Electron Attachment to Ni(PF₃)₄ and Pt(PF₃)₄

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Abstract

An experimental study has been made of thermal electron attachment to the transition-metal phosphine compounds Ni(PF₃)₄ and Pt(PF₃)₄, using a flowing-afterglow Langmuir-probe apparatus. The electron attachment rate constant was found to increase with temperature for both compounds. In both cases, a PF₃ ligand is ejected upon electron attachment. Molecular structure calculations have been carried out to aid in understanding the electron attachment process.

1. Introduction

We have used a flowing afterglow Langmuir probe (FALP) apparatus to study electron attachment to metallic phosphines over the temperature range 300-450 K. (At higher temperatures, thermal decomposition of the reactant molecules was evident.) We are motivated by the fact that Pt(PF₃)₄ is one of the few gaseous forms of platinum and has been used to deposit platinum metal. The assumed mechanism in plasma vapor deposition is:

\[ \text{Pt(PF₃)}₄ + e^- \rightarrow \text{Pt(PF₃)}₃ + \text{PF₃} \]

followed by surface decomposition into Pt₄.

Electrons are initially attached into short-lived resonant states in the continuum. How do the ligands affect the low-lying states of the metal core? All metal carbonyls attach electrons at the gas kinetic rate. The metal-PF₃ compounds which we have examined do not. We wished to study the entire series Ni(PF₃)₄, Pd(PF₃)₄, and Pt(PF₃)₄, but Pd(PF₃)₄ is not very stable thermally.

2. Flowing-Afterglow Langmuir-Probe Experiment

The FALP apparatus is sketched in Fig. 1. Reactions take place in a weak plasma in a fast flow of helium carrier gas along the length of a flow tube. Knowing the velocity of the
flowing plasma allows us to convert the distance scale into a time scale and deduce reaction rate constants. In the FALP, a cylindrical, movable Langmuir probe is used to measure the electron density along the axis of the flow tube. In absence of an electron-attaching gas the only loss of electron density is through ambipolar diffusion to the walls of the flow tube. When an electron-attaching gas is present in the flow tube, the electron density decays much more rapidly, to the point where eventually a pure positive-ion/negative-ion plasma obtains. The FALP method, and this particular instrument at the U. S. Air Force Research Laboratory, have been described previously [1].

![Fig. 1. A sketch of the FALP apparatus.](image)

Helium gas flows in the FALP at typically 16 std. L min⁻¹, giving a bulk gas velocity of 63 m s⁻¹ in a flow tube of 3.6-cm radius, at 133 Pa pressure and room temperature. The electron/He⁺ source in the FALP is a 3.45-GHz microwave discharge at the upstream end of the flow tube. The discharge additionally creates metastable-excited He⁺, which are undesirable because suprathermal electrons would be released in the reaction zone when reactant neutrals are Penning ionized by the He⁺. Because of this, a small flow of 60 std. cm⁻³ min⁻¹ of Ar gas is injected into the flow tube 10 cm downstream of the discharge for the purpose of deexciting the He⁺ via Penning ionization with Ar, well ahead of the reaction zone. Electrons created in the discharge and in Penning ionization thermalize readily in the He carrier gas prior to the reaction zone. The Ar also removes He₂⁺ by ion-molecule reaction yielding Ar⁺. Thus, following Ar reaction the plasma consists of electrons, He⁺, and Ar⁺, undergoing ambipolar diffusion.

Halfway down the flow tube, the electron attaching gas under study is added through a 3-radial-needle port with a known flow rate resulting in a known concentration nᵣ in the flow tube. At this point, the electron density nₑ(0) has been adjusted to be in the range 0.8-3 x 10⁸ cm⁻³: small enough that nₑ(0) << nᵣ, so that first-order kinetics holds, and small enough that electron-ion recombination is negligible. (Thermal electron-ion recombination rate constants are only significant for molecular ions, such as those produced in ion-molecule reactions with the gas under study. However, since the recombination rate depends on the square of the plasma density, that rate is entirely negligible at the low plasma densities used in the electron attachment experiments, provided the electron attachment rate constant is larger than ca. 10⁻¹⁰ cm⁻³ s⁻¹.)

