Prototypical Triplet Alkyl Phosphonatocarbenes[†]

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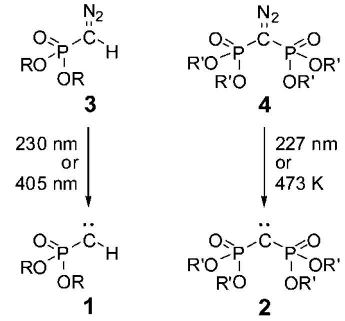
The current case study focuses on the generation, identification, and characterization of two representative mono- and disubstituted alkyl phosphonatocarbenes by means of matrix isolation techniques in conjunction with density functional theory [B3LYP/6-311++G(d,p)] and coupled cluster [CCSD(T)/cc-pVXZ, X = D, T] computations. The EPR measurements identify both carbenes as triplet ground-state species with *D* values of 0.660 and 0.623 cm^{-1}, respectively, exhibiting persistency toward intramolecular reactions (the EPR signal observable in perfluoromethylcyclohexane up to around 70 K for the disubstituted molecule). While the reaction of the carbene center of the conformationally rich tetramethyl bisphosphonatocarbene with the CH bonds of the methyl groups leads to phosphaoxetane at room temperature, its fragmentation via a Wittig-type reaction during high vacuum flash pyrolysis (HVFP) results in dimethyl vinylphosphonate and methyl metaphosphate. The latter has been observed for the first time as an isolated entity.

Introduction

Studies of triplet carbenes have given birth to an impressive number of compounds belonging almost exclusively to the class of arylcarbenes,[1] some of which are observable even at room temperature.[2] Such substitution stabilizes these inherently electronically deficient species with radical-like reactivity kinetically by σ-bonds strengthened against homolysis *and* thermodynamically by conjugation. The price of the increased thermodynamic stability is often the delocalization of unpaired electrons away from the divalent carbon, as documented by EPR zero field splitting (ZFS) parameters[1,2a,3−5] and products[1,2b,6] from reactions of the separate radical centers of these paramagnetic molecules. To counter the principal drawback of decoupling of the unpaired electron spins by aryl substituents, we have conceptualized triplet ground-state carbenes gaining kinetic stability through polar bonds surrounding the carbene carbon atom.[7] Substituting the carbene center with electropositive atoms that bear otherwise polar bonds to highly electronegative elements as in $F_3Si{-}C{-}SiF_3$ assures triplet multiplicity on the one hand and accounts for the electronic deficit immanent to carbenes on the other. Indeed, arene-free carbenes with substituents containing polar bonds to atoms more electropositive than the carbene carbon, e.g., $F_3C{-}C{-}CF_3$,[8] $H{-}C{-}Si(OCH_3)_3$,[9] $H{-}C{-}SiCl_2H$,[10] and $H{-}C{-}SiH_3$[11] possess triplet ground states. A recent theoretical investigation[12] on dimethyl phosphonatonitrene supports validity of this general concept also for nitrenes. Given the prediction[7] of a triplet ground-state multiplicity for the parent bisphosphonatocarbene combined with the persistency toward intramolecular rearrangements of some of their alkylated derivatives,[13] alkyl phosphonatocarbenes should expand the list of stabilized triplet carbenes. In the present case study we have examined these aspects for mono- and bisphosphonatocarbene **1** and **2** (Scheme 1) by the matrix isolation technique and electronic structure computations.

SCHEME 1: Studied Phosphonatocarbenes and Their Respective Diazo Precursors: R = Ethyl, R′ = Methyl



