Structure and Properties of Phosphaketene (H–P=C=O): Phosphorus *versus* Oxygen Protonation?

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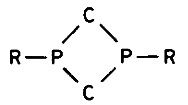
Phosphaketenes carrying bulky substituents to limit dimerization have recently been reported and for comparison the simple model phosphaketene (**1**) was investigated using *ab initio* methods. It has an *E*-bent structure with a CP bond length of 1.728 Å and a CPH bond angle of 90.6° (using the 4-31G basis set). This is rationalized in terms of stabilizing interactions between the PH and CO fragments so that the C–P bond is essentially a dative single bond enforced by π-back-donation. Both P and O centres carry an overall negative charge; of five possible structures of protonated HPCO considered, phosphorus protonation is unambiguously preferred and the perpendicular structure (**11**) calculated to be the most stable. Inclusion of polarization functions and correlation energies favours phosphorus protonation further. Also reported are the vibrational frequencies, dissociation energies of the protonated and neutral phosphaketene, and the predicted reactivity in both cycloadditions and additions of HX; comparison is made with reported experimental data where available.

Phosphaketenes (I), phosphorus analogues of isocyanates, belong to the newly developed class of phospha-allenes R–C=P=X. The first examples of (I) have recently been synthesized and characterized by Appel and Paulen.[1,2] The t-butylphosphaketene is stable only below −60 °C and rapidly dimerizes to diphosphatenedione (II) at higher temperature, whereas the 2,4,6-tri-t-butylphenylphosphaketene is stable at room temperature. The stabilization of this class of compounds is thus crucially dependent upon the steric protection of bulky substituents.

$R{-}P{=}C{=}O$ (I)


(II)

One of the unusual properties of phospha-allenes is the site of protonation. Theoretical studies predict an α-carbon-site protonation either for carbodiphosphene (HP=C=PH) or for ethylidenephosphine (H_2C=C=PH) whereas the carboimidophosphine (HN=C=PH) prefers *P*-site-protonation.[3] In connection with our continuing theoretical studies on phosphorus compounds containing multiple bonds,[4] we report here theoretical results on related properties of the simplest phosphaketene, HPCO. In particular, we consider the geometry, linearity, vibrational frequencies, charge distribution, sites of protonation, and the mechanisms of some chemical reactions of HPCO.

Calculations

The calculations were carried out by using four basis sets: 4-31G,[5] 4-31G* [with *d*-functions on C, O, and P, $\alpha_d(P) = 0.5$], 6-31G** (with *d*-functions on C, O, P and *p*-functions on H), and DZP[6] [with the contraction (11*s*7*p*2*d*/6*s*4*p*2*d*) for P, (9*s*5*p*1*d*/4*s*2*p*1*d*) for C, N, O, and (4*s*1*p*/2*s*1*p*) for H]. The molecular geometries of the species considered were optimized by the force method with analytical gradient[7a] along with the optimally conditioned algorithm[7b] employing both 4-31G and 4-31G* basis sets for HPCO and only 4-31G for protonated HPCO species. Relative energies were obtained from single-point calculations at the Hartree–Fock (HF), second-, third-, and fourth-order Møller–Plesset perturbation theory[8] (MP2, MP3, MP4SDQ) employing the 6-31G** basis set and the 4-31G-optimized geometries. The designation of energy calculation level should be denoted by, for example, MP3/6-31G**//HF/4-31G. For simplicity, the second descriptor will, however, be omitted. The full harmonic force fields of HPCO (with 4-31G and 4-31G*) and protonated HPCO (with 4-31G) were calculated by gradient difference using the VA05AD subroutines.[9] The corresponding harmonic frequencies and normal co-ordinates were computed by the standard GF-matrix method.[10]

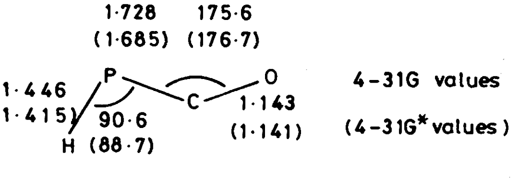
To maintain consistency with previous work on phosphorus compounds,[3,4] the electronic and molecular properties of HPCO are analysed from the DZP//4-31G wave functions. The localized molecular orbitals were obtained by means of the Foster–Boys procedure.[11,12] The molecular electrostatic potentials were computed by employing a modified version of the Denpot program[13] including the calculations with polarization *d*-functions.

All calculation procedures are implemented in the Monstergauss program[14a] except for the MPn/6-31G** for which an IBM-VM/CMS version of the Gaussian-80 program[14b] was used. The optimized geometries of the species considered will be displayed within the text.

Results and Discussion

(1) *Geometry and Molecular Deformation.*—The phosphaketene molecule is calculated to possess a planar *E*-bent structure (**1**). As expected, the 4-31G* basis set yields smaller values for both CP and PH bond lengths with respect to those of the 4-31G basis set. By comparison with the corresponding bond lengths in the parent H_2C=PH (**2**) and HN=C=O (**3**) molecules, we note that both PH and CO distances in (**1**) remain quasi-unchanged. As a matter of fact, the PH of bond length (**2**) was calculated at 1.449 and 1.419 Å with 4-31G and 4-31G*, respectively[3] and the CO of (**3**) at 1.146 Å with 4-31G*[15] (the CO distance in HNCO is incorrectly reproduced by the 4-31G basis set[15]).

