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Detection of PO, Cl and P from the Photodissociation of $POCl_3$ at 193 nm

Deirdre A. Belle-Oudry, Sunita Satyapal[a],

Thibaud Mussillon and Paul L. Houston*

Department of Chemistry
Cornell University
Ithaca, NY 14853-1301

Abstract

The photodissociation of $POCl_3$ has been investigated using the unfocussed radiation of an excimer operating at 193 nm. PO, P and Cl radicals were probed by resonance-enhanced multiphoton ionization (REMPI), and signal intensities were studied as a function of excimer laser power. The probe laser was found to produce a non-resonant PO^+ background signal in addition to the resonant ionization signal of neutral PO. A set of possible dissociation pathways has been postulated.

[a] Present address: United Technologies Research Center, East Hartford, CT 06108

1. Introduction

During the last three decades there have been numerous laser photolysis studies of a variety of small polyatomic molecules.[1-4] These studies have provided much information on energy equilibration, excited state lifetimes and product quantum yields as a function of photolysis wavelength. Although most simple organic polyatomic molecules have been studied in detail, there have been very few studies of phosphorus compounds. Because of recent interest in the disposal of organophosphorus pesticides and chemical weapons, there is a growing need for information on the decomposition and detection of phosphorus species. For example, on-site incineration has been recommended as the safest method for the destruction of thousands of tons of obsolete chemical warfare agents that are stored in eight continental US locations. However, little is known about the combustion process, and only a few methods have been devised for sensitive, real-time detection of the combustion products. One goal of the present work was to investigate detection schemes for such products.

A second goal was to investigate the photodissociation dynamics of phosphoryl chloride (phosphorus oxychloride) at 193 nm. To the best of our knowledge, there have been no studies on the photolysis of $POCl_3$ reported previously. Emission studies of flames containing this molecule have been performed,[5] and light absorption by $POCl_3$ has been reported to be nearly 100% for 35 torr in a 20 cm cell at wavelengths between 220 nm and 190 nm.[6] It appears that no other information on the gas phase absorption spectrum of $POCl_3$ is available, but it is reasonable to expect a strong contribution from the P=O chromophore and similarities with spectra of organophosphonates. Dimethyl methyl phosphonate (DMMP), for example, does not absorb between 200 nm and the near IR.[7] Phosphorus trihalides by comparison, absorb strongly below about 244 nm.[8]

The only phosphorus compounds studied in detail by laser photolysis are DMMP,[7,9,10] triethyl phosphite,[11] PBr_3,[8] and PCl_3.[8,12] PO radicals have been detected by LIF from the multiphoton dissociation of DMMP at 193 and 248 nm.[7,9] The absorption at 193 nm and subsequent dissociation of $POCl_3$ and DMMP may be similar. In this study we have detected PO, PO^+, P and Cl and see evidence of several channels occurring during the photolysis of $POCl_3$ at 193 nm.

2. Experimental

A stainless steel six-way cross vacuum chamber pumped by a Varian 6" diffusion pump served as the "cell" for the experiments. The pressure in the cell was 4×10^{-7} torr and increased to $1\text{-}2\times10^{-5}$ torr when the phosphoryl chloride (Aldrich, 99%, 28 torr vapor pressure at 20°C) was leaked into the chamber through a needle valve. The unfocussed output of a Lambda Physik EMG101 excimer laser was used to photolyze the molecules at 193 nm (ArF). The laser intensity varied between 0.5 and 4.5 mJ/cm^2.

The various photofragments (PO, P, and Cl) were probed using REMPI techniques. The REMPI wavelengths were generated by doubling the output of a Lumonics dye laser (HD-500) which was pumped by either the second harmonic (532 nm) or the third harmonic (355 nm) of a Spectra-Physics Nd:YAG laser. Doubling was accomplished using an Inrad autotracker equipped with a BBO crystal. For PO and P fragments, the dye used was a mixture of Rhodamine 610 and 640, which provided the desired output wavelength range of 300-315 nm. For probing Cl atoms, Coumarin 480 was used to produce light in the 233-247 nm region with a linewidth of 0.1 cm^{-1}. The probe and photolysis beams were counter-propagated through the cell. Probe laser focussing conditions were varied according to the fragment being detected.

Ions were detected using time-of-flight mass spectrometry (TOFMS). The mass spectrometer was of the Wiley-McLaren design.[13] The ionization region consisted of a 2" diameter repeller plate held at 2300 V, situated 1.27 cm below a grid held at 1700 V. This grid was positioned 1.27 cm below a second grid, held at ground potential. The ion drift tube (1.05 m in length) was positioned vertically above this second grid. After travelling up the flight tube, the ions hit the detector, a Johnston MM-1 electron multiplier. The output signal was sent through a preamplifier (gain=20) before being averaged in a computer which recorded the full mass spectrum of fragments. For the REMPI spectra, a boxcar was used to record the signal at a particular time-of-flight corresponding to the fragment of interest as the wavelength of the probe laser was varied. The excimer laser power dependence of particular fragments was measured by placing a series of attenuators in the excimer beam.