Methods

Experimental Methods. The diazo precursors **3** and **4**, synthesized according to the procedures developed by Seyferth et al.[14] and McKenna et al.[15] were evaporated at 268 and 326 K, respectively, and co-condensed with Ar on a sample holder (CsI or BaF_2 crystal window for IR/UV, Cu rod for EPR measurements) of the matrix apparatus. Achieving optimal spectral quality of the deposited matrix as well as improving the efficiency of the photolysis of conformationally flexible **4** required increasing the temperature from 12 to 35 K. For homogeneity, the matrices containing **1** and **2** were tempered for 1−2 h at 35 K ahead of EPR (X-band; 0−6950 G) sampling at 18 K. To determine the temperature of disappearance of the EPR signal, the sample was irradiated, warmed and cooled to 18 K iteratively. IR and UV spectra were taken at 12 K, independent of the temperature maintained during the preceding experiment. IR spectroscopic measurements cover the range of 760−4000 cm^{-1} (in single cases additionally beginning with 400 cm^{-1}), UV spectra were recorded in the 200−1100 nm window. Photolysis at 248, 254, and 227−405 [227, 230, 313, 366, 405] nm were performed with a KrF-Excimer-LASER (LPX 100 Lambda Physik), a mercury low-pressure spiral lamp (Graentzel) equipped by either vycor or interference filter, and

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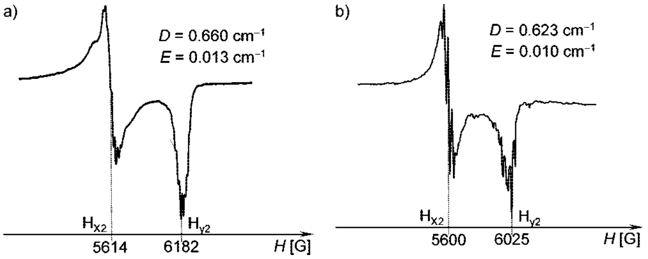


Figure 1. Key parts of EPR spectra of (a) **1** and (b) **2** obtained through irradiation of **3** and **4** at 230 and 227 nm in an Ar matrix (18 K), respectively.

a mercury high-pressure lamp (HBO 200 Osram) combined with a monochromator (Bausch & Lomb) respectively. All NMR measurements were undertaken in DMSO.

Theoretical Methods. Geometry optimizations along with analytic determination of the harmonic vibrational frequencies were carried out by utilizing the three-parameter gradient corrected B3LYP density functional, in combination with a segmentally contracted Pople-type basis set supplied with diffuse and polarization basis functions for all kinds of atoms, 6-311++G(d,p).[16,17] Stationary points were characterized by their number of imaginary frequencies and transition structures were verified to connect the anticipated potential energy minima by the intrinsic reaction coordinate[18] algorithm. For selected (parent) systems geometries were additionally optimized and harmonic frequencies computed analytically[19] with the higher accuracy coupled cluster method truncated to single and double substitutions as well as perturbatively added triple excitations CCSD(T)[20] with generally contracted correlation consistent multiple ζ basis sets including polarization basis functions for valence electrons (cc-pVDZ and cc-pVTZ).[21] Unrestricted reference wave functions were employed for open-shell species; all other structures were computed with the restricted formalism. Reported electronic energies are corrected for zero-point vibrational energies (ZPVEs). In the graphical depiction of simulated IR spectra the widths at half-maximum are uniformly set to 4 cm^{-1} except for Figure 5, where it amounts to 1 cm^{-1} for the methyl metaphosphate monomer; no weighting was applied for the conformers contributing for the computed spectra (Figures 2 and 3). ZFS parameters were calculated[22] on the basis of the recorded EPR signals, assuming the equivalence of the g_x and g_y parameters to the Landé factor in the frame of the classic model of exclusive dipolar spin−spin coupling.

Results and Discussion

We attempted the preparation of monosubstituted diethyl phosphonatomethylene **1** both through HVFP and through photolysis of the diazo precursor **3**. Diethyl diazomethylphosphonate (**3**) underwent formal ester pyrolysis reaction upon thermal treatment at 970−1170 K and spectroscopic data showed the formation of ethylene but no evidence for **1**. Light of 254 and 313 nm causes destruction of the photolysis product due to the broad absorption around 265 nm (cf. Supporting Information) prior to complete conversion of **3**. In contrast, photolysis of the matrix isolated **3** at 230 or 405 nm gave a product that could be identified as a triplet carbene by its EPR transitions (Figure 1a). The triplet ground state with singlet−triplet energy splitting, ΔE_{ST}, of 7.9 kcal mol^{-1} is favored by B3LYP/6-311++G(d,p); for parent H−C−PO(OH)$_2$ $\Delta E_{\text{ST}} = 10.3$ kcal mol^{-1} at the same level of theory, whereas it amounts to 11.9 kcal mol^{-1} at CCSD(T)/cc-pVDZ. The values refer to the most stable syn conformer of the triplet carbene with respect to relative positions of H and the formal[23] PO double bond.