More interesting, of course, are the values of the CP bond length and CPH bond angle. Table 1 shows that there are two opposite effects when the C=P bond has been cumulated with another C=X bond. For instance, the C=P is slightly compressed



(1)

$H_2C{=}Ph$

(2)

HN=C=O

(3)

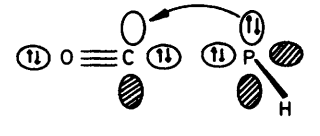


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Table 1. CP bond lengths (Å) and CPH bond angles (°) in some dico-ordinated phosphorus molecules calculated with the 4-31G basis set

Molecule	CP	Δ(CP)[a]	CPH	Δ(CPH)[b]
$H_2C{=}PH$[c]	1.672		98.5	
$H_2C{=}C{=}PH$[d]	1.657	−0.015	96.3	−2.2
$HP{=}C{=}PH$[c]	1.644	−0.028	97.5	−1.0
$HN{=}C{=}PH$[c]	1.718	0.046	92.3	−6.2
$O{=}C{=}PH$	1.728	0.056	90.6	−7.9

[a] Δ(CP) = CP (molecule) − CP ($H_2C{=}PH$). [b] Δ(CPH) = CPH (molecule) − CPH ($H_2C{=}PH$). [c] Ref. 3. [d] Ref. 20.

in cumulating either with a C=C or with a second C=P (as would be expected in cumulative systems), while it is significantly stretched under the action of a C=N or C=O bond. The latter geometric variation can easily be explained by considering the more electronegative character of the C=X (X = N or O) moiety with respect to the C=P.[3] Depopulation of the C=P bond by withdrawing its electrons *via* an inductive effect by the C=N or C=O group stretches their cumulating partner. The larger CP bond length in HPCO (**1**) is in line with the relative electronegativity of oxygen and nitrogen (see Table 1).

Furthermore, the geometry of phosphaketene (**1**) can also be regarded as a result of a stabilizing interaction between PH and CO fragments. The conjugation of the PH lone pair with the empty *p*-orbital of the CO carbon as illustrated by (**4**) becomes larger if the PH lone-pair electron has more π-character.

In spite of its apparent complex-like structure, HPCO is reluctant to undergo molecular deformation. In contrast to HNCO, where the barrier to linearity was previously calculated[16] at < 5 kcal mol^{-1} (*e.g.*, 0.1 kcal mol^{-1} at 4-31G and < 5 kcal mol^{-1} at MP3/6-311G**), the barrier in HPCO is 73 kcal mol^{-1}[*,†] at the 4-31G level. This barrier height arises essentially from the inversion of the P atom.[17]

(2) *Electronic Structure.*—The ground-state electronic configuration of HPCO (**1**) and HNCO (**3**) can be written as:

HPCO: $\cdots\cdot(1a'')^2(6\text{—}8a')^6(2a'')^2(9\text{—}12a')^8(3a'')^2(13a')$

HNCO: $\cdots\cdot(1a'')^2(8a\cdot)^2(9a')^2(2a'')^2(10a')$

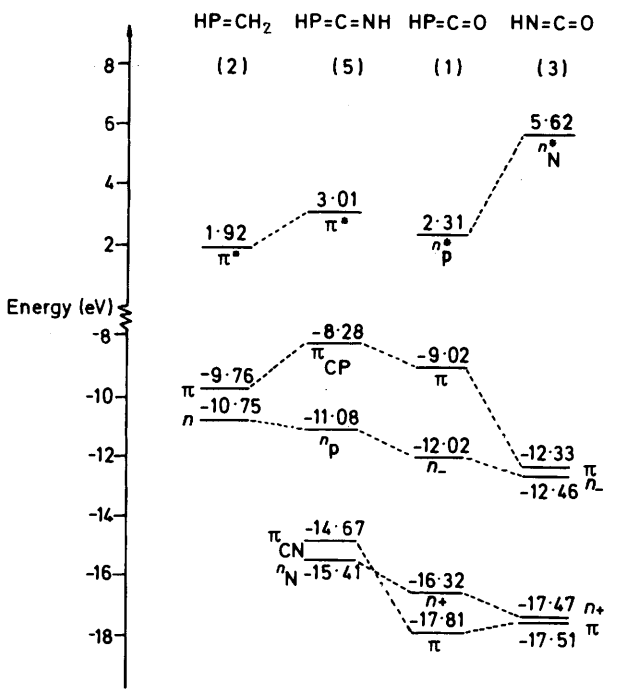

Figure 1. Orbital correlation diagram for the LUMOs and some HOMOs of HPCO (**1**), H_2CPH (**2**), HNCO (**3**), and HPCNH (**5**). Orbital energies calculated at DZP//4-31G level

The HOMOs in both molecules are π-orbitals. Each is delocalized on the molecular skeleton with the largest coefficients on P or N, respectively. Unlike other cumulenes,[3] the LUMOs of (**1**) and (**3**) can be described as n^*-orbitals of P and N rather than the usual π^*-orbitals. The electronic configuration of HPCO is between those of HNCO (**3**) and HP=C=NH (**5**) (Figure 1).

