Intramolecular Stabilization of the Phosphine Radical Cation by the Second Phosphorus Atom during the Photooxidation of Diphosphines: ^{31}P NMR Spectroscopic Analysis

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Diphosphines, $Ph_2P(CH_2)_nPPh_2$ **1** ($n = 1$, 2, 3, 4, and 6), were photolyzed by a xenon lamp in air. The ^{31}P NMR spectroscopic analysis of the reaction showed that **1** is oxidized, according to first-order kinetics, to the monoxide, which is further oxidized to the dioxide. The dependence of the rate constants for the first oxidation on the chain-length n in **1** is interpreted in terms of the orientation of the p-orbitals on the two phosphorus atoms in the intermediate, the diphosphine radical cation.

Scheme 1. Photoreaction of diphosphine **1**.

The trivalent phosphorus radical cation, $Z_3P^{•+}$, which is readily generated upon treatment of trivalent phosphorus compounds, Z_3P, with electron-deficient compounds, behaves as either a radical or a cation.[1] Sometimes, the parent Z_3P acts as a nucleophile to promote the cationic character of $Z_3P^{•+}$. For example, electron impact on triarylphosphines, Ar_3P, during ion cyclotron resonance mass spectrometry (ICR-MS) affords the dimeric radical cation, $[Ar_3P–PAr_3]^{•+}$,[2] which certainly results from the nucleophilic attack of the parent phosphine, Ar_3P, on the initially generated radical cation, $Ar_3P^{•+}$. This occurs because Ar_3P exists in large excess under the stated conditions, but even a small amount of Ar_3P may assist in the formation of $Ar_3P^{•+}$ through a nucleophilic interaction. To disclose how a neutral phosphine interacts with the phosphine radical cation, diphosphine, which has two phosphine moieties in a single molecule, may be useful. Thus, the radical cation generated on a phosphine moiety could be intramolecularly stabilized by the other phosphine moiety. The difference in the structure of the spacer between the two phosphine moieties would result in the difference in stabilization due to the different spatial arrangements of the two phosphorus atoms.

We have found that the steady-state photolysis of triarylphosphines, Ar_3P, under aerobic conditions generates the radical cation, $Ar_3P^{•+}$, very likely through electron transfer from Ar_3P in the excited state to oxygen.[3,4] The radical cation is then trapped by oxygen to eventually form the phosphine oxide, $Ar_3P=O$. In this system, no sensitizer is required and no significant by-products are produced. Based on these features, this system is a convenient way to generate $Ar_3P^{•+}$. In the present study, we carried out the steady-state photolysis of bis(diphenylphosphino)alkanes, $Ph_2P(CH_2)_nPPh_2$ **1** ($n = 1$, 2, 3, 4, and 6), as listed in Scheme 1, using a xenon lamp in air. By analyzing the reaction mixture periodically, by ^{31}P NMR spectroscopy, it was found that **1** disappears according to first-order kinetics with the appearance of diphosphine monooxide **2** as well as diphosphine dioxide **3**. The first-order rate constants of the disappearance of **1** were variable, depending on the length of the methylene-chain spacer. This observation is interpreted in terms of the difference in the geometry of the phosphine radical cation intermediate.
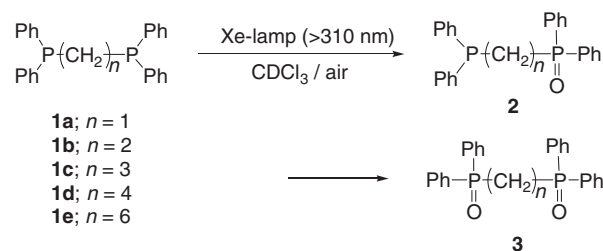
The diphosphines **1** were purchased (Aldrich) and purified by recrystallization from ethanol, except for **1c**. Recrystallization of **1c** was not feasible due to its rather low melting point (mp: 63–65 °C) compared to those of the others (ranging from 118 to 142 °C). The **1c** sample was used without purification because its solution gave no appreciable signal other than that from **1c** on the ^{31}P NMR spectrum. The deuterochloroform ($CDCl_3$) solution of **1** (20 mM) was prepared in a quartz NMR tube. The solution was irradiated with light from a xenon lamp (an Ushio xenon short arc UXL-500D-0 lamp), in which light of wavelengths shorter than 310 nm was cutoff by a glass filter (a Toshiba sharp-cut glass filter UV-31). The solution was periodically analyzed by ^{31}P NMR spectroscopy using a Varian INOVA400 operating at 161.9 MHz. The external 85% phosphoric acid was used as the reference standard (0.0 ppm). The intensity of each signal was quantitatively evaluated using triethyl phosphate as the internal standard.[5]

The time-course of the spectral change for the photooxidation of **1d**, as a representative example, is shown in Figure 1. The signal (-14.2 ppm) from the phosphorus of the starting diphosphine **1d** gradually disappeared with the concomitant appearance of two new signals. One of them (-14.2 ppm) resonated at only a slightly higher field than the signal of **1d**, and another appeared at a low field (34.1 ppm).[6] Consulting the literature data,[7] these signals are judged to result from diphosphine monooxide **2d**. These signals disappeared, being accompanied by the appearance of another new signal at a low field (34.1 ppm), which is assignable to diphosphine dioxide **3d**.[7c] These observed spectrum changes correspond to the consecutive oxidation of two phosphorus atoms in the starting material; namely, the oxidation of **1** to **2** and further to **3** (Scheme 1).[8] Several unidentified signals also appeared in the ^{31}P NMR spectra, e.g., the signals at 23.5 and 43.4 ppm during the photolysis of **1b**. A possibility is the abstraction of chlorine atom(s) from the solvent $CDCl_3$ by a radical intermediate to afford the chlorinated products. We have not tried to identify these products at this stage of the present study.

Table 1 summarizes the chemical shifts δ of **1**–**3**. The downfield δ shifts of **1** were observed as the reaction proceeded.
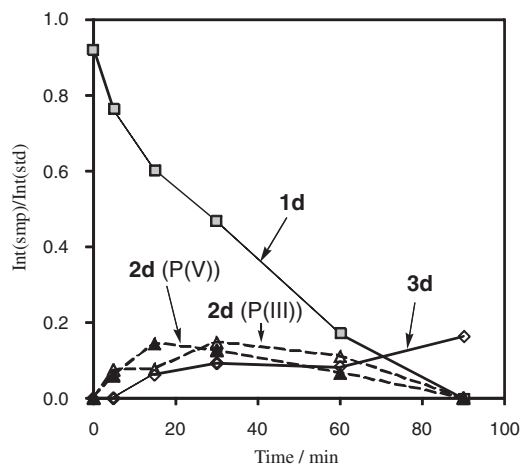
Figure 1. Time-course of the photolysis of **1d**. The ordinate is a scale for the ratio of the signal intensity of a sample (Int(smp)) versus that of the internal standard $(EtO)_3P=O$ (Int(std)).

Table 1. ^{31}P NMR chemical shifts of **1–3**[a]

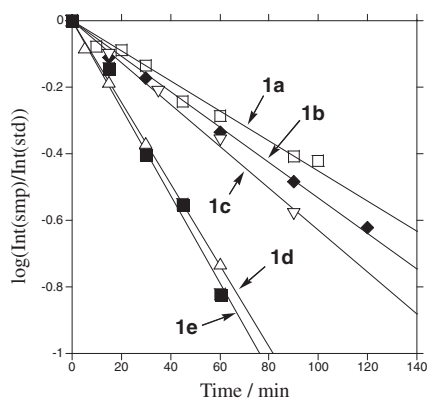|	n	**1**	P(III) in **2**	P(V) in **2**	**3**
a	1	−20.4	−26.5	31.3	27.0
b	2	−10.6	−9.9	34.9	34.8
c	3	−15.4	−15.9	34.5	34.2
d	4	−14.2	−14.2	34.1	34.1
e	6	−14.1	−13.5	34.6	34.5

[a] δ in ppm from 85% H_3PO_4.

Figure 2. Logarithmic plots of the decrease in the amounts of **1** during the steady-state photolysis. As for the abbreviations of the ordinate, refer to the caption of Figure 1.

Control experiments confirmed the concentration shift with respect to the δ value of **1**. For example, the δ values (in ppm) of **1b** are −10.6, −10.4, and −10.2 at 20, 16, and 7.8 mM, respectively.

The logarithm of the relative amount of **1**, evaluated by the ratio of the ^{31}P NMR intensities of **1** and the internal standard, was plotted versus time in Figure 2, which gave a linear line within the period of the measurement. That is, **1** disappears according to first-order kinetics during the early stage of the

Table 2. First-order rate constant k_{obs} for the oxidation of **1** to **2**, and the computed distance between two phosphorus atoms in the radical cation **4** at the optimized structures

1	n	$(10^4/2.30)\,k_{obs}/s^{-1}$	$k_{obs}(rel)$[a]	$d(P–P)$ in **4-C$^{(\prime)}$**/Å[b]
1a	1	0.744	1	—
1b	2	0.872	1.17	2.85
1c	3	1.05	1.41	2.85
1d	4	2.03	2.73	2.76
1e	6	2.18	2.93	3.10

[a] Relative rate. [b] Computed for the cyclic structure by DFT B3LYP/6-31G(d).
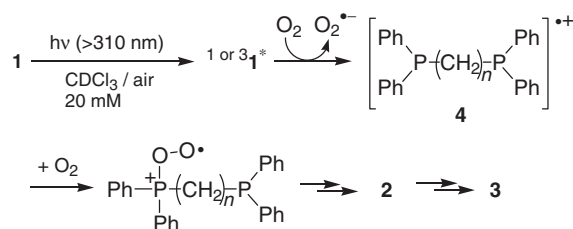
Scheme 2. A plausible mechanism for the photooxidation of diphosphine **1**.
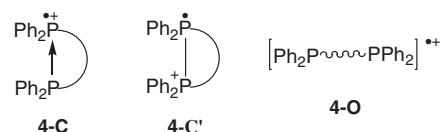
Scheme 3. The "cyclic" structure **4-C** or **4-C′** and the "open-chain" structure **4-O** of the diphosphine radical cation.

