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The gas-phase thermochemistry of PCl_4^+: A test of lattice energy calculations

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Dedicated to the memory of Sharon Lias in honor of her many contributions to the understanding of ion thermochemistry.

Abstract

The bond dissociation energy for loss of Cl atom from PCl_4^+ has been measured to be $411 \pm 17\,\mathrm{kJ\,mol^{-1}}$ at 0 K using energy-resolved collision-induced dissociation in a flowing afterglow-guided ion beam tandem mass spectrometer. Density functional calculations give bond energies that are lower than experiment, while MP2 calculations are in good agreement. The bond energy can be combined with the ionization energy of PCl_3 to derive the 0 K heat of formation of PCl_4^+, $378 \pm 18\,\mathrm{kJ\,mol^{-1}}$. This value is in good agreement with the value derived from lattice energy calculations.

Keywords: Thermochemistry; Lattice energy; Guided ion beam; Ab initio calculations

1. Introduction

Thermodynamic properties of molecules are key factors in understanding chemical bonding and reactivity. Massive amounts of thermodynamic data have been collected over a period of more than a century, and great efforts have gone into systematizing the results into a coherent body of knowledge. A prominent contribution in this area is the NIST Standard Reference Data Program [1], of which one of the strongest components is the ion energetics databases [2,3] developed by Sharon Lias and coworkers.

One of the difficulties of thermodynamic measurements is that parameters are strongly affected by the phase of the material studied. It is necessary to determine thermodynamic quantities in the solid, liquid, and gas phases, as well as in varying solutions. Any method for predicting thermodynamic properties in one phase from values in another phase can multiply the usefulness of the experimental data.

Knowledge of the lattice energy of ionic materials allows the interconversion of solid-state and gas-phase thermochemistry. Methods for calculating the lattice energy have been available for over 80 years [4], and have been developed into more generalized techniques, such as Volume-Based Thermodynamics (VBT) [5]. In 1996, Jenkins and coworkers [6] predicted the enthalpies of formation for PCl_4^+ and PCl_6^- to be 384 ± 10 and $-813 \pm 10\,\mathrm{kJ\,mol^{-1}}$, respectively, through a detailed analysis of crystals such as $(PCl_4^+)_2(PCl_6^-)(Cl^-)$. Jolly and Gin also estimated $\Delta_f H(PCl_4^+) = 430 \pm 40\,\mathrm{kJ\,mol^{-1}}$ by comparison to the isoelectronic $SiCl_4$ [7]. We report here an experimental determination of the heat of formation of PCl_4^+ that tests the predictions.

This type of thermodynamic investigation depends upon the availability of reliable and reasonably precise auxiliary thermochemistry. In this case, the availability of a precisely measured ionization energy, $\mathrm{IE}(PCl_3) = 9.90 \pm 0.01$ eV [8], is particularly important ($1\,\mathrm{eV} = 96.485\,\mathrm{kJ\,mol^{-1}}$). The history of measurements of this value is detailed on the NIST database [3]. Unfortunately, this is the only phosphorus trihalide where such an accurate IE value is available.

2. Methods

2.1. Experimental

The dissociation energy of PCl_4^+ was measured using the energy-resolved collision-induced dissociation (CID) technique

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[9,10] in a flowing afterglow-tandem mass spectrometer (MS) [11]. The instrument consists of an ion source region, a flow tube, and the tandem MS. The dc discharge ion source used in these experiments is typically set at 2000 V with 2 mA of emission current. The flow tube operates at a buffer gas pressure of 0.35 Torr and an ion residence time of 10 ms. The buffer gas is helium with up to 10% argon added to stabilize the dc discharge.

To make PCl_4^+ for this study, PCl_3 was added to the ion source. PCl_4^+ was presumably produced either by direct electron impact ionization followed by chlorine atom transfer from another neutral precursor, or by formation of Cl^+ (or a Cl^+ transfer agent such as PCl_3^+ or Cl_2^+) followed by addition to PCl_3. Approximately 10^5 collisions with the buffer gas cool the resulting PCl_4^+ ions to room temperature. The identity and purity of the PCl_4^+ reactant ions was confirmed by the isotopic peak pattern. Attempts to make sufficient PBr_4^+ for similar studies by addition of PBr_3 to the ion source were unsuccessful, although addition of Br_2 gave sufficient reactant ion intensity to see that PBr_3^+ was the main dissociation product.

The tandem MS includes a quadrupole mass filter, an octopole ion guide, a second quadrupole mass filter, and a detector, contained in a stainless steel box that is partitioned into five differentially pumped chambers. During CID experiments, the ions are extracted from the flow tube and focused into the first quadrupole for mass selection. The reactant ions are then focused into the octopole, which passes through a reaction cell that contains xenon collision gas. After the dissociated and unreacted ions pass through the reaction cell, the second quadrupole is used for mass analysis.

