Heats of Formation for PO_n and PO_nH ($n = 1-3$)

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The geometries and frequencies are determined using density functional theory. The atomization energies are computed at the coupled cluster level of theory. The complete basis set limit is obtained by extrapolation. The scalar relativistic effect is computed using the Douglas−Kroll approach. Spin−orbit and core−valence effects are accounted for.

I. Introduction

We recently reported[1] the heats of formation and the change in heat of formation, entropy, and heat capacity as a function of temperature for the PH_n species, for $n = 1-3$. These data are required for any computer modeling of chemical vapor deposition (CVD) processes using PH_3 as a feedstock. It has been found that some processes involving PH_3 can be improved by the addition of oxygen to the reaction chamber. Since it is known[2] that the reaction of PH_3 with oxygen can produce PO_n and PO_nH species, accurate heats of formation are required for these species if the CVD processes with the oxygen and PH_3 are to be modeled. Unfortunately, excluding PO, the thermodynamic properties of these species are poorly known. We have therefore extended our studies to include the PO_n and PO_nH species.

II. Methods

The geometries are optimized using the hybrid[3] B3LYP[4] functional and the 6-31+G* and 6-31+G(2df) basis sets.[5] The harmonic frequencies are computed using the 6-31+G* basis set; they confirm that the stationary points correspond to minima and are used to compute the zero-point energies.

Using the B3LYP 6-31+G(2df) geometries, the energetics are computed using the restricted coupled cluster singles and doubles approach[6,7] including the effect of connected triples determined using perturbation theory,[8,9] RCCSD(T). In the valence RCCSD(T) calculations, the P 3s and 3p electrons, the oxygen 2s and 2p electrons, and the hydrogen 1s electrons are correlated. The H and P basis set are the correlation-consistent valence-polarized (cc-pV) sets developed by Dunning and coworkers.[10−13] For O, the augmented (aug) cc-pV basis sets[12,13] are used. The triple-ζ (TZ), quadruple-ζ (QZ), and quintuple-ζ (5Z) sets are used. Note that a tight d function is added to the P basis set; the exponents are 1.956, 3.11, and 8.00, for the TZ, QZ, and 5Z sets, respectively.

To improve the accuracy of the CCSD(T) results, we extrapolate to the complete basis set (CBS) limit using the n^{-3} scheme.[14] We should note that after adding the tight d functions, the n^{-3} {T,Q}Z and {Q,5}Z extrapolations for the PO dissociation energy agree to within 0.04 kcal/mol, whereas they differed by 1.1 kcal/mol without the tight d functions. With the addition of the tight d function, the results obtained using the {T,Q,5}Z $n^{-4} + n^{-6}$ and variable α extrapolation approaches[15] agree with the {Q,5}Z n^{-3} result to within 0.3 kcal/mol, whereas without the tight d functions, the spread in the three methods is 1.4 kcal/mol.

The core−valence (CV) effect is computed at the RCCSD(T) level, as the difference between the treatment correlating the valence electron and one in which the phosphorus 2s and 2p and the oxygen 1s electrons are also correlated. These calculations are performed using the CV basis set, which is derived from the P cc-pVTZ and O aug-cc-pVTZ sets. For phosphorus, the inner 10 s and inner 4 p primitives are contracted to two and one function, respectively. The remaining s and p primitives are uncontracted. Three tight d (17.604, 5.868, and 1.956) and two tight f (4.07 and 1.356) functions are added to the normal polarization set. For oxygen, the inner five s primitives are contracted to one function and the remaining s and all of the p primitives are uncontracted. Two tight d (20.83 and 6.94) primitives and a tight f (4.284) primitive are added to the normal polarization set.

Of the molecules, only PO is expected to have a significant spin−orbit effect, and we compute this as half the difference between the sublevels of the $^2\Pi$ state, which we take from Huber and Herzberg.[16] The atomic spin−orbit effects are computed using the tabulation of Moore.[17]

The scalar relativistic effects are computed as the differences between results obtained using the nonrelativistic and Douglas Kroll (DK) approaches.[18] More specifically, the systems are studied at the modified coupled pair functional[19] (MCPF) level of theory using the cc-pVTZ basis set (aug-cc-pVTZ for O). Note that the contraction coefficients used in the molecular DK calculations are taken from DK atomic Hartree−Fock (HF) calculations.

