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Citation: The Journal of Chemical Physics **109**, 578 (1998); doi: 10.1063/1.476594 View online: http://dx.doi.org/10.1063/1.476594 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/109/2?ver=pdfcov Published by the AIP Publishing

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Electron attachment to PCI₃ and POCI₃, 296–552 K

Thomas M. Miller,^{a)} John V. Seeley,^{b)} W. B. Knighton,^{c)} Roger F. Meads,^{d)} A. A. Viggiano, and Robert A. Morris *Air Force Research Laboratory, Space Vehicles Directorate/VSBP, 29 Randolph Road, Hanscom Air Force Base, Massachusetts 01731-3010*

Jane M. Van Doren

Department of Chemistry, College of the Holy Cross, 1 College Street, Worcester, Massachusetts 01610-2395

Jiande Gu and Henry F. Schaefer III

Center for Computational Quantum Chemistry, University of Georgia, Athens, Georgia 30602

(Received 2 February 1998; accepted 2 April 1998)

Rate constants for electron attachment to PCl₃ and POCl₃ have been measured over the temperature range 296–552 K in 135 Pa of helium gas, using a flowing-afterglow Langmuir-probe apparatus. Electron attachment to PCl₃ is dissociative, producing only Cl⁻ ions in this temperature range. The rate constant is $6.4 \pm 1.6 \times 10^{-8}$ cm³ s⁻¹ at 296 K and increases with temperature in a way that may be described by an activation energy of 43 ± 10 meV. Electron attachment to POCl₃ is a richer process in which a nondissociative channel (POCl₃⁻) competes with two dissociative ones (POCl₂⁻ and Cl⁻). The rate constant for electron attachment to POCl₃ is $1.8\pm0.4\times10^{-7}$ cm³ s⁻¹ at 296 K and is relatively temperature independent in our temperature range. POCl₂⁻ is the major product over the entire temperature range. *Ab initio* MP2 and MP4 calculations have been carried out on ground-state neutral and anionic PCl_n and POCl_n for n=1-3. The calculated adiabatic electron affinities agree with experimental estimates where available. The calculations yield C_{3v} structural symmetries for PCl₃ and POCl₃, and C_s symmetries for PCl₃⁻ and POCl₃⁻. The degree of distortion between the respective neutrals and anions is explored in the calculations, and the implications for electron attachment reactions are outlined. © *1998 American Institute of Physics*. [S0021-9606(98)02726-3]

INTRODUCTION

The solution phase chemistry of phosphorous trichloride and phosphoryl chloride is well characterized as these molecules are used in a number of industrial processes including the synthesis of important organophosphorous compounds,¹ such as flame retardants, plasticizers, insecticides, and fuel additives.² In contrast, the gas phase chemistry of PCl₃ and POCl₃, including the ion-molecule and electron-molecule reactions, has not been well studied despite the fact that the pure substances have relatively high vapor pressures. The gas phase structures of the neutral molecules are known: PCl₃ is pyramidal while gas phase POCl₃ is a distorted tetrahedron in which the PCl₃ group is pyramidal.^{3,4} The formation of positive and negative ions by electron bombardment on PCl₃ and POCl₃ was studied in the 1960s by Halmann and Klein.⁵ A decade later, Mathur et al.⁶ carried out a crossed beam experiment in which PCl₃ or POCl₃ molecules collided with energetic Cs atoms. From the thresholds for production of various negative ions, Mathur et al. were

^{b)}Air Force Geophysics Scholar, 1995–1997. Present address: Department of Chemistry, Oakland University, Rochester, MI 48309-4401. able to determine the electron affinities of PCl₃ (0.82 eV), POCl₃ (1.41 eV), and POCl₂ (3.83 eV) within an uncertainty of about 0.15 eV. More recently, our laboratory undertook a study of the reactivity of POCl₃ with a variety of negative ions.⁷ In the present work, we have investigated the reactivity of PCl₃ and POCl₃ with thermal electrons, measuring rate constants and product branching ratios over the temperature range 296–552 K. We have also calculated the structures and energies of neutral and anionic PCl_n and POCl_n, seeking information on the energetics of dissociative electron attachment and clues about the role played in the attachment process by geometry changes induced by the added electron.

