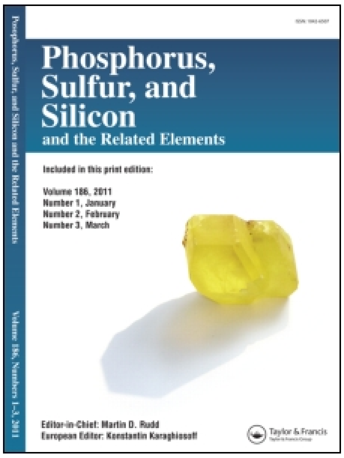

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# ION CYCLOTRON RESONANCE MASS SPECTROMETRIC STUDY ON THE GAS-PHASE REACTION OF TRIARYLPHOSPHINE RADICAL CATIONS

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***The gas-phase reaction of triarylphosphine radical cations was examined by ion cyclotron resonance mass spectrometry. Triarylphosphine radical cations generated from triphenylphosphine, tris(*m*-tolyl)phosphine, and *p*-tolyldiphenylphosphine underwent bimolecular reaction with the parent phosphine that exists in large excess. On the other hand, radical cations generated from tris(*p*-toly)phosphine, *o*-tolyldiphenylphosphine, tris(*o*-toly)phosphine, and trimesitylphosphine gave totally different products. This is the first observation that a small substituent such as a methyl group on the aryl ligand results in dramatic change of the reactivity of triarylphosphine radical cations.***

**Keywords** Gas-phase reaction; ion cyclotron resonance mass spectrometry; radical cation; trivalent phosphorus compound

## INTRODUCTION

Electron transfer (ET) from a trivalent phosphorus compound $Z_3P$ to many types of acceptors takes place in solution to give the corresponding radical cation $Z_3P^{\bullet+}$.[1–10] In principle, the radical cation can act as either a cation or a radical to undergo either an ionic or a radical reaction, respectively. We have investigated the reactions of $Z_3P^{\bullet+}$ generated in condensed phase, and found that the relative ease of ionic and radical reactions is determined not only by the structure of $Z_3P^{\bullet+}$ but also by the environment surrounding the radical cation.[4,8] For example, $Z_3P^{\bullet+}$ undergoes an ionic reaction with a trace amount of water in the solvent so rapidly that its reactivity as a radical is sometimes obscured.[4–6] That is, the reactions in condensed phase afford only limited information about the reactivity of $Z_3P^{\bullet+}$. In this matter, the reactions should be carried out under the conditions without solvent to elucidate the intrinsic reactivity of $Z_3P^{\bullet+}$.

To study gaseous organic ion-molecule reactions, a number of instruments and experimental methods have been developed in the past three decades. These techniques have

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proven to be powerful tools for studying intrinsic reactivities of highly reactive species such as cations, anions, and radical ions in the gas phase.[11–15] In the present study, we investigated the reactivity of triarylphosphine radical cations $Ar_3P^{\bullet+}$ in gas phase by Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry. We generated seven radical cations from the corresponding triarylphosphines $Ar_3P$ (**1a–g**) (Chart 1) and followed their reactions using an FT-ICR mass spectrometer.

| $Ar_3P$ | |
|---|---|
| **1a**; $Ph_3P$ | **1e**; *o*-Tol$Ph_2P$ |
| **1b**; *m*-$Tol_3P$ | **1f**; *o*-$Tol_3P$ |
| **1c**; *p*-Tol$Ph_2P$ | **1g**: $Mes_3P$ |
| **1d**; *p*-$Tol_3P$ | |

**Chart 1** Triarylphosphines used in the present study.

## RESULTS AND DISCUSSION

Triarylphosphine radical cations $\mathbf{1}^{\bullet+}$ were generated by electron impact ionization of triarylphosphines **1** and were isolated in the ICR cell by ejection sweeps. The reaction of $\mathbf{1}^{\bullet+}$ was followed by an FT-ICR mass spectrometer, with the temperature of the chamber being kept constant throughout the reaction (80∼100°C). The product ions observed were those corresponding formally to 2M (**2**), M+Ar (**3**), M−Me (**4**), M−Me+2Ar−2 (**5**), M+2Ar−3 (**5′**), 2M−Ar−2 (**6**), and 2M−Ar (**7**), where M refers to the molecular weight of the starting phosphine **1**. After several seconds (depending on the pressure of the neutrals), the ratio of the abundances of these product ions as well as $\mathbf{1}^{\bullet+}$ were obtained in the stationary state. Table I reports the abundances of these ions at this stage (except for run 6) as normalized values.[16,17] Reproducibility of each run was satisfactory.

