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Demonstration of the branching ratio inversion for the electron attachment to phosphoryl chloride POCl_3 in the gas phase between 300 and 200K

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Abstract

Electron attachment to phosphoryl chloride (phosphorus oxychloride) POCl_3 has been studied in the gas phase by mass spectrometry at several low temperatures (47.7, 74.5, 169.7 and 199.5K) with the CRESU method. By measuring over this temperature range and data from (11), we have demonstrated the inversion of the branching ratio between the exothermic non-dissociative exit channel POCl_3^- and the thermo-neutral dissociative exit channel $\text{POCl}_2^- + \text{Cl}$. A kinetic model in terms of statistical theory is used to fit the experimental data.

Keywords: Electron attachment – branching ratio

1. Introduction

Phosphorus oxychloride (POCl_3) is an organophorous compound widely used in several industrial processes including the synthesis of flame retardant and plasticizers for PVC (5), the chemical dehydration process to obtain nitrile from amide (1), the gas diffusion for the solar cells N-type silicon solar cells (8). However, from a more fundamental point of view, POCl_3 is a molecule that has proved to have a very interesting behaviour with respect to electron attachment. The reaction has been found (7) to have a large rate coefficient ($0.6 - 1.8 \times 10^{-7} \text{ cm}^3 \cdot \text{s}^{-1}$ in the range from 296-552 K), but what is particularly noteworthy is that the attachment products depend upon both pressure and temperature (18; 17).

The attachment process can be represented by the following dissociative processes:



all of which pass through an excited intermediate state POCl_3^* that subsequently dissociates. ΔE are the reaction enthalpies at 298 K from G3 model chemistry calculations(4). An additional non-dissociative exit channel is also possible:



where the excited intermediate state POCl_3^* is stabilized. This has been modeled and discussed in several experimental studies using a Flowing Afterglow Langmuir Probe (FALP), an ion mobility mass spectrometer apparatus, and also an electron beam experiment (18; 11; 12; 17). In swarm experiments, under low pressure conditions at temperature of between 300 and 600K, the dissociative attachment leading to a POCl_2^- product dominates representing more than 90% of the reaction. The non-dissociative attachment yielding POCl_3^- becomes more and more apparent as the ambient pressure is increased. At higher temperatures between 600 and 1200K, the other dissociative pathways open up yielding Cl^- which dominates above 1000K with a small contribution from Cl_2^- . POCl^- has been detected as a fragment product but only at higher electron energies in the beam experiment.

In this paper, we explore the electron attachment on POCl_3 in the gas phase, for a temperature range between 200 and 47.7K and for an electron energy near 0eV using the CRESU (Cinétique des Reactions en Ecoulement

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Supersonique Uniforme) apparatus. This experimental setup has previously been used in this laboratory for the study of electron attachment to CF_3Br , CF_2Cl_2 , SF_6 (6), CH_3I (15), HBr , HCl (14) and HI , DI (2). In the latter publication, evidence was presented that in the supersonic flow of the CRESU apparatus, the electron temperature is not in equilibrium with the nitrogen buffer gas temperature due to the presence of vibrationally excited N_2 ($v=1$) that can transfer energy to the electrons. Thus, the present experiments are not under true thermal equilibrium conditions, with the internal energy of the attaching molecules at the buffer gas temperature, but the electrons initially at an elevated temperature and undergoing thermalization on the time scale of the experiment. A detailed modeling of the electron temperatures in the experiment has been presented elsewhere (2). At pressures approaching 1 atm (18), stabilization (i.e. reaction (5)) dominates and the branching ratios for attachment to POCl_3 appear insensitive to electron energy over the range of 0.04 -0.33 eV. The present experiments are at much lower densities, where more interesting effects can be explored.

2. Experimental Method

The CRESU experiment has been described in detail elsewhere (9), only a brief description of this method illustrated by Figure 1 and details useful for understanding the present measurements are given here. The CRESU method consists of generating a supersonic uniform flow by the expansion of a buffer gas, here N_2 , through a Laval nozzle. The design of the Laval nozzle and its upstream and downstream pressures, maintained by a powerful pumping system (24,000 m^3/hour), determine the temperature, the density, and the speed of the flow. The present design of the apparatus allows for a temperature range of 20 - 300K. An important characteristic of the flow is its high density (10^{16} - 10^{17} molecule cm^{-3} depending on the Laval nozzle design and the pressure conditions), which ensures local thermodynamic equilibrium of the gas. This expansion is uniform in gas temperature, speed, and density over tens of centimeters which corresponds to a hydrodynamic time from about 100 to 1000 μs . This supersonic uniform flow can be regarded as a low temperature chemical reactor without walls, thus precluding condensation of the neutral species. The production of charged species is achieved with an electron beam crossing the neutral supersonic jet, a few millimeters downstream from the nozzle generating a weakly charged plasma (10^7 - 10^9 $\text{e}^- \text{cm}^{-3}$). The electrons and ions in that

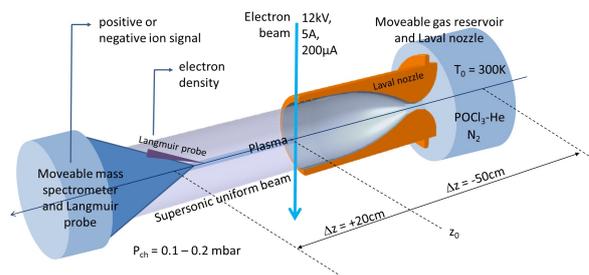


Figure 1: Supersonic cold uniform beam in the CRESU apparatus at Rennes.

plasma react with a neutral species, continuously introduced as a minority species into the buffer gas, to form anions and/or cations via collisional processes (charge transfer, dissociative electron attachment, etc.). The ions and electrons are monitored along the flow axis using a movable quadrupole mass spectrometer coupled with an electrostatic Langmuir probe constituted by a thin thoriated tungsten wire (25 μm diameter and 1.5 cm length).

The neutral reactant phosphoryl chloride POCl_3 was obtained from the Aldrich® (98% purity). The vapour pressure of POCl_3 , which is solid at room temperature, is sufficient to obtain a He - POCl_3 mixture with a dilution factor $f = 1.2 \times 10^{-4}$. This mixture is continuously injected into the reservoir via a flow controller with a typical flow rate of $Q_m = 0.1$ -0.2 standard liters per minute. The density of this neutral reactant is obtained using the following formulae:

$$[\text{POCl}_3] = n_{\text{tot}} \frac{Q_m}{Q_{\text{tot}}} f \quad (\text{molecule cm}^{-3}) \quad (6)$$

where $[\text{POCl}_3]$ is the injected POCl_3 density, n_{tot} is the total molecular beam density, and Q_{tot} is the total flow rate of all the injected gases in the experiment. The $[\text{POCl}_3]$ density is known with an accuracy of 5%.

3. Results and Discussion

Figure 2 shows normalized mass spectra for anions produced by non-dissociative attachment and dissociative attachment to POCl_3 . Measurements were made at three different temperatures 47.7, 74.5 and 199.5K at corresponding flow densities of 2.74, 1.67 and 5.29×10^{16} molecules/ cm^3 respectively and a neutral POCl_3 density of $2.3 \times 10^{11} \text{ cm}^{-3}$. Two sets of peaks have been observed between 0 and 200 Daltons and are primarily associated with the POCl_3^- and POCl_2^- exit channels (1) and (5) taking into account the major natural isotopes

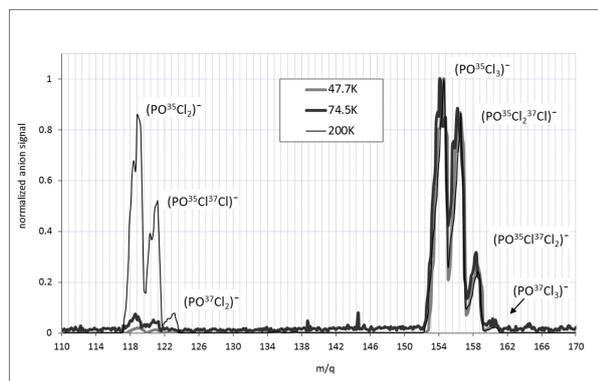


Figure 2: Normalized negative mass spectra for three different temperatures: 47.7, 74.5 and 199.5K. The typical density is about $n_{tot} = 10^{16}$ molecules cm^{-3} (see Table 1 for details) and the distance between the mass spectrometer and the electron beam is 9 cm.

of the chlorine atom ^{35}Cl and ^{37}Cl . We did not observe POCl^- , Cl^- , or Cl_2^- anions, which correspond to the exit channels (2) (3) and (4) products, consistent with the endothermicity ΔE of these reactions.

At lower temperatures, 74.5 and 47.7K, neutral clusters may be formed, however, these species lie above the observable 0 - 200 Dalton range of the mass spectrometer. A process which could contribute to the POCl_3^- signal is the dissociative electron attachment to $(\text{POCl}_3)_{n \geq 2}$ clusters: $(\text{POCl}_3)_n + e^- \rightarrow \text{POCl}_3^- + (\text{POCl}_3)_{n-1}$. Dissociative electron attachment to clusters is expected to be energetically more favourable than the studied non-dissociative attachment to POCl_3 (3) and could correspond to an additional source term for the evolution of the anion signal and a loss term for the electron density. To verify the absence of this process for both the 74.5K and 47.7K temperatures, we have monitored the electron density as a function of the Laval nozzle distance from the electron beam (see Figure 1) while injecting a large concentration $1 \times 10^{11} \text{ cm}^{-3}$ of POCl_3 . By moving the nozzle backwards, clusters would have more time to form in the supersonic beam before intersecting the electron beam. This would lead to a change in the electron density if they were present. The measured electron density was found to be constant for a Laval nozzle displacement of $\Delta z = -30$ cm, and therefore, cluster formation can be neglected.

Table 1 shows the proportions of anion signals at 47.7, 74.5, and 199.5K. Contrary to the situation at 199.5K, where competition between the two exit channels (1) and (5) is evident, at the lower temperatures there is a clear predominance of the non-dissociative exit channel (5).

Table 1: Proportions of POCl_2^- and POCl_3^- anion signals in this work. The gray lines are branching ratios from 4

T (K)	n_{tot} ($\times 10^{16}$ molecules. cm^{-3})	POCl_2^- (%)	POCl_3^- (%)	Cl_2^- (%)	Cl^- (%)
550	3.2	94	2	4	0.5
500	3.2	93	3.5	3	0.3
400	3.2	89	10	2	-
300	3.2	74	25	1.2	-
199.5	5.29	41	59	-	-
169.7	0.572	56	44	-	-
74.5	1.67	5	95	-	-
47.7	2.74	2	98	-	-

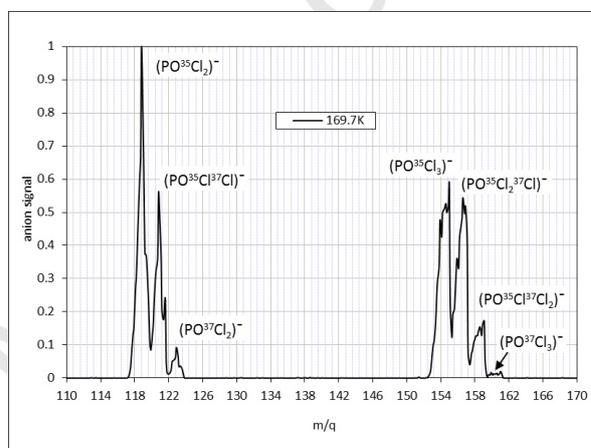


Figure 3: Normalized negative mass spectra for a molecular beam corresponding to a temperature $T=169.7\text{K}$ and a density $n_{tot} = 0.572 \times 10^{16}$ molecules/ cm^3 .

We have explored the density effect with an additional measurement which has been performed with a supersonic gas flow at 169.7K and a density lower by one order of magnitude, *i.e.* 0.572×10^{16} molecule cm^{-3} . The corresponding normalized mass spectrum for anions (Figure 3) shows that the fraction of the dissociative exit channel (1) is increased compared to the higher density data at the slightly higher temperature of 199.5K. This is qualitatively consistent with the need of a third body stabilization process for the non-dissociative channel (17). Note that the decrease in temperature from 200 to 170K will promote the non-dissociative exit channel over the dissociative one, all else being equal. That the dissociative channel is increased in the 170K data indicates that this effect is much smaller than the decrease in the non-dissociative channel due to the lowered density.

Figure 4 provides a comparison between the POCl_2^- and POCl_3^- anion signal proportions (%) obtained at

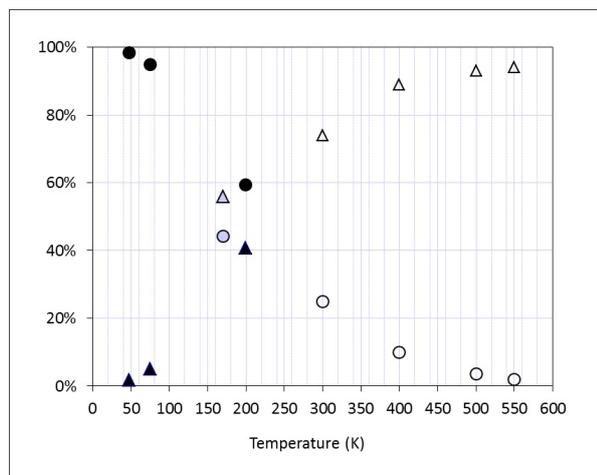


Figure 4: (●, ▲) Black full circles and triangles correspond to the observed POCl_3^- and POCl_2^- signal proportions (%) for the different temperatures 47.7, 74.5 and 199.5K. (○, △) Gray circles and triangles correspond to the POCl_3^- and POCl_2^- signal proportions respectively at 169.7K for which the density is lower, *i.e.* 0.572×10^{16} molecule. cm^{-3} . (○, △) Open circles and triangles are the POCl_3^- and POCl_2^- branching ratios from (11).

the 47.7, 74.5, 169.7 and 199.5K temperatures and the branching ratios of the exit channel (5) and (1) from (11).