The energy threshold for CID is determined by modeling the cross-section for product formation as a function of the reactant ion kinetic energy in the center-of-mass frame. The ion kinetic energy distribution for the present data is typically Gaussian with an average full width at half maximum of 0.8–1.6 eV (1 eV = 96.5 kJ mol^{-1}). All experiments were performed with both mass filters at low resolution to improve ion collection efficiency and reduce mass discrimination. Average atomic masses were used for all elements. Data taken at several pressures is extrapolated to a zero pressure cross-section before fitting the data to avoid the effects of secondary collisions [12].

Threshold energies are derived by fitting the data to a model function given in Eq. (1), where $\sigma(E)$ is the cross-section for formation of the product ion at center-of-mass energy E, E_T the desired threshold energy, σ_0 the scaling factor, n an adjustable parameter, and i denotes rovibrational states having energy E_i, and population g_i ($\sum g_i = 1$). Doppler broadening and the kinetic energy distribution of the reactant ion are also accounted for in the data analysis, which is done using the CRUNCH program written by Armentrout and collaborators [13].

$$\sigma(E) = \sigma_0 \sum_i \frac{g_i(E + E_i - E_T)^n}{E} \tag{1}$$

Experimental vibrational frequencies are available [14] for PCl_4^+ and PCl_3, but not for PCl_3^+. Therefore, vibrational and rotational frequencies were calculated using the B3LYP model [15] and the aug-cc-pV(T + d)Z basis set (which is designed to improve results for elements including P and Cl [16]) to give a consistent set of frequencies, given in Table 1. The calculated frequencies reported here for PCl_4^+ and PCl_3, average 4% lower than experiment [14], with a standard deviation of 1%. B3LYP calculations with the aug-cc-pVTZ basis set [17] give frequencies 5–6% lower than experiment, indicating that the aug-cc-pV(T + d)Z basis set is more accurate for these systems. B3LYP/aug-cc-pVTZ frequencies are typically 0–5% lower than experimental frequencies for this type of system [18,19]. Uncertainties in the derived thresholds due to possible inaccuracies in the frequencies were estimated by multiplying the entire sets of frequencies by 0.9 and 1.1. The resulting changes in internal energies are less than 2 kJ mol^{-1}. Because the effect of varying the frequencies on the energies is small, and the condensed-phase vibrational frequencies may not be appropriate for gas-phase ions, no scaling was applied to the calculated frequencies. Polarizabilities for neutral molecules were also taken from the computational results; varying these parameters has a negligible effect on the derived energies.

Table 1
Experimental and computed vibrational frequencies

PCl_4^+		PCl_3	
Experimental[a]	Calculated[b]	Experimental[a]	Calculated[b]
178 (×2)	167 (×2)	186 (×2)	179 (×2)
255 (×3)	246 (×3)	258	250
458	439	504 (×2)	475 (×2)
662 (×3)	640 (×3)	515	495

Values in cm^{-1}. Multiplicities given in parentheses.
[a] Values from Ref. [14].
[b] Computed at the B3LYP/aug-cc-pV(T + d)Z level.

Collisionally activated metastable complexes can have sufficiently long lifetimes that they do not dissociate on the experimental timescale (*ca.* 50 μs). Such kinetic shifts are accounted for in the CRUNCH program by RRKM lifetime calculations, where the reaction transition states are presumed to be essentially product-like [20]. The uncertainty in the derived thresholds is again estimated by multiplying reactant or product frequency sets by 0.9 and 1.1, and by multiplying the time window for dissociation by 10 and 0.1. This last variation is equivalent to multiplying the dissociation rate by 0.1 and 10. The effect of these variations is less than 3 kJ mol^{-1}. Because systematic deviations for both reactant and products tend to give cancelling errors in the derived thermochemistry, the calculated frequencies were used without scaling.

Electronic states must also be considered in the present study. The reactant ion has no excited electronic states with a significant population at room temperature. The main product ion PCl_3^+ has a $^2A_1$ ground state [21], with no important excited states. However, the main neutral product (the chlorine atom) has a $^2P_{3/2}$ ground state and a $^2P_{1/2}$ excited level that is 10.6 kJ mol^{-1} higher in energy [22]. If dissociation were to occur entirely to the excited $^2P_{1/2}$ level (conserving an overall J value of zero for reactants and products), then the measured threshold would be higher than the reaction energy by 10.6 kJ mol^{-1}. However, it is unlikely that J is well conserved in this reaction because molecular rotations can couple with the electronic angular momentum. As noted in the above paragraph, even if a need to cross from a $J = 1/2$ surface to a $J = 3/2$ surface reduces the dissociation efficiency by a factor of 10, the effect on the derived threshold will be less than 3 kJ mol^{-1}. The effect of electronic excited states is therefore assumed to be negligible compared to the overall uncertainty given below.