reaction, and the disappearance of **1** represents the oxidation of **1** to **2**. We evaluated the rate constant k_{obs}, as summarized in Table 2, which shows that k_{obs} increases with the increasing number of methylene groups in the spacer; namely, **1a** < **1b** < **1c** < **1d** ≈ **1e**. As in the steady-state photolysis of triarylphosphines, Ar_3P, under these conditions,[3] the present reaction certainly proceeds via the radical cation **4** (Scheme 2). According to this mechanism, a factor to determine k_{obs} is the stability of **4**. The second phosphorus atom would stabilize **1$^{•+}$** through a coordination bond (**4-C**) or a covalent bond (**4-C′**), as schematically depicted in Scheme 3. In any event, the spatial arrangement of the two phosphorus atoms, which is regulated by the number of methylene groups in the spacer, plays a crucial role.

To determine the optimized geometry of the "cyclic" structure of the radical cation **4-C** or **4-C′**, we performed a theoretical calculation based on the density function theory (DFT) at B3LYP/6-31G(d).[9] The values of the P–P distances ($d(P–P)$) in the optimized structures (Table 2) are too long to be those of covalent bonds between the trivalent tricoordinate phosphorus atoms, for which 2.22 Å is reported as a representative value.[10] That is, **4-C** is a more proper description than **4-C′**. Meanwhile, the same calculation was made on the "open-chain" structure of the radical cation **4-O**. The calculations indicated that **4a-O**–**4e-O** is 4–13 kJ mol^{-1} less stable than **4a-C**–**4e-C**, suggesting that the radical cation center is somewhat stabilized
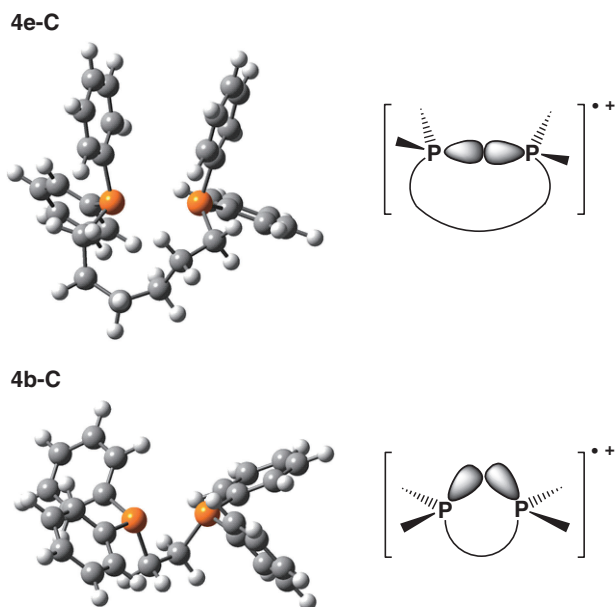
4e-C

4b-C

Figure 3. Optimized structures of **4e-C** and **4b-C** computed by DFT B3LYP/6-31G(d) (left) and their schematic illustrations (right).

by the second phosphorus atom. It has been reported that the interaction of nitrogen lone pairs in diamines is destabilized in the neutral form, but stabilized in the radical cation.[11] A three-electron σ bond has been used to explain the stabilization. More importantly, in the present study, as d(P–P) in **4-C** becomes longer, k_{obs} increases. In other words, the close proximity of the two phosphorus atoms in **4-C** is not a factor to stabilize the radical cation **4**. This result, in turn, requires another factor than d(P–P) to explain the reactivity of **1** under the photochemical conditions. The orientations of the two p-orbitals on the phosphorus atoms in **4-C** may play a role. The DFT computations suggest that these two p-orbitals are linearly arranged in **4e-C** (upper part of Figure 3), whereas **4b-C** has a bent structure (lower part of Figure 3). The spacer with methylene units smaller than four is too short for the radical cation to have a favorite geometry. This difference in geometry may result in the difference in the stability of the phosphine radical cation, thus causing the difference in the oxidation rate.

This study has suggested the importance of the orientation of the p-orbitals in stabilizing the diphosphine radical cation. A more detailed consideration, by taking into account the SOMO–LUMO interaction in the radical cation, would be needed to obtain new insights into the chemistry of the trivalent phosphorus.

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8 Since the ratio, (Int(smp)/Int(std)), was not calibrated except for **1**, a direct comparison of the intensities among the different compounds **1–3** provides the wrong information. The intensity of the phosphorus signal is largely dependent on the relaxation time of the phosphorus nucleus, therefore variable depending on the environment of the nucleus under consideration.

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