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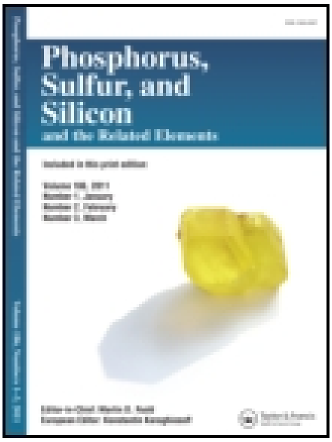

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Mechanistic Study on Photooxidation of Triarylphosphines by Time-Resolved Infrared Spectroscopy

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MECHANISTIC STUDY ON PHOTOOXIDATION OF TRIARYLPHOSPHINES BY TIME-RESOLVED INFRARED SPECTROSCOPY

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Abstract *Upon laser flash photolysis on a solution of triarylphosphine* Ar_3P *in acetonitrile or dichloromethane using a YAG laser at 266 nm, transient absorption was observed by time-resolved infrared spectroscopy. Rate constants were determined for the formation step of the absorption. Dependency of the rate on* $[Ar_3P]$ *and atmosphere, along with independent observation in laser flash photolysis/UV-Vis spectroscopy of the* Ar_3P *solutions, suggests that electron transfer occurs from* Ar_3P *to the singlet photoexcited state of* Ar_3P*, generating triarylphosphine radical cation* $Ar_3P^{\cdot+}$*, which reacts with a trace amount of* H_2O *in the solvent to give the final product* $Ar_3P{=}O$*, which has been observed in steady-state photolysis.*

Keywords Laser flash photolysis; radical cation; time-resolved infrared spectroscopy; triarylphosphine

INTRODUCTION

Trivalent phosphorus compounds Z_3P, including phosphines, phosphinites, phosphonites, and phosphites, are oxidized by many types of oxidants in the dark to afford the corresponding pentavalent oxo-compounds $Z_3P{=}O$.[2–3] The oxidation reactions are exothermic, and the mechanistic aspects of these oxidation processes have been well explored. On the other hand, photo-oxidation of Z_3P has been studied much less often. Thus, although some publications report the oxidation of phosphines to phosphine oxides initiated by photo-irradiation, the species that is initially excited under the conditions is not phosphine itself.[4,5]

Recently, we observed that upon steady-state irradiation of UV light from a Xe lamp, triarylphosphines Ar_3P (Figure 1) are oxidized quantitatively to the corresponding phosphine oxides $Ar_3P{=}O$. Quite interestingly, the oxidation took place even under an argon atmosphere, except for the reaction of Mes_3P. In the reaction of Mes_3P, O_2 is a prerequisite for formation of $Mes_3P{=}O$. Certainly, Ar_3P is photoexcited directly because

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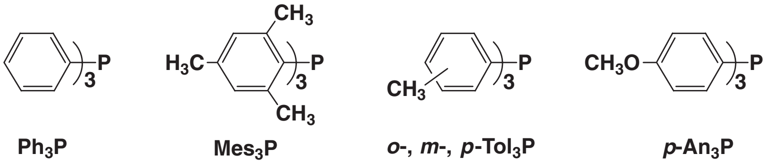

Figure 1 Triarylphosphines used in this study.

there is no species other than Ar_3P in the system. In an attempt to reveal the mechanism of this peculiar oxidation, we investigated the photoreaction of Ar_3P by using laser flash photolysis (LFP) with time-resolved infrared spectroscopy (TRIR). An advantage of IR spectroscopy is that the spectrum obtained involves much more definite information than its UV-Vis counterpart.

RESULTS AND DISCUSSION

The photoreaction of Ar_3P was followed by laser flash photolysis time-resolved infrared spectroscopy (LFP-TRIR). Thus, when the acetonitrile or dichloromethane solution of Ar_3P was photolyzed by using a YAG laser at 266 nm, a transient absorption was observed at the region of 1110 cm^{-1} ~1220 cm^{-1}, showing existence of an intermediate. The appearance of the transient absorption and its decay occurred with microsecond timescale and with millisecond timescale, respectively. Pseudo-first order rate constants $k^F{}_{obs}$ for the formation of the intermediate were determined by varying the concentration of Ar_3P as well as the atmosphere (argon, air, or oxygen). $k^F{}_{obs}$ was found to depend linearly on $[Ar_3P]$ (Figure 2). Interestingly, $k^F{}_{obs}$ for the reaction of Mes_3P depended linearly on $[O_2]$, whereas those for other Ar_3P's were almost constant irrespective of atmosphere. These observations finally give a rate Equation (1).

$$k^F_{obs} = k^F_2[Ar_3P] + k^F_o[O_2] \tag{1}$$

Importantly, $k^F{}_O$ exerts meaningful values only for the reaction of Mes_3P.

The acetonitrile solution of Ar_3P was also photolyzed at 266 nm to be followed by time-resolved UV-Vis spectroscopy. Within 100 ns, the transient spectrum that was assignable to triarylphosphine radical cation $Ar_3P^{\cdot+}$ appeared, in comparison with the

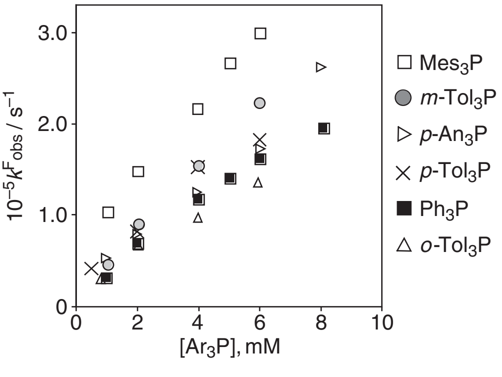

Figure 2 Dependence of $k^F{}_{obs}$ on $[Ar_3P]$. In CH_2Cl_2 under air.

spectra previously observed in the LFP of the acetonitrile solution of Ar_3P in the presence of dicyanoanthracene[1] and also in the pulse radiolysis on the benzonitrile solution of Ar_3P.[6] The spectrum decayed at a rate approximately identical to that of the formation rate observed on the TRIR. This observation in LFP-TRUV-Vis spectroscopy strongly suggests that the intermediate observed in the LFP-TRIR experiment results from $Ar_3P^{\cdot +}$.[7]

Since there is no acceptor in the solution of these LFP experiments, electron transfer may take place from Ar_3P to the singlet photoexcited state of Ar_3P, generating $Ar_3P^{\cdot +}$. The kinetics represented by Eq. (1) support this mechanism. Radical cation $Ar_3P^{\cdot +}$, once formed, reacts with a trace amount of H_2O in the solvent to give the final product $Ar_3P{=}O$.[2] In the reaction of Mes_3P, three mesityl ligands are bulky enough to prevent a water molecule from attacking the central phosphorus atom. This may be the reason why O_2 is prerequisite to the photooxidation of Mes_3P to $Mes_3P{=}O$.

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7. A brief outline of experiments is given here: Triarylphosphines were purchased (Aldrich) and recrystallized from ethanol before use. TRIR experiments were conducted with a JASCO TRIR-1000 dispersive-type IR spectrometer. Sample solutions flowing through a CaF_2 cell were excited by pulses (266 nm) from a Continuum cw Q-sw Nd:YAG laser. Changes in IR intensity were monitored by an MCT photovoltaic IR detector.