As in carbodi-imide (HN=C=NH) or carbodiphosphene (HP=C=PH),[3] HNCO (**3**) exhibits two quasi-degenerate *n* and π sets of orbitals. In contrast, *n* and π of each orbital set in both HPCO (**1**) and HP=C=NH (**5**) are widely separated. The *n*–π separation energies show larger values for both sets in HPCO (**1**). As expected from the respective electronegativies of the O and N atoms, an overall shift to lower electron affinity and ionization potential occurs in HPCO (**1**) with respect to HP=C=NH (**5**). As a consequence, the CO group appears to stabilize the *n*-orbital noticeably [1.27 eV; by comparison with that in the uncumulated $H_2C{=}PH$ (**2**)], whereas the CNH group destabilizes the π-orbital (1.48 eV, see Figure 1). These differences might imply a variation in the nature of their low-lying excited states as well as their complexation reactions with transition metals. Phosphaketenes might therefore prefer to form π-complexes with metals.

It is also interesting to examine the distribution of localized orbital charge centroids obtained from the Foster–Boys procedure. The main point seen from Figure 2 is the centroid picture for the HPCO molecule.

There is only one LMO centroid between the C and P atoms in (**1**), but there are two LMO centroids in the immediate neighbourhood of the P atom. The latter are best described as the lone pairs of the P atom rather than as a CP bond. Moreover, the centroid connecting the C and P atoms is positioned closer to the C atom in clear contrast to the distribution in HNCO (**3**) (see Figure 2a) where two equivalent centroids forming the C=N bond are on the side of N atom. Thus, it can be concluded that the carbon–phosphorus bond in

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[*] 4-31G data of the linear HPCO are: PH = 1.370, CP = 1.570, CO = 1.167 Å, and E = 453.304 39 a.u.

[†] We don't find a transition structure corresponding to the rotation of PH around the CP bond.

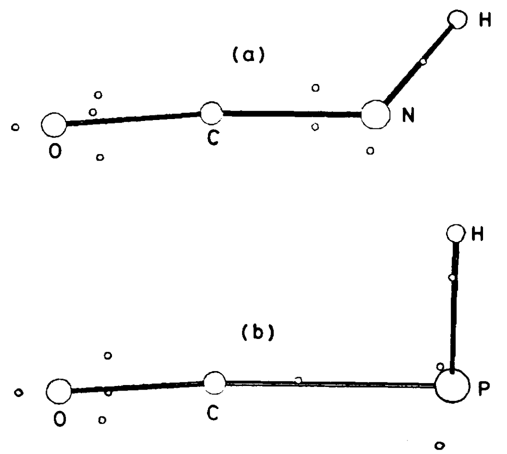
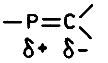
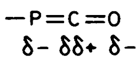


Figure 2. Localized orbital centroids in (a) HNCO and (b) HPCO


$-P=C\langle$ $\delta+\ \delta-$

(6)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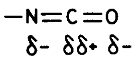

$-N=C=O$ $\delta-\ \delta\delta+\ \delta-$

(8)

Table 2. Net charges and overlap populations (DZP//4-31G)[a]

	$HP=CH_2$[b] (2)	$HP=C=NH$[b] (5)	$HP=C=O$ (1)	$HN=C=O$ (3)
Net charges				
C	−0.494	−0.062	0.099	0.474
P or N	0.173	−0.009	−0.056	−0.450
O or N		−0.253 (N)	−0.106 (O)	−0.338 (O)
Overlap populations				
C=P	1.084	0.850	0.729	
C=O			1.492	1.448
C=N		1.506		1.606
Dipole moment (D)				
μ	1.02	2.76	0.67	3.21
Second moment (a.u.)				
$\langle r^2 \rangle$	−45.5	−53.8	−56.3	−34.9

[a] The DZP//4-31G energies of HPCO and HNCO are −454.024 18 and −167.790 30 a.u., respectively. [b] Ref. 3.

HPCO (**1**) is essentially a dative single bond enforced by a π-back-donation.

(3) *Charge Distribution.*—Consistent with its long bond length, the overlap population of the CP bond in HPCO (**1**) is calculated to be the smallest among the molecules considered (see Table 2). Also the CO population is somewhat larger in (**1**) than in (**3**). The polarizations of HPCO and HNCO are similar but reversed relative to $H_2C=PH$ (see also ref. 1). The net negative charge on P in HPCO is in part reflected by the strongly negative values observed for the ^{31}P chemical shift in phosphaketenes, namely δ_P −180[1] and −207.4 p.p.m.[2] in t-butyl- and 2,4,6-tri-t-butylphenyl-phosphaketene, respectively. By comparison, δ_P for phospha-alkenes is normally observed at >200 p.p.m.[17]

