which uses the PF<sub>5</sub> polarizability<sup>25</sup> of 6.10 × 10<sup>-24</sup> cm<sup>3</sup>. Table II gives the present results for PF<sub>5</sub><sup>-</sup> reactant. In Table III are given the temperature dependences of rate coefficients for reactions (1) and (2) and for the reaction of PF<sub>5</sub><sup>-</sup> with O<sub>2</sub>.

#### A. Electron transfer channel

Electron transfer to PF<sub>5</sub> was observed in reaction with all anions which have electron binding energies less than 0.76 eV (±0.10 eV), except for Fe<sup>-</sup>. For three anions with electron binding energies in the range 0.77–0.86 eV (±0.10 eV), only the C<sub>6</sub>F<sub>5</sub>CF<sub>3</sub><sup>-</sup> reaction showed an electron transfer channel producing PF<sub>5</sub><sup>-</sup>. No anion with an electron binding energy greater than 0.86 eV reacts with PF<sub>5</sub> via electron transfer. Figure 2 displays the electron transfer efficiency (branching fraction times the overall efficiency given in Table I) vs electron binding energy of the reference anion (EA of the corresponding neutral). Three data points in Fig. 2 need special note: those for *o*-, *m*-, and *p*-CF<sub>3</sub>C<sub>6</sub>F<sub>4</sub>CN<sup>-</sup>. These three ions are structurally similar. The partial rate coefficient for the association channel (overall rate coefficient times the association branching fraction) is approximately the same for these three ions (3.0–3.1 × 10<sup>-10</sup> cm<sup>3</sup> s<sup>-1</sup>). The decrease in overall rate coefficient (Table I) in going from *m*- to *o*- to *p*-CF<sub>3</sub>C<sub>6</sub>F<sub>4</sub>CN<sup>-</sup> is entirely due to a decrease in reaction via the electron transfer channel, which may be correlated with the energy available for electron transfer. The data of Fig. 2 imply an upper bound for EA(PF<sub>5</sub>) in the neighborhood of 0.9 eV.

TABLE II. Rate coefficients for PF<sub>5</sub><sup>-</sup> reaction with various molecules at 300 K.

Reactant neutral	Reaction rate coefficient <sup>a</sup> (10 <sup>-10</sup> cm <sup>3</sup> s <sup>-1</sup> )	Calculated reaction efficiency <sup>b</sup>	Terminal ionic product
O <sub>2</sub>	0.53	0.091	O <sub>2</sub> ·PF <sub>5</sub> <sup>-</sup>
C <sub>6</sub> F <sub>6</sub>	3.3	0.38	C <sub>6</sub> F <sub>6</sub> ·PF <sub>5</sub> <sup>-</sup>
C <sub>3</sub> F <sub>3</sub> N	3.1	0.25	C <sub>3</sub> F <sub>3</sub> N·PF <sub>5</sub> <sup>-</sup>
PF <sub>5</sub>	6.2	0.87	PF <sub>6</sub> <sup>-</sup>
C <sub>6</sub> F <sub>5</sub> Cl	3.6	0.34	C <sub>6</sub> F <sub>5</sub> Cl·PF <sub>5</sub> <sup>-</sup>
C <sub>6</sub> F <sub>5</sub> CF <sub>3</sub>	10.6	0.80	C <sub>6</sub> F <sub>5</sub> CF <sub>3</sub> ·PF <sub>5</sub> <sup>-</sup>

<sup>a</sup>Effective binary rate coefficient, measured in a helium buffer at a pressure of 0.4 Torr (He number density 1.25 × 10<sup>16</sup> cm<sup>-3</sup>). The pressure dependence of the reactions was not studied.

<sup>b</sup>Defined as in Table I.

<sup>c</sup>For O<sub>2</sub> and PF<sub>5</sub>, the product listed is the *only* ionic product. In the other cases, the ionic product listed is the most intense one observed, and is likely the direct product of reaction. However, because both the reactant neutral and PF<sub>5</sub> were present in the flow tube simultaneously, it is difficult to rule out minor products or a PF<sub>6</sub><sup>-</sup> product; see the text.