3. Results

Three different photofragments were observed in our study: Cl atoms, P atoms, and PO radicals. In its most general form, the process studied consists of two steps. In the first step, the excimer laser breaks one or more of the P-Cl bonds. Further dissociation and ionization of products may occur due to subsequent absorption of probe or pump laser photons. Measurement of the dependences of each of the photofragments on the power of the excimer laser can provide insight into the products formed in the first step. Figure 1 shows various possible dissociation channels and the photon energies required for each. Bond dissociation energies were calculated from refs. 14 and 15.

Detection of Cl and Cl_2

Ground state ($^2P_{3/2}$) and excited state ($^2P_{1/2}$) chlorine atoms were probed by (2+1) REMPI through transitions involving the 4p Rydberg state.[16] The probe beam was slightly defocussed using a 33 cm focal length lens to avoid fragmentation. It was found that with a tightly focussed probe beam, Cl was produced with the probe laser alone. The (2+1) REMPI spectrum of Cl was obtained between 233 and 238 nm. By slowly scanning over the 4p $^2P_{3/2} \leftarrow$ 3p $^2P_{3/2}$ resonance and monitoring the TOF signal at mass 35, the Doppler profile of Cl shown in Fig. 2 was obtained. The width of the Doppler profile was measured to be 0.36 cm^{-1}. This corresponds to an average translational energy of 0.64 eV for the Cl fragment assuming a Gaussian velocity distribution. However, because more than one Cl may be produced the translational energy does not provide conclusive information on the dynamics of the photodissociation. The Cl signal dependence on the excimer laser power appeared to be nearly quadratic, indicating that at least two excimer photons are absorbed by $POCl_3$ to produce Cl atoms.

The photodissociation of numerous chlorinated compounds has previously been investigated by different groups.[17-20] Some of these studies show that the production of Cl_2 in a highly excited electronic state[19,20] is a very likely channel at 193 nm for species containing two or more Cl atoms. We thus looked for molecular chlorine resulting from the photodissociation of $POCl_3$ using a (2+1) REMPI scheme.[21] The dye used was the same Rhodamine 610/640 mixture used to probe PO. The light was doubled, focussed in the center of the chamber with a 30 cm focal length lens, then scanned over the range of the dye between 300 and 315 nm. We were not able to detect any Cl_2 in this fashion, but the wavelength scanned enabled us to probe only the ground state. Although our study did not show evidence of Cl_2, we can not exclude the possibility of its being present in a long-lived excited state.

Detection of PO^+ and PO

The results of our study show that PO^+ is produced both by resonant ionization of PO and by another “non-resonant” channel. As long as both the photolysis and probe lasers were present, the signal at mass 47 corresponding to the PO^+ ion was seen at all probe laser wavelengths between 233 nm and 247 nm and between 304 nm and 310 nm. The observation that the non-resonant PO^+ signal depends on both lasers suggests that the first step involves absorption of 193 nm to produce an intermediate (possibly POCl or $POCl_2$) that subsequently absorbs the probe laser and dissociates to produce PO^+.

In order to obtain information on the absorption spectrum of the intermediate, we scanned the doubled dye laser in the 233-247 and 304-310 nm regions. The signal at mass 47 was continuous throughout these wavelength regions with broad peaks at 238 nm and 245 nm, but the signal increased sharply at resonances corresponding to REMPI of neutral PO. By using a Pellin Broca prism to separate the fundamental from the doubled light, we were able to verify that the doubled light was necessary for production of non-resonant PO^+.

The excimer laser power dependences of the resonant and non-resonant PO^+ signals were measured in the range 0.5 - 4.5 mJ/cm^2 (unfocussed). The resonant PO^+ signal varied with laser intensity as I^n, where the average dependence was with $n \approx 1.3$. For the non-resonant PO^+, $n = 1.5$ when measured with a 306.78 nm probe laser wavelength, for which there may still be some resonant signal contribution even though the probe wavelength was tuned off any of the major bandheads. However, when the 233.36 nm probe laser was used, the dependence was quadratic ($n = 2.0$). As discussed below, this observation seems to indicate that there are two different pathways giving rise to the resonant and non-resonant PO^+ signals.

Similar measurements were made for the probe laser power dependences of the two signals. The resonant signal was measured on the 5-3 transition at 306.63 nm, and the non-resonant contribution to this signal, which was measured at 306.78 nm, was subtracted to determine the "purely" resonant part at each laser power from 0.5 - 2.0 mJ using a 30 cm f.l. lens. The resonant PO^+ displayed a power dependence of about $n = 1.1$, while the non-resonant signal (measured at 306.78 nm) showed a quadratic dependence ($n = 2.0$). However, since the probe power may be very high due to the tight focussing conditions, we do not place too much emphasis on these measurements.

Figure 3 shows the (1+1) REMPI spectrum of PO probed through the $B^2\Sigma^+ \leftarrow X^2\Pi$ transition.[22] The spectrum shows the $4\leftarrow2$ and $5\leftarrow3$ vibrational bands, indicating some vibrational excitation in the PO products. The $4\leftarrow2$ bands of both ground state PO ($^2\Pi_{1/2}$) and the excited spin-orbit state ($^2\Pi_{3/2}$) were observed. We were unable to probe lower vibrational levels (v=0,1) in our experiment, because two-photon excitation in this wavelength region is not sufficient to ionize PO.

Detection of P Atoms

A significant signal at mass 31 corresponding to phosphorus atoms was observed at particular wavelengths of the probe laser. While 2+1 REMPI transitions had been observed in this region on unspecified transitions,[23] they were reported only after this work was begun.[24] Figure 4 shows a sample REMPI spectrum of P atoms in the 303.5-306 nm region. The P atom signal was seen with the excimer unfocussed and focussed (as in the spectrum of the figure). Under tight focusing conditions, appreciable P^+ signal is present when only the probe laser and not the excimer laser is on, indicating that the doubled dye light also dissociates the $POCl_3$. While the largest peaks in the spectrum correspond to transitions from the ground state, $3p^4S_{3/2}$, to the $4p^4D_{x/2}$ (x=1,3,5,7) Rydberg states,[25,26] some very small REMPI peaks corresponding to transitions from the $3p^2D_{5/2,3/2}$ to the $5p^2P_{3/2,1/2}$ states[25,26] also appeared only when both lasers were on, indicating that some excited state P atoms are produced in a channel which involves the excimer laser. The excimer laser power dependence of the P atom signal was very similar to that of the resonant PO^+ signal.

4. Discussion

Figure 5 shows a possible, though by no means unique, dissociation mechanism consistent with our results. In the first step, if $POCl_3$ absorbs one 193 nm photon, there is sufficient energy to produce either $POCl_2$ or POCl (see Fig. 1). The production of PO requires at least one more photon from either the pump or probe laser. We hypothesize two routes to PO^+ because this species is produced both resonantly by the probe laser with a low-order dependence on the pump laser power ($n \approx 1.3$) and non-resonantly by the probe laser with a quadratic dependence on the pump laser power. We will call the two routes implicated by these different power dependences the resonant route and the non-resonant route.

Resonant Production of PO^+

The resonant route must have a PO intermediate in order to carry out the resonant 1+1 ionization signal for this species. Because the resonant signal depends nearly linearly on the power of the pump laser and because three more ~307-nm photons are required to reach PO^+, we look first for a route to PO^+ involving production of PO by one 193-nm photon and one ~307-nm photon. PO ionization would then follow via the 1+1 process involving two ~307-nm photons. It is possible that the second photon needed to produce PO is a 193-nm photon, but in either case, this second photon absorption must be saturated ($n < 2$). For the 193-nm photon, saturation follows from the observed power dependence ($n \approx 1.3$), whereas for the ~307-nm photon saturation follows from the observed nearly linear power dependence on this 1+1 transition. We assume that the saturated step involves POCl; that is, that this step is $POCl + h\nu \rightarrow PO + Cl$. Our reasoning is that the only other possible intermediate is $POCl_2$, and that either $POCl_2 \rightarrow PO + Cl_2$ or $POCl_2 \rightarrow PO + 2\ Cl$ is likely to require absorption of two photons, whereas $POCl \rightarrow PO + Cl$ requires only one. The mechanism just described thus gives the resonant branch on the left-hand side of Fig. 5. Although P^+ is produced from the probe laser alone, the P^+ signal that was due to the excimer had a nearly linear pump laser power dependence, similar to that of PO^+. We assume that P^+ is produced by ~305-nm dissociation of PO followed by 2+1 ionization in this wavelength region.

Non-resonant Production of PO^+

The non-resonant route cannot involve a PO intermediate because PO^+ is observed at wavelengths that do not ionize PO by REMPI. Neither $POCl^+$ nor $POCl_2^+$ is observed in the mass spectrum, so either it is unlikely that PO^+ is produced by fragmentation of these species or these species must be extremely short-lived. The most likely final route to the non-resonant PO^+ is $POCl + 3\ h\nu_{probe} \rightarrow PO^+ + Cl + e^-$ (or $PO^+ + Cl^-$). The non-resonant PO^+ production probably involves at least two 193-nm photons in order to have the observed dependence on the pump laser power ($n = 1.5, 2.0$). Thus, a plausible sequence is $POCl_3 + h\nu(\lambda=193\ nm) \rightarrow POCl_2 + Cl$; $POCl_2 + h\nu(\lambda=193\ nm) \rightarrow POCl^‡$; $POCl^‡ + (2\text{-}3)\ h\nu_{probe} \rightarrow PO^+ + Cl + e^-$, as shown on the right-hand side of Fig. 5. Here, $POCl^‡$ is distinct from $POCl^*$ in the resonant route and denotes POCl in a long-lived electronically or vibrationally excited state. Note that the non-resonant PO^+ was observed for probe wavelengths of both ~307 nm and ~235 nm, so that the final step in the process must have a rather broad spectrum. In fact, broad peaks at 238 and 245 nm were observed in the spectrum. Unfortunately, there is no other conclusive information to our knowledge on the absorption spectrum of either POCl or $POCl_2$.[27,28]

A qualitative comparison of the importance of the resonant and non-resonant channels can be made from the relative intensities of the respective PO^+ signals. The non-resonant PO^+ signal represents a current indicative of a certain number of PO^+ ions. The resonant PO^+ signal appears above this background, and the band heads we have observed are roughly twice as strong as the non-resonant background (see Fig. 4). Because the resonant ionization efficiency for PO is less than unity, our observation implies that there must be at least as many PO neutral radicals as there are non-resonant PO^+ ions. According to this result, the channel shown on the left-hand side of Fig. 5 is most probably the dominant channel at the laser intensities we have used.

While the mechanism of Fig. 5 plausibly accounts for our observations, other possibilities might still exist. One possibility we have not discussed is the production of Cl_2. We are reasonably confident from our measurements that if produced, the Cl_2 is not in its lowest vibrational state. Nor have we addressed the possible *coherent* two-photon absorption by $POCl_3$ of the 193-nm light. The Cl REMPI signal showed a puzzling quadratic dependence on the excimer laser power. If the resonant route is the dominant channel as we have argued, one might have expected a linear dependence, similar to that for the resonant PO^+. However, it is still possible that the first step in the dissociation produces Cl_2 rather than 2 Cl, and that the quadratic power dependence arises because 2/3 of the Cl atoms are actually produced by Cl_2 absorption of a second 193-nm photon. Similar processes have been proposed for other systems in which Cl atoms are produced.[19,20] Thus, several questions about the dissociation of this molecule remain to be answered.

5. Conclusion

PO, P and Cl radicals are observed following photolysis of $POCl_3$ at 193 nm. All three species have been probed by resonance-enhanced multiphoton ionization (REMPI). The Doppler profile of the Cl atoms indicates that they appear with an average translational energy of 0.64 eV. Two routes to the observed PO^+ were indicated by differing dependences on the excimer laser power. A resonant ionization signal was observed corresponding to known PO transitions. A non-resonant ionization signal was also observed in the range from 233-247 nm. A plausible mechanism has been proposed to account for the results.

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Figure Captions

Figure 1. Relative energies of potential fragment combinations produced in the photodissociation of $POCl_3$ at 193 nm. Arrows indicate energies of photolysis and probe photons and are drawn to scale.

Figure 2. Doppler profile of the $4p^2P_{3/2} \leftarrow 3p^2P_{3/2}$ transition of Cl produced in the photolysis of $POCl_3$. The width of the fitted Gaussian is 0.36 cm^{-1}, corresponding to an average translational energy of 0.64 eV.

Figure 3. (1+1) REMPI spectrum of the PO radical through the $B^2\Sigma \leftarrow X^2\Pi_{1/2,3/2}$ transition. PO was probed in the v"=2 and v"=3 levels of the ground electronic state using the $4 \leftarrow 2$ and $5 \leftarrow 3$ transitions. Bandhead values agree quite well with those in reference 22.

Figure 4. (2+1) REMPI spectrum of phosphorus. The four largest peaks correspond to transitions from the ground state ($3p^4S_{3/2}$) to $4p^4D_j$ Rydberg levels indicated. The small peaks are due to excited state phosphorus ($3p^2D_{5/2,3/2}$) transitions to $5p^2P_{1/2,3/2}$ levels. Wavelength values agree with those in reference 24 to within 0.01 nm.

Figure 5. One plausible mechanism for the dissociation of $POCl_3$ at 193 nm using the probe laser wavelengths indicated in the text. The dotted lines show radiationless processes.