**Table I** Product ions from the reaction of $\mathbf{1}^{\bullet+}$

| Run | **1** | Reaction Time (ms) | Product ions (%)[a] | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | **2** | **3** | **4** | **5** | **5′** | **6** | **7** | Others |
| 1 | **1a** | 30000 | 49 | 17 | 0 | 0 | 0 | 19 | 15 | |
| 2 | **1b** | 5000 | 30 | 33 | 0 | 0 | 0 | 19 | 10 | 8 (501)[b] |
| 3 | **1c** | 6000 | 35 | 9[c]+34[d] | 0 | 0 | 0 | 4[e]+7[f] | 4[g]+7[h] | 3 (426)[i] |
| 4 | **1d** | 2000 | 0 | 3 | 0 | 11 | 0 | 31 | 48 | |
| 5 | **1e** | 6000 | 3 | 0 | 0 | 31[j] | 0 | 21[e]+18[f] | 8[g]+5[h] | 7 (547),[b] 7 (549)[b] |
| 6 | **1f** | 100 | 0 | 0 | 100 | 0 | 0 | 0 | 0 | |
| 7 | **1f** | 3000 | 0 | 0 | 13 | 19 | 12 | 12 | 25 | 19 (501)[b] |
| 8 | **1g** | 1500 | 0 | 0 | 100 | 0 | 0 | 0 | 0 | |

[a] Normalized abundances determined by ICR mass spectrometry based on the peak intensity. Observed after 2∼30 s.

[b] Numbers in parentheses denote mass numbers. Structure not characterized.

[c] M+Ph (353).

[d] M+Tol (367).

[e] 2M−Tol−2 (459).

[f] 2M−Ph−2 (473).

[g] 2M−Tol (461).

[h] 2M−Ph (475).

[i] 2M−2Tol.

[j] M−Me+2Tol−2 (441).

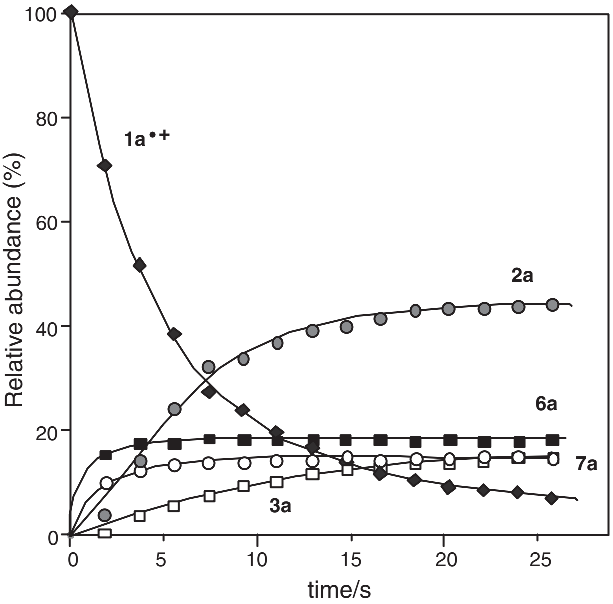
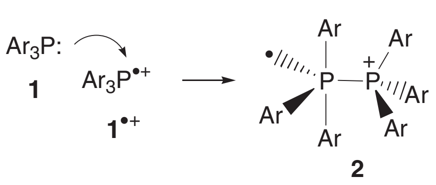


**Figure 1** Time dependence of the normalized abundances of the ions formed upon reaction of $\mathbf{1a}^{\bullet+}$ that was isolated after 4 s of the electron-impact ionization pulse. $\mathbf{1a}^{\bullet+}$ (diamonds), **2a** (open squares), **3a** (closed squares), **6a** (closed circles), and **7a** (open circles).