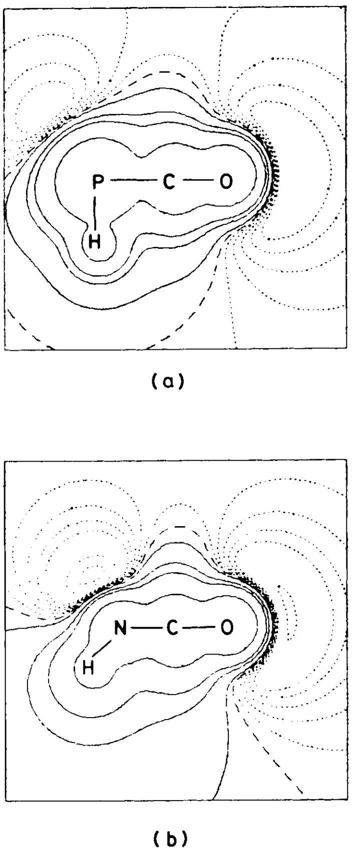


Figure 3. Molecular electrostatic potential in molecular planes: (a) HPCO, (b) HNCO. Isopotentials contours are given in 10^{-2} atomic units: 50.0, 10.0, 5.0, 1.0, 0.0, −0.5, −1.0, −1.5, −2.0, −2.5, −4.5, and −5.5

The rather small difference between the negative charges on P and O ($0.05e^-$) indicates that both centres may be in competition for attracting electrophilic agents. The calculated molecular electrostatic potentials (m.e.p.s) at 4-31G*//4-31G* level for HPCO and HNCO are displayed in Figure 3. In each molecule there are two minima corresponding to the lone pairs of the O and the P or N atoms, respectively. The most pronounced minima are of course located around nitrogen (−37.3 kcal mol^{-1}) in HNCO and oxygen (−25.3 kcal mol^{-1}) in HPCO.

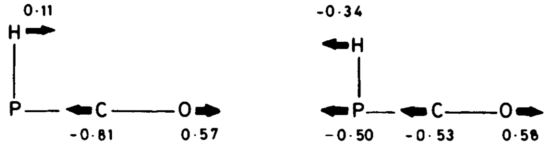
Furthermore, the absolute values of the charge in HNCO (**3**) (see Table 2) are all much larger than the corresponding ones in HPCO (**1**). This large difference in polarities is for instance shown by a larger dipole moment found for HNCO, namely 3.21 D at DZP//4-31G instead of 0.67 D for HPCO. The quota of the respective extents of the charge distribution for the couple HNCO/HPCO is estimated from the second moments $\langle r^2 \rangle$ at *ca.* 2/3.

(4) *Vibrational Frequencies of* HPCO.—The harmonic vibrational frequencies calculated with both 4-31G and 4-31G* basis sets (using their respective optimized parameters as reference geometries) are listed in Table 3.

The 4-31G frequencies are systematically smaller than the 4-31G* values as in other molecules containing only first-row atoms (C,N,O,H).[18] The stretching frequencies of C=X double bonds are slightly underestimated by 4-31G calculations (*ca.* 95% of experimental values). In such cases, the larger frequencies obtained from the 4-31G* basis set should thus be considered as a relative improvement which may be an overestimation. At the moment, the only i.r. experimental datum

Table 3. Harmonic vibrational frequencies of HPCO

		Wavenumber (cm^{-1})		
		4-31G	4-31G*	Assignment
A'	ν_1	2 239	2 462	PH stretching
	ν_2	2 164	2 195	PCO asymmetric stretching
	ν_3	970	1 000	HPC bending
	ν_4	635	738	PCO symmetric stretching
	ν_5	436	479	PCO bending
A''	ν_6	481	549	torsion



(9) (10)

Figure 4. Normal co-ordinates of two P=C=O stretching modes: (**9**) asymmetric (ν_2) and (**10**) symmetric (ν_4) with 4-31G basis set

reported for phosphaketenes is the value of 1 953 cm^{-1} assigned as the frequency of the asymmetric stretching of the whole P=C=O group in tri-t-butylphenylphosphaketene.[2] Figure 4 indicates that there are, as in other cumulenes,[3] two stretching modes involving the PCO skeleton: one is asymmetric and vibrates at 2 167 cm^{-1} and another symmetric and at 630 cm^{-1} (4-31G values). The former is comparable with the experimental frequency of 1 953 cm^{-1}. It can be in fact expected that a substituent such as the tri-t-butylphenyl does reduce the multiple-bond stretching frequency.[19]

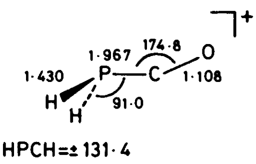
The PH stretching frequency is also close to the 4-31G value of 2 220 cm^{-1} calculated for the *E*-diphosphene.[20] On the other hand, the torsion mode of HPCO has a smaller frequency (808 cm^{-1} in HP=PH [19]).

In summary, a comparison between harmonic frequencies calculated by 4-31G and 4-31G* basis sets suggests that the *d*-functions on phosphorus as well as on first-row atoms [18] are not necessary in the calculations of harmonic vibrational frequencies for dico-ordinated phosphorus molecules. As a result of a balanced mutual cancellation between polarization and correlation effects,[21] the 4-31G structural data seem to be closer to the experimental ones for this type of compound. More computed data are of course necessary to point out the general trend.