The B3LYP calculations are performed using Gaussian 94,[20] the CCSD(T) calculations are performed using Molpro,[21] and the MCPF calculations are performed using Molecule-Sweden.[22] The DK integrals are computed using a modified version of the program written by Hess.

The heat capacity, entropy, and temperature dependence of the heat of formation are computed for 300−4000 K using a rigid rotor/harmonic oscillator approximation. The B3LYP frequencies are used in these calculations. These results are fit in two temperature ranges, 300−1000 K and 1000−4000 K, using the Chemkin[23] fitting program and following their constrained three-step procedure.

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TABLE 1: Summary of the PO_n, $n = 1-3$, B3LYP/6-31+G(2df) Geometries

	r(P−O)(Å)	∠(OPO)(deg)
	PO $^2\Pi$ $C_{\infty v}$	
present work (B3LYP)	1.483	
Lohr[24](HF)	1.456	
expt[16]	1.475	
	PO_2 $^2A_1$ C_{2v}	
PW	1.476	134.0
Lohr	1.446	134.4
expt[28]	1.467	135.3
	PO_3 $^2A'$ D_{3h}	
PW	1.481	
Lohr	1.455	

TABLE 2: Summary of the PO_nH, $n = 1-3$, B3LYP/6-31+G(2df) Geometries (Bond Lengths in Angstroms, Angles in Degrees)

HPO $^1A'$ C_s

	r(P═O)	r(P−H)	∠(HPO)
present work	1.488	1.475	104.1
Lohr[24](HF)	1.461	1.430	105.4
Roos[26](CASPT2)	1.490	1.452	104.2
Gordon[25](HF)	1.439	1.409	104.5
expt[27]	1.480 ± 0.005	1.456 ± 0.003	103.5 ± 2.5

OPOH $^1A'$ C_s (cis)

	r(P═O)	r(P−O$_H$)[a]	r(P−H)	∠(OPO)	∠(POH)
PW	1.476	1.620	0.972	110.7	114.5
Lohr	1.450	1.602	0.956	109.4	114.4
Gordon	1.427	1.582	0.995	109.8	110.6

O_2 POH $^1A'$ C_s

	r(P═O$_c$)[b]	r(P═O$_t$)	r(P−O$_H$)	r(P−H)
PW	1.462	1.456	1.585	0.969
Lohr	1.437	1.431	1.564	0.954

	∠(O$_c$PO$_H$)	∠(O$_c$PO$_t$)	∠(POH)
PW	112.1	134.0	112.1
Lohr	133.2	133.8	113.3

[a] The "H" subscript indicates the oxygen bonded to the hydrogen. [b] The "c" subscript indicates the oxygen cis to the hydrogen, while the "t" indicates the trans oxygen.

III. Results and Discussion

We first consider the geometries and vibrational frequencies of the PO_n and PO_n H species. While the data on the heats of formation of these compounds are very limited, the geometries have been the subject of previous computational studies.[24−26] One rather complete series of work is that by Lohr and co-workers,[24] who have optimized, at the HF level, the geometries of all of the species considered in this work. They studied several isomers in many cases. We have also considered different isomers, and our most stable structure is similar to the ones reported by Lohr and co-workers. We should note that the cis and trans structures of PO_2H are sufficiently close in energy that, for both isomers, we extrapolated the CCSD(T) results to the basis set limit, accounted for core−valence correlation and scalar relativistic effects, and found the cis structure to be lower, as found by Lohr and co-workers. The B3LYP approach also favors the cis structure.