EXPERIMENT

The present measurements utilized a flowing-afterglow Langmuir-probe (FALP) apparatus. The apparatus and technique have been discussed in detail in the literature.^{8,9} A weak electron-He⁺, -Ar⁺ plasma (10^9 cm^{-3}) is generated in a fast flow of He buffer gas (a plasma velocity of 10^4 cm s^{-1} , measured by timing the propagation along the flow tube axis of a pulse disturbance of the electron density). The decay in electron density was measured along the axis of the flow tube with a movable Langmuir probe before and after introduction of an electron-attaching gas at a level of 200–500 ppb. The data were fit to the solution of the rate equation governing the coupled effects of ambipolar diffu-

^{a)}Under contract (F19628-95-C-0020) to Visidyne, Inc., Burlington, MA.

^{c)}AFOSR University Resident Research Program participant, 1996. Permanent address: Department of Chemistry, Montana State University, Bozeman, MT 59717.

^{d)}Under contract to Wentworth Institute of Technology, Boston, MA.

TABLE I. Measured rate constants k_a for electron attachment to PCl₃ and POCl₃, accurate to ±25%. The branching fractions for the ion products of attachment to POCl₃ are also given in the table. Attachment to PCl₃ yields solely Cl⁻ ions in the temperature range indicated.

	PCl ₃	POCl ₃	Branching fractions for e^- + POCl ₃ products		
T (K)	$(10^{-7} \text{ cm}^3 \text{ s}^{-1})$	$(10^{-7} \text{ cm}^3 \text{ s}^{-1})$	$POCl_3^-$	$POCl_2^-$	Cl^{-}
296	0.64	1.8	0.29	0.70	0.006
372	0.91	2.1	0.14	0.85	0.014
457	1.1	1.8	0.06	0.91	0.03
552	1.4	1.5	0.01	0.94	0.05

sion and electron attachment^{8,9} to give the electron attachment rate constant. The use of PCl₃ and POCl₃ offered no special problems. PCl3 and POCl3 were used as obtained from the manufacturer¹⁰ without further purification aside from several freeze-pump-thaw cycles to outgas the samples. Because very low concentrations of reactant are needed in the experiment, mixtures of typically 0.26% PCl₃ or POCl₃ in liquid-nitrogen-purified He gas were made immediately prior to use. No "stickiness" or passivation problems were observed. These mixtures allow the reactant flowmeters¹¹ to be operated in a range where they are most accurate. An additional benefit of the dilute mixtures comes about because the flowmeters are calibrated for He gas, and no correction is needed for such low fractions of trace reactant gas. The FALP apparatus was operated at 135 Pa (1 Torr) helium buffer pressure at all temperatures.

The rate constants are considered accurate to $\pm 25\%$.^{8,9} The relative uncertainty is approximately $\pm 15\%$. (Only relative values of the electron densities are needed for the determination of the electron attachment rate constant, provided that the electron densities are low enough that electron–ion recombination may be ignored.) Periodically, measurements were made for electron attachment to SF₆ for comparison with accurately known rate constants.^{9,12}

EXPERIMENTAL RESULTS

Table I gives the rate constants measured for electron attachment to PCl_3 and $POCl_3$. Attachment to PCl_3 is dissociative, yielding Cl^- ionic product over the temperature range 296–552 K:

$$e^{-} + \mathrm{PCl}_{3} \rightarrow \mathrm{Cl}^{-} + \mathrm{PCl}_{2} + 0.33 \,\mathrm{eV}. \tag{1}$$