We carried out FT-ICR experiments with triphenylphosphine **1a** with different reaction times. A set of the data provided a time dependence of the normalized abundances of the product ions observed here, in **2a**, **3a**, **6a**, and **7a**, as well as the starting radical cation $\mathbf{1a}^{\bullet+}$. As seen in Figure 1, increases in the abundances of **2a** and **3a** as well as a decrease in the abundance of $\mathbf{1a}^{\bullet+}$, respectively, obey first-order kinetics. For the increases and the decrease in the abundances of these ions, a nearly identical value was obtained as pseudo-first order rate constants ($6 \times 10^{-2}$ s$^{-1}$). The value became about twice larger when the pressure of **1a** was raised approximately to twice the initial one. The observations suggest that the bimolecular reactions of $\mathbf{1a}^{\bullet+}$ with neutral **1a** that exists in large excess give **2a** and **3a** simultaneously. Meanwhile, **6a** and **7a** appeared within a very short reaction time (< 1 sec), and their abundances did not show further change with the reaction time.

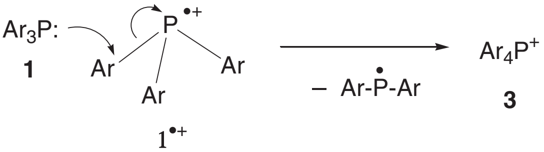
A major product ion **2** (2M) in the reactions with triphenylphosphine (**1a**), tris(*m*-tolyl)phosphine (**1b**), and *p*-tolyldiphenylphosphine (**1c**) is assignable to dimeric product $Ar_3P^{\bullet}$-$P^{+}Ar$ (Table I, runs 1–3). Certainly, this product ion is formed through nucleophilic attack by the phosphorus atom in **1** upon the phosphorus atom in $\mathbf{1}^{\bullet+}$ (Scheme 1). Similar



**Scheme 1** Pathway to give **2**.

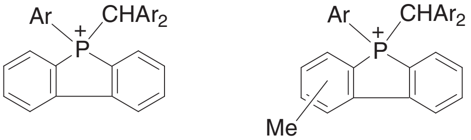
dimerization of $Z_3P^{\bullet+}$ (where Z is OR, $NR_2$, or R; R = alkyl) generated upon the $\gamma$-ray irradiation in solution to the dimer radical cation $Z_3P^{\bullet}$-$P^{+}Z_3$ has been observed during the ESR measurement.[18]

Another major product ion **3** (M+Ar) observed in the reactions with **1a**–**c** is assignable to tetraarylphosphonium cation $Ar_4P^+$. The structure was confirmed by a collision-induced dissociation (CID) MS/MS experiment. It is difficult to find a route leading to this product because one cannot detect intermediates in reactions with such a reactive species. A possibility is ipso-substitution of Ar-$P^{\bullet}$-Ar moiety in $\mathbf{1}^{\bullet+}$ by **1** (Scheme 2).



**Scheme 2** A possible pathway to give **3**.

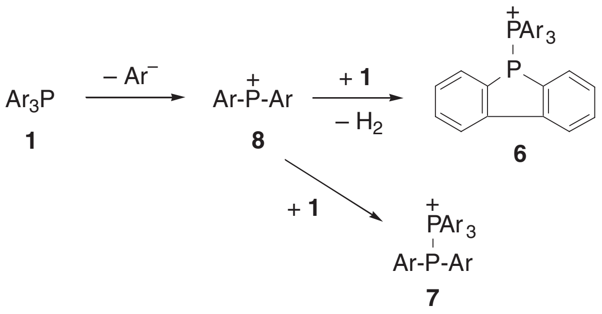
Dramatic change in the product distributions is seen in the reactions with the phosphines having the methyl groups at the *ortho* positions on the aryl ligand, *o*-tolyldiphenylphosphine (**1e**), tris(*o*-toly)phosphine (**1f**), and trimesitylphosphine (**1g**), which gave neither **2** nor **3** but gave **5** (M−Me+2Ar−2) and **5′** (M+2Ar−3) along with **4** (M−15) (Table I, runs 5, 7, and 8). Possible structures of **5** and **5′** are given in Scheme 3. Indeed, a semiempirical calculation (PM3) predicts that the nucleophilic attacks by **1e**–**g** on $\mathbf{1e}$–$\mathbf{g}^{\bullet+}$, respectively, are only slightly exothermic, while the counterpart of **1a**–**c** is highly exothermic. The reaction with **1f** gave **4f** at very a early stage (Table I, run 6), and **5f** and **5f′** appeared at the expense of **4f** in the further reaction (run 7). The observation suggests that the loss of a methyl group prevails in the reactions of $\mathbf{1e}$–$\mathbf{g}^{\bullet+}$ over the nucleophilic path, and that the resulting **4** is a precursor of **5** or **5′**. The reaction of $\mathbf{1g}^{\bullet+}$ only gave **4g** probably because the highly congested structure of **4g** prevents further reaction. Interestingly, the cation radical $\mathbf{1d}^{\bullet+}$ from tris(*p*-tolyl)phosphine (**1d**) undergoes this reaction to give **5d** as well, but with competitively affording **3d** in a smaller abundance (Table I, run 4). It is worth noting here that an *ortho*-methyl group on the aryl ligand results in significant change in the reaction path.