PCl_3 was obtained from Aldrich. He and Ar were obtained from BOC, and Xe was obtained from Spectra Gases, Inc. All reagents were used as received.

2.2. Computational

Computational work on these systems was performed using the Gaussian 03 suite [23]. All optimized geometries were identified as true minima by their lack of imaginary frequencies. The specialized thermochemical methods G3 [24] and G3B3 [25] were used as implemented in the Gaussian code. The aug-cc-pV(T + d)Z basis set was used for all other calculation because of its demonstrated effectiveness for elements including P and Cl. [16] Several density functional methods (B3LYP [26], B3P86 [27,28], MPW1PW91 [29], and PBE1PBE [30]) were used in addition to the MP2 method.

The ionization energy of PCl_3 was also studied computationally; the bond energy in PCl_4^+ and IE(PCl_3) are closely related because of their common product and the fact that both reactants are closed-shell, phosphorus chloride species. Fig. 1 shows the thermodynamic scheme for the species studied here.

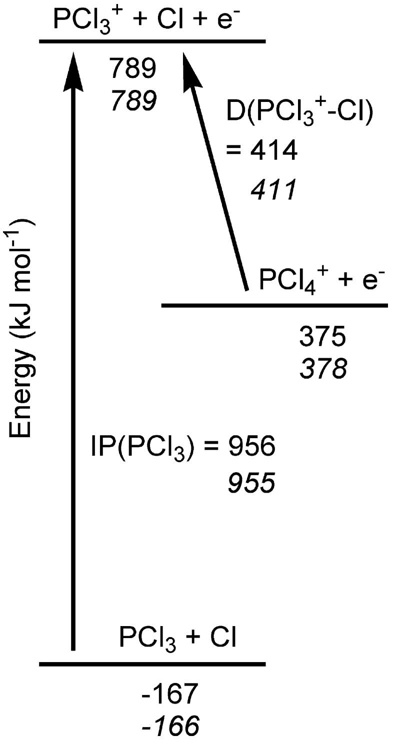

Fig. 1. Experimental energy diagram for PCl_4^+ and related species; 298 K values are in regular type and 0 K values are in italics. For details see text.

3. Results and discussion

3.1. Experimental results

CID of PCl_4^+ gives loss of Cl, reaction (2), as the predominant product at low energy. Reaction (3) is the predominant product at higher energy. The neutral products cannot be directly measured, so reaction (3) can correspond to either loss of Cl_2 or to loss of two Cl atoms.

$$PCl_4^+ \rightarrow PCl_3^+ + Cl \tag{2}$$

$$PCl_4^+ \rightarrow PCl_2^+ + [2Cl] \tag{3}$$

Loss of Cl_2 is calculated at the levels of theory discussed above to be 15–38 kJ mol^{-1} *lower* in energy than reaction (2). Because D(Cl–Cl) = 239 kJ mol^{-1} at 0 K [31], loss of 2Cl from PCl_4^+ is roughly 201–224 kJ mol^{-1} higher in energy than reaction (2). The apparent threshold for reaction (3) is somewhat more than 2 eV (200 kJ mol^{-1}) above the apparent threshold for reaction (2), consistent with loss of two Cl atoms. The large cross-section for reaction (3) at higher energies is also more consistent with loss of two atoms, which is entropically favored because it results in three product particles.

Appearance curves and fits to the data are shown in Fig. 2. The total cross-section for reactions (2) and (3) was fit because this sum corresponds to the production of ions that lose a Cl atom (regardless of whether or not they lose a second atom). Eq. (1) fitting parameters are $n = 0.9 \pm 0.1$ and $E_T = 4.26 \pm 0.16$ eV. Because the effects of reactant and product internal energy are included in the fitting procedure, the thresholds correspond to dissociation energies at 0 K. The final uncertainties in the dissociation energies are derived from the standard deviation of the thresholds determined for individual data sets (0.16 eV), the uncertainty in the reactant internal energy (0.02 eV), the effects of kinetic shifts (0.05 eV), and the uncertainty in the energy scale (±0.15 eV lab, 0.065 eV CM). This gives a final reaction energy of 4.26 ± 0.18 eV (411 ± 17 kJ mol^{-1}).