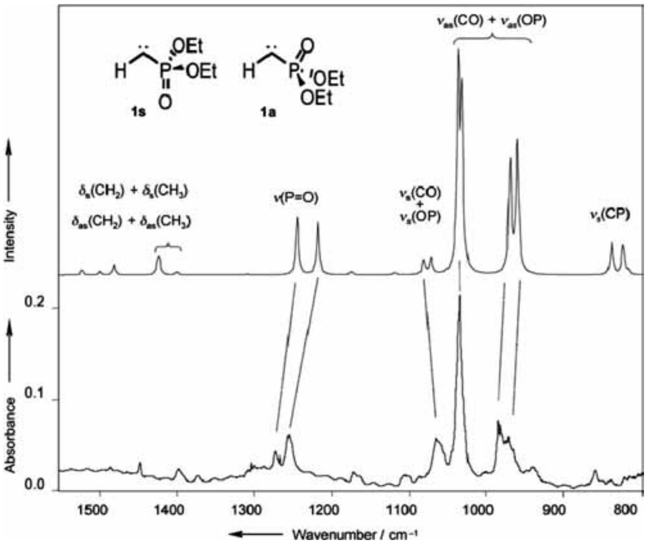


Figure 2. Representative parts of computed (top: B3LYP/6-311++G(d,p)) and experimental (bottom: 50% conversion after 2 h irradiation at 230 nm of **3** in Ar matrix; bands of unreacted starting material removed by subtraction) IR spectra of ^{3}**1**. Simulated spectrum considers both most stable conformers of ^{3}**1** (*syn* and *anti*).

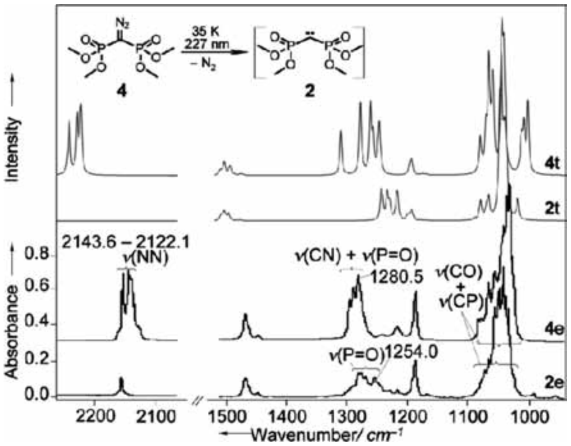
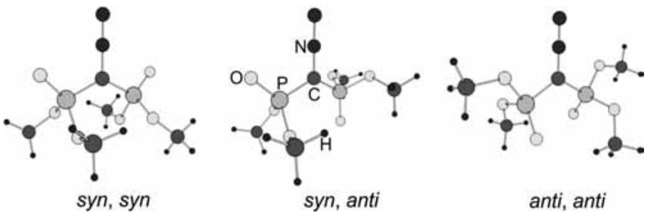


Figure 3. IR spectra of tetramethyl diazomethyldiphosphonate prior to (**4**e) and after (**2**e) 3.5 h irradiation at 227 nm and 35 K in an Ar matrix. **2**t, **4**t: excerpts of summed spectra for three conformers of ^{3}**2** and **4** computed at B3LYP/6-311++G(d,p), respectively.

