Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

A kinetic study of α- and β-scission of phosphoranyl radicals, $R_n\dot{P}(OR)_{4-n}$

ALWYN G. DAVIES, R.W. DENNIS, D. GRILLER and B.P. ROBERTS
Department of Chemistry, University College London, 20 Gordon Street, London WC1H OAJ (Great Britain).

(Received May 15th, 1972)

Compounds of tervalent phosphorus react with alkoxyl radicals in solution to form phosphoranyl radicals (I) which may then undergo α- or β-scission.[1]

$$\begin{tikzcd} & & ROPX_2 + X\cdot & (1a) \\ RO\cdot + PX_3 \arrow[r] & \underset{(I)}{RO\dot{P}X_3} \arrow[ru, "\alpha\text{-scission}"] \arrow[rd, "\beta\text{-scission}"'] & & \\ & & R\cdot + O{=}PX_3 & (1b) \end{tikzcd}$$

Using ESR spectroscopy to monitor the concentrations of the phosphoranyl and t-butyl radicals, we have studied the decomposition of the t-butoxytriethoxyphosphoranyl radical which undergoes exclusive β-scission (eqn. lb, R = t-Bu, X = EtO)[2].

Only the spectrum of the ethyl radical was detected during the photolysis of di-t-butyl peroxide in the presence of triethylphosphine at low temperature, and it was concluded that the intermediate phosphoranyl radical, $t\text{-BuO}\dot{P}Et_3$, (which was not detected) underwent exclusive α-scission[3], although β-scission is the thermodynamically favoured process[1].

$$t\text{-BuO}\cdot + PEt_3 \longrightarrow Et\cdot + t\text{-BuOPEt}_2 \qquad (2)$$

We have determined the rate constant for the overall reaction (2) by causing triethylphosphine and triethyl phosphite to compete for t-butoxyl radicals[2]*, at low conversions, and at temperatures sufficiently high that the concentration of $t\text{-BuO}\dot{P}(OEt)_3$ was small. In the temperature range +34 to −42° in cyclopentane,

---

*For the reaction $t\text{-BuO}\cdot + P(OEt)_3 \longrightarrow t\text{-Bu}\cdot + OP(OEt)_3$ the rate constant is given[2] by log $k(l\cdot mol^{-1}\cdot sec^{-1}) = 9.83 - 2.24/\theta$.

$$\log k_2(\mathrm{l \cdot mol^{-1} \cdot sec^{-1}}) = 9.34 - 1.34/\theta$$

where $\theta = 2.303\,RT$ kcal·mol^{-1}.

After a few minutes' photolysis of a mixture of triethylphosphine and di-t-butyl peroxide in isopentane, an ESR spectrum assigned to the radical $(\text{t-BuO})_2\dot{\text{P}}\text{Et}_2$ [a(P) 705G, a(H) 2.3G (binomial quintet) at −80°] appeared and became progressively more intense as the photolysis continued.

A similar radical [a(P) 707G, a(H) 2.3G] was detected when di-t-butyl peroxide was photolysed in the presence of diethylethoxyphosphine. Ethyl radicals (and no t-butyl radicals) were also detected.

$$\text{t-BuO}\cdot + \text{Et}_2\text{POEt} \longrightarrow \text{Et}_2\dot{\text{P}}(\text{OEt})\text{OBu-t} \qquad (3)$$

$$\text{Et}_2\dot{\text{P}}(\text{OEt})\text{OBu-t} \longrightarrow \text{Et}\cdot + \text{EtP}(\text{OEt})\text{OBu-t} \qquad (4)$$

The radical $\text{Et}_2\dot{\text{P}}(\text{OEt})\text{OBu-t}$ was sufficiently stable to allow its unimolecular decay to be followed by ESR at low temperatures (−128° to −96°) without the aid of computer averaging techniques. At higher temperatures (−88° to −37°) the steady state method[2] was used to study the reaction. In both temperature ranges in isopentane k_4 was given by:

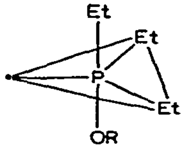
$$\log k_4(\mathrm{sec^{-1}}) = 10.91 - 8.16/\Theta$$

Similar treatment of $\text{EtP}(\text{OEt})_2$ gave rise to a weak spectrum of $\text{Et}_2\dot{\text{P}}(\text{OEt})_2$ and a stronger signal from the ethyl radical, but the spectrum of the radical $\text{Et}\dot{\text{P}}(\text{OEt})_2\text{OBu-t}$ [a-(P) 793G at −100°] was extremely weak even at −120°. After some time tetraalkoxyphosphoranyl and t-butyl radicals were detected in addition, and these probably arise[2] from reaction of t-butoxyl radicals with the trialkyl phosphite resulting from α-scission of $\text{Et}\dot{\text{P}}(\text{OEt})_2\text{OBu-t}$. The $\text{Et}_2\dot{\text{P}}(\text{OEt})_2$ radicals probably arise from reaction (5) and indeed the radical $\text{MeEt}\dot{\text{P}}(\text{OEt})_2$ was detected during photolysis of azomethane in the presence of ethyldiethoxyphosphine.

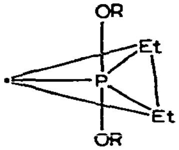
$$\text{Et}\cdot + \text{EtP}(\text{OEt})_2 \rightleftharpoons \text{Et}_2\dot{\text{P}}(\text{OEt})_2 \qquad (5)$$

The thermodynamically most stable configurations[2] of the various radicals are shown in (II), (III) and (IV). We attribute the differences in stability (III > IV > II) partly to a configurational selectivity for α-scission in these trigonal bipyramidal[2] species, loss of an apical alkyl group being favoured[★].

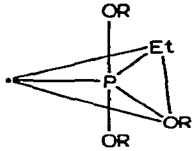
[★] On the other hand, β-scission of an alkoxyphosphoranyl radical appears to occur most readily when it involves an equatorial alkoxy group.



(II)



(III)



(IV)

The radical (II) has an apical ethyl group and will thus be less stable towards α-scission than (III) which has not. Pseudo-rotation[4] of (III) about the unpaired electron as pivot results in interchange of the apical and equatorial groups and in fact α-scission of $(RO)_2\dot{P}Et_2$ probably involves, as the slowest step, positional exchange of the ethyl and alkoxyl groups to give the thermodynamically and kinetically less stable form with apical ethyl groups. The barrier to pseudo-rotation of (IV) about the unpaired electron should be less than in the case of (III) because the new structure has one and not two apical ethyl groups.

Other effects, especially substitutent electronegativity, also appear to be important and a full discussion will be given later.

REFERENCES

1 A.G. Davies and B.P. Roberts, *Nature (London), Phys. Sci.*, 229 (1971) 221; K.U. Ingold and B.P. Roberts, *Free Radical Substitution Reactions*, Wiley-Interscience, New York, 1971, Ch. 6.
2 A.G. Davies, D. Griller and B.P. Roberts. *Angew. Chem. Intern. Ed. Engl.*, 10 (1971) 738; *J. Chem. Soc. Perkin II*, in the press.
3 J.K. Kochi and P.J. Krusic, *J. Amer. Chem. Soc.*, 91 (1969) 3944.
4 S.R. Berry, *J. Chem. Phys.*, 32 (1960) 933; G.M. Whitesides and H.R. Mitchell, *J. Amer. Chem. Soc.*, 91 (1969) 5384.