Photoinduced oxidation of triphenylphosphine isolated in a low-temperature oxygen matrix

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Photooxidation reactions of triphenylphosphine (Ph3P) monomers isolated in matrices of solid oxygen at 10 K were characterized by means of infrared spectroscopy. Upon UV (λ > 280 nm) irradiation of O2 matrices, ca. 90% of Ph3P was converted to triphenylphosphine oxide (Ph3P=O), with concomitant formation of ozone. In the competing photoreaction, ca. 10% of Ph3P was converted to diphenyl-phenyl-phosphinate, Ph2(Ph–O–Ph)P=O. The interpretation was assisted by theoretical [DFT(B3LYP)/6-31G(d,p)] calculations of vibrational spectra, as well as by comparison with the experimental vibrational data from separate experiments in which monomeric Ph3P and Ph3P=O were isolated in argon and oxygen matrices at 10 K.

1. Introduction

The rich chemistry of phosphines is dominated by strong nucleophilicity and reducing character of these compounds. Trivalent phosphorus can be easily oxidized and converted into quinquevalent phosphorus (see Scheme 1). Recently, it has been reported that singlet molecular oxygen (generated photochemically with intermediary of a photosensitizer) reacts with phosphines (1) in solutions at room temperature. In such reactions, the corresponding phosphoxide oxides (2) are generated as dominating products, whereas phosphinates (3) are produced only in very small amounts[1–4].

The aim of the present work is an investigation of photochemical behavior of triphenylphosphine (triphenylphosphane according to the IUPAC nomenclature) embedded in low-temperature matrices of solid oxygen at 10 K. Solid O2 is optically transparent in a broad spectral region: from far IR to visible and UV. In spite of this advantage, solid oxygen was only scarcely applied as a host in matrix-isolation studies[5–12]. As far as matrix-isolation photochemistry is concerned, low-temperature solid oxygen environment enables selective delivery of UV-excitation as well as structural characterization of photogenerated products based on their vibrational spectra. The excess of O2 creates the most favorable conditions for the photooxidation reactions. Moreover, in the low-temperature matrices of solid O2, the photoproducts can be stabilized and subsequently identified using stationary spectroscopic techniques.

2. Experimental and computational methods

Commercial samples of Ph3P (99%) and Ph3P=O (98%) supplied by Aldrich were used in this study. Matrix gases Ar and O2 of spectral purity were supplied by Linde AG. Matrices were prepared by deposition of the studied compounds, together with a large excess of the matrix gas (Ar or O2), onto a cold CsI window (10 K) directly attached to the cold tip of a continuous flow liquid helium cryostat. The compounds were sublimated from a miniature glass oven by resistive heating. The FTIR spectra were recorded in the 4000–400 cm−1 range, with 0.5 cm−1 resolution, using a Thermo Nicolet Nexus 670 FTIR spectrometer, equipped with a KBr beamsplitter.

The samples were irradiated through the outer quartz window of the cryostat with the light from HBO200 high-pressure mercury lamp. This lamp was fitted with a water filter to remove IR radiation. The energy of the incident UV light was controlled by cutoff filters UG5, UG11 or WG295 (Schott). In particular, photoreaction of Ph3P was induced using WG295 long pass filter transmitting light with λ > 280 nm. In addition, the 400–680 nm range of the visible spectrum was suppressed with a band pass filter (UG5, Schott). Other details of the experimental setup can be found in our recent publications[13,14].

Theoretical calculations were performed using the GAUSSIAN 03 program package[15] at the DFT(B3LYP) level of theory[16–18], with the standard 6-31G(d,p) basis set. This basis set was adopted from our previous study on triphenylamine[19], where it produced vibrational data quantitatively comparable with the aug-cc-pVDZ basis set. The scaling factor of 0.975, used in the present work for the calculated frequencies, was obtained from the least squares linear fit (R = 0.99985).
3. Results and discussion

The Raman [20–22] and infrared [22–24] spectra of triphenylphosphine (Ph₃P) in condensed phases were the subject of several studies, however, no vibrational spectra of monomeric Ph₃P have been reported hitherto.

Within the current work, the experimental FTIR spectra were recorded for monomers of Ph₃P isolated in O₂ and Ar low-temperature matrices. These spectra are presented in Fig. 1, where they are compared with the IR spectra of Ph₃P monomers calculated at the DFT(B3LYP) level of theory, with the standard 6-31G(d,p) basis set. The theoretical DFT(B3LYP)/6-31G(d,p) calculations were performed for the optimized geometry of Ph₃P. In agreement with the previous gas-phase electron diffraction experimental data [25], this optimized structure was predicted to be of C₃ symmetry. The similarity of the vibrational signatures of Ph₃P isolated in O₂ and Ar matrices (Fig. 1a and b) with the theoretically calculated IR spectrum for (Fig. 1c) is in line with a non-planar structure at the central phosphorus atom of Ph₃P and the overall C₃ symmetry of the molecule. The complete optimized geometry of the Ph₃P monomer agrees with an earlier study [25] and can be found in the Supplementary material (Table S1). The most prominent bands correspond to the modes involving P–C stretching (1092.4 cm⁻¹); out-of-plane CH bending (746.5 cm⁻¹); out-of-plane ring bending (696.4 and 499.7 cm⁻¹).

In order to investigate the photophysical behavior of Ph₃P isolated in solid O₂, the matrix was subjected to series of UV-irradiations, where the wavelength of the incident light was controlled by cut-off filters. Upon exposure to UV light with λ > 280 nm, the IR spectrum of the starting compound disappeared completely within several minutes. The new IR spectrum of the photogenerated products was recorded after the UV-irradiation. This spectrum is presented in Fig. 2a.

In separate experiments, IR spectra of monomeric triphenylphosphine oxide Ph₃P=O isolated in O₂ and Ar matrices were recorded. These spectra are presented in Fig. 2b and c, respectively. A very good agreement between spectra 2a and 2b strongly suggests that the main photoproduct, generated upon UV (λ > 280 nm) irradiation of Ph₃P isolated in an O₂ matrix, can be reliably identified as Ph₃P=O.

The experimental IR spectra of Ph₃P=O are well reproduced by the results of theoretical simulations performed at the DFT(B3LYP)/6-31G(d,p) level (Fig. 2d). These calculations were carried out for the optimized geometry of the compound (see Table S2 in the Supplementary material). Using the calculated forms of normal modes, the strong band found in the spectrum of Ph₃P=O at 1219/1216 cm⁻¹ was assigned to the stretching vibration of the P=O group. This band does not have its analogue in the spectrum of Ph₃P. Other strong bands found in the spectrum of Ph₃P=O at positions clearly different from any IR absorptions of Ph₃P were observed at 1123.7/1121.2 and at 544.8/542.3 cm⁻¹.

Comparison of the spectra presented in Fig. 2 as traces (a) and (b) shows also that Ph₃P=O is not the only photoproduct generated upon exposure of Ph₃P isolated in an O₂ matrix to UV (λ > 280 nm) light. Alongside the bands belonging to the spectrum of Ph₃P=O, a new band around 1036 cm⁻¹ was found in the spectrum recorded after UV-irradiation of Ph₃P monomers. This band is characteristic of ozone (O₃) isolated in an O₂ matrix [26].

Hence, the main UV-induced process observed for Ph₃P isolated in an O₂ matrix can be summarized as follows:

\[
\text{Ph}_3\text{P} + 2\text{O}_2 \xrightarrow{h\nu} \text{Ph}_3\text{P} = \text{O} + \text{O}_3
\]

There are several reasons to believe that the driving force of the studied photoreaction is the promotion (by absorption of UV photon) of Ph₃P to its excited state and not a direct excitation of O₂ matrix host. It has been demonstrated within the present work, as well as in the previous work of Schriffer-Mazzuoli et al. [27], that exposure of neat O₂ matrices to UV radiation of a lamp fitted with a cut-off filter transmitting light with λ > 280 nm (or with a monochromatic laser light λ = 266 nm [27]) does not result in generation of ozone. Direct excitation of solid oxygen and generation of ozone requires irradiation with UV light of shorter wavelengths.
However, the UV ($\lambda > 280$ nm) light, used in the current experiments, can be effectively absorbed by the molecules of Ph$_3$P trapped in O$_2$. The UV absorption spectrum of this species (as it was shown for Ph$_3$P dissolved in cyclohexane) exhibits a broad band that has maximum around 260 nm and extends approximately to 300 nm [28]. Hence, the energy of the UV ($\lambda > 280$ nm) light must be a very good match to promote direct excitation of Ph$_3$P. Generation of ozone in the current experiments must also be related with initial excitation of Ph$_3$P. Indeed, upon the total consumption of Ph$_3$P, the subsequent UV ($\lambda > 280$ nm) irradiations did not result in any increase of the O$_3$ absorption band.

A careful inspection of the spectrum recorded after UV ($\lambda > 280$ nm) irradiation of Ph$_3$P isolated in an O$_2$ matrix reveals the presence of a new absorption around 900 cm$^{-1}$ (marked by 'X' in Fig. 2a). Absorption in this spectral region is characteristic of the P–O–C moiety. For matrix-isolated trimethyl phosphate, a strong infrared absorption due to the P–O–C stretching vibration was observed at 860 cm$^{-1}$ [29]. In the present case, appearance of a similar absorption indicates occurrence of an additional photo-reaction, where an oxygen atom is inserted in a P–C bond to produce diphenyl-phenyl-phosphinate, Ph$_2$(Ph–O–P)$\equiv$O (or simply ‘phosphinate’). In order to assess the efficiency of such photochemical reaction, several theoretical spectra were simulated, where the phosphinate and Ph$_3$P$\equiv$O photoproducts contributed with varying percentage. These simulated spectra (shown in Fig. 3b) are compared with the experimental spectrum (Fig. 3a). This comparison leaves no doubt that (in the reported experiment) ca. 10% of matrix-isolated Ph$_3$P was converted to the phosphinate photoproduc

The three-membered ring peroxides with the form R$_3$PO$_2$, where the R group represents alkyl or aryl substituents, were reported to act as intermediates in reactions of singlet oxygen with organic phosphines in solutions and in the gaseous phase at room temperature and higher temperatures [1–4,30–32]. There has been much recent interest to such ‘exotic peroxides’ – to quote from the title of a recent review by Sawwan and Greer [33]. Under the present matrix-isolation conditions, at low temperatures, no absorption bands ascribable to the peroxide intermediate could be observed experimentally.

The present matrix-isolation study is the first experimental evidence of phosphinate photoproduc formed from Ph$_3$P and O$_2$ without addition of any photosensitizers. The experiments carried out in the current work demonstrated that excitation of Ph$_3$P with UV ($\lambda > 280$ nm) light induces the oxygenation of this compound. No direct excitation of O$_2$ molecules of the matrix host (that would require irradiation with the more energetic UV light $\lambda \approx 248$ nm [27]) was necessary to promote this photooxidation.

The pattern of photochemical reactions of Ph$_3$P with molecular oxygen, investigated in the current work, shows similarities with the pattern of thermal oxidations of phosphines. These latter processes were investigated already as early as in XIX century [34–37]. Elucidation of the complicated mechanisms of these reactions is important for many practical applications. For example, substituted arylphosphines are being evaluated as potential additives for enhancing the stability of future jet fuels toward thermal oxidation [32,38]. Ph$_3$P was shown to improve the thermal oxidative stability of jet fuel by at least 50% [39].

4. Conclusions

New vibrational data on monomeric Ph$_3$P and Ph$_3$P$\equiv$O isolated in Ar and O$_2$ matrices are reported. The O$_2$ matrices can be considered inert in absence of UV-irradiation. The photochemical changes could be triggered by the excitation of Ph$_3$P with UV ($\lambda > 280$ nm) light. Under such conditions, the direct excitation of molecular oxygen and formation of ozone is not possible. The main UV-induced process, observed upon irradiation of Ph$_3$P isolated in an O$_2$ matrix, concerns generation of Ph$_3$P$\equiv$O and O$_3$ products. In the competing minor photoreaction, where both atoms of O$_2$ molecule are incorporated into the photoproduc structure [4], diphenyl-phenylphosphinate Ph$_2$(Ph–O–P)$\equiv$O was formed. In the present study, both Ph$_3$P$\equiv$O and Ph$_2$(Ph–O–P)$\equiv$O products were photochemically generated and trapped in a low-temperature oxygen matrix. The recorded IR spectral characteristics of these species allowed their positive identification. The isolation of the photochemical targets in low-temperature oxygen matrices proved to be very instrumental for studies of UV-induced oxygenation reactions, where the photochemical products can be preserved at low temperatures and studied spectroscopically.

Appendix A. Supplementary material

Supplementary data associated with this Letter can be found, in the online version, at doi:10.1016/j.cplett.2008.11.034. These data contain the complete optimized geometries of the Ph$_3$P, Ph$_3$P$\equiv$O, and Ph$_2$(Ph–O–P)$\equiv$O monomers (Tables S1, S2, S3, respectively).

References