In Tables 1 and 2, we summarize our computed geometrical results for the most stable isomer, along with some previous calculations and experiment.[27,28] We first note that our results are in good agreement with the limited experimental data. The error in our X−H bond distances is a bit larger than for the P−O distances, since polarization functions are not included on H. We also note that our B3LYP bond lengths are a bit longer than the HF results of Lohr and co-workers, where in general the HF and B3LYP results bracket experiment. The small (STO-2G*) basis set HF results of Gordon and co-workers[25] have bond lengths that are too short, as noted by Gordon. For HPO, our B3LYP results are in good agreement with the much higher level CASPT2 results of Roos and co-workers.[26]

Our computed vibrational frequencies are summarized in Table 3 along with experiment[2,29] and the high-level CASPT2 treatment for HPO. For HPO, the agreement between the B3LYP and CASPT2 results is very good. Excluding PO_3, our results are in good agreement with experiment. However, we find the vibrational frequencies of PO_3^- agree very well with experiment; in addition, the computed PO_3^- isotopic ratios for the 480.3 and 1273.3 cm^{-1} bands agree very well with experiment. Despite that fact that the computed isotopic ratio for the 435.2 cm^{-1} band is in poor agreement with experiment, we believe that the bands assigned to PO_3 are in fact due to PO_3^-. This reassignment is currently being investigated.[30] Thus, while it is possible that the PO_3 zero-point energy is less accurate than for the other systems, we see no definitive evidence to support this view, and therefore, we use the B3LYP frequencies to compute the PO_3 zero-point energy. If our reassignment is incorrect, and the observed species is PO_3, using the B3LYP frequencies for the zero-point will introduce an error of approximately 1 kcal/mol.

Using the B3LYP/6-31+G(2df) geometries, the atomization energies (AE) are computed using higher levels of theory; these results are summarized in Table 4. For all systems except PO_3H, we are able to perform the 5Z calculation; thus, the best results are obtained using the {Q5}Z extrapolation, except for PO_3H, where we use the {TQ}Z extrapolation. For the PO_n species, there are essentially no differences between between the {TQ}Z and {Q5}Z extrapolations, while for the PO_nH systems the difference grows from −0.26 kcal/mol for HPO to −0.55 kcal/mol for PO_2H. Therefore, we assume that using the {TQ}Z extrapolation for PO_3H could lead to an atomization energy that is about 0.85 kcal/mol too large.

Woon and Dunning[31] studied PO and their MRCI CBS D_e value is 138.3 kcal/mol, which is about 5 kcal/mol smaller than our CCSD(T) CBS value. Since their 5Z value is almost 5 kcal/mol smaller than our 5Z value, we suspect that most of the difference arises from their use of an MRCI wave function.

The MCPF atomization energies are in good agreement with the CCSD(T) results. Since correlation tends to reduce the scalar relativistic effect on the atomization energy, we assume that the computed scalar relativistic effect is slightly too large. The spin−orbit effects are taken from experiment and, therefore, expected to be accurate. The effect of core−valence correlation increases the atomization energies slightly. Our AE best 0 K value is computed as

$$\text{AE CCSD(T) CBS}(n^{-3}) + \text{spin orbit} + \text{scalar rel} + \text{CV effect} + \text{ZPE} \quad (1)$$

Our best atomization energy at 0 K is converted to 298 K using the rigid rotor/harmonic oscillator approximation. Using these atomization energies and the P, O, and H heats of formation[32] (75.619, 59.553, 52.103 kcal/mol, respectively), the PO_n and PO_nH, $n = 1-3$, heats of formation are computed as

$$\Delta H_{298}(\mathrm{PO}_n\mathrm{H}_m) = \Delta H_{298}(\mathrm{P}) + n\Delta H_{298}(\mathrm{O}) + m\Delta H_{298}(\mathrm{H}) - \text{AE best 298 K} \quad (2)$$

and are in Table 4. Also given in Table 4 are the values from

TABLE 3: Summary of the B3LYP/6-31+G* Harmonic Frequencies,[a] in cm^{-1}

PO						
PW	1226(53)					
expt[16]	1233.3					
PO_2						
PW	381(31)	1047(4)	1277(101)			
expt[28]	377	1090	1278			
PO_3						
PW	143(4)	143(4)	410(57)	995(0)	1083(32)	1083(32)
expt[2]	435.2	435.2	480.3		1273.3	1273.3
PO_3^-						
PW	458(61)	458(61)	463(36)	972(0)	1239(322)	1239(322)
HPO						
PW	1004(37)	1192(66)	2142(329)			
Roos[26]	977	1115	2096			
expt[29]	985	1188	2095			
PO_2H						
PW	377(53)	564(178)	819(243)	941(23)	1242(143)	3661(75)
expt[2]		523.9	841.5		1252.6	3550.7
PO_3H						
PW	386(21)	409(36)	431(51)	515(156)	870(117)	
	1048(113)	1159(129)	1432(205)	3711(136)		
expt[2]	412.0	428.0	447.2	492.0	913.4	
	1044.8	1192.6	1451.3	3585.4		

[a] The intensities, in km/mol, are given in parentheses.