The bandwidth in the measured vibrational spectrum (Figure 2) of ^{3}**1** indicates the presence of more than one conformer in the Ar matrix. Consideration of the computed IR spectra of the most stable conformers with respect to the ethoxy group of the syn and anti rotamers reproduces the main features of the recorded spectrum. The energy difference of these conformers of triplet diethyl phosphonatomethylene at B3LYP/6-311++G(d,p), $\Delta E_{\text{anti-syn}} = 1.1$ kcal mol^{-1}, compares well with that of H−C−PO(OH)$_2$ at CCSD(T)/cc-pVDZ ($\Delta E_{\text{anti-syn}} = 1.0$ kcal mol^{-1}), which, however, should be more conformationally flexible than ^{3}**1** with $E_{\text{Rot(anti}\rightarrow\text{syn)}} < 1$ kcal mol^{-1}. Strikingly, the vibrational frequencies for ν(P═O) in the experimental IR spectra of ^{3}**1** appear at *higher* wavenumbers than computed in the frame of the harmonic oscillator approximation ($\nu_{\text{exp}}(^3\mathbf{1}) = 1255.1{-}1272.2$ cm^{-1} vs $\nu_{\text{theor}}(^3\mathbf{1}_{\mathbf{syn}}) = 2119.0$ cm^{-1}, $\nu_{\text{theor}}(^3\mathbf{1}_{\mathbf{anti}}) = 1245.6$ cm^{-1}). The same tendency is found for the corresponding diazo compound **3** ($\nu_{\text{exp}}(\mathbf{3}) = 1263.1$ cm^{-1} vs $\nu_{\text{theor}}(\mathbf{3}) = 1255.9$ cm^{-1}, 1258.6 cm^{-1}) as well as for the disubstituted ^{3}**2** ($\nu_{\text{exp}}(^3\mathbf{2}) = 1254.0{-}1281.8$ cm^{-1} vs $\nu_{\text{theor}}(^3\mathbf{2}) = 1216.9{-}1244.9$ cm^{-1}) and **4** $\nu_{\text{exp}}(\mathbf{4}) = 1280.5{-}1295.4$ cm^{-1} vs $\nu_{\text{theor}}(\mathbf{4}) = 1244.9{-}1278.8$ cm^{-1}). In part, this observation can be rational-

SCHEME 2: Representation of Selected Conformers of 4 (B3LYP/6-311++G(d,p)) with Varying Relative Orientations of CNN and formal P═O Moieties



ized in terms of elongation (10^{-3} Å with respect to $CH_3PO(OH)_2$) of the PO bonds with maximal double bond character due to the well-known overestimation[24] of the degree of p-electron delocalization by the DFT methods. Basis set incompleteness and inclusion of diffuse basis functions on the P atom lengthen the PO bonds (10^{-2} Å for the formal double bonds) and weaken the respective vibrations, as exemplified for PO_2H, PO_2OH, and PO_2OCH_3 (cf. Supporting Information).

Tetramethyl bisphosphonatocarbene **2** was obtained in an Ar matrix by irradiation of the diazo precursor **4** at its absorption maximum (227 nm). By analogy to **1**, generation of **2** at 248, 254, 313, and 366 nm proves inefficient owing to two broad absorptions around 272 and 345 nm (cf. Supporting Information) of **2**, which, however, is not affected by light of 227 nm. Some starting material (<10%) remains even after prolonged photolysis (8.5 h) at 227 nm, and at 35 K **2** recombines with N_2 in line with chemical behavior reported[25] for triplet ground-state carbenes lacking bonds labile toward intramolecular reactions. The energetic differences between the conformers of **4** (Scheme 2) with syn and anti orientations of the formal P═O bonds relative to the diazo group (*syn*, *syn*; *anti*, *syn*; *anti*, *anti*) are insubstantial with ≤ 2 kcal mol^{-1}, similar to **3** ($\Delta E_{\text{syn-anti}} < 1$ kcal mol^{-1}) at B3LYP/6-311++G(d,p). In contrast to the diazocarbonyl compounds,[26] the interactions between the CNN and P═O units aligned as *syn*, *anti*, and almost perpendicularly (97.3°) are comparable in magnitude: these three kinds of conformations are predicted to be potential energy minima with $\Delta E < 1$ kcal mol^{-1} for the monosubstituted parent H−C(N_2)-PO$(OH)_2$ at the CCSD(T)/cc-pVDZ level of theory. The flatness of the respective potential energy hypersurface ($E_{\text{A(anti→perpendicular)}} < 1$ kcal mol^{-1}) implies the weakness of the interactions between the phosphonato and the diazo group.

Apart from the disappearance of the characteristic ν(NN) band associated with N_2 extrusion, the IR spectral changes accompanying carbene formation are marginal (Figure 3). They concern mainly frequencies of vibrations involving bonds to the central carbon atom and the PO bonds with maximal double-bond character. The lack of unique bands hampers assignments of matrix isolated **2** by IR spectroscopy only. This task is further complicated by the presence of a multitude of rotamers in the vibrational spectrum of **2** (and **4**), leading to band broadening. Much like the monosubstituted parent triplet carbene and ^{3}**1**, ^{3}**2** appears to be relatively insensitive to conformational changes: In the energy interval of 3.3 kcal mol^{-1} at least four conformers with dihedral angles between the P═O bonds (OPPO) varying over 40° (82°−122°) can be located, all of which represent ground-state configurations with the smallest $\Delta E_{\text{ST}} = 5.2$ kcal mol^{-1} within the applied theoretical model (cf. ΔE_{ST}-$(CH_2)_{\text{B3LYP/6-311++G(d,p)}}$) = 11.8 kcal mol^{-1} vs experimental[27] 9.1 kcal mol^{-1}).

The absence of the typical ν(NN), ν(C═O), and ν(C═P) vibrations in the IR spectrum of photolyzed **4** excludes the corresponding diazirine, azine, as well as products of intramolecular carbene rearrangements. To gain additional evidence for the transformation of **4** to **2** and N_2, we conducted photolysis at 227 nm in an Ar matrix doped with 1%$_{\text{vol}}$ CO. The resulting IR spectrum (Figure 4) displays bands in positions indicative for the C═O (2162.2 cm^{-1}) and C═C (1327.8 cm^{-1}) stretching modes of ketenes, undermining intermediate formation of carbene **2** during irradiation. IR spectra reflect weakening of the CP bonds upon reaction of **2** to the corresponding ketene **5** and their strengthening on going from **4** to **2**.

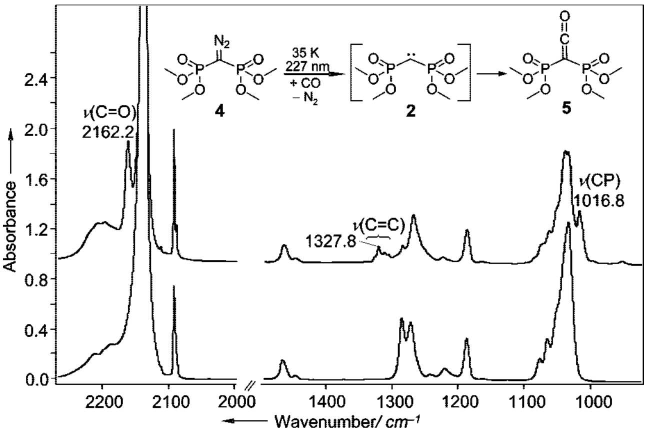


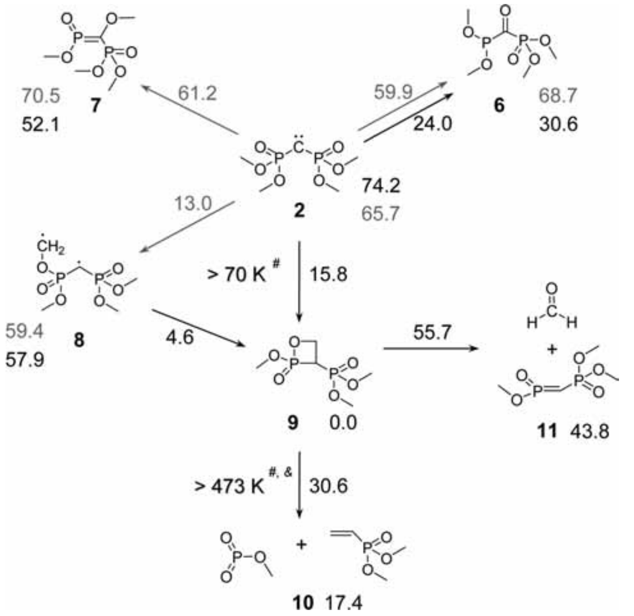
Figure 4. IR spectra of **4** in an Ar/CO (1%$_{\text{vol}}$) matrix recorded at 35 K before (bottom) and after (top) 4.5 h photolysis at 227 nm and 8 h annealing to 35 K, yielding ketene **5**.

Finally, the triplet nature of **2** has been confirmed by its EPR transitions. Despite the conformational richness of ^{3}**2**, no differences in transitions attributable to single conformers are noticeable in the EPR spectrum in contrast to 1-naphthyl-, 2-naphthyl-, formyl-, and vinylcarbenes.[28] The unique value of the *D* parameter derived for bisphosphonatocarbene $D(\mathbf{2}) = 0.623$ cm^{-1} falls between the data for the monosubstituted phosphonatocarbene $D(\mathbf{1}) = 0.660$ cm^{-1} and the phenyl-substituted $D(C_6H_5{-}C{-}PO(OCH_3)_2) = 0.487$ cm^{-1}.[13d]

The EPR transitions are observable up to about 70 K in perfluoromethylcyclohexane (mp = 236 K), and no new signals, e.g., of biradical **8**, arising from hydrogen abstraction from one of the methoxy groups emerge. The disappearance of signals is likely to be dominated by recombination of **2** with N_2, because repeated irradiation at 18 K restores the initial intensity. Given the narrowness of the temperature range, allowing meaningful analysis of species isolated in Ar matrices by EPR, IR, and UV/vis spectroscopy, collected reaction products forming subsequent to irradiation of **4** were examined the ^{1}H, ^{13}C, and ^{31}P NMR at room temperature. Samples of **4** photolyzed in perfluoromethylcyclohexane were slowly warmed (20 K/h) without permanent evacuation of the matrix apparatus. The same procedure was applied to amend the study of the products of the gas phase thermolysis.

Annealing of the photolytically generated carbene should lead to the most stable molecule (Scheme 3) attainable from **2** in unimolecular reactions, namely 4-dimethylphosphonato-1-methoxyphosphaoxetane **9**. Indeed, we could identify **9** by comparison of experimental and computed NMR spectra, whereas no peaks denoting products of the Wolff-type rearrangement (**7**), insertion into the formal PO double bond (**6**) or phosphaoxetane decomposition (**10**, **11**) could be detected. In contrast, HVFP in the 470−970 K temperature interval results in the products of the Wittig-type reaction of the phosphaoxetane: Both NMR and IR (Figure 5) reveal the presence of one of the fragments of **9**, dimethyl vinylphosphonate, by comparison with spectra

SCHEME 3: Computed (B3LYP/6-311++G(d,p)) and Observed ([#]Ar Matrix; [&]Vacuum Pyrolysis) Reactivity of 2[a]



[a] Gray for structures of triplet multiplicity, black for singlets. Numbers at arrows are the activation barriers for the reactions of selected conformers in the indicated direction; beneath the structures are their relative energies with respect to **9**. For carbenes of both multiplicities the relative energy of the respective most stable conformer is given. All values in kcal mol^{-1} and refer to $T = 0$ K.

of the commercially available substance. Its coproduct, methyl metaphosphate $PO_2(OCH_3)$, has been known to polymerize readily,[29] precluding[30] direct[31] (NMR) spectroscopic identification at room temperature. Nevertheless, fairly sharp and intense bands at 1427.4, 1166.7, 1026.0, and 1022.5 cm^{-1} in the IR spectrum of the matrix isolated products of the thermolysis of **4** suggest the presence of the monomer, which was proposed as a source of ADP/ATP formation in prebiotic environments.[31−33] Insubstantial differences in the computed (CCSD(T)/cc-pVTZ) harmonic vibrational frequencies of two rotamers, as compared to their absolute deviations from the experimental values, do not allow for assignment to a specific form; both are computed to be isoenergetic (cf. Supporting Information). The intensity of the ν(PO+OC) mode (1237.6 and 1217.2 cm^{-1}) exhibits strong basis set sensitivity: on going from CCSD(T)/cc-pVDZ to CCSD(T)/cc-pVTZ this mode grows by factors of 2−3 for both conformers. Studies aiming at the independent generation and detailed characterization of methyl metaphosphate by means of matrix isolation are in progress.