(5) *Site of Protonation*.—The 4-31G-optimized geometries of five possible structures of protonated HPCO species are given in (**11**)—(**15**) which are formed from P-, α-C-, and O-site protonation of (**1**) respectively. The calculated total energies of neutral and protonated HPCO at different levels using 4-31G geometries are summarized in Table 4. The proton affinities at each site can be estimated from equation (1) where ΔE is the calculated energy difference $E(H_2PCO^+) - E(HPCO)$ and ΔZPE is the zero-point vibrational energy difference $ZPE(H_2PCO^+) - ZPE(HPCO)$.

$$PA = \Delta E - \Delta ZPE \qquad (1)$$

The remaining contributions have been omitted. Table 5 shows the energy differences ΔE and the calculated proton affinities by employing ΔE values at MP4/6-31G** level and ΔZPE values at HF/4-31G level.



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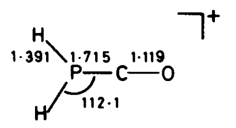

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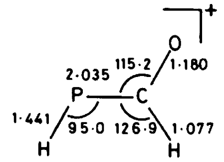

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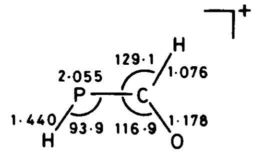

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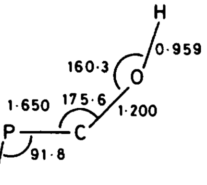

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(a) *Geometries of protonated species*. The eigenvalues of the energy second-derivatives matrix show that the pyramidal (**11**) and the planar (**12**) P-site protonated structures are both local minima in the energy surface. The α-C-site protonation yields, as expected, two formylphosphenium cation isomers, namely the *cis*-(**13**) and the *trans*-(**14**) which are both planar. Finally there is only one stable structure (**15**) (also planar) formed from the *O*-protonation.

The CP bond lengths in (**11**), (**13**), and (**14**) are unusually long so that we can say that the O atom continues to lengthen the CP bond in the cations, as in the neutral (**1**), by means of an inductive effect. The pyramidal (**11**) has a long CP distance (1.967 Å) by comparison with those in the planar (**12**) (1.715 Å) or in the neutral (**1**) (1.728 Å). Further, it is seen that the CO bond lengths become shorter in both *P*-protonated (**11**) and (**12**). The values of 1.11—1.12 Å are in fact typical of the CO triple bond. Such an observation has also previously been made for the *N*-protonated HNCO species.[22]

The nearly perpendicular configuration of (**11**) also suggests that this structure can be best regarded as a stable complex between two PH_2^+ and CO fragments rather than a normal cation. The CP distances of 2.035—2.055 Å in (**13**) and (**14**) are also far larger than the CP bond length of 1.75 Å (4-31G) in the vinyl phosphenium cation ($H_2C=CH=PH^+$) or of 1.84 Å in the imidoylphosphenium cation ($HN=CH=PH^+$).[3] Here again, both (**13**) and (**14**) appear more likely as stable complexes involving PH and HCO^+ groups. Concerning the structure (**15**), the positive charge is mainly localized at the O atom so that its valence structure is best described as $H{-}P{=}C{=}\overset{+}{O}{-}H$.

(b) *Proton affinities*. The main conclusion which emerges from the data listed in Tables 4 and 5 is that *P*-protonation is unambiguously preferred. For instance, structure (**11**) shows the lowest energy among five minima considered for H_2PCO^+. Inclusion of polarization functions and correlation energies acts in favour of the *P*-protonation and particularly the most stable structure (**11**). With an energy difference of 52—60 kcal mol^{-1} (PAs, Table 5), which separates (**11**) on one hand from (**14**) (α-C-

Table 4. Calculated total energies (a.u.) of neutral and protonated HPCO species[a]

Species	HF/4-31G	HF/6-31G**	MP2/6-31G**	MP3/6-31G**	MP4/6-31G**
HPCO (**1**)	−453.410 36	−454.000 40	−454.410 43	−454.416 07	−454.428 75
H_2PCO^+ (**11**) (*P*-protonation)	−453.708 97	−454.314 41	−454.712 83	−454.723 28	−454.738 48
H_2PCO^+ (**12**) (*P*-protonation)	−453.663 28	−454.259 71	−454.669 11	−454.676 57	−454.690 07
H_2PCO^+ (**13**) (α-*C*-protonation)	−453.630 39	−454.215 77	−454.610 80	−454.628 35	−454.641 72
H_2PCO^+ (**14**) (α-*C*-protonation)	−453.634 21	−454.216 08	−454.611 35	−454.628 48	−454.642 01
H_2PCO^+ (**15**) (*O*-protonation)	−453.640 64	−454.221 32	−454.631 68	−454.645 14	−454.656 40

[a] Energies calculated with 4-31G-optimized geometries given in (**1**) and (**11**)—(**15**). [b] MP4 denotes MP4SDQ: Møller–Plesset fourth-order perturbation theory including single, double, and quadrupole substitutions.