TABLE 4: Summary of Atomization Energies (AE) and Heats of Formation at 298 K (ΔH_{298}), in kcal/mol

	PO $^2\Pi$	PO_2 $^2A_1$	PO_3 $^2A'$	HPO $^1A'$	PO_2H $^1A'$	PO_3H $^1A'$
AE						
AE CCSD(T) TZ	134.495	252.191	345.061	203.745	350.965	465.297
AE CCSD(T) QZ	139.611	260.812	356.664	209.764	360.248	478.563
AE CCSD(T) 5Z	141.452	263.917	360.819	211.781	363.284	
AE CCSD(T) CBS(n^{-3})	143.384	267.175	365.177	213.898	366.470	488.244
AE MCPF TZ	128.539	240.669	327.914	197.274	340.303	450.210
AE MCPF(DK)TZ	128.264	239.813	326.761	196.853	339.821	448.580
scalar rel	−0.275	−0.856	−1.152	−0.421	−0.731	−1.630
spin−orbit (Moore[17])	−0.126[a]	−0.446	−0.669	−0.223	−0.446	−0.669
AE CCSD(T) CV	136.562	255.823	347.332	205.847	354.124	470.307
AE(CV) CCSD(T) CV	137.225	256.733	348.406	206.455	355.267	471.709
CV effect	+0.663	+0.910	+1.074	+0.607	+1.143	+1.402
ZPE (B3LYP)	−1.752	−3.866	−5.513	−6.202	−10.871	−14.240
AE best 0 K	142.146	262.917	358.917	207.660	355.815	473.107
AE best 298 K	142.989	265.010	361.781	209.825	359.188	477.745
ΔH_{298}						
PW	−7.82	−70.29	−107.50	−22.55	−112.36	−171.36
JANAF[32]	−5.63 ± 1.0	[−75.17]				
Gurvich[33]	−6.66 ± 0.8	−67.3 ± 2.4		−13.6 ± 9.6		

[a] Includes the effect of spin−orbit for PO $^2\Pi$.

Gurvich[33] and JANAF.[32] The present value for PO is in good agreement with the Gurvich value. Since we expect that our values are accurate to about 1 kcal/mol, the computed value overlaps with that of Gurvich. This is also true for PO_2, where the Gurvich value is more uncertain. Clearly the Gurvich value is far better than the estimate of JANAF, but the computed value is clearly the most accurate of the three. For HPO, the computed value is clearly more accurate than the uncertain value of Gurvich.

Using our heats of formation at 298 K and the B3LYP frequencies and geometries, we evaluate the heat capacity, entropy, and heat of formation from 300 to 4000 K. The parameters obtained from the resulting fits can be found on the Web.[34]

IV. Conclusions

The heats of formation of the PO_n and PO_nH, $n = 1-3$, species have been computed. The geometries are in good agreement with the available experimental values. Excluding PO_3, the frequencies also agree well with experiment. For PO_3, we have reassigned the observed bands to PO_3^-, thus there appears to be no experimental values for PO_3; however, we do not expect the PO_3 frequencies to be less accurate than those of the other systems. The complete basis set limit CCSD(T) atomization energies have been obtained by extrapolation. The scalar relativistic effect has been computed using the DK approach in conjunction with an MCPF wave function. The effect of core−valence has also been accounted for. For PO_n and PO_nH, $n = 1-2$, the error is estimated to be ±1 kcal/mol. For PO_3 and PO_3H, we increase the error bars to ±2 kcal/mol to account for the possibility that the experimental assignment of the PO_3 frequencies is correct and to account for using only the {T,Q}Z extrapolation for PO_3H. The computed results are in good agreement with limited, and sometimes uncertain, experimental data.

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