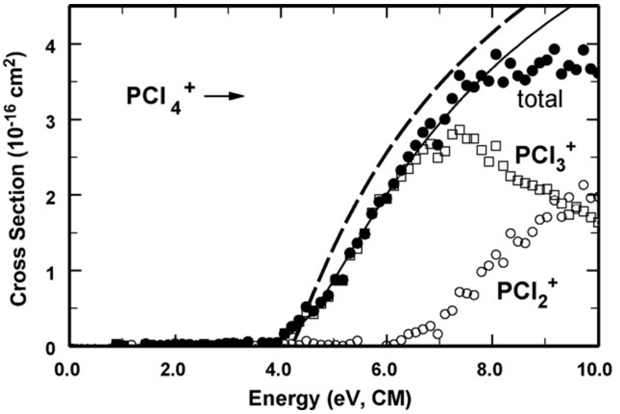

Fig. 2. Product ion appearance curves for collision-induced dissociation of PCl_4^+ with xenon collision gas as a function of translational energy in the center-of-mass frame. The solid and dashed lines represent convoluted and unconvoluted fits to the total reaction cross-section, as described in the text. Eq. (1) fitting parameters for this data are $n = 1.02$ and $E_T = 4.23$.

Table 2
Experimental and computed geometries[a]

	PC_4^+		PCl_3^+	PCl_3	
	Experimental[b]	Calculated[c]	Calculated[c]	Experimental[b]	Calculated[c]
∠Cl–P–Cl	109.5	109.5	111.5	100.3	100.8
r(P–Cl)	1.91	1.96	1.97	2.04	2.07

[a] Bond lengths in Å, angles in °.
[b] Values from Ref. [32].
[c] Computed at the B3LYP/aug-cc-pV(T + d)Z level.

The experimental 0 K dissociation energy determined this way can be converted into a 298 K dissociation enthalpy using the integrated heat capacities of the reactants and products, which are determined using the frequencies in Table 1. The 298 K enthalpy is 3 kJ mol^{-1} larger than the 0 K value, or 414 ± 17 kJ mol^{-1}.

3.2. Computational results

Computational geometries are compared to experimental values in Table 2. The calculations indicate that PCl_4^+ has tetrahedral symmetry, while PCl_3^+ and PCl_3 have C_{3v} symmetry, in agreement with experiment [21,32]. The bond angles are in good agreement, while the B3LYP method gives slightly long bond lengths, as observed previously [33].

Computational thermochemical results are summarized in Table 3. The directly calculated bond energies are significantly lower than the experimental value, and the same is true for the computed values of IE(PCl_3). Many density functional methods systematically underestimate homolytic bond strengths [28]. It is likely that the difficulties on the calculation of IE(PCl_3) are due to error in the energy of the radical PCl_3^+ rather than the closed-shell PCl_3 [34]. This means that the calculated energy of PCl_3^+ is too low, which would directly affect the calculated values of $D(PCl_3^+\text{–}Cl)$. A simple correction for this is given in Eq. (4),

$$D_{\mathrm{corr}}(PCl_3^{+}\text{–}Cl) = D_{\mathrm{calc}}(PCl_3^{+}\text{–}Cl) + \mathrm{IE}_{\mathrm{exp}}(PCl_3) - \mathrm{IE}_{\mathrm{calc}}(PCl_3) \quad (4)$$

Table 3
Calculated bond dissociation energy (kJ mol^{-1}) of PCl_4^+ and ionization energy (eV) of PCl_3 at 0 K

Model	BDE	IE(PCl_3)	BDEcorr[a]
G3	377	9.85	383
G3B3	375	9.86	379
B3LYP/aug-cc-pV(T + d)Z	328	9.74	342
MPW1PW91/aug-cc-pV(T + d)Z	351	9.63	377
B3P86/aug-cc-pV(T + d)Z	357	10.22	326
MP2/aug-cc-pV(T + d)Z	390	9.67	413
PBE1PBE/aug-cc-pV(T + d)Z	358	9.60	387
Exp.	411[b]	9.90[c]	411

[a] For derivation of corrected bond energies see text.
[b] This work.
[c] Ref. [8].

where $D_{\mathrm{corr}}(PCl_3^+\text{–}Cl)$ is the calculated bond strength corrected for the probable error in the energy of PCl_3^+. The corrected values are generally closer to the experimental values, Table 3. The MP2 value is in good agreement with experiment; it has been noted [35] that MP2 usually gives better results for radicals than density functional theory. The G3X values are significantly lower than experiment. Improved methods for G3X calculations on radicals have been documented recently [36]. Calculations with the aug-cc-pVTZ basis set give substantially lower values for $D(PCl_3^+\text{–}Cl)$ than aug-cc-pV(T + d)Z calculations, although the simpler basis set often gives better agreement on IE(PCl_3).