Table 5. Relative energies of neutral and protonated HPCO and calculated proton affinities of HPCO (kcal mol^{-1})

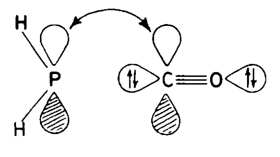
Species	4-31G	6-31G**	MP2/6-31G**	MP3/6-31G**	MP4/6-31G**	ZPE[a]	PA[b]
HPCO (**1**)	0.0	0.0	0.0	0.0	0.0	9.9	
H_2PCO^+ (**11**) (*P*-protonation)	−187.3	−197.0	−189.7	−192.7	−194.3	16.5	187.7
H_2PCO^+ (**12**) (*P*-protonation)	−158.7	−162.7	−162.3	−163.4	−163.9	16.3	157.5
H_2PCO^+ (**13**) (α-*C*-protonation)	−138.0	−135.1	−125.7	−133.2	−133.6	17.3	126.2
H_2PCO^+ (**14**) (α-*C*-protonation)	−140.4	−135.3	−126.0	−133.3	−133.8	17.4	126.3
H_2PCO^+ (**15**) (*O*-protonation)	−144.4	−138.6	−138.8	−143.7	−142.8	17.0	135.7

[a] Zero-point vibrational energies calculated at HF/4-31G level (kcal mol^{-1}). [b] Proton affinities calculated from MP4/6-31G** energy differences and corrected by ZPEs: PA = $-[E(H_2PCO^+) - E(HPCO)] - [ZPE(H_2PCO^+) - ZPE(HPCO)]$, see text.

site) or (**15**) (O-site) on the other hand, it is reasonable to postulate that α-*C*- and *O*-protonated species (**13**)—(**15**) respectively, can be excluded as candidates for the protonated structure of HPCO (**1**). Although *N*-protonation was also found to be the most favoured process for the HNCO molecule,[22] the energy difference between both to be N-site and O-site proton affinities was however calculated only 18 kcal mol^{-1} with a double-zeta basis set.[22]

From these results, it is clear that a consideration based only on the charge distribution has failed once again to predict the behaviour of the protonation process in cumulenes[23] (the O atom having in fact the most negative charge, see above). A correct charge-based prediction thus appears to be fortuitous. This approach has recently been improved by Klopman *et al.*[24,25] by including in the reaction potential, in addition to the electrostatic potential, other components such as the charge transfer, the polarization, *etc.* Further applications are no doubt necessary to assess the generality of the approach.

It is surprising to note that the 4-31G proton affinity (PA) of 187 kcal mol^{-1} of HPCO (Table 5 with ZPE correction) is slightly larger than the N-site PA of 182 kcal mol^{-1} in HNCO at DZ level.[22] The relative basicities of P and N atoms are thus reversed by comparison with the couple PH_3–NH_3 where the experimental PA of the former is *ca.* 15 kcal mol^{-1} smaller (187 in PH_3 and 202 in NH[26]). Within the two *P*-protonated species (**11**) and (**12**), the energy difference is calculated at 30 kcal mol^{-1} (MP4/6-31G**) in favour of the pyramidal (**11**). A reverse situation has been found for the *N*-protonated HNCO[23] for which the (**12**)-like planar structure has lower energy. This difference can be partially rationalized by the orbital interaction argument. A planar structure (**12**) involves inevitably a face-to-face position between two empty orbitals on P and C atoms [see (**16**)]. To avoid such a repulsive orbital interaction and meanwhile to gain an attractive interaction between the C lone pair and the P empty orbital, the PH_2 group adopts a perpendicular configuration [see (**17**)]. In contrast, the positive charge in H_2NCO^+ is most likely concentrated on the CO group so that only a planar structure allows a full delocalization of the N lone pair into the empty orbital of either C or O atom and hence stabilizes the cation [see (**18**)]. This view can be supported by the CN distance of 1.27 Å, as previously calculated (DZ)[22] for the planar H_2NCO^+, which is a typical carbon–nitrogen double bond.



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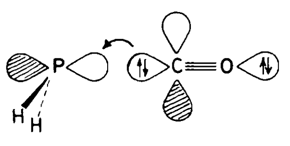

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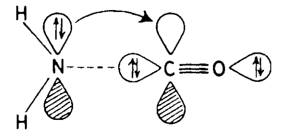

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Finally, our best value (MP4/6-31G** together with ΔZPE) predicts a proton affinity of 188 kcal mol^{-1} for the HPCO molecule. This value is comparable to that of 184 kcal mol^{-1} calculated for the P-site PA of phosphaethene (**2**) (H_2C=PH) at nearly the same level, MP4/6-31G**//HF/6-31G*.[27]

(6) *Dissociation of* (**1**) *and* (**11**).—To provide further insight into the stability of the neutral (**1**) and protonated (**11**) HPCO, we have also considered the related dissociations of both molecules to fragments. In recent studies ,[27,28] $PH_2{}^+$ (**19**) was shown to have a singlet ground state. Therefore we consider only equation (4). For PH, both singlet (**20**) and triplet (**21**) states are calculated [equations (2) and (3)]. The calculated

$$\text{HPCO } (\mathbf{1}) \longrightarrow \text{PH (singlet) } (\mathbf{20}) + \text{CO} \qquad (2)$$

$$\text{HPCO } (\mathbf{1}) \longrightarrow \text{PH (triplet) } (\mathbf{21}) + \text{CO} \qquad (3)$$

$$H_2PCO^+ \ (\mathbf{11}) \longrightarrow PH_2{}^+ \text{ (singlet) } (\mathbf{19}) + \text{CO} \ (4)$$

Table 6. Calculated energies of fragments PH_2^+, PH, and CO at different levels[a]

	HF/6-31G**	MP2/6-31G**	MP3/6-31G**	MP4/6-31G**	ZPE[b]
PH (singlet)	−341.191 20	−341.278 27	−341.297 06	−341.301 78	3.0
PH (triplet)[c]	−341.266 28	−341.341 68	−341.357 78	−341.361 29	3.0
CO[d]	−112.737 26	−113.020 13	−113.018 37	−113.029 15	3.3
PH_2^+ (singlet)	−341.510 35	−341.602 58	−341.622 65	−341.627 60	8.1

[a] Energy calculations with 4-31G geometries, 4-31G energies are omitted. [b] Zero-point vibrational energies at HF/4-31G (in kcal mol^{-1}). [c] With UHF method. [d] We found that MP3 energy is higher than MP2 energy (!).