Formation of the parent ion PCl_3^- is exothermic by 0.8 eV, but this channel is not observed in the present work. At 296 K, the attachment mass spectrum shows additionally PCl_4^- as a result of Cl⁻ clustering with PCl_3 . This ion-molecule reaction is almost negligible at 383 K with the very low PCl_3 concentrations used in the electron attachment work, and imperceptible at still higher temperatures. The mass spectra also show small (1%) amounts of $POCl_2^-$ and $POCl_3^-$ which we take to indicate the presence of trace oxygen in the He buffer gas in the flow tube, despite liquid-nitrogen trapping of the He gas. The attachment results for PCl_3 contrast with those for PF_3 ,¹³ for which thermal electron attachment is endothermic. The electron attachment rate constants for PCl₃ are plotted versus 1/kT in Fig. 1. Over the temperature range 296– 552 K the data may be described by an activation energy of 43 ± 10 meV. The fitted line in Fig. 1 is given by

$$k_a(\text{PCl}_3) = 3.4 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1} \exp(-0.043 \text{ eV/kT}).$$
 (2)

The prefactor in this expression is essentially identical to the collisional rate constant calculated from a Maxwell–Boltzmann average at 296 K of the theoretical s-wave capture cross section of Klots:¹⁴

$$\sigma_{\rm cap} = (\pi a_0^2 / 2E) \{ 1 - \exp[-(32\alpha E)^{1/2}] \},$$
(3)

though there is no reason, in principle, that it must be. In Eq. (3) a_0 is the Bohr radius, *E* is the electron energy (in hartrees), and α is the molecular polarizability (in a_0^3 , from Ref. 15). A comparison of the measured and collisional rate constants implies that attachment to PCl₃ occurs on one out of every six collisions, on average, at 296 K. The dipole moment (0.56 D for PCl₃ and 2.54 D for POCl₃)¹⁶ affects the collisional rate constant for PCl₃ by less than 1%, and at the level of several percent for POCl₃.¹⁷

Electron attachment to POCl₃ gives three ionic products in the same temperature range:



FIG. 1. Arrhenius plot for electron attachment to PCl₃. The slope of the fitted line is -42.9 ± 0.8 meV, but considering the statistical uncertainty in the measurements, an activation energy of 43 ± 10 meV is appropriate.



FIG. 2. Arrhenius plot for the two dissociative channels observed in electron attachment to POCl₃. The slopes of the fitted lines are -16 ± 2 meV (POCl₂⁻) and -118 ± 11 meV (Cl⁻). Considering the statistical uncertainties in the data, activation energies of 16 ± 5 meV and 120 ± 40 meV, respectively, are appropriate.

$$\rightarrow \text{POCl}_3^- + 1.41 \text{ eV}$$
 (4a)

 $e^- + \text{POCl}_3 \rightarrow \text{POCl}_2^- + \text{Cl} + 0.32 \text{ eV}$ (4b)

$$\rightarrow \text{Cl}^- + \text{POCl}_2 + 0.10 \text{ eV}. \tag{4c}$$

The reaction enthalpies for the electron attachment product channels for PCl_3 and $POCl_3$ were calculated from results reported in Ref. 6 and do not include the thermal energy of the electron. The uncertainties in the exothermicities are typically 0.15 eV.

The measured rate constants for electron attachment to $POCl_3$ show little dependence on temperature within experimental uncertainty. The decrease observed at our highest temperature is likely that predicted by Eq. (3). Attachment to $POCl_3$ is seen to occur in one of every two collisions at 296 K.

Branching fractions for reaction (4) are given in Table I for the temperatures at which electron attachment rate constants were measured. Branching fractions were obtained at 68 and 135 Pa buffer gas pressures, and the results are shown in Fig. 2. A possible pressure dependence in the Cl⁻ branching fraction is evident in the figure, but the branching fractions are so small that we hesitate to make much of the difference between the 68 and 135 Pa results. Branching fractions for the two dissociative attachment channels, (4b) and (4c), were found to increase with temperature, while the branching fraction for the nondissociative channel decreased with temperature. Over our entire temperature range the $POCl_2^-$ ion product was dominant. The branching fractions for the two dissociative channels (4b) and (4c) were modeled as Arrhenius-type processes as shown in Fig. 2, combining data at 68 and 135 Pa, with the results (296–552 K)

fraction $(POCl_2^-) = 1.4 \exp(-0.016 \text{ eV/kT}),$ (5)

fraction
$$(Cl^{-})=0.6 \exp(-0.120 \text{ eV/kT}).$$
 (6)