Assuming that the quadrupole mass filter transmission is at least greater for the lighter anions and is independent of the temperature and considering that all the measurements have been performed under the same experimental detection conditions (same biasing on the electrostatic lens and same resolution), the signal proportion of POCl_3^- is probably underestimated compared to that for POCl_2^- . We deduced from these observations that the branching ratio inversion between the exit channels (5) and (1) occurs between 300 and 200K.

A temperature dependent branching ratio inversion has also been observed for the electron attachment reaction to CF_3 between 300 and 600K (13). The competition between the dissociative and a non-dissociative exit channels as a function of temperature and pressure were successfully analysed using a kinetic model. Details of the modeling have been presented elsewhere (11; 10; 16). A similar kinetic modeling approach has been previously applied to the system of interest here, electron attachment to POCl_3 , at temperatures between 300 - 1200K. We have extended the kinetic modeling to the temperature and pressure conditions here, using the system-dependent parameters previously determined from the higher temperature data and treating the

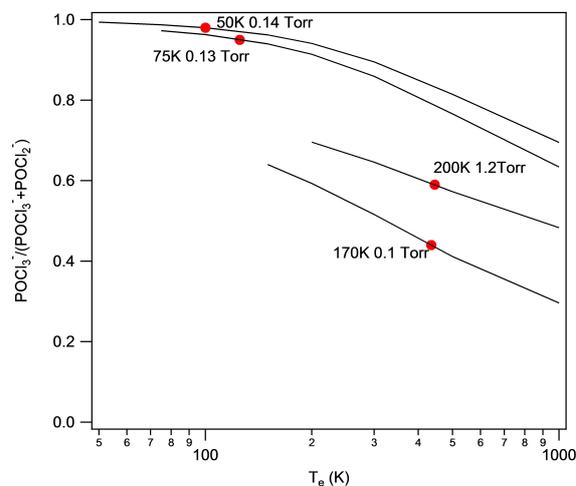


Figure 5: Non-dissociative branching fraction of attachment to POCl_3 (solid lines) from the kinetic model at the indicated densities and gas temperatures as a function of electron temperature. Full circles (●) are CRESU experimentally measured branching fractions at ill-defined electron temperatures and are plotted at the T_e where agreement with the modeling is best.

electron temperature as a variable parameter. The resulting branching ratios calculated using the model are presented in Figure 5 as a function of electron temperature. At 170 and 200K, the product branching fraction is a strong function of electron temperature, and the data is only explained by assuming electron temperatures of 450K. This value is in good agreement with prior results (2) indicating that the CRESU apparatus produces an initial electron temperature distribution of 500 - 1000K, which thermalizes on the timescale of the experiment. Note that the kinetic modeling was fairly constrained, and could only have reasonably explained a product branching fraction of 0.5-0.7 at 200K and of 0.35-0.65 at 170K. At the lower temperatures of 50 and 75K, the product branching fraction is dominated by the non-dissociative channel and is a weaker function of the electron temperature. The kinetic modeling can explain the observed data by assuming electron temperatures of 100 and 150K, respectively.

4. Conclusions

In this work we have demonstrated that a temperature dependent branching ratio inversion for the electron attachment to phosphoryl chloride POCl_3 in the gas phase between occurs 300 and 200K. This reaction leads to four dissociative exit channels including the thermoneutral dissociative $\text{POCl}_2^- + \text{Cl}$ channel and one exother-

mic non-dissociative POCl_3^- exit channel. In this latter process, the POCl_3^- anion formation requires a third body for its stabilization thus the pressure condition is fundamental. In this work, the POCl_2^- and POCl_3^- ion signals have been observed by mass spectrometry for several temperatures 47.7, 74.5 and 199.5K and a high density about few 10^{16} molecule/cm³. A kinetic model has been used to obtain the branching fraction of attachment to POCl_3 as a function of the electron temperature. It has been demonstrated that at very low temperature (47.7K), the non-dissociative exit channel predominates while as the temperature is increased, competition begins between the two exit channels. The data confirm that electron temperatures in the CRESU experiment are not thermalized, and is consistent with the previously modeled behavior of the electron temperature (2). The success of the kinetic modeling in explaining the present data suggests that its extrapolation is robust for temperatures down to 50K.

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Highlights

- Charged products from electron attachment reaction on POCl_3 in gas phase are observed by mass spectrometry;
- Temperature dependence of the corresponding exit channels is studied down to 47.7K;
- A kinetic model is used to fit the experimental data.

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