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Formation of Benzyl Radicals by Pulse Radiolysis of Benzyltriphenylphosphonium Chloride in Aqueous Solutions

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Synopsis. The reaction of benzyltriphenylphosphonium ion ($PhCH_2P^+Ph_3$) with e_{aq}^- has been studied. The benzyl radical and triphenylphospine are formed by the reaction: $PhCH_2P^+Ph_3 + e_{aq}^- \rightarrow PhCH_2\cdot + Ph_3P$, with the rate constant $(2.7 \pm 0.3) \times 10^{10}$ M^{-1} s^{-1}. The benzyl radical decays in a bimolecular reaction with $2k = (2.7 \pm 0.4) \times 10^9$ M^{-1} s^{-1}.

Tetraphenylphosphonium ions (Ph_4P^+) are reduced with hydrated electrons to form $Ph_4P\cdot$ radicals which decay by disproportionation.[1]

On the other hand, optically active tertiary phosphines have been prepared without racemization by electrochemical reduction of quaternary phosphonium salts having the benzyl group.[2,3] This indicates that the electron is transferred directly to the benzyl group and not to the phosphorus atom, causing fission to form a tertiary phosphine and benzyl radical, since nucleophilic attack on phosphorus leads to inversion of configuration.[4] The present investigation deals with the direct confirmation of this scheme by the pulse radiolysis method.

Experimental

The experimental details and dosimetry were reported.[5] A 500 W Xe lamp was used to follow the decay of the hydrated electron and observe other transient and permanent absorptions. All solutions were prepared from triply distilled water. The solutions were buffered with 1 mM phosphate. Deaeration of solutions was performed by argon bubbling for about 2 h. The reagents were of analytical grade and used without further purification. A fresh solution was used for each pulse. Ph_3P aqueous solution used for the absorption spectra was prepared by mixing 5×10^{-5} M Ph_3P EtOH solution with H_2O.

Results and Discussion

Pulse radiolysis of deaerated neutral aqueous solutions of benzyltriphenylphosphonium chloride yielded a transient species and products. Figure 1 shows the spectra observed immediately and 5 ms after the cessation of pulse in a buffered solution at pH 7 of 2×10^{-5} M benzyltriphenylphosphonium chloride containing 0.2 M *t*-butyl alcohol as an OH radical scavenger. The absorption at 5 ms after cessation of the pulse seems to be permanent from oscilloscopic tracing. On saturating the solution with dinitrogen oxide which converts e_{aq}^- into OH radicals, the transient absorption almost disappeared. Thus, transient and permanent absorptions are caused by the reaction of the phosphonium ion with e_{aq}^-.

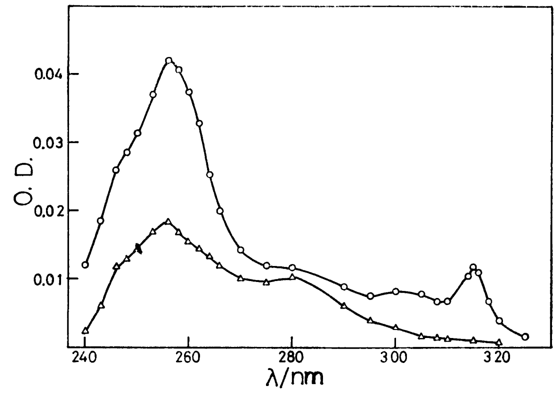

Fig. 1. Absorption spectra observed after pulse irradiation in a deaerated aqueous solution of 2×10^{-5} M benzyltriphenylphosphonium chloride, 0.2 M *t*-butyl alcohol at pH 7. Dose, 430 rad: (○) end of the pulse; (△) 5 ms after the pulse.

Figure 2 shows the spectrum of the intermediate obtained by subtraction of the absorption taken 5 ms after cessation of the pulse from that taken immediately on cessation (Fig. 1). The spectrum has three maxima at 258, 305, and 315 nm with the estimated extinction coefficients 13300, 3400, and 5900 M^{-1} cm^{-1}, respectively, taking $G(e_{aq}^-) = 2.7$. The spectrum is very similar to that of the benzyl radical[6] in aqueous solutions, which has three maxima at 258, 307, and 317.5 nm with extinction coefficients 14000, 3300, and 5500 M^{-1} cm^{-1}, respectively.

Figure 3 shows the absorption spectrum at 5 ms after the pulse corrected for the depletion of the solute ($PhCH_2P^+Ph_3Cl^-$), and that of aqueous Ph_3P solution

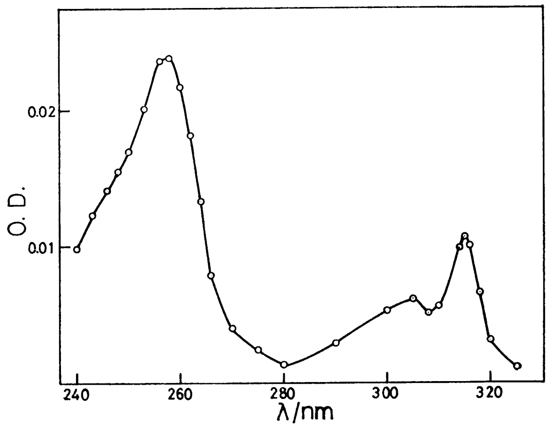

Fig. 2. Transient spectrum corrected for the permanent absorption obtained from Fig. 1.

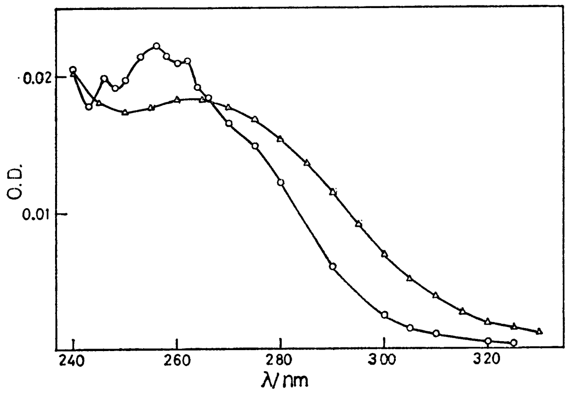

Fig. 3. Absorption spectra of the stable products corrected for depletion of the substrate obtained from Fig. 1 (○) and that of ethanolic aqueous solution of Ph_3P corresponding to the e_{aq}^- concentration in Fig. 1 (△).

corresponding to the concentration of the e_{aq}^- produced under the conditions of Fig. 1. The absorption spectrum of Ph_3P in Fig. 3 was obtained from that of 9×10^{-6} M Ph_3P aqueous solution containing 20 vol% EtOH, which has an absorption maximum at 260—265 nm with $\varepsilon = 10300\ M^{-1}\ cm^{-1}$. The permanent absorption spectrum formed by pulse radiolysis probably comes from PPh_3, since the two spectra are considerably similar. The small difference in the absorption spectra below 260 nm may be due to bibenzyl[7] produced by the recombination of benzyl radicals and the one beyond 270 nm may arise from undissolved triphenylphosphine in water.

The transient absorption at 315 nm (Fig. 2) disappears in a bimolecular reaction with $2k=(2.7\pm0.4)\times10^9\ M^{-1}\ s^{-1}$. The absorption at 258 nm, which is corrected for the permanent one, decays by a second-order kinetics with the same rate constant as that at 315 nm within an experimental error. This indicates that the permanent absorption takes place immediately on cessation of the pulse. The rate constant agrees with the previous values $(3.1\pm0.3)\times10^9$,[6] $2.4\times10^9\ M^{-1}\ s^{-1}$.[8]

The results suggest that the $PhCH_2P^+Ph_3$ ion is reduced with e_{aq}^- to dissociate into the benzyl radical and triphenylphosphine. The following reaction scheme may be suggested:

$$H_2O \rightsquigarrow e_{aq}^-,\ H,\ OH,\ etc. \qquad (1)$$

$$OH + t\text{-BuOH} \longrightarrow t\text{-BuOH radical} + H_2O \qquad (2)$$

$$PhCH_2P^+Ph_3 + e_{aq}^- \longrightarrow PhCH_2\cdot + Ph_3P \qquad (3)$$

$$PhCH_2\cdot + PhCH_2\cdot \longrightarrow \text{Products} \qquad (4)$$

$$e_{aq}^- + N_2O \longrightarrow OH + OH^- + N_2 \qquad (5)$$

The rate constant for the reaction of the $PhCH_2P^+Ph_3$ ion with e_{aq}^- is $(2.7\pm0.3)\times10^{10}\ M^{-1}\ s^{-1}$, which was determined from the decay of e_{aq}^-. The rate constant is diffusion controlled, similar to that[1] of Ph_4P^+ with e_{aq}^-.

The phosphoranyl radical $PhCH_2\dot{P}Ph_3$ might not be sufficiently stable to be observed in the microsecond pulse radiolysis. It seems reasonable to assume that e_{aq}^- attacks the $PhCH_2$ group, and causing release of the benzyl radical before the electron is delocalized to form the phosphoranyl radical.

The reaction mechanism might be similar to that of the electroreduction of quaternary ammonium compound.[9,10]

References

1) H. Horii, S. Fujita, T. Mori, and S. Taniguchi, *Int. J. Radiat. Phys. Chem.*, **8**, 521 (1976).

2) L. Horner, H. Winkler, A. Rapp, A. Mentrup, H. Hoffmann, and P. Beck, *Tetrahedron Lett.*, **1961**, 161.

3) L. Horner and H. Winkler, *Tetrahedron Lett.*, **1964**, 175.

4) R. F. Hudson, "Structure and Mechanism in Organophosphorus Chemistry," Academic Press, London (1965), pp. 211—212.

5) S. Fujita, H. Horii, and S. Taniguchi, *J. Phys. Chem.*, **77**, 2868 (1973).

6) H. C. Christensen, K. Sehested, and E. J. Hart, *J. Phys. Chem.*, **77**, 983 (1973).

7) H. C. Christensen and R. Gustafsson, *Acta Chem. Scand.*, **26**, 937 (1972).

8) K. Sehested, H. Corfitzen, H. C. Christensen, and E. J. Hart, *J. Phys. Chem.*, **79**, 310 (1975).

9) M. Finkelstein, R. C. Petersen, and S. D. Ross, *J. Am. Chem. Soc.*, **81**, 2361 (1959); **82**, 1582 (1960).

10) J. S. Mayell and A. J. Bard, *J. Am. Chem. Soc.*, **85**, 421 (1963).