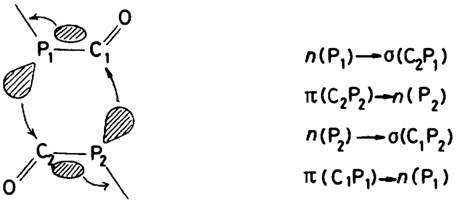
Table 7. Dissociation energies of HPCO and H_2PCO^+ at different level of calculations (kcal mol^{-1})

Dissociation energy[a]	HF/6-31G**	MP2/6-31G**	MP3/6-31G**	MP4/6-31G**
HPCO ⟶ PH (singlet) + CO [equation (2)]	41.5	66.7	59.5	57.8
HPCO ⟶ PH (triplet) + CO [equation (3)]	−5.6	26.9	21.4	20.4
H_2PCO^+ ⟶ PH_2^+ (singlet) + CO [equation (4)]	36.5	51.1	46.2	45.9

[a] ZPE are taken into account at all levels.

total energies at different levels and ZPE at 4-31G level of fragments are collected in Table 6. The dissociation energies are recorded in Table 7. We note that when the size of the correlation energy increases, the dissociation energy in all cases decreases. With larger basis sets, these quantities will be slightly reduced. At MP4/6-31G** level, HPCO (**1**) lies only 20 kcal mol^{-1} below the PH and CO fragments in their ground states. This value is relatively small to ensure the stability of the HPCO molecule. In contrast, the protonated HPCO (**11**) is 46 kcal mol^{-1} below the fragments PH_2^+ and CO and may thus be a candidate for experimental observation.

(7) *Chemical Reactions of Phosphaketenes.*—(a) *Addition to* HX. As pointed out by Appel and Paulen,[1] the addition of proton-acidic reagents HX to phosphaketenes can be well explained by their polarity [see (7)]. In the reaction of HCl with t-butylphosphaketene (the first and the only reaction actually realized at present[1]), a phosphino-chloro-acid (**22**; X = Cl) has been obtained. We can imagine a transition state being formed



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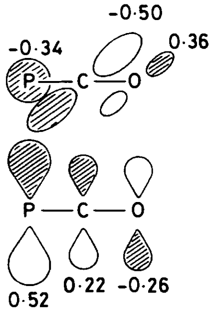

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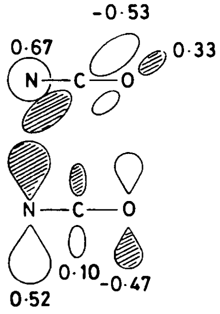

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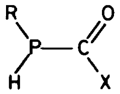

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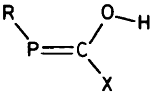

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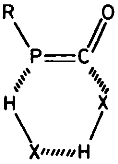

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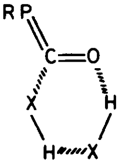

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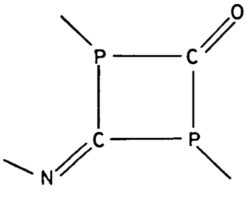

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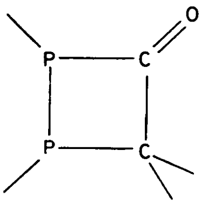

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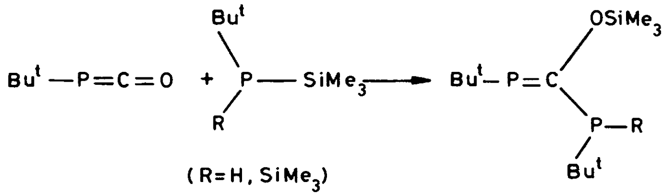

$$\mathrm{Bu^t{-}P{=}C{=}O} + \mathrm{P(Bu^t)(R){-}SiMe_3} \longrightarrow \mathrm{Bu^t{-}P{=}C(OSiMe_3){-}P(R)Bu^t} \quad (5)$$

(R=H, $SiMe_3$)

from R–P=C=O and at least two HX molecules as displayed in (**24**). The question is whether (**22**) is formed directly *via* (**24**) or only in a subsequent step. In other words, the formation of (**23**) *via* the transition state (**25**) in the rate-determining step should not be ruled out because the C=O bond in cumulated systems reacts more easily than, for example, the C=C bond with the water dimer.[29,30]

In fact, compounds (**23**) have also been prepared by Appel and Paulen[1] in reaction (5). It is well established that the $SiMe_3$ group stabilizes considerably the enol structure with respect to the ketone structure.[31]

(b) *Cycloadditions*. The dimerization of phosphaketenes[1] occurs exclusively as a head-to-tail addition of two C=P bonds leading to diphosphetane (II). From the charge movement, the P atom behaves like a σ-bond donor centre in a cyclic movement of the electron pairs [see (**26**)].