Since the total rate constant for reaction (4) is temperature independent (within our experimental uncertainty), the energies in expressions (5) and (6) may be taken as apparent activation energies for the two product channels. Thus, there is a small activation energy $(16\pm 5 \text{ meV})$ for process (4b), production of $POCl_2^-$. This process is exothermic by 0.32 eV according to the results of Ref. 6, with an uncertainty of +0.10/-0.25 eV. Similarly, process (4c), production of Cl⁻, is exothermic by 0.10 eV according to the results of Ref. 6, with an uncertainty of +0.10/-0.30 eV. Ab initio calculations to be described below indicate that reaction (4c) is endothermic by 0.09 eV; unfortunately, the calculations are only accurate to about 0.5 eV. The uncertainties in either determination of the reaction enthalpy are such that the 120 ± 40 meV activation energy [Eq. (6)] observed in the present work may represent an endothermicity, although activation energies in electron attachment are common even for exothermic processes.

There have been no previous measurements of electron attachment rate constants for PCl₃ and POCl₃, but the formation of negative ions upon electron bombardment of these gases was studied by Halmann and Klein⁵ in the 1960s. They found Cl⁻ ionic product from attachment to both PCl₃ and POCl₃, peaked at 50 ± 50 meV electron energy. PCl₂⁻ from POCl₃ was observed at 400 ± 400 meV electron energy. Their observations for PCl₃ are in agreement with the present work, but that for POCl₃ is not. We note, however, that Halmann and Klein's electron energies exceeded ours, and their gas pressures were far lower than ours, so a direct comparison of ion products may be misleading. On the other hand, Halmann and Klein themselves noted that finding PCl₂⁻ from POCl₃ is an unlikely turn of events.

AB INITIO CALCULATIONS

Ab initio calculations were carried out on neutrals and anions relevant to the present work in order to provide an understanding of the structural and energetic changes which occur upon addition of an electron to PCl₃ and POCl₃. The results of these calculations provide information about relative positioning of the potential energy surfaces for PCl₃ and POCl₃ including adiabatic and vertical electron attachment energies, vertical detachment energies of PCl₃⁻ and POCl₃⁻, and the energy of dissociation products relative to reactants. These results are compared to experimental data (Ref. 6) where possible. For completeness, the calculations included smaller molecules (e.g., PCl) uninvolved in the present experiments except for estimating reaction enthalpies for energetically closed channels. Below is given a general description of the calculations. In two cases, convergence problems required a higher level of theory to be used, and these exceptions are noted in the tables (footnote a of Table IV and footnote b of Table V). The calculations were performed on several computers: a 200 MHz Micron-PC based on the Pentium-Pro processor at AFRL, an IBM SP-2 at the AFRL High Performance Computing Center at Maui, and IBM RS/ 6000 machines at the CCQC of the University of Georgia.

The GAUSSIAN 94 package¹⁸ of molecular structure programs was used to calculate the geometries of neutral and anionic PCl_n and POCl_n at the MP2(Full)/6-311+G(d) level of theory. These results are given in Table II, and in Fig. 3



FIG. 3. Sketches of the neutral and anionic MP2(Full)/6-311+G(d) structures of PCl₃ and POCl₃. The Cl atoms are labeled with superscripts for identification with the bond lengths and angles given in Table II and charges given in Table III.