**5** **5'**

**Scheme 3** Possible structures of **5** and **5′**.

As shown in Table I, the radical cations examined here afforded **6** and **7** except for $\mathbf{1g}^{\bullet+}$. It has been reported that **6a** and **7a** are readily formed from **1a** under the ICR-MS experimental conditions.[19] The literature discusses the mechanism only briefly, proposing that phosphenium cation **8a** (Ar = Ph in Scheme 4) intermediate is initially produced by electron-impact of **1a**. In fact, a semiempirical calculation performed in the present study suggests that the "hot" phosphine $\mathbf{1}^*$ in a high energy state loses aryl anion $Ar^-$



**Scheme 4** Pathway to give **6** and **7**.

spontaneously to produce **8** to some extent, which in turn is trapped by **1** with or without being accompanied by the loss of two *ortho*-hydrogens to give **6** and **7**, respectively (Scheme 4).

## CONCLUSION

The examination of the gas-phase reactions of triarylphosphine radical cations $Ar_3P^{\bullet+}$ by FT-ICR mass spectrometry has shown that the distribution of the product ions from these reactions depends significantly on the methyl substituent(s) on the aryl ligand(s) of $Ar_3P$ (M). The radical cations $Ar_3P^{\bullet+}$ from $Ph_3P$, *m*-$Tol_3P$, and *p*-$TolPh_2P$ are efficiently trapped by the parent phosphine $Ar_3P$ that exists in large excess to eventually give the product ions 2M as well as M+Ar. On the other hand, $Ar_3P^{\bullet+}$ from *o*-$TolPh_2P$, and *o*-$Tol_3P$ give neither 2M nor M+Ar, but give the product ions M−Me+2Ar−2 and M+2Ar−3. To the best of our knowledge, this is the first observation that a small substituent such as a methyl group on the aryl ligand of $Ar_3P^{\bullet+}$ results in dramatic change of the reactivity of $Ar_3P^{\bullet+}$.

## EXPERIMENTAL

Triarylphosphines **1a–g** were purchased (Aldrich) and recrystallized from ethanol. Their purities were checked by $^1H$ NMR as well as mass spectra on an FT-ICR spectrometer.

The FT-ICR experiments were performed on an Extrel FTMS 2001 spectrometer (3.0 T) equipped with an IonSpec Data Station. Since all the compounds **1a–g** investigated in the present study are poorly volatile solids, a solid sample direct-inlet system was used. All vacuum chamber systems were kept at 80∼100°C. Typical pressures of neutral compounds were maintained between $5 \times 10^{-5}$ and $1 \times 10^{-4}$ Pa, by varying the temperature of the direct-inlet system. The reactions were initiated by an electron-impact ionization (electron energy = 30 eV, 10 ms pulse) of **1**. The triarylphosphine radical cation $\mathbf{1}^{\bullet+}$ was isolated by broad band ejection of any other unwanted ions, and mass spectra were recorded at a variable reaction time.

Semiempirical calculations were performed at the PM3 level of theory using the Spartan program (Wavefunction, Inc.) to obtain heats of formation ($AH_f^o$) in the gas phase at 298.15 K.

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