# Polar Effects on the Addition of Alkyl Radicals to Diethyl Vinylphosphonate

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Summary Absolute rate constants for addition of alkyl radicals (R·) to diethyl vinylphosphonate at 233 K increase in the order R = Me < Et < Pr^i < Bu^t, indicating the predominance of polar effects over steric or thermodynamic factors.
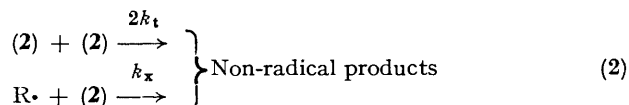
Alkyl radicals generally add more rapidly to electron deficient alkenes than to electron rich ones.[1] This reactivity pattern is usually taken as evidence for the importance of polar effects in stabilising the transition state for addition, and the alkyl radical appears to exhibit nucleophilic properties.[2] However, this conclusion is often not entirely justified, since it is usually difficult to assess the part played by polar factors, as distinct from steric or thermodynamic effects, in determining the relative rates. During the course of our e.s.r. studies of radical addition to unsaturated molecules, we have obtained quantitative evidence for the importance of polar effects on the rates of addition of alkyl radicals to the electron deficient alkene diethyl vinylphosphonate (1) [equation (1)].

$$R\cdot + CH_2=CHP(O)(OEt)_2 \xrightarrow{k_{add}} RCH_2\dot{C}HP(O)(OEt)_2 \quad (1)$$
$$(1) \qquad\qquad\qquad (2)$$
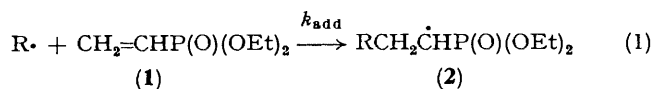
Photolysis at 233 K of a hydrocarbon solution containing azoisobutane (as a source of t-butyl radicals) and (1) (0·3 M) gave rise to the e.s.r. spectrum† of (2; R = Bu^t), whilst the signal from ·Bu^t was barely detectable. Alternative photochemical sources of t-butyl radicals [Bu$^t_2$CO; Bu^{t}OOBu^t + (EtO)$_3$P] gave similar results. However, photolysis of azomethane in the presence of the same concentration of (1) at 233 K afforded spectra of both (2; R = Me) and Me·, and the signals were now of similar intensity. E.s.r. parameters for the α-phosphonylalkyl radicals (2) are given in the Table.

The values of a(P) are similar to those reported previously for related radicals in the solid state[3] and close to that shown by H$_2$ĊP(O)(OEt)$_2$‡ in cyclopropane solution [a(P) 42·7, a(2H) 22·0 G, g 2·0024 at 236 K].

Rate constants for addition of alkyl radicals to (1) were measured relative to those for self-reaction of the adduct radicals (2).

$$(2) + (2) \xrightarrow{2k_t} \left.\begin{array}{c} \\ \\ \end{array}\right\}$$
$$R\cdot + (2) \xrightarrow{k_x} \left.\begin{array}{c} \\ \end{array}\right\} \text{Non-radical products} \quad (2)$$

As expected, for a given concentration of (1) the ratio [(2)] : [R·] increased with increasing temperature. Addition of the electrophilic α-phosphonylalkyl radicals (2) to (1), which would lead to polymerisation of the phosphonate, was not detected by e.s.r. below 270 K. It may be shown that the steady-state radical concentrations during continuous photolysis are given by equation (3).

$$[(1)]/[(2)] = (2k_t/k_{add}) \, [(2)]/[R\cdot] + k_x/k_{add} \quad (3)$$

Radical concentrations were measured at 233 K as a function of [(1)] (0·30—1·25 M) in cyclopentane solvent, and plotting [(2)]/[R·] against [(1)]/[(2)] yielded 2k$_t$/k$_{add}$, values of which are given in the Table. The rate constant for self-reaction of (2; R = Bu^t) was measured by kinetic e.s.r. spectroscopy[4] in cyclopentane at 230 K, with a concentration of (1) (1·25 M) such that only (2) was detectable, and a value of 4·0 × 10^8 l mol^{-1} s^{-1} was obtained. The values of k$_{add}$ listed in the Table were calculated assuming that 2k$_t$ was independent of the nature of R·. If 2k$_t$ increases somewhat as the size of the adduct decreases, this will only serve to increase the differences in k$_{add}$.

It is evident that k$_{add}$ increases appreciably along the series R = Me < Et < Pr^i < Bu^t, contrary to expecta-

TABLE. E.s.r. parameters (in cyclopropane) for the adducts RCH$_2$ĊHP(O)(OEt)$_2$ and rate constants (in cyclopentane at 233 K) for addition of R· to CH$_2$=CHP(O)(OEt)$_2$

| R· | Addendum radical source[a] | Temp./K | g-Factor | Hyperfine splittings/G[b] | | | 2k$_t$/k$_{add}$ | k$_{add}$/ l mol^{-1} s^{-1} |
				a(1P)	a(1H$_\alpha$)	a(2H$_\beta$)		
Me·	A	230	2·0025	40·9	21·0	25·2	2·3 × 10^6	1·7 × 10^2
Et·	B	225	2·0025	41·9	21·1	25·2[c]	9·6 × 10^5	4·2 × 10^2
·Pr^i	B	243	2·0025	41·8	21·1	25·3[d]	1·6 × 10^5	2·5 × 10^3
·Bu^t	A, C, D, E	239	2·0024	41·3	21·1	25·5[e]	1·3 × 10^4	3·1 × 10^4

[a] A = RN=NR; B = Bu^{t}OOBu^t + R$_3$P; C = Bu$^t_2$CO; D = Bu^{t}OOBu^t + (EtO)$_3$P; E = Bu^{t}OOBu^t + RH. [b] γ-Proton splittings unresolved unless otherwise stated. [c] a(2Hγ) 0·7 G. [d] a(1Hγ) 1·0 G. [e] a(2Hβ) 26·1 G at 170 K; a(P) and a(H$_\alpha$) did not vary significantly with temperature.

† Assignment to (2; R = Bu^t) is based upon the magnitudes of the hyperfine splittings and their temperature dependences, which are not consistent with the structure H$_2$ĊCH(Bu^t)P(O)(OEt)$_2$ (X). A 1,2-shift of the (EtO)$_2$P(O) group in (X) would yield (EtO)$_2$P(O)CH$_2$ĊHBu^t (Y), but the latter was eliminated by generating authentic (Y) [a(P) 69·5, a(H$_\alpha$) 22·1, a(2H$_\beta$) 22·1 G at 209 K] by addition of (EtO)$_2$PO to Bu^{t}CH=CH$_2$.

‡ Generated by photolysis of solutions containing either ICH$_2$P(O)(OEt)$_2$ and Me$_3$SnSnMe$_3$ or Bu^{t}OOBu^t, Et$_3$SiH, and BrCH$_2$P(O)(OEt)$_2$.

tions if either steric or thermodynamic effects are predominant. We conclude that polar effects are of overriding importance in determining the rate of addition of alkyl radicals to (1). In valence bond terms, the transition state for addition must be stabilised by contributions from the charge-transfer structure (3), and this stabilisation

$$R^+ \; CH_2\!\!=\!\!CHP(O)(OEt)_2^{\,\overline{\cdot}}$$

(3)
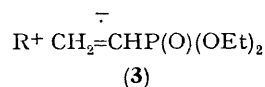
would become greater as the ionisation potential of R· decreases on going from Me· to ·Bu^t.

The same conclusion may be expressed in the terminology of frontier orbital theory.[5] The SOMO–LUMO (C=C π^*) interaction will predominate for addition of R· to (1), and will become increasingly important as the ionisation potential of R· decreases.

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[2] P. I. Abell in 'Free Radicals,' ed. J. K. Kochi, Wiley-Interscience, 1973, vol. 2, ch. 13; B. Giese and W. Zwick, Angew. Chem. Internat. Edn, 1978, 17, 66; B. Giese and J. Meister, ibid., 1977, 16, 178.

[3] A. Begum and M. C. R. Symons, J.C.S. Faraday II, 1973, 69, 43.

[4] R. W. Dennis and B. P. Roberts, J.C.S. Perkin II, 1975, 140.

[5] I. Fleming, 'Frontier Orbitals and Organic Chemical Reactions,' Wiley-Interscience, 1976, pp. 182—186.