The reaction of PF<sub>5</sub><sup>-</sup> with O<sub>2</sub> was studied over the temperature range 303–543 K in order to place a lower bound on EA(PF<sub>5</sub>); the results are given in Table III. The O<sub>2</sub> reaction was favored over other possibilities listed in Table I because of the clear product picture for the forward reaction, i.e., O<sub>2</sub><sup>-</sup> reacts only by electron transfer. Despite the experimental difficulties outlined above in regard to identifying products in PF<sub>5</sub><sup>-</sup> reactions, it was evident that PF<sub>5</sub><sup>-</sup> does not charge transfer with O<sub>2</sub> even at 543 K. If we take the ratio of the rate coefficient for the PF<sub>5</sub><sup>-</sup> + O<sub>2</sub> reaction to that for O<sub>2</sub><sup>-</sup> + PF<sub>5</sub> as an upper limit to an equilibrium constant relating PF<sub>5</sub><sup>-</sup> and O<sub>2</sub><sup>-</sup> at 543 K, we obtain a lower limit to [EA(PF<sub>5</sub>)–EA(O<sub>2</sub>)] of 0.19 eV.<sup>31</sup> Thus, EA(PF<sub>5</sub>) > 0.64 eV.

Combining the considerations above, we assign EA(PF<sub>5</sub>) = 0.75 ± 0.15 eV. The uncertainty is slightly larger than implied by the discussion above because of the corresponding uncertainties in the reference EAs, typically ±0.11 eV, except for O<sub>2</sub> [EA(O<sub>2</sub>) = 0.451 ± 0.007 eV],<sup>32</sup> and the possible influence of internal energy on the electron transfer rates. The measured EA(PF<sub>5</sub>) is 1 eV smaller than what is apparently the best calculated value,<sup>3</sup> and in fact is in good agreement with a cruder theoretical estimate (0.7 eV, Ref. 4). We assume that this agreement is fortuitous.

TABLE III. Reaction rate coefficients (in units of 10<sup>-10</sup> cm<sup>3</sup> s<sup>-1</sup>) as a function of temperature. The estimated uncertainty is ±30% for the first two reactions, and ±40% for the third.

Reaction	303 K	390 K	483 K	543 K
O <sub>2</sub> <sup>-</sup> + PF <sub>5</sub> → PF <sub>5</sub> <sup>-</sup> + O <sub>2</sub>	9.7	10.6	11.2	12.3
PF <sub>5</sub> <sup>-</sup> + O <sub>2</sub> → O <sub>2</sub> ·PF <sub>5</sub> <sup>-</sup>	0.53 <sup>a</sup>	0.39 <sup>a</sup>	0.21 <sup>a</sup>	0.12 <sup>a</sup>
PF <sub>5</sub> <sup>-</sup> + PF <sub>5</sub> → PF <sub>6</sub> <sup>-</sup> + PF <sub>4</sub>	6.2	4.6	3.6	4.0

<sup>a</sup>Effective binary rate coefficient measured in a helium buffer at the following pressures (and number densities): 303 K, 0.39 Torr (1.24 × 10<sup>16</sup> cm<sup>-3</sup>); 390 K, 0.44 Torr (1.08 × 10<sup>16</sup> cm<sup>-3</sup>); 483 K, 0.46 Torr (9.3 × 10<sup>15</sup> cm<sup>-3</sup>); and 543 K, 0.49 Torr (8.7 × 10<sup>15</sup> cm<sup>-3</sup>). Pressure dependences were not studied at the various temperatures.

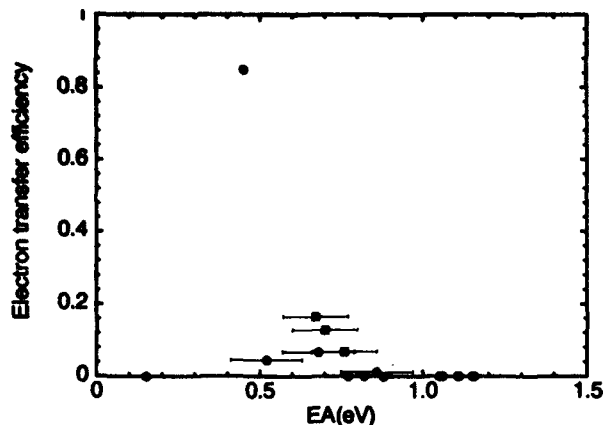


FIG. 2. Efficiency for electron transfer from reference anions to PF<sub>5</sub>, vs electron binding energy for the reference anion (electron affinity of the corresponding neutral molecule). The data points labeled ■ are for *m*-, *o*-, and *p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CN<sup>-</sup>.