for the PCl₃ and POCl₃ systems. In these calculations the molecules were not confined to any particular symmetry, but if bond lengths or angles came out to be the same within the precision given in Table II, they are grouped together to simplify the table. Table III presents results from a natural population analysis^{18,19} (NPA) of the MP2 electron densities to tell, within the NPA model, where the "extra" electron on the anion resides. Energies of these same neutral and anionic species were calculated at the MP4/6-311+G(d) level using the MP2 geometries. Hartree–Fock calculations [HF/6-311 + G(d)] were performed to determine zero-point energy (ZPE) corrections. It is common to multiply the HF ZPEs by an empirical factor¹⁹ of approximately 0.9, but we chose not to do so because such scaling only amounted to about 3 meV

correction to the energy differences needed in the present work. The results of the energy calculations are given in Table IV. Finally, Table V presents adiabatic electron affinities (EAs), vertical electron attachment energies, and vertical electron detachment energies calculated at the MP4/6-311 +G(d) level of theory. The vertical electron attachment energy is defined as the energy of the neutral molecule at its equilibrium geometry minus the energy of the corresponding anion evaluated at the equilibrium geometry of the neutral. The vertical detachment energy is defined as the energy of the neutral molecule evaluated at the equilibrium geometry of the anion, minus the energy of the anion at its equilibrium geometry. Figure 4 shows estimated potential energy curves for the POCl₃ system to illustrate the vertical energies. The vertical attachment and detachment energies in Table IV include ZPE correction for the neutral molecule in the case of attachment, and the anion in the case of detachment. The vertical attachment energies were calculated to give us an idea of where the anion potential surface intersects that of the neutral, if at all. The vertical detachment energy was calculated to give us a feeling for the degree of structural distortion between neutral and anion, in energy units.

The calculated adiabatic EAs (Table V) agree with those for PCl₃, POCl₃, and POCl₂ determined from collisional ionization measurements⁶ within experimental and estimated calculational uncertainty. Interestingly, the calculated EAs for the PCl_n do not show the odd/even oscillation in magnitude noted strikingly for the SF_n series,⁹ and somewhat for the PF_n series.^{13,20} The NPA data (Table III) on where the "extra" electron is placed to form the ground state anion show that in both PCl₃⁻ and POCl₃⁻ 80% of the extra negative charge is localized on the Cl atoms. In contrast, the extra negative charge is localized more on the P atom (53–73%) than on the Cl atoms in PCl₂⁻, PCl⁻, and POCl⁻¹. In all of the POCl_n species the O atom is largely a spectator to the attachment process: its charge and bond length (to P) hardly

TABLE II. Equilibrium geometries for PCl_n and POCl_n neutrals and anions calculated at the MP2(Full)/6-311+G(d) level of theory. The Cl atoms are labeled with a superscript where needed (to cross reference bond lengths and angles). No symmetry was assumed in the calculations, but if bond lengths or angles came out equal within the precision quoted below, they are combined to simplify the table. Dihedral angles are viewed along the P–Cl¹ axis in PCl₃ and along the O–P axis in POCl₃. The bond lengths are in Å and bond angles are in degrees.