The decay in the electron density following addition of the gas under study is due to the coupled effects of ambipolar diffusion and electron attachment. The solution to the relevant rate equation is

\[ nₑ(t) = nₑ(0) (vₑ - vₑ)⁻¹ \left[ vₑ \exp(-vₑt) - vₑ \exp(-vₑt) \right], \]

where \( vₑ \) is the electron attachment frequency, \( vₑ \) is the diffusion loss frequency, and \( t \) is the reaction time. The electron attachment rate constant is \( kₑ \) and is equal to \( vₑ nₑ \). The
diffusion loss frequency $\nu_D$ is equal to the ambipolar diffusion coefficient divided by the square of the diffusion length characteristic of the apparatus, and is measured directly from the electron density decay along the flow tube axis in absence of the electron-attaching gas. The reaction time $t$ is the distance between the gas inlet port and the movable Langmuir probe, divided by the plasma velocity. The plasma velocity (typically 100 m/s) is measured by pulse-modulating the microwave discharge and timing the arrival of the disturbance on the Langmuir probe, at different distances in the reaction zone. The plasma velocity as measured on the flow tube axis is greater than the bulk gas velocity by a factor of about 1.6 because of the way the parabolic velocity profile of the gas in laminar flow overlaps the fundamental diffusion mode of the plasma.

The Langmuir probe in these experiments is 25 $\mu$m in diameter, 4 mm long, and is made of tungsten. The diameter is much smaller than the plasma sheath diameter as required by orbital-limited cylindrical probe theory. Furthermore, the He pressure is kept low enough (usually 133 Pa) that the collisionless-sheath condition is satisfied. The probe potential is swept from about -2 to 2 V around the local plasma potential, and the current collected is typically a few $\mu$A. The electron-attracting portion of the probe I-V characteristic is parabolic in shape, as indicated by probe theory. A plot of the square of the probe current yields a straight line; the slope of this line is readily determined and yields the electron density at the position of the probe along the axis of the flow tube. Hysteresis in the probe characteristic is eliminated by cleaning the probe in the plasma to white-hot appearance through application of a high bias voltage (100-200 V). We note that only relative electron densities are needed in electron attachment measurements, and the major uncertainty is the probe surface area. This uncertainty is mainly due to the question of where current collection terminates at the boundary between probe and a coaxial glass support. The relative electron density measurements are estimated uncertain to $\pm 10\%$. The absolute electron attachment results are estimated uncertain to $\pm 25\%$. The major uncertainty in the latter figure is measurement of the flow rates of the He, Ar, and electron-attaching gas. An example of the data obtained is shown in Fig. 2.

Fig. 2. Sample data for electron density decay with Ni(PF$_3$)$_4$ concentration of $1.2 \times 10^{10}$ cm$^{-5}$. The solid line through the data is a fit using Eq. (1) with $k_D = 1.05 \times 10^{-7}$ cm$^3$ s$^{-1}$ and $\nu_D = 521$ s$^{-1}$. The "positive ions" line is obtained from measurements of electron density in absence of an attaching gas. The "negative ions" line is the difference between the other two curves.
As electron attachment proceeds, the negative charge in the plasma becomes increasingly composed of negative ions. However, ambipolar diffusion is still determined by electron diffusion to the walls of the flow tube because of the high mobility of electrons. Negative ions are confined by the space charge field to the axial region of the flow tube as long as the electron density is at least 1/100th that of the negative ions. Eventually, the space charge field collapses and the plasma becomes a negative-ion/positive-ion plasma.

The data shown in Fig. 2 were obtained for a case where the negative ions are stable enough that thermal electron detachment will not take place at the temperatures of the measurement. If the electron detachment energy of the negative ion is low enough, thermal electron detachment will take place, and that process would have to be taken into account in the rate equations used to analyze the decay in the electron density [2].

At the downstream end of the flow tube there is an orifice leading to a high-vacuum region where an rf quadrupole mass spectrometer is used to determine the ion products and branching fractions of the electron attachment reactions studied.

3. Experimental Results

Both Ni(PF₃)₄ and Pt(PF₃)₄ attach electrons efficiently, with Ni(PF₃)₄ more so. The only attachment channels observed are:

\[
\text{Ni(PF₃)₄} + e^- \rightarrow \text{Ni(PF₃)}^+ + \text{PF₃},
\]
\[
\text{Pt(PF₃)₄} + e^- \rightarrow \text{Pt(PF₃)}^+ + \text{PF₃}.
\]

Rate constants for electron attachment to Ni(PF₃)₄ are shown in Fig. 3 in Arrhenius form.

![Arrhenius plot](image)

Fig. 3. The temperature dependence of the electron attachment rate constant may be described with an activation energy of 40 meV for Ni(PF₃)₄. This energy may be interpreted as the amount of vibrational energy needed to access a dissociation surface, or the endothermicity of the attachment reaction. Data for Ni(PF₃)₄ and Pt(PF₃)₄ will be compared at the Symposium.