As seen from (**27**) and (**28**) the HOMO and LUMO coefficients of HPCO (**1**) and HNCO (**3**) are very similar. Nevertheless, from the orbital energies reported in Figure 1, it is somewhat difficult to predict the major adduct that could be obtained from the 1,1-condensation, for example, between phosphaketenes and isocyanates (RNCO).

The condensation of –P=C=O to –P=C=N– can be considered as a (2 + 2) addition controlled by a HOMO(P=C=N)–LUMO(P=C=O) interaction (Figure 1) giving the diphosphetanes (**29**). Furthermore, the condensation of –P=C=O to phospha-alkenes >C=P– may lead to a head-to-head addition by forming the diphosphetanes (**30**).

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References

1 R. Appel and W. Paulen, *Tetrahedron Lett.*, 1983, **24**, 2639.
2 R. Appel and W. Paulen, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 785.
3 M. T. Nguyen and A. F. Hegarty, *J. Chem. Soc., Perkin Trans. 2*, 1985, 2005.
4 T. K. Ha, M. T. Nguyen, and P. Ruelle, *Chem. Phys.*, 1984, **87**, 23.
5 (*a*) R. Ditchfield, W. J. Hehre, and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724; (*b*) W. J. Hehre and W. A. Lathan, *ibid.*, 1972, **56**, 5244.
6 (*a*) T. H. Dunning and P. J. Hay, 'Modern Theoretical Chemistry,' ed. H. F. Schaefer, Plenum Press, New York, 1976, vol. 3, p. 24; (*b*) For details of the DZP basis set, see ref. 22.
7 (*a*) H. B. Schlegel, *J. Comput. Chem.*, 1982, **3**, 214; (*b*) W. C. Davidon, *Mathematical Programming*, 1975, **9**, 1.
8 R. Krishnan, M. J. Frisch, and J. A. Pople, *J. Chem. Phys.*, 1980, **72**, 4244.
9 M. J. D. Powell: 'VA05AD Program,' Harwell Subroutines Library, Atomic Energy Research Establishment, Harwell.
10 E. B. Wilson, J. C. Decius, and P. C. Cross, 'Molecular Vibrations,' McGraw-Hill, New York, 1955.
11 J. M. Foster and S. F. Boys, *Rev. Mod. Phys.*, 1960, **32**, 300.
12 D. Peeters, Boyloc Program, QCPE 330.
13 D. Peeters and M. Sana, Denpot Program, QCPE 360.
14 (*a*) R. A. Poirier and M. A. Peterson, Monstergauss Program, University of Toronto, Canada; (*b*) J. S. Binkley, R. A. Whiteside, R. Krishnan, R. Seeger, D. J. DeFrees, H. B. Schlegel, S. Topiol, L. R. Kahn, and J. A. Pople, Gaussian 80 Program, QCPE 406.
15 C. Glidewell and C. Thomson, *Chem. Phys. Lett.*, 1982, **86**, 340.
16 C. Glidewell and C. Thomson, *J. Mol. Struct., THEOCHEM*, 1983, **104**, 287.
17 R. Appel, F. Knoll, and I. Ruppert, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 731.
18 J. A. Pople, H. B. Schlegel, R. Krishnan, D. J. DeFrees, J. S. Binkley, M. J. Frisch, R. A. Whiteside, R. F. Hout, and W. J. Hehre, *Int. J. Quant. Chem., Quant. Chem. Symp.*, 1981, **15**, 269.
19 P. O'Neill, personal communication.
20 M. T. Nguyen and A. F. Hegarty, following paper.
21 M. T. Nguyen, *Z. Naturforsch, Teil A*, 1984, **39**, 169.
22 S. Green, *J. Phys. Chem.*, 1981, **85**, 1676.
23 T. K. Ha and M. T. Nguyen, *J. Mol. Struct., THEOCHEM*, 1982, **88**, 335.
24 G. Klopman, H. Moriishi, O. Kikucki, and K. Suzuki, *Tetrahedron Lett.*, 1982, **23**, 1027.
25 H. Moriishi, O. Kikuchi, K. Suzuki, and G. Klopman, *Theor. Chim. Acta*, 1984, **64**, 319.
26 S. Ikuta and P. Kebarle, *Can. J. Chem.*, 1983, **61**, 97.
27 L. L. Lohr, H. B. Schlegel, and K. Morokuma, *J. Phys. Chem.*, 1984, **88**, 1981.
28 J. F. Harrison, *J. Am. Chem. Soc.*, 1981, **103**, 7406.
29 M. T. Nguyen and T. K. Ha, *J. Am. Chem. Soc.*, 1984, **106**, 599.
30 M. T. Nguyen and A. F. Hegarty, *J. Am. Chem. Soc.*, 1984, **106**, 1552.
31 J. E. Dubois and G. Axiotis, *Tetrahedron Lett.*, 1984, **25**, 2143.

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