### B. Other reaction channels

Fluoride transfer to PF<sub>5</sub> is observed with most of the fluorine-containing anions used in this work. In the cases of *o*-, *m*-, and *p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CN<sup>-</sup>, fluoride transfer does not appear to take place, but the secondary reaction of the PF<sub>5</sub><sup>-</sup> product to yield PF<sub>6</sub><sup>-</sup> made it difficult to rule out a direct fluoride-transfer channel occurring at the few percent level. Fluoride transfer is generally expected, since according to Larson and McMahon,<sup>33</sup> PF<sub>5</sub> has the largest fluoride affinity known; they estimate it to be 85 ± 10 kcal mol<sup>-1</sup> (3.7 ± 0.4 eV). They also showed<sup>33</sup> that chloride affinities of perfluoro compounds are ~0.3–0.5 of the corresponding fluoride affinities. Chloride transfer from C<sub>6</sub>F<sub>5</sub>Cl<sup>-</sup> (and Br<sup>-</sup> transfer from C<sub>6</sub>F<sub>5</sub>Br<sup>-</sup>) occurs instead of F<sup>-</sup> transfer, presumably because the halide affinity in the reactant anion is much less than the F<sup>-</sup> affinity. Association of F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup> with PF<sub>5</sub> is observed in the present work; the reaction rate coefficients decrease markedly in the order given, probably indicative of the decreasing halide affinities of PF<sub>5</sub> in the order F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup>. A similar decrease in efficiency of halide association is seen in their reactions with SF<sub>4</sub>.<sup>9</sup>

An association channel was active in about half of the reactions reported here. Indeed, the association channel was generally the main competition faced by the electron transfer channel; without association, our conclusion for EA(PF<sub>5</sub>) would be more clear-cut. Association is probably a result of the five-coordinate nature of PF<sub>5</sub>, as is the strong fluoride transfer channel that was observed.

It is interesting to contrast the Fe<sup>-</sup> reaction with PF<sub>5</sub> to the Fe<sup>-</sup> reactions with SF<sub>4</sub> and SF<sub>6</sub>.<sup>9</sup> In reaction with SF<sub>*n*</sub> the major product ion observed is F<sup>-</sup>, and charge transfer takes place as a minor channel. In the reaction of Fe<sup>-</sup> with PF<sub>5</sub> the favored channel is PF<sub>4</sub><sup>-</sup> + FeF, and simple electron transfer does not take place at all. Comparison may also be made between the FeCO<sup>-</sup> reactions with SF<sub>*n*</sub> and PF<sub>5</sub>; all yield predominantly FeF<sub>*n*</sub><sup>-</sup> products, but PF<sub>5</sub> reactant also produces PF<sub>4</sub><sup>-</sup> + FeF (25%). The PF<sub>4</sub><sup>-</sup> ion was also observed by Sullivan and Beauchamp<sup>34</sup> and by Larson and McMahon<sup>35</sup> in fluoride transfer to PF<sub>3</sub>.

Note that the reactions of NH<sub>2</sub><sup>-</sup> and OH<sup>-</sup> with PF<sub>5</sub> are characterized by the production of HF, analogous to their reactions with PF<sub>3</sub> and OPF<sub>3</sub>.<sup>34</sup>

### IV. CONCLUSIONS

We have determined rate coefficients and product branching fractions for ion–molecule reactions with PF<sub>5</sub> and/or PF<sub>5</sub><sup>-</sup>. Ion–molecule association is observed in about half the reactions studied. Amide and hydroxide reaction with PF<sub>5</sub> result in HF formation. Fluoride transfer and electron transfer channels are also observed in many of the reactions studied. Examination of the energetics of reactions *vis-à-vis* electron transfer leads to the conclusion that the electron affinity of PF<sub>5</sub> is 0.75 ± 0.15 eV.

### ACKNOWLEDGMENTS

We acknowledge partial support for this work from the National Science Foundation (NSF/EPSCoR-OU-88 and CHE-9008860) and from the Donors of The Petroleum Research Fund, administered by the American Chemical Society (to A. E. S. M.). We wish to thank Professor David Smith for a critical reading of the manuscript.

<sup>1</sup>T. M. Miller, A. E. S. Miller, J. F. Friedman, and J. F. Paulson (to be published). See *Bull. Am. Phys. Soc.* **38**, 1100 (1993).

<sup>2</sup>T. M. Miller, A. E. S. Miller, J. F. Paulson, and X. Liu, *J. Chem. Phys.* (to be published).

<sup>3</sup>G. L. Gutsev, *J. Chem. Phys.* **98**, 444 (1993).

<sup>4</sup>G. L. Gutsev, A. I. Boldyrev, and A. A. Ovchinnikov, *Russ. J. Phys. Chem.* **62**, 168 (1988), translated from *Zh. Fiz. Khim.* **62**, 378 (1988).

<sup>5</sup>An experimental EA(PF<sub>5</sub>) ≈ 3.5 eV was quoted in Ref. 3, due to N. Bartlett and B. W. McQuillan, in *Intercalation Chemistry*, edited by M. S. Whittingham and A. J. Jacobson (Academic, New York, 1982), p. 19. However, the quoted value was in fact 1/2 Δ*H* estimated for the reaction 3PF<sub>5</sub>(g) + 2e<sup>-</sup> → 2PF<sub>6</sub><sup>-</sup>(g) + PF<sub>3</sub>(g); i.e., an "effective" electron affinity based on the oxidizing ability of PF<sub>5</sub>. No estimate for EA(PF<sub>5</sub>) can be made from this enthalpy of reaction. Similarly, the experimental bond energy *D*(F<sub>4</sub>P–F) given in Table VII of Ref. 3 is misquoted: it is actually a calorimetric measurement of the energy required to remove all five F atoms from the P core, divided by 5 (see Ref. 20).

<sup>6</sup>G. L. Gutsev, *Int. J. Mass Spectrom. Ion Processes* **115**, 185 (1992).

<sup>7</sup>T. Ziegler and G. L. Gutsev, *J. Chem. Phys.* **96**, 7623 (1992).

<sup>8</sup>M. L. Polak, M. K. Gilles, and W. C. Lineberger, *J. Chem. Phys.* **96**, 7191 (1992).

<sup>9</sup>A. A. Viggiano, T. M. Miller, A. E. S. Miller, R. A. Morris, J. M. Van Doren, and J. F. Paulson, *Int. J. Mass Spectrom. Ion Processes* **109**, 327 (1991); also, A. E. S. Miller, T. M. Miller, A. A. Viggiano, R. A. Morris, J. F. Paulson, and J. M. Van Doren (to be published).

<sup>10</sup>E. P. Grimsrud, S. Chowdhury, and P. Kebarle, *J. Chem. Phys.* **83**, 1059 (1985).

<sup>11</sup>R. N. Compton, P. W. Reinhard, and C. D. Cooper, *J. Chem. Phys.* **68**, 2023 (1978). In this work EA(SF<sub>3</sub>) = 3.07 ± 0.2 eV and EA(SF<sub>2</sub>) = 2.71 ± 0.2 eV were determined from differences in thresholds for collisional ionization coupled with the best estimates of EA(SF<sub>4</sub>) and EA(SF<sub>6</sub>) and neutral bond energies available at the time. If we substitute presently accepted EAs and neutral bond energies, we obtain EA(SF<sub>3</sub>) = 3.8 eV and EA(SF<sub>2</sub>) = 4.2 eV (with some ambiguity as to 298 → 0 K adjustment).

<sup>12</sup>M. Fenzlaff, R. Gerhard, and E. Illenberger, *J. Chem. Phys.* **88**, 149 (1988). EA(SF<sub>3</sub>) = 3.8 ± 0.14 eV was estimated from the activation energy for production of SF<sub>3</sub><sup>-</sup> in electron attachment to SF<sub>4</sub>, using the best available value for *D*(F<sub>3</sub>S–F). If we substitute *D*<sub>298</sub>(F<sub>3</sub>S–F) = 4.35 ± 0.10 eV [based upon a reexamination of more recent data by W. Tsang and J. T. Herron, *J. Chem. Phys.* **96**, 4272 (1992)], we obtain EA(SF<sub>3</sub>) = 4.2 eV (with some ambiguity as to 298 → 0 K adjustment).

<sup>13</sup>K. W. Hansen and L. S. Bartell, *Inorg. Chem.* **4**, 1775 (1965).

<sup>14</sup>A. R. Boate, A. J. Colussi, J. R. Morton, and K. F. Preston, *Chem. Phys. Lett.* **37**, 135 (1976).

- <sup>15</sup>E. Yabe, *Rev. Sci. Instrum.* **58**, 1 (1987); E. Yabe and R. Fukui, *Jpn. J. Appl. Phys.* **26**, 1179 (1987); A. Grob, J. J. Grob, and A. Golanski, *Nucl. Instrum. Methods Phys. Res. B* **19/20**, 55 (1987); A. Grouillet, *Vacuum* **39**, 163 (1989); J. C. Muller and P. Siffert, *Radiat. Effects* **63**, 81 (1982); A. Slaoui, F. Foulon, and P. Siffert, *J. Appl. Phys.* **67**, 6197 (1990).
- <sup>16</sup>N. Bartlett and B. W. McQuillan, in *Intercalation Chemistry*, edited by M. S. Whittingham and A. J. Jacobson (Academic, New York, 1982), p. 19; K. O. Christe and R. D. Wilson, *Inorg. Chem.* **28**, 4175 (1989).
- <sup>17</sup>B. J. Dalton, *J. Chem. Phys.* **54**, 4745 (1971).
- <sup>18</sup>R. Wyatt, J. T. Roberts, R. E. Wentz, and P. M. Wilt, *J. Chem. Phys.* **50**, 2552 (1969).
- <sup>19</sup>R. S. Berry, *J. Chem. Phys.* **32**, 933 (1960).
- <sup>20</sup>C. J. Marsden, *J. Chem. Phys.* **87**, 6626 (1987); *J. Chem. Soc. Chem. Commun.* **1984**, 401.
- <sup>21</sup>L. S. Bernstein, S. Abramowitz, and I. W. Levin, *J. Chem. Phys.* **64**, 3228 (1976).
- <sup>22</sup>A. A. Viggiano, R. A. Morris, F. Dale, J. F. Paulson, K. Giles, D. Smith, and T. Su, *J. Chem. Phys.* **93**, 1149 (1990).
- <sup>23</sup>D. Smith and N. G. Adams, *Adv. At. Mol. Phys.* **24**, 1 (1988).
- <sup>24</sup>N. M. Rodiguin and E. N. Rodiguina, *Consecutive Chemical Reactions*, English edition, edited by R. F. Schneider (Van Nostrand, Princeton, 1964), p. 9.
- <sup>25</sup>T. M. Miller, in *Handbook of Chemistry and Physics*, 74th ed., edited by D. R. Lide (Chemical Rubber, Boca Raton, 1993), p. 10-180 (electron affinities) and 10-192 (polarizabilities).
- <sup>26</sup>P. Kebarle and S. Chowdhury, *Chem. Rev.* **87**, 513 (1987).
- <sup>27</sup>P. W. Villalta and D. G. Leopold, *J. Chem. Phys.* **98**, 7730 (1993).
- <sup>28</sup>R. N. Compton and P. W. Reinhardt, *Chem. Phys. Lett.* **91**, 268 (1982).
- <sup>29</sup>E. P. Grimsrud, S. Chowdhury, and P. Kebarle, *J. Chem. Phys.* **83**, 1059 (1985).
- <sup>30</sup>T. Su, *J. Chem. Phys.* **89**, 5355 (1980); **88**, 4102 (1988); see also T. Su and W. J. Chesnavich, *ibid.* **76**, 5183 (1982).
- <sup>31</sup>The upper limit to the equilibrium constant leads to a lower limit to  $\Delta G^\circ$  of 0.22 eV for electron transfer from PF<sub>5</sub><sup>-</sup> to O<sub>2</sub> at 543 K. The entropy of the reaction is determined from the known entropies of O<sub>2</sub> and O<sub>2</sub><sup>-</sup> (Ref. 26); the entropy change for PF<sub>5</sub><sup>-</sup> to PF<sub>5</sub> is estimated from the ratio of the symmetry numbers ( $\sigma=4$  for PF<sub>5</sub><sup>-</sup> and  $\sigma=6$  for PF<sub>5</sub>) to yield the rotational entropy change, and from the loss of the twofold electronic multiplicity. (Insufficient data exist to make predictions about vibrational entropy changes between PF<sub>5</sub><sup>-</sup> and PF<sub>5</sub>; the change is assumed small.) Thus,  $T \Delta S$  is  $-0.026$  eV, and therefore  $\Delta H^\circ > 0.19$  eV. We assume that the heat capacity change for the PF<sub>5</sub>/PF<sub>5</sub><sup>-</sup> pair vs that for O<sub>2</sub>/O<sub>2</sub><sup>-</sup> between 0 and 543 K is small, allowing us to equate  $\Delta H^\circ$  to the difference in electron affinities (0 K) between PF<sub>5</sub> and O<sub>2</sub>.
- <sup>32</sup>M. J. Travers, D. C. Cowles, and G. B. Ellison, *Chem. Phys. Lett.* **164**, 449 (1989).
- <sup>33</sup>J. W. Larson and T. B. McMahon, *J. Am. Chem. Soc.* **107**, 766 (1985).
- <sup>34</sup>S. A. Sullivan and J. L. Beauchamp, *Inorg. Chem.* **17**, 1589 (1978).
- <sup>35</sup>J. W. Larson and T. B. McMahon, *J. Am. Chem. Soc.* **105**, 2944 (1983).

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