Thermal decomposition of the compound on surfaces is evident in the difference between results obtained with the compounds diluted in He and PF₃. Even in PF₃, decomposition occurs at elevated temperatures, though Ni(PF₃)₄ is apparently more stable.
3. Calculations Using Density Functional Theory

We used the Gaussian-98W program package to investigate the molecular structures of neutral Ni(PF$_3$)$_4$, isolated PF$_3$, and neutral and anionic Ni(PF$_3$)$_3$ and to obtain estimates of the energetics of the electron attachment process. The Pt compound cannot be reliably treated at this time because a relativistic method is needed. Calculations of the total energies of the parent molecules and fragments were carried out using density functional theory, in particular Becke’s three parameter hybrid functional denoted by B3LYP, which includes the Lee, Yang, and Parr correlation functional, which contains both local and non-local terms [3].

The parent and fragment molecules were first geometry-optimized using the B3LYP/6-31G(d) functional and basis set, and a harmonic frequency analysis was performed at the same level of theory to give the zero-point energies (ZPE). The vibrational frequencies were scaled by the empirical factor 0.9613 in calculating both the ZPE and thermal corrections [4]. Next, single-point energies were calculated using the 6-311+G(3df) basis set and tight convergence of the SCF integrals. ZPE corrections were then applied to the total energies; both quantities are given in Table 1.

Table 1. Total energies and zero-point energies (ZPE) for Ni(PF$_3$)$_4$, Ni(PF$_3$)$_3$, Ni(PF$_3$)$_3^-$ and PF$_3$, all in hartree units.

<table>
<thead>
<tr>
<th>molecule</th>
<th>ZPE$^a$</th>
<th>total energy$^b$ (0 K)</th>
</tr>
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<tbody>
<tr>
<td>Ni(PF$_3$)$_4$</td>
<td>0.04065</td>
<td>-4072.91651</td>
</tr>
<tr>
<td>Ni(PF$_3$)$_3$</td>
<td>0.02998</td>
<td>-3431.75533</td>
</tr>
<tr>
<td>Ni(PF$_3$)$_3^-$</td>
<td>0.02907</td>
<td>-3431.82222</td>
</tr>
<tr>
<td>PF$_3$</td>
<td>0.00816</td>
<td>-641.127034</td>
</tr>
</tbody>
</table>

$^a$B3LYP/6-31G(d) level of theory, and scaled by 0.9613.
$^b$B3LYP/6-311+(3df)//B3LYP/6-31G(d) plus ZPE.

Derived quantities are given in Table 2. The adiabatic electron affinity of Ni(PF$_3$)$_3$ was calculated from the difference in 0 K total energies of Ni(PF$_3$)$_3$ and Ni(PF$_3$)$_3^-$. Bond strengths were calculated from differences in total energies of parent-molecule and the sum of fragment energies. The exothermicity for dissociative electron attachment (yielding Ni(PF$_3$)$_3^-$ product ion) was calculated from the total energies given in Table 1. We have calculations in progress for determining reaction enthalpy and bond dissociation enthalpies at 298 K and higher. Our own experience is that an uncertainty of ±0.3 eV is a reasonable estimate of the accuracy of this computational method [5], but we have not heretofore applied the method to such large molecules.
Table 2. Quantities derived from the 0 K energies in Table 1: the energy (ΔE) released in the dissociative electron attachment reaction, the electron affinity (EA) of the fragment molecule Ni(PF$_3$)$_3$, and the ligand bond energy ($D_0^0$) in Ni(PF$_3$)$_4$.

<table>
<thead>
<tr>
<th>quantity</th>
<th>energy (eV)</th>
</tr>
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<tbody>
<tr>
<td>ΔE</td>
<td>0.84</td>
</tr>
<tr>
<td>EA[Ni(PF$_3$)$_3$]</td>
<td>1.82</td>
</tr>
<tr>
<td>$D_0^0$[Ni(PF$_3$)$_3$—PF$_3$]</td>
<td>0.98</td>
</tr>
</tbody>
</table>

4. Conclusions

The FALP experiment confirms the expectation that Ni(PF$_3$)$_4$ and Pt(PF$_3$)$_4$ attach electrons dissociatively, throwing off a PF$_3$ ligand in the process. The process is very efficient, being roughly half the collisional rate at 298 K and increasing to the collisional rate at temperatures ca. 400 K. Decomposition of Ni(PF$_3$)$_4$ and Pt(PF$_3$)$_4$ was indicated in the data at elevated temperatures, as illustrated in Fig. 3. The calculations show that the electron attachment reaction for Ni(PF$_3$)$_4$ is exothermic, by 0.8 eV, meaning that the activation energy derived from the data in Fig. 3 is most likely interpreted as related to the energy given to the molecule by the incoming electron, enabling the system to reach a dissociation pathway. The calculated Ni(PF$_3$)$_3$—PF$_3$ bond energy is consistent with reactant decomposition being observed in the experiment at temperatures above 450 K; a more careful analysis will be carried out once the enthalpy computation has been completed for temperatures other than 0 K. The calculated EA[Ni(PF$_3$)$_3$] is consistent with lack of any electron detachment signature in the electron density decay data.

References