An Electron Spin Resonance Study of Alkyl Radical Addition to Diethyl Vinylphosphonate

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The irreversible addition of alkyl radicals to diethyl vinylphosphonate to give the α-phosphorylalkyl radicals (1) has been studied by e.s.r. spectroscopy at 233 K in hydrocarbon solvents. The rate constants for addition (k_{add}) have

$$R\cdot + H_2C{=}CHP(O)(OEt)_2 \xrightarrow{k_{add}} RCH_2\dot{C}HP(O)(OEt)_2 \qquad (1)$$

been determined relative to those ($2k^A_t$) for self-reaction of (1) for a series of addenda. The values of $2k^A_t$ have been measured in separate kinetic e.s.r. experiments for (1 ; R = Me) (2.0×10^9 dm^3 mol^{-1} s^{-1}) and (1 ; R = Bu^t) (5.0×10^8 dm^3 mol^{-1} s^{-1}) and thus absolute values of k_{add} were obtained. The rate constant k_{add} increases along the series R· = Me· (2.5×10^3 dm^3 mol^{-1} s^{-1}) < $R^{prim.}$ < $R^{sec.}$ < $Bu^{t}\cdot$ (5.9×10^4 dm^3 mol^{-1} s^{-1}) and this order is interpreted in terms of the over-riding importance of polar effects in determining the size of the barrier for addition of these nucleophilic radicals to the electron deficient alkene.

A NUMBER of factors are thought to be significant in determining the rate of radical addition to alkenes.[1] The overall thermochemistry of addition is important, as are polar, steric, and stereoelectronic effects which influence the energy of the transition state. Alkyl radicals are generally considered to exhibit nucleophilic character in their addition to alkenes and appear to add more rapidly to electron-deficient C=C bonds than to electron-rich ones.[2,3] However, it is often difficult to disentangle the various effects when attempting to interpret relative reactivity data[4] and, as has been pointed out,[5] a complete understanding of the factors involved in homolytic addition to alkenes awaits further quantitative kinetic studies of these reactions.

In this paper we report an e.s.r. study of the addition of alkyl radicals to the electron-deficient alkene diethyl vinylphosphonate to give α-phosphorylalkyl radicals (1) [equation (i)].

$$R\cdot + H_2C{=}CHP(O)(OEt)_2 \xrightarrow{k_{add}} \underset{(1)}{RCH_2\dot{C}HP(O)(OEt)_2} \qquad (i)$$

Absolute rate constants (k_{add}) for addition have been determined and these provide strong evidence for the over-riding importance of polar effects in determining the height of the barrier to reaction (i). Some of our results were reported in a preliminary communication.[6]

RESULTS

Cyclopropane or cyclopentane solutions containing diethyl vinylphosphonate (DEVP) and an appropriate source of radical addenda were photolysed with high intensity u.v.-visible light from a high-pressure mercury arc lamp whilst the sample was in the cavity of the e.s.r. spectrometer. The spectra of the addenda and the adduct radicals (1) were monitored during continuous photolysis.†

Photolysis at 233 K of a cyclopentane solution containing DEVP (0.16M), triethyl phosphite (15% v/v), and di-t-butyl peroxide (15% v/v) (the latter two reagents provide a clean source of t-butyl radicals at this temperature [7]) gave rise to the spectra shown in Figure 1a. A strong spectrum assigned to the adduct (1; R = Bu^t) may be seen together with a weaker signal from the t-butyl radical [equations (ii)—(iv)].

$$Bu^tOOBu^t \xrightarrow{h\nu} 2Bu^tO\cdot \qquad (ii)$$

$$Bu^tO\cdot + (EtO)_3P \longrightarrow Bu^t\cdot + (EtO)_3PO \qquad (iii)$$

$$Bu^t\cdot + H_2C{=}CHP(O)(OEt)_2 \longrightarrow Bu^tCH_2\dot{C}HP(O)(OEt)_2 \qquad (iv)$$

Other photochemical sources of t-butyl radicals (Bu^{t}N=NBu^t, Bu$^t_2$CO, Bu^{t}OOBu^t + Bu^{t}H) gave similar results and with higher concentrations of DEVP the value of [(1; R = Bu^t)]/[Bu^t·] was larger. Photochemical generation of methyl radicals (from MeN=NMe or Bu^{t}OOBu^t + Me$_3$B) in the presence of DEVP similarly gave rise to spectra of Me· and (1; R = Me), although for a given concentration of DEVP the value of [(1)]/[R·] was much greater when R = Bu^t than when R = Me (see Figure 2).

The spectral assignment to (1; R = Me) was confirmed by generating this radical independently by abstraction of bromine from diethyl 1-bromopropylphosphonate using photochemically produced triethylsilyl radicals [equations (v) and (vi)] (see Figure 3).[8]

$$Bu^tO\cdot + Et_3SiH \longrightarrow Bu^tOH + Et_3Si\cdot \qquad (v)$$

$$Et_3Si\cdot + CH_3CH_2CHBrP(O)(OEt)_2 \longrightarrow Et_3SiBr + CH_3CH_2\dot{C}HP(O)(OEt)_2 \qquad (vi)$$

The spectra of (1; R = Me) derived from the two sources were identical, but when the radical was generated by reaction (vi) no trace of the spectrum of Me· could be detected. The latter result confirms that addition of Me· to DEVP is irreversible under the experimental conditions, since the methyl radical may be readily detected in the

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† Photolysis of DEVP alone in hydrocarbon solvents afforded no e.s.r. signals. Photolysis of a mixture of di-t-butyl peroxide and DEVP in cyclopropane at 233 K gave rise only to a weak, poorly defined spectrum of broad lines (ΔB_{p-p} *ca.* 2 G) which might have been due to an adduct of the type XCH$_2\dot{C}$HP(O)(OEt)$_2$, but if so the nature of X is unknown. At lower temperatures (160 K) some sharper weak lines were also apparent, but we were unable to assign these. After prolonged photolysis unidentified persistent radicals were produced and the spectra of these could be detected for long periods after shuttering the light.

presence of Et_3SiH (photolysis of a solution containing Bu^tOOBu^t, Et_3SiH, and MeBr afforded a very intense spectrum of Me· at 233 K).

A number of other adducts of the type (1) were generated in a similar way by addition of carbon centred radicals to DEVP and the e.s.r. parameters are given in Table 1. Figure 1b shows the spectra obtained during generation of the n-butyl radical in the presence of DEVP. Addition of benzyl radicals to DEVP was undetectable at 233 K and only the spectrum of $Ph\dot{C}H_2$ was observed during photolysis of a cyclopropane solution containing DEVP, Bu^tOOBu^t, and toluene. Cyclopropane was always used as the solvent when hydrogen abstraction from cyclopentane to give cyclopentyl radicals might compete with reaction of $Bu^tO\cdot$ to give R· and hence give rise to a mixture of adducts. In contrast to the result with Me·, addition of $CF_3\cdot$ (from $CF_3I + Me_3SnSnMe_3$) was essentially complete even at low concentrations of DEVP (0.3M) and only a very weak signal from the addendum was detected at 233 K.

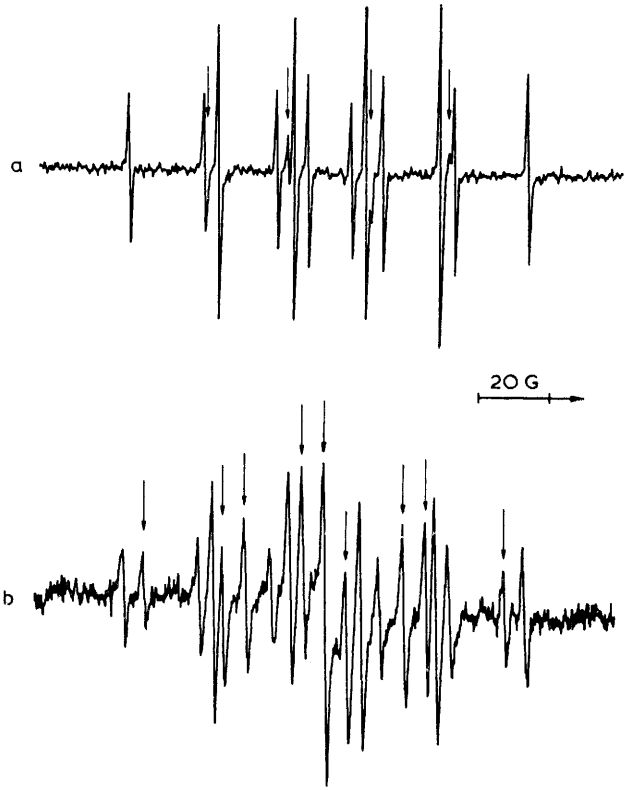

FIGURE 1 a, E.s.r. spectrum of (1; R = Bu^t) obtained during photolysis of a cyclopentane solution containing DEVP (0.16M), di-t-butyl peroxide, and triethyl phosphite at 233 K. The arrows mark the positions of the four central lines in the spectrum of the t-butyl radical. b, E.s.r. spectrum of (1; R = Bu^n) obtained during photolysis of a cyclopropane solution containing DEVP (0.60M), di-t-butyl peroxide, and tri-n-butylborane at 233 K. The arrows mark the positions of the lines due to the n-butyl radical

Addition of the adduct radicals (1) to DEVP was not detectable by e.s.r. spectroscopy under the conditions employed in these experiments. Although the major hyperfine splittings for (1) are virtually independent of the nature of R, the detection of γ-proton splittings serves to confirm the structures of the adducts (see Table 1).

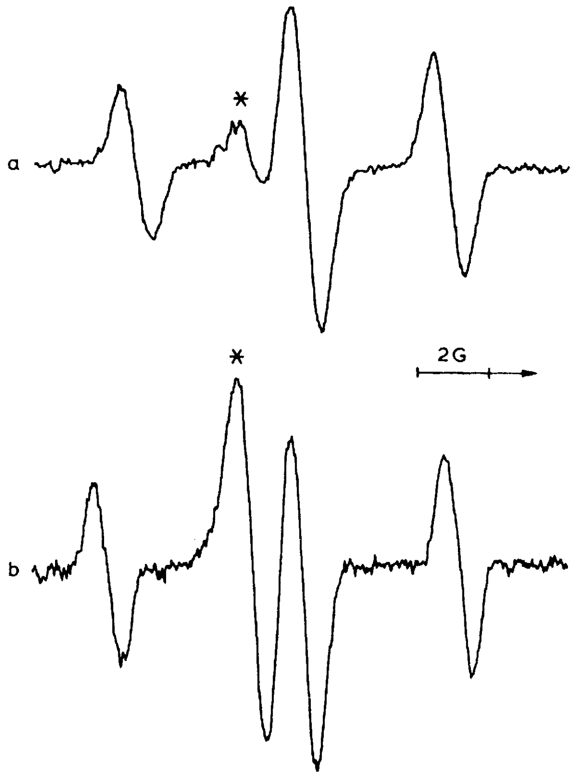

FIGURE 2 Lines 4—6 of the e.s.r. spectra of (1; R = Me or Bu^t) and (marked *) line 2 of Me· or line 5 of $Bu^t\cdot$ at 233 K. a, R = Bu^t, cyclopentane solvent, [DEVP] 0.16, [(1; R = Bu^t)] 1.2×10^{-6}, [$Bu^t\cdot$] 1.3×10^{-7}M; b, R = Me, cyclopropane solvent, [DEVP] 0.63, [(1; R = Me)] 3.8×10^{-7}, [Me·] 2.0×10^{-7}M

Measurement of $(2k^{A}_{t}/k_{add})$.—The rate constants for addition of a number of radicals to DEVP were measured relative to those for self-reaction of the adducts (1) using an extension of the method employed previously for unimolecular reactions.[9,10] If the irreversible addition reaction

$$\left.\begin{array}{l}(1) + (1) \xrightarrow{2k^{A}_{t}} \\[1em] (1) + R\cdot \xrightarrow{k_{x}} \end{array}\right\}\text{non-radical products}\qquad\begin{array}{r}\text{(vii)}\\[1em]\text{(viii)}\end{array}$$

(i) is the only source of (1) which is removed only by reactions (vii) and (viii), it may be shown readily that

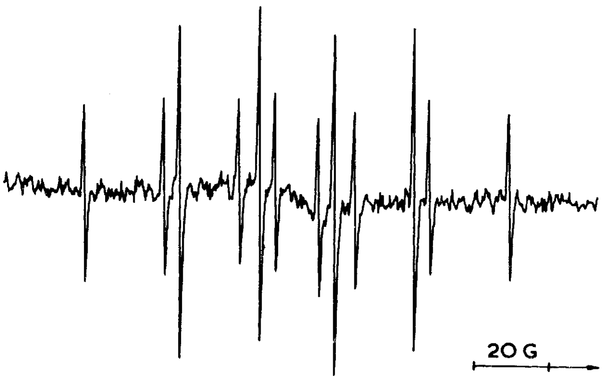

FIGURE 3 E.s.r. spectrum of (1; R = Me) obtained during photolysis of a cyclopropane solution containing diethyl 1-bromopropylphosphonate, di-t-butyl peroxide, and triethylsilane at 235 K

equation (ix) holds under steady-state conditions during continuous photolysis.

$$[\mathrm{DEVP}]/[(1)] = (2k^{\mathrm{A}}_{\mathrm{t}}/k_{\mathrm{add}})[(1)]/[\mathrm{R}\cdot] + (k_{\mathrm{x}}/k_{\mathrm{add}}) \quad \text{(ix)}$$

The concentrations of adduct and alkyl radicals were measured for different values of [DEVP] (usually between 0.3 and 1.2M) and the value of $(2k^{\mathrm{A}}_{\mathrm{t}}/k_{\mathrm{add}})$ was obtained as the slope of a graph of [DEVP]/[(1)] against [(1)]/[R·]. Results using cyclopropane or cyclopentane solvents were the same within experimental error. Examination of Figure 1 shows that the effects of chemically induced dynamic electron polarisation (CIDEP) [11] are apparent in the spectra. The lines appearing at low magnetic field have intensities different from those of the corresponding lines to high field of the centre. Such polarisation was more apparent in the spectrum of (1) than in that of the alkyl radical addendum. The degree of polarisation was less at lower radical concentration (lower incident light intensities) in accord with theory.[11,12] It was assumed that there was no net polarisation of the spectra [11] and radical concentrations were measured using the average of the double integrals of corresponding lines at low and high fields.

TABLE 1

E.s.r. parameters for the α-phosphorylalkyl radicals (1)

R	Solvent [a]	T/K	Hyperfine splittings [b] (G)			
			a(P)	$a(1\mathrm{H}_\alpha)$	$a(2\mathrm{H}_\beta)$	$a(n\mathrm{H}_\gamma)$
Me	A	233	40.9	21.1	25.3	not resolved
Et	A	225	41.9	21.1	25.2	0.7 (2)
$\mathrm{Bu^n}$	B	230	41.3	21.0	25.0	0.7 (2)
$\mathrm{Bu^i}$	B	235	41.1	21.1	25.1	not resolved
$\mathrm{MeOCH_2}$	B	235	41.3	21.1	25.3	
$\mathrm{Pr^i}$	A	243	41.8	21.1	25.3	1.0 (1)
cyclo-$\mathrm{C_5H_9}$	A	230	41.3	21.1	25.1	1.0 (1)
$\mathrm{Bu^t}$	A	232	41.4	21.0	25.1	
$\mathrm{CF_3}$	B	230	41.1	21.4	24.8	*d*

[a] A = Cyclopentane, B = cyclopropane. [b] All g factors were 2.0025 ± 0.0001 corrected to second-order. [c] Number of equivalent nuclei shown in parentheses. [d] Fluorine splitting not resolved.

The values of $(2k^{\mathrm{A}}_{\mathrm{t}}/k_{\mathrm{add}})$ at 233 K are given in Table 2, and where these differ from those given in our preliminary communication [6] the present results are considered more reliable. The only appreciable difference is in the value of $(2k^{\mathrm{A}}_{\mathrm{t}}/k_{\mathrm{add}})$ for R = Me. In the preliminary work we employed only photolysis of azomethane as the source of Me· and radical concentrations were low, especially at high DEVP concentrations. We have now also generated methyl radical addenda from the $\mathrm{Me_3B} + \mathrm{Bu^tO\cdot}$ couple [13] which affords much stronger spectra (see Figure 2b) and hence more reliable results. The relatively large error associated with $(2k^{\mathrm{A}}_{\mathrm{t}}/k_{\mathrm{add}})$ for R = Me reflects the fact that agreement between the results obtained using the different sources of Me· was not particularly good. However, agreement was good between values of $(2k^{\mathrm{A}}_{\mathrm{t}}/k_{\mathrm{add}})$ obtained with $\mathrm{R_3B} + \mathrm{Bu^tO\cdot}$ or $\mathrm{R_3P} + \mathrm{Bu^tO\cdot}$ as sources of addenda.

TABLE 2

Kinetics of alkyl radical addition to diethyl vinylphosphonate at 233 K in cyclopropane or cyclopentane

R·	Addendum radical source [a]	$(2k^{\mathrm{A}}_{\mathrm{t}}/k_{\mathrm{add}})$	k_{add}/ $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$
Me·	A, C	$(8.0 \pm 4.0) \times 10^5$	2.5×10^3
Et·	B	$(5.0 \pm 2.0) \times 10^5$	2.6×10^3
$\mathrm{Bu^n\cdot}$	B, C	$(2.6 \pm 0.5) \times 10^5$	5.0×10^3
$\mathrm{Bu^i\cdot}$	C	$(3.5 \pm 0.8) \times 10^5$	3.7×10^3
$\mathrm{MeOCH_2\cdot}$	D	$(1.9 \pm 0.4) \times 10^5$	6.8×10^3
$\mathrm{Pr^i\cdot}$	B	$(1.1 \pm 0.3) \times 10^5$	1.2×10^4
cyclo-$\mathrm{C_5H_9\cdot}$	D	$(2.0 \pm 0.5) \times 10^5$	6.5×10^3
$\mathrm{Bu^t\cdot}$	E	$(8.5 \pm 2.0) \times 10^3$	5.9×10^4

[a] A = RN=NR, B = $\mathrm{R_3P} + \mathrm{Bu^tOOBu^t}$, C = $\mathrm{R_3B} + \mathrm{Bu^tOOBu^t}$, D = $\mathrm{RH} + \mathrm{Bu^tOOBu^t}$, E = $\mathrm{(EtO)_3P} + \mathrm{Bu^tOOBu^t}$.

Measurement of $2k^{\mathrm{A}}_{\mathrm{t}}$.—The rate constants for self-reaction of (1; R = $\mathrm{Bu^t}$) and (1; R = Me) were measured at 233 K using the rotating sector technique.[14,15] Both cyclopropane and cyclopentane were used as diluents and the viscosities of the samples used for measurements of $(2k^{\mathrm{A}}_{\mathrm{t}}/k_{\mathrm{add}})$ and $2k^{\mathrm{A}}_{\mathrm{t}}$ were similar. To overcome CIDEP effects, measurements were made on corresponding lines to high and low field of the spectrum centre and the peak height at a given time after interrupting photochemical generation was taken as the mean of the two measured heights. This mean value was then converted to an absolute radical concentration using the mean double integral and mean height of the two peaks recorded during continuous photolysis.

The adduct (1; R = $\mathrm{Bu^t}$) was generated by photolysis of a mixture of DEVP (1.2M), $\mathrm{Bu^tOOBu^t}$, and $\mathrm{(EtO)_3P}$, since at this phosphonate concentration only the spectrum of the adduct was detectable. The adduct (1; R = Me) was generated by photolysis of a mixture of diethyl 1-bromopropylphosphonate (*ca.* 0.3—0.6M), $\mathrm{Bu^tOOBu^t}$ (*ca.* 0.9M), and $\mathrm{Et_3SiH}$ (*ca.* 1—2M) as described above. The concentrations of both adducts during continuous photolysis were proportional to the square-root of the incident light intensity (100—3% of the maximum), confirming second-order removal of the radicals. No meaningful differences in $2k^{\mathrm{A}}_{\mathrm{t}}$ were found on changing the solvent from cyclopentane to cyclopropane. With low concentrations of $\mathrm{Et_3SiH}$ in cyclopentane a weak spectrum of the cyclopentyl radical could be detected alongside that of (1; R = Me) and thus such systems were unsuitable for measurement of $2k^{\mathrm{A}}_{\mathrm{t}}$. The values of $2k^{\mathrm{A}}_{\mathrm{t}}$ at 233 K were $(2.0 \pm 0.5) \times 10^9$ (R = Me) and $(5.0 \pm 1.0) \times 10^8$ (R = $\mathrm{Bu^t}$) $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ with initial radical concentrations of *ca.* 2×10^{-7} and 6×10^{-7}M, respectively. These rate constants are probably quite close to the diffusion-controlled limiting values.

The absolute values of k_{add} are given in Table 2. For adducts of radicals other than Me· or $\mathrm{Bu^t\cdot}$, $2k^{\mathrm{A}}_{\mathrm{t}}$ was taken to be the mean of the values for (1; R = Me or $\mathrm{Bu^t}$), that is $1.3 \times 10^9\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$.

In principle, k_{x} may be obtained from the intercept of straight-line plots according to equation (ix). However, we did not consider that the accuracy of these rate constants would justify their calculation. If we make the questionable assumption that k_{x} is equal to the geometric mean of $2k^{\mathrm{A}}_{\mathrm{t}}$ and $2k^{\mathrm{R}}_{\mathrm{t}}$ [reaction (x)], we may rewrite equation (ix) as equation (xi) in which r is $(2k^{\mathrm{R}}_{\mathrm{t}}/2k^{\mathrm{A}}_{\mathrm{t}})$.

$$\mathrm{R}\cdot + \mathrm{R}\cdot \xrightarrow{2k^{\mathrm{R}}_{\mathrm{t}}} \text{non-radical products} \qquad \text{(x)}$$

$$k_{\mathrm{add}} = 2k^{\mathrm{A}}_{\mathrm{t}} \frac{[(1)]}{[\mathrm{DEVP}]} \left\{ \frac{[(1)]}{[\mathrm{R}\cdot]} + r^{1/2} \right\} \qquad \text{(xi)}$$

The values of k_{add} obtained using equation (xi) and taking [16] $2k^{\mathrm{R}}_{\mathrm{t}}$ as $1 \times 10^{10}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$ independent of the nature of R· [r = 5 (R· = Me·), 20 ($\mathrm{Bu^t\cdot}$), 8 (other addenda)] were within experimental error of those given in Table 2.

DISCUSSION

The errors in the absolute value of k_{add} determined by the e.s.r. method are relatively large, partly because of the difficulty of measuring the absolute radical concentrations needed to determine both $(2k^{A}_{t}/k_{add})$ and $2k^{A}_{t}$. However, even taking the maximum value of k_{add} (R = Me) and the minimum value of k_{add} (R = Bu^{t}), it is clear that t-butyl radicals add to DEVP more rapidly than methyl radicals at 233 K. The complete set of relative values of k_{add} is given in Table 3.

The *A* factor for addition of t-butyl radicals to DEVP is probably somewhat smaller than that for addition of methyl radicals [17] and hence the difference in rates of addition of Me· and Bu^{t}· results from a smaller activation energy for addition of the latter radical. There can be little doubt that addition of Bu^{t}· is less exothermic than that of Me· and any steric compression in the transition state would also favour addition of the less bulky methyl radical. Thus we are forced to conclude that *polar effects* are of over-riding importance in determining the relative rates of addition of Me· and Bu^{t}· to DEVP.

TABLE 3

Relative rate constants for addition of carbon-centred radicals to diethyl vinylphosphonate at 233 K

R·	Me·	Et·	Bu^{n}·	Bu^{i}·	$MeO\dot{C}H_2$	$Ph\dot{C}H_2$	Pr^{i}·	cyclo-C_5H_9·	Bu^{t}·	$\dot{C}F_3$
k_{add} (rel.)	(1)	1.0	2.0	1.5	2.7	<1	4.8	2.6	23.6	>10

Addition of alkyl radicals to DEVP is significantly faster than their addition to ethylene (although the latter is probably the more reactive towards $\dot{C}F_3$). For example, the rate constants for addition of Me·, Bu^{t}·, and $\dot{C}F_3$ to ethylene in the gas phase extrapolated to 233 K are 20, 4, and 2×10^5 dm^3 mol^{-1} s^{-1} respectively.* Polar effects are probably mainly responsible for the relatively high rate of addition of alkyl radicals to DEVP, although stabilisation of (1) by the α-P(O)(OEt)$_2$ group may also be significant.[22]

There have been a number of theoretical studies of the addition of Me· to ethylene.[23] The transition state occurs early along the reaction co-ordinate. Although certainly small in magnitude, the charge on the methyl group in the transition state has been calculated to be either positive [23b] or negative.[23a,c] Fukui and his coworkers [23b] concluded that whilst both the SOMO–LUMO (C=C π^*) and SOMO–HOMO (C=C π) interactions were important in the addition reaction, the former predominates and the methyl group carries a small positive charge in the transition state. The electron-withdrawing (EtO)$_2$P(O) substituent in DEVP will *lower* the energies of both LUMO and HOMO and thus we expect the SOMO–LUMO interaction to be relatively more important for addition of Me· to DEVP than to ethylene.[24] The SOMO energy of Bu^{t}· is higher than that of Me· (the vertical ionisation potentials [25] are 6.92 and 9.84 eV, respectively) and thus the stabilising interaction with the LUMO of DEVP will be greater for Bu^{t}· than for Me· and the rate of addition will be greater for the former radical.[24]

The primary alkyl radicals (Et·, Bu^{n}·, and Bu^{i}·) add to DEVP somewhat more rapidly than methyl but less rapidly than the secondary radicals (Pr^{i}· and cyclo-C_5H_9·) which are in turn less reactive than Bu^{t}·. The relative reactivities of the primary and secondary alkyl radicals, which are admittedly less well established than those of Me· and Bu^{t}·, can be similarly rationalised by assuming the over-riding importance of polar effects on the energy of the transition state for addition. In simple valence-bond terms, contributions from (2) and (3), leading to stabilisation of the transition state, will increase as the ionisation potential of R· decreases [25] along the series Me· > R$^{prim.}$· > R$^{sec.}$· > Bu^{t}·.

$$R^{+}\ \bar{C}H_2\text{-}\dot{C}HP(O)(OEt)_2 \longleftrightarrow R^{+}\ \dot{C}H_2\text{-}\bar{C}HP(O)(OEt)_2$$

(2) (3)

The methoxymethyl radical is more nucleophilic (has a higher SOMO energy) [24] than methyl and thus we may understand the higher rate of addition of the former to DEVP, despite the probable greater exothermicity of methyl radical addition. Addition of (1) to DEVP could not be detected under our conditions, whereas simple primary and secondary alkyl radicals add readily. This is probably due mainly to the lower nucleophilicity of (1), although stabilisation of this addendum by the α-(EtO)$_2$-P(O) substituent may also be important [22] and thus addition may also be less favourable thermodynamically. Relatively unfavourable thermochemistry is the probable reason for the slow addition of the stabilised, but nucleophilic,[26] benzyl radical.

The trifluoromethyl radical (vertical ionisation potential 10.85 eV) [27] is expected to be much less nucleophilic than Me·, although the former appears to add much more rapidly to DEVP. Additions of CF_3· and Me· are probably similarly exothermic and it is likely that charge transfer *from* DEVP *to* the addendum, represented by a contribution from structure (4), is important in the transition state for addition of CF_3·.

$$\bar{C}F_3\ H_2\overset{+}{C}\text{-}\dot{C}HP(O)(OEt)_2 \quad (4)$$

The SOMO–HOMO interaction appears to predominate for addition of $\dot{C}F_3$ to both DEVP and ethylene.[17] The latter reaction is very rapid (see above), probably more rapid than addition of $\dot{C}F_3$ to DEVP which has a lower HOMO energy (is less electron rich) than ethylene.

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* The following Arrhenius equations were used to obtain these values (k_{add} in dm^3 mol^{-1} s^{-1}, $\theta = 2.303RT$ kJ mol^{-1}):

$Me\cdot + CH_2{=}CH_2 \longrightarrow MeCH_2CH_2\cdot$
$\log k_{add} = 8.52 - 32.2/\theta$ (ref. 18)
$Bu^{t}\cdot + CH_2{=}CH_2 \longrightarrow Bu^{t}CH_2CH_2\cdot$
$\log k_{add} = 7.24 - 29.7/\theta$ (ref. 19 in conjunction with ref. 20)
$\dot{C}F_3 + CH_2{=}CH_2 \longrightarrow CF_3CH_2CH_2\cdot$
$\log k_{add} = 8.0 - 11.9/\theta$ (ref. 21)

EXPERIMENTAL

Materials.—Diethyl vinylphosphonate (Lancaster Synthesis) was purified by distillation (b.p. 50 °C at 1 Torr); the material as received sometimes gave rise to e.s.r. spectra of unidentified long-lived radicals.

Di-t-butyl peroxide, triethyl phosphite, triethyl- and tri-n-butyl-phosphines, and triethylsilane were commercial products which were purified before use. Di-t-butyl ketone, hexamethylditin, trifluoromethyl iodide, cyclopropane, cyclopentane, isobutane, toluene, and dimethyl ether were high quality commercial products and were used as received. Tri-isopropylphosphine and tri-n-butyl- and tri-isobutyl-boranes were prepared from the appropriate alkylmagnesium bromide and PCl_3 or BF_3–Et_2O. Trimethylborane was liberated from its pyridine complex by addition of 2M aqueous H_2SO_4 under 200 Torr of nitrogen and transferred to a vacuum line. After fractionation to remove traces of water, the Me_3B was used without further purification. Azomethane [28] and azoisobutane [29] were prepared by published methods.

Diethyl 1-bromopropylphosphonate [30] was prepared by the reaction of Ph_3PBr_2 with diethyl 1-hydroxypropylphosphonate [31] in acetonitrile. Bromine (3.6 cm^3, 0.070 mol) was added dropwise to a stirred solution of triphenylphosphine (19.0 g, 0.073 mol) in dry acetonitrile (100 cm^3) under nitrogen. During addition the temperature of the solution was allowed to rise to 50 °C. A solution of diethyl 1-hydroxypropylphosphonate (13.7 g, 0.070 mol) and pyridine (5.6 g, 0.070 mol) in acetonitrile (25 cm^3) was then added dropwise to the stirred solution of Ph_3PBr_2, keeping the internal temperature between -15 and -20 °C. After addition the mixture was stirred and allowed to warm to room temperature during 2 h. The acetonitrile was removed at 35 °C (water pump) and the residue was distilled as a liquid, b.p. 55—65 °C at 0.02 Torr. Redistillation gave the product, b.p. 58.5—59.5 °C at 0.02 Torr (Found: C, 32.7; H, 6.0; Br, 30.7. $C_7H_{16}BrO_3P$ requires C, 32.5; H, 6.2; Br, 30.8%). The ^{1}H n.m.r. spectrum (200 MHz in C_6D_6) was complicated by the presence of two types of diastereotopic methylene protons, δ 1.00 (3 H, t, $^3J_{H-H}$ 7.2 Hz, CH_3CH_2CHBr), 1.13 (6 H, t, $^3J_{H-H}$ 7.1 Hz, CH_3-CH_2O), 1.98 (2 H, m, CH_2CHBr), 3.74 (1 H, d of t, $^2J_{H-P} = {}^3J_{H-H^1} = 9.8$, $^3J_{H-H^2}$ 3.8 Hz, CHBr), and 4.06 (4 H, m, CH_2O).

E.s.r. Spectroscopy.—Spectra were recorded using a Varian E-4 spectrometer equipped with the standard variable-temperature accessory. The magnetic field was calibrated using a ^{1}H n.m.r. gaussmeter and g values were determined using this in conjunction with an EIP Autohet microwave counter (model 331). Differences in magnetic field at the sample and n.m.r. probe could be corrected for using the g factor of the pyrene radical anion (Na^+ counter ion) in tetrahydrofuran as standard (g 2.002 71).[32]

Photolysis was carried out with light from a Philips CS 500 W/2 (D.C.) high-pressure mercury arc lamp filtered through 8 cm of 0.04M aqueous $NiSO_4$ solution and focused onto the entrance grid of the cavity using fused silica lenses. The incident light intensity could be varied using calibrated metal gauze screens.

Radical concentrations were determined by comparison of the intensities of suitable lines in the spectra with the signal obtained from a solution of *NN*-diphenyl-*N'*-picrylhydrazyl (DPPH; Aldrich) (*ca.* 4×10^{-5}M) in carbon tetrachloride, using the signal from a synthetic ruby fixed to the inside of the microwave cavity as a standard. The concentration of the DPPH solution was checked by measuring its absorbance at 520 nm (ε 12 934 dm^3 mol^{-1} cm^{-1}).[33] The intensities of lines in the e.s.r. spectra were determined by electronic integration of the first-derivative curves followed by mechanical integration of the derived absorption traces. In relating the intensity of the DPPH resonance (at 295 K) to that of the adduct radicals (at 233 K) it was assumed that signal intensity was proportional to the reciprocal of the absolute temperature.

Temperature Measurement.—A calibrated digital thermometer (Comark type 5335) fitted with Cu/Cu–Ni thermocouples (10 inputs are available) was employed. The sample temperature without photolysis was determined by positioning a thermocouple in the Dewar insert alongside the sample tube. In separate experiments, this insert thermocouple was calibrated against a second thermocouple contained in an open sample tube filled with cyclopentane. The heating effect of photolysis was determined by monitoring the spectrum of the isobutyl radical, formed in a sample containing Bu^i_3B and Bu^tOOBu^t in cyclopropane, and the value of $a(H_\beta)$ was measured as a function of incident light intensity. Extrapolation to zero light intensity gave the value of $a(H_\beta)$ corresponding to the known dark temperature. Over the range 130—300 K, $a(H_\beta)/G$ ($\equiv A$) was given by equation (xii).*

$$T/K = 2.703\,94A^2 - 198.419A + 3\,763.56 \quad \text{(xii)}$$

Equation (xii) was used to determine the heating effect of photolysis under given conditions and at *ca.* 230 K the effect was +6 K for maximum light intensity. Actual sample temperatures during photolysