

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

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ABSTRACT

Photooxidation reactions of triphenylphosphine (Ph_3P) monomers isolated in matrices of solid oxygen at 10 K were characterized by means of infrared spectroscopy. Upon UV ($\lambda > 280$ nm) irradiation of O_2 matrices, ca. 90% of Ph_3P was converted to triphenylphosphine oxide ($\text{Ph}_3\text{P}=\text{O}$), with concomitant formation of ozone. In the competing photoreaction, ca. 10% of Ph_3P was converted to diphenyl-phenyl-phosphinate, $\text{Ph}_2(\text{Ph}-\text{O}-)\text{P}=\text{O}$. 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 Ph_3P and $\text{Ph}_3\text{P}=\text{O}$ were isolated in argon and oxygen matrices at 10 K.

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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 intermediacy of a photosensitizer) reacts with phosphines (**1**) in solutions at room temperature. In such reactions, the corresponding phosphine 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 O_2 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 O_2 creates the most favorable conditions for the photooxidation reactions. Moreover, in the low-temperature matrices of solid O_2 , the photoproducts can be stabilized and subsequently identified using stationary spectroscopic techniques.

2. Experimental and computational methods

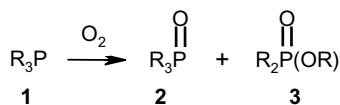
Commercial samples of Ph_3P (99%) and $\text{Ph}_3\text{P}=\text{O}$ (98%) supplied by Aldrich were used in this study. Matrix gases Ar and O_2 of spectral purity were supplied by Linde AG. Matrices were prepared by deposition of the studied compounds, together with a large excess of the matrix gas (Ar or O_2), 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 cut-off filters UG5, UG11 or WG295 (Schott). In particular, photoreaction of Ph_3P was induced using WG295 long pass filter transmitting light with $\lambda > 280$ 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 ($R = 0.99985$).

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Scheme 1. Reaction products that may result from oxidation of trisubstituted phosphine (1): phosphine oxide (2) and phosphinate (3).

3. Results and discussion

The Raman [20–22] and infrared [22–24] spectra of triphenylphosphine (Ph_3P) in condensed phases were the subject of several studies, however, no vibrational spectra of monomeric Ph_3P have been reported hitherto.

Within the current work, the experimental FTIR spectra were recorded for monomers of Ph_3P isolated in O_2 and Ar low-temperature matrices. These spectra are presented in Fig. 1, where they are compared with the IR spectra of Ph_3P 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 Ph_3P . In agreement with the previous gas-phase electron diffraction experimental data [25], this optimized structure was predicted to be of C_3 symmetry. The similarity of the vibrational signatures of Ph_3P isolated in O_2 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 Ph_3P and the overall C_3 symmetry of the molecule. The complete optimized geometry of the Ph_3P 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 photochemical behavior of Ph_3P isolated in solid O_2 , 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 $\lambda > 280 \text{ nm}$, 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 $\text{Ph}_3\text{P}=\text{O}$ isolated in O_2 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 sug-

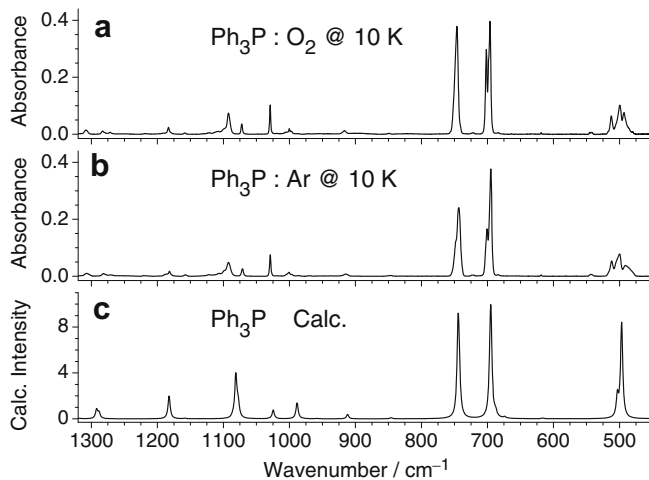


Fig. 1. Experimental FTIR spectra of Ph_3P isolated in O_2 (a) and Ar (b) matrices at 10 K compared with the spectrum of Ph_3P monomer simulated at the DFT(B3LYP)/6-31G(d,p) level (c).

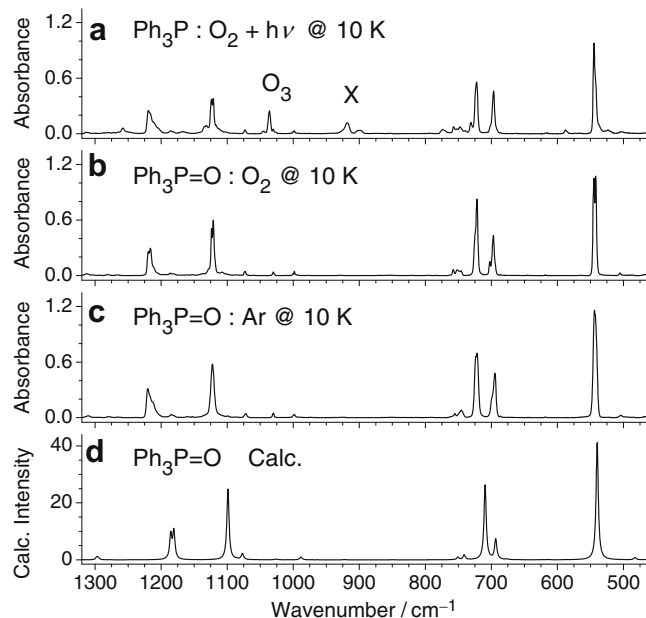


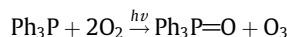
Fig. 2. Experimental FTIR spectrum of the photoproduct(s) obtained upon 20 min of UV-irradiation ($\lambda > 280 \text{ nm}$) of Ph_3P isolated in O_2 matrix at 10 K (a) compared with experimental FTIR spectra of $\text{Ph}_3\text{P}=\text{O}$ isolated in O_2 (b) and Ar (c) matrices at 10 K and with the theoretically simulated spectrum of $\text{Ph}_3\text{P}=\text{O}$ monomer (d). The ‘ O_3 ’ mark designates the band due to the matrix-isolated ozone photoproduct. The ‘X’ mark (in frame a) designates the absorption due to a photoproduct other than $\text{Ph}_3\text{P}=\text{O}$ or O_3 .

gests that the main photoproduct, generated upon UV ($\lambda > 280 \text{ nm}$) irradiation of Ph_3P isolated in an O_2 matrix, can be reliably identified as $\text{Ph}_3\text{P}=\text{O}$.

The experimental IR spectra of $\text{Ph}_3\text{P}=\text{O}$ 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 $\text{Ph}_3\text{P}=\text{O}$ at $1219/1216 \text{ cm}^{-1}$ was assigned to the stretching vibration of the P=O group. This band does not have its analogue in the spectrum of Ph_3P . Other strong bands found in the spectrum of $\text{Ph}_3\text{P}=\text{O}$ at positions clearly different from any IR absorptions of Ph_3P were observed at $1123.7/1121.2$ and at $544.8/542.3 \text{ cm}^{-1}$.

Comparison of the spectra presented in Fig. 2 as traces (a) and (b) shows also that $\text{Ph}_3\text{P}=\text{O}$ is not the only photoproduct generated upon exposure of Ph_3P isolated in an O_2 matrix to UV ($\lambda > 280 \text{ nm}$) light. Alongside the bands belonging to the spectrum of $\text{Ph}_3\text{P}=\text{O}$, a new band around 1036 cm^{-1} was found in the spectrum recorded after UV-irradiation of Ph_3P monomers. This band is characteristic of ozone (O_3) isolated in an O_2 matrix [26].

Hence, the main UV-induced process observed for Ph_3P isolated in an O_2 matrix can be summarized as follows:



There are several reasons to believe that the driving force of the studied photoreaction is the promotion (by absorption of UV photon) of Ph_3P to its excited state and not a direct excitation of O_2 matrix host. It has been demonstrated within the present work, as well as in the previous work of Schriver-Mazzuoli et al. [27], that exposure of neat O_2 matrices to UV radiation of a lamp fitted with a cut-off filter transmitting light with $\lambda > 280 \text{ nm}$ (or with a monochromatic laser light $\lambda = 266 \text{ nm}$ [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_3P trapped in O_2 . The UV absorption spectrum of this species (as it was shown for Ph_3P 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_3P . Generation of ozone in the current experiments must also be related with initial excitation of Ph_3P . Indeed, upon the total consumption of Ph_3P , 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_3P 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 phosphite, 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, $\text{Ph}_2(\text{Ph-O})\text{P=O}$ (or simply 'phosphinate'). In order to assess the efficiency of such photochemical reaction, several theoretical spectra were simulated, where the phosphinate and $\text{Ph}_3\text{P=O}$ 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_3P was converted to the phosphinate photoproduct. The new bands, which arise (upon UV $\lambda > 280$ nm irradiation) at 1258, 1205, 1168, 1132, 918, 900, 774, 740, 731, 588, 536, 523 cm^{-1} (marked by crosses in Fig. 3a), have their counterparts in the calculated spectrum of the phosphinate photoproduct (see Fig. 3b). The complete optimized geometry of the $\text{Ph}_2(\text{Ph-O})\text{P=O}$ monomer can be found in the Supplementary material (Table S3).

As an additional test for the reaction mechanism, monomers of $\text{Ph}_3\text{P=O}$ deposited at 10 K with a large excess of oxygen (to form an O_2 matrix) were exposed to prolonged UV ($\lambda > 280$ nm) irradiation. No bands ascribable to the phosphinate photoproduct appeared upon such experimental conditions. This proves that phosphinate is not a product of a secondary, UV-induced reaction of $\text{Ph}_3\text{P=O}$ with oxygen, but that it is generated as a result of the branched character of the photochemistry of Ph_3P .

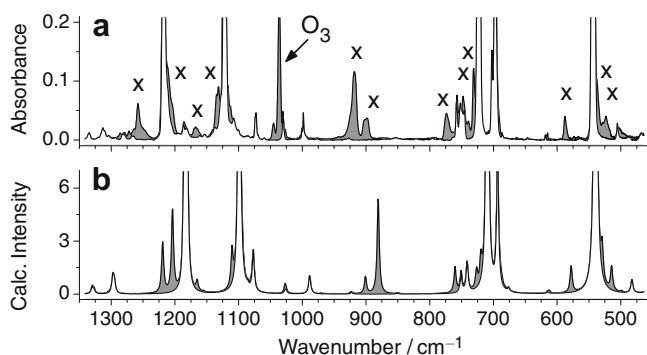


Fig. 3. (a, foreground layer): FTIR spectrum of $\text{Ph}_3\text{P=O}$ isolated in an O_2 matrix (the area under the spectrum trace is filled white); (a, background layer): the FTIR spectrum of photoproducts generated upon UV ($\lambda > 280$ nm) irradiation of Ph_3P isolated in an O_2 matrix (the area under the spectrum trace is filled grey). Crosses designate absorption bands due to the minor photoproduct; (b, foreground layer): IR spectrum calculated for $\text{Ph}_3\text{P=O}$ (the area under the spectrum trace is filled white); (b, background layer): sum of the IR spectra calculated for $\text{Ph}_3\text{P=O}$ and for $\text{Ph}_2(\text{Ph-O})\text{P=O}$: the spectra were added with weights 9 and 1, respectively (the area under the spectrum trace is filled grey). The theoretical spectra were calculated at the DFT(B3LYP)/6-31G(d,p) level. The theoretical frequencies were scaled by a uniform factor of 0.975.

The three-membered ring peroxides with the form R_3PO_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 photoproduct formed from Ph_3P and O_2 without addition of any photosensitizers. The experiments carried out in the current work demonstrated that excitation of Ph_3P 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_3P 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_3P was shown to improve the thermal oxidative stability of jet fuel by at least 50% [39].

4. Conclusions

New vibrational data on monomeric Ph_3P and $\text{Ph}_3\text{P=O}$ 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_3P 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_3P isolated in an O_2 matrix, concerns generation of $\text{Ph}_3\text{P=O}$ and O_3 products. In the competing minor photoreaction, where both atoms of O_2 molecule are incorporated into the photoproduct structure [4], diphenyl-phenylphosphinate $\text{Ph}_2(\text{Ph-O})\text{P=O}$ is formed. In the present study, both $\text{Ph}_3\text{P=O}$ and $\text{Ph}_2(\text{Ph-O})\text{P=O}$ 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_3P , $\text{Ph}_3\text{P=O}$, and $\text{Ph}_2(\text{Ph-O})\text{P=O}$ monomers (Tables S1, S2, S3, respectively).

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