Molecule	Calculated structure
PCl ₃	$r(P-Cl^{1})=2.0579, r(P-Cl^{2,3})=2.0573, angle(Cl^{1}-P-Cl^{2,3})=100.82$
	dihedral(Cl ² ,Cl ³) = 103.37 r(P, Cl ¹) = 2.0060, r(P, Cl ^{2,3}) = 2.2842, angle(Cl, P, Cl ^{2,3}) = 02.81
rCl ₃	$(Cl^2, Cl^3) = 162.19$
PCl ₂	r(P-Cl) = 2.0497, angle(Cl-P-Cl) = 101.99
PCl_2^-	r(P-Cl) = 2.1753, angle(Cl-P-Cl) = 98.84
PCl	r = 2.0166
PC1 ⁻	r = 2.1936
POCl ₃	$r(O-P) = 1.4642$, $r(P-Cl^{1,3}) = 2.0105$, $r(P-Cl^2) = 2.0104$, angle $(O-P-Cl^1) = 114.89$,
	$angle(O-P-Cl^2) = 114.85$, $angle(O-P-Cl^3) = 114.93$,
	dihedral(Cl^{1}, Cl^{2}) = 119.97, dihedral(Cl^{1}, Cl^{3}) = -120.03
$POCl_3^-$	$r(O-P) = 1.4811$, $r(P-Cl^1) = 2.1633$, $r(P-Cl^{2.3}) = 2.3081$, angle $(O-P-Cl^1) = 109.63$,
	$angle(O-P-Cl^{2,3}) = 108.26$, dihedral(Cl ¹ ,Cl ²) = -dihedral(Cl ¹ ,Cl ³) = 109.95
POCl ₂	r(O-P) = 1.4732, $r(P-Cl) = 2.0417$, angle $(O-P-Cl) = 116.00$, dihedral $(Cl,Cl) = 122.35$
$POCl_2^-$	r(O-P) = 1.494, $r(P-Cl) = 2.2800$, angle $(O-P-Cl) = 106.28$, dihedral $(Cl,Cl) = 101.22$
POCl	r(O-P) = 1.4830, r(P-Cl) = 2.0869, angle(O-P-Cl) = 109.87
POC1 ⁻	r(O-P) = 1.5258, $r(P-Cl) = 2.3528$, angle $(O-P-Cl) = 108.29$

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TABLE III. Natural population analysis of the MP2 charge density on neutral and anionic PCl_n and $POCl_n$. The "extra electron" number is the difference in the neutral and anionic charge. The Cl atoms are labeled with superscripts so that they may be identified with particular bond lengths and angles given in Table II.

	Charge associated with atom				
System	0	Р	Cl ¹	Cl ²	Cl ³
PCl ₃		0.760	-0.253	-0.253	-0.253
PCl_3^-		0.553	-0.351	-0.601	-0.601
Extra electron		0.21	0.10	0.35	0.35
PCl ₂		0.552	-0.276	-0.276	
PCl_2^-		-0.100	-0.450	-0.450	
Extra electron		0.65	0.17	0.17	
PCl		0.236	-0.236		
PCl ⁻		-0.496	-0.504		
Extra electron		0.73	0.27		
POCl ₃	-0.950	1.547	-0.199	-0.199	-0.199
POCl ₃	-1.0120	1.399	-0.404	-0.492	-0.492
Extra electron	0.06	0.15	0.21	0.29	0.29
POCl ₂	-0.929	1.405	-0.238	-0.238	
POCl ₂	-1.022	1.117	-0.547	-0.547	
Extra electron	0.09	0.29	0.31	0.31	
POCI	-0.840	1.119	-0.349		
POC1 ⁻	-1.028	0.655	-0.628		
Extra electron	0.19	0.53	0.28		

change as an electron is added to the system.²¹

The vertical electron detachment energies (Table V) are too large to have any relevance to the thermal attachment results but are interesting from the point of view of stability of the anions, especially against photodetachment. It is seen that POCl₂ not only has a large EA (3.7 eV), but its photodetachment threshold is also large (4.6 eV). The vertical detachment energy for PCl₃⁻ is surprisingly large (3.3 eV) given the moderate adiabatic EA (1.2 eV), but the difference in these two energies is consistent with the large difference in the P–Cl bond length between the neutral and anion. The

P–Cl bond length change is the greatest (0.32 Å) for PCl_3 , among the molecules studied in this work.

DISCUSSION

First, let us consider reaction (1) for dissociative electron attachment to PCl_3 . Table V shows that the PCl_3^- surface lies slightly *above* that of the neutral (a small negative value for the vertical attachment energy) at the equilibrium geometry of the neutral molecule. Thus, the most likely explanation for

TABLE IV. Total energies for netural and anionic PCl_n and POCl_n evaluated for geometries calculated at the MP4/6-311+G(d)//MP2(Full)/6-311 +G(d)+ZPE[HF/6-311+G(d)//HF/6-311+G(d)] level. The zero-point energies (ZPE) have not been scaled in any way. The ZPE-corrected energies were used to evaluate EAs (Table V) and dissociation energies (text).

TABLE V. Adiabatic electron affinities, vertical attachment	energies, and
vertical detachment energies, in eV, calculated at the	MP4/6-311
+ G(d) / (MP2(Full)/6-311 + G(d)) level of theory except as no	ted. The ZPE
corrections are included (see text and Fig. 4). The adiabatic	EAs are ex-
pected to be accurate to $\pm 0.5 \text{ eV}$, and the vertical energies	are probably
good to within ± 0.6 eV.	

Molecule	ZPE	MP4 energy+ZPE
PCl ₃	0.005 270	- 1719.887 785
PCl ₃	0.002 991 ^a	-1719.933503
PCl ₂	0.002 971	-1260.183752
PCl_2^-	0.002 270	-1260.234410
PCl	0.001 284	$-800.432\ 140$
PC1 ⁻	0.000 857	-800.506558
POCl ₃	0.010 609	-1794.996462
POCl ₃	0.007 707	-1795.057555
POCl ₂	0.007 542	-1335.275 044
$POCl_2^-$	0.006 386	- 1335.409 581
POCl	0.005 268	-875.637465
POC1 ⁻	0.004 060	-875.676534

^aNo stable HF structure could be found for PCl_3^- , so this ZPE value was calculated at the MP2(Full)/6-311+G(d) level.

Molecule	Adiabatic electron affinity ^a	Vertical electron attachment energy	Vertical electron detachment energy
PCl ₃	1.24	-0.50^{b}	3.26
PCl ₂	1.38	1.16	1.48
PCl	2.03	1.81	2.17
POCl ₃	1.66	0.15	2.95
POCl ₂	3.66	2.60	4.57
POCI	1.06	0.81	1.96

^aCollisional ionization experiments (Ref. 6) yield EAs of 0.82 $\pm 0.10 \text{ eV}(\text{PCl}_3)$, $1.41 \pm 0.20/-0.10 \text{ eV}(\text{POCl}_3)$, and $3.83 \pm 0.25/-0.10 \text{ eV}(\text{POCl}_2)$.

^bA larger basis set [6-311+G(2df)] was needed for this energy difference in order to obtain convergence of the SCF series for the energy of the anion at the geometry of the neutral.

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FIG. 4. A cut through the potential energy surfaces of POCl₃ (upper curve) and POCl₃⁻ (lower curve) along an arbitrary reaction coordinate connecting the POCl₃ and POCl₃⁻ minima. The shapes of the potential energy curves are crude estimates based on the energies given in Tables IV and V. The vibrational levels shown are the zero point energies. VAE denotes the vertical attachment energy, and VDE denotes the vertical detachment energy. Experimental data place the POCl₂+Cl⁻ and POCl₂⁻+Cl asymptotes closer together [see Eq. (4)].

the 43 meV activation energy that we observe for electron attachment to PCl_3 is that the incoming electron must give the molecule enough internal energy to access the anion potential surface. Once accessed, the PCl_3^- system does not stabilize (under our conditions) but dissociates into Cl^-+PCl_2 . The geometry calculations for PCl_3 and PCl_3^- (Table II) show that while one of the P–Cl bonds is little changed by the attachment process, the other two elongate by 0.33 Å, and therefore the attachment process leaves the anion well on the way to dissociation of one P–Cl bond if the parent complex is not stabilized collisionally or radiatively.

Reaction (4) for electron attachment to POCl₃ is more complex since the parent anion is partially stabilized at the lower temperatures of the present work, in 135 Pa of helium gas. At all temperatures studied, the formation of POCl₂⁻ is favored, and a small amount of Cl⁻ is observed. From Table V and Fig. 4 it is seen that the POCl₃⁻ surface intersects the neutral surface in the vicinity of the POCl₃ minimum. Since the attachment rate coefficient is large, we surmise that the anion potential surface is readily accessible to the electronmolecule system, and the question of whether POCl₃⁻ or POCl₂⁻ is the major final product depends solely on the time required for collisional or radiative stabilization of the parent anion. Thus the 16 meV activation energy for the POCl₂⁻ product channel may be quite different if measured in an ion cyclotron resonance experiment (no collisions) or in an atmospheric pressure drift tube. The weak Cl⁻ product channel is nearly thermoneutral according to available data⁶ and results of the present calculations, so the observed 120 meV activation energy may be due to a genuine endothermicity or may be a result of the relative rates of dissociation and stabilization of POCl₃⁻. The dominance of the POCl₂⁻ product channel over the Cl⁻ product channel, differing only in the location of the electron, is likely due to energetics but should also be favored on the basis of structure if the temporary POCl₃⁻ can access its equilibrium geometry (POCl₂⁻ is structurally similar to POCl₃⁻ while POCl₂ is not).

As noted in the previous section, the calculations imply that the O atom in POCl₃ is unimportant from structural and charge density points of view in forming the anion. However, the presence of the additional atom (over PCl₃) provides more vibrational modes in which the energy gained upon addition of an electron can be stored. As a result, the lifetime of the initially formed, internally excited POCl₃⁻ is sufficiently long that collisional stabilization occurs and the parent anion is observed—in contrast to the PCl₃ case, where the parent anion is not observed in these experiments.

The calculations verify that $POCl_2$ has a large EA (3.8 eV experimentally, and 3.7 eV calculated). The structure (Table II) of $POCl_3^-$ is similar to that of $POCl_2^-$ joined to an additional Cl atom. The only significant difference is that the dihedral angle (looking down along the O–P bond) between the two identical Cl atoms in $POCl_3^-$ is 101°, while in $POCl_2^-$ these same two Cl atoms quite reasonably open up to 140° (but note, not to 180°, the planar configuration). The NPA data in Table III show that these two Cl atoms carry about the same amount of negative charge in both $POCl_3^-$ and $POCl_2^-$ (the P atom in $POCl_2^-$ carries most of the negative charge that a third Cl atom would claim). The structural similarity between $POCl_3^-$ and $POCl_2^-$ may contribute to the dominance of the $POCl_2^-$ ion product in electron attachment to $POCl_3$.

CONCLUSIONS

Rate constants have been measured for electron attachment to PCl₃ and POCl₃ over the temperature range 296–552 K. Attachment to PCl₃ yields only Cl⁻ ionic product in this temperature range, with an activation energy of 43 \pm 10 meV. Attachment to POCl₃ results in a competition between a nondissociative channel (yielding POCl₃⁻ ionic product) and two dissociative channels (POCl₂⁻ and Cl⁻). POCl₂⁻ is the major ionic product observed at all temperatures studied. Branching fractions were determined, as well as activation energies for the two dissociative channels.

Ab initio structure and energy calculations were carried out for neutral and anionic PCl_n and POCl_n, for n = 1-3. The calculated adiabatic EAs agree with those for PCl₃, POCl₃, and POCl₂ determined from collisional ionization measurements⁶ within experimental and estimated calculational uncertainty. In particular, the EA of POCl₂ is large, 3.8 eV experimentally or 3.7 eV calculated. The calculations show that both PCl₃⁻ and POCl₃⁻ have C_s symmetry. POCl₃⁻ has a structure very similar to that of POCl₂⁻, with an extra Cl atom appended, taking negative charge from the P atom. The O atom in the POCl_n series appears to be unimportant to the initial electron attachment process, but the additional vibrational modes related to this O atom are crucial to the survival of the POCl₃⁻ ion product of attachment to POCl₃.

ACKNOWLEDGMENTS

We appreciate continued support for this Laboratory by the Air Force Office of Scientific Research. Some of the calculations reported here were carried out at the Maui High Performance Computing Center of the Air Force Research Laboratory. JMVD would like to acknowledge support from the Camille and Henry Dreyfus Foundation. We also wish to thank Professor Keiji Morokuma for some helpful discussions.

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