The variations in the computational results for PCl_4^+ can be compared to those for the isoelectronic reaction (5). The experimental 0 K energy for this reaction is 466 ± 4 kJ mol^{-1} [37].

$$SiCl_4 \rightarrow SiCl_3 + Cl \quad (5)$$

This value is higher than the dissociation energy in PCl_4^+. The computational bond energies are 416 kJ mol^{-1} at the B3LYP/aug-cc-pV(T + d)Z level, 472 kJ mol^{-1} at the MP2/aug-cc-pV(T + d)Z level (adjusted for zero point energies with the B3LYP frequencies), and 439 kJ mol^{-1} at the B3P86/aug-cc-pV(T + d)Z level. Once again, the MP2 result is in good agreement with experiment while density functional theory give bond strengths that are substantially lower.

3.3. Thermochemical implications

Fig. 1 shows how known thermodynamics can be combined with the bond energy determined here to derive the heat of formation of PCl_4^+. The 298 K enthalpies of formation of PCl_3 and Cl are −288.7 ± 5.4 and 121.3 kJ mol^{-1}, respectively [31]; these sum to −167.4 kJ mol^{-1}. The ionization energy of PCl_3 is 9.90 eV (955.2 kJ mol^{-1}) at 0 K [8], which can be adjusted up by 1.26 kJ mol^{-1} to give the ionization energy at 298 K. This value uses the ion convention [3], where the heat capacity of the electron is taken to be zero. The IE can be added to the enthalpy of formation of [PCl_3 + Cl] to give $\Delta_f H_{298} = 789$ kJ mol^{-1} for [$PCl_3^+ + Cl + e^-$]. This in turn can be combined with the 298 K bond energy of 414 ± 17 kJ mol^{-1} to give $\Delta_f H_{298}(PCl_4^+) = 375 \pm 18$ kJ mol^{-1}. The corresponding value using the electron convention [3], where the heat capacity of an electron is taken to be that of an ideal gas, is 381 kJ mol^{-1}. The 0 K thermodynamic cycle, starting with $\Delta_f H(PCl_3) = -285.5$ kJ mol^{-1} and $\Delta_f H(Cl) = 119.6$ kJ mol^{-1} [31], gives $\Delta_f H_0(PCl_4^+) = 378 \pm 18$ kJ mol^{-1}.

Because the computations performed here give generally lower values than experiment for the bond energy in PCl_4^+, the computed heats of formation are higher than experiment. Starting from the experimental heats of formation of PCl_3 and Cl, the theoretical results in Table 3 give values for $\Delta_f H_0(PCl_4^+)$ ranging from 376 to 463 kJ mol^{-1}.

The lattice energy estimate [6] $\Delta_f H_{298}(PCl_4^+) = 384 \pm 10$ compares well to the experimental result, being well inside the combined error limits. The other estimated value, 430 ± 40 kJ mol^{-1}, is in moderate agreement considering the substantial uncertainty ascribed to the value. The good agreement with the prediction from lattice energy calculations is consistent with the nature of the ion: it is not likely to be involved in covalent bonding with neighboring ions (which is not accounted for in the lattice energy model) and the ion is highly symmetric, minimizing the importance of how the ion packs into a lattice with a particular anion.

The sum of the three homolytic bond energies in PCl_3 equals $\Delta_f H_{298}(P) + 3\Delta_f H_{298}(Cl) - \Delta_f H(PCl_3)$. Values given above can be combined with $\Delta_f H_{298}(P) = 316.5 \pm 1.0$ kJ mol^{-1} [31] to give an average bond energy at 298 K of 323 ± 2 kJ mol^{-1}. This is substantially lower than the homolytic bond strength in PCl_4^+, 414 ± 17 kJ mol^{-1}. Part of this difference is due to promotion energy effects. As the three bonds in PCl_3 are broken, some of the energy cost is returned as the phosphorus atom relaxes to the ground ^4S atomic state from a state that partly correlates to the ^2D and ^2P atomic states, which are 136–224 kJ mol^{-1} higher in energy. Thus, the PCl_3^+–Cl bond appears to have a typical dissociation energy after electronic states are taken into account.

The above data can also be combined with IE(P) = 10.487 eV [3] to derive average homolytic bond energies in PCl_4^+ and PCl_3^+ of 360 and 343 kJ mol^{-1}, respectively. The electronic state effects are more complex here, but the average bond strengths are in between the other P–Cl bond energies discussed.

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