The observed reactivity pattern of ^{3}**2** is in line with our computations: (a) inaccessibly high activation energies for intramolecular reactions with both kinds of PO bonds, (b) the lowest activation energy for the formation of a four-membered ring among the reactions considered, and (c) a kinetic disadvantage of its decomposition via the Wittig route.

Conclusions

Both monosubstituted alkyl phosphonatocarbene **1** and bisphosphonatomethylene **2** possess triplet ground states. The findings for carbene **2** summarize the reactivity picture of phosphonatocarbenes: (i) the formal PO double bonds prove generally unreactive, (ii) unlike phosphinylcarbenes,[32] the alkoxy groups do not undergo Wolff-type rearrangements even under pyrolysis conditions,[33] and (iii) decomposition products[33] of phosphaoxetanes form only at elevated temperatures. As the CH bonds of the methoxy groups are responsible for the disappearance of ^{3}**2**, photolysis of perfluoromethoxy- or phenoxy-substituted diazomethyldiphosphonates will result in triplet ground-state carbenes that are likely to be persistent toward intramolecular reactions even at room temperature.

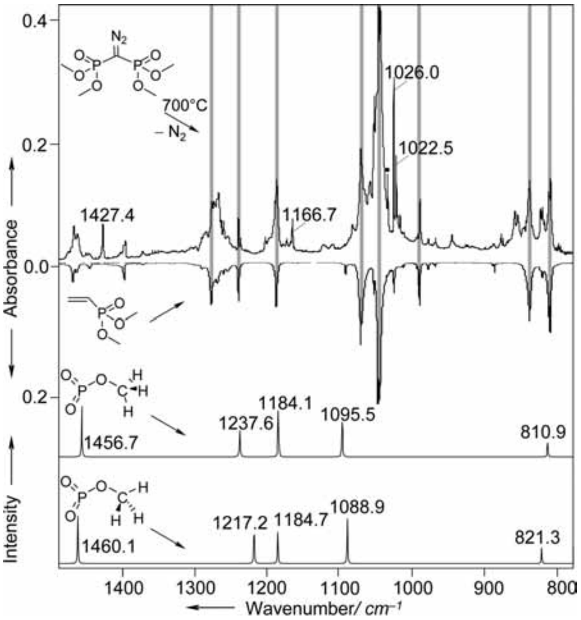


Figure 5. IR spectra of thermolysis product (positive direction of *y*-axes) and pure dimethyl vinylphosphonate as reference (negative direction of ordinate) scaled to the band at 990 cm^{-1} (Ar matrix). For eye guidance areas of agreement are highlighted in gray. IR spectrum of methyl metaphosphate (bottom) is computed at CCSD(T)/cc-pVTZ. ● at 1033 cm^{-1} marks ν(CO) vibration of methanol.

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Supporting Information Available: Cartesian coordinates, electronic energies, and ZPVEs of optimized structures; computed (GIAO B3LYP/6-311++G(d,p)) and measured ^{31}P NMR chemical shifts for isomers of **2**; experimental UV/vis spectra recorded prior to and after irradiation of matrix isolated **3** and **4** along with electronic excitation energies and the respective oscillator strengths for closed shell species, computed by TD B3LYP/6-311++G(d,p); computed vibrational frequencies with corresponding intensities for **1**, **2**, **3**, **4**, PO_2OCH_3 (**10**), PO_2OH, and POOH. This material is available free of charge via the Internet at http://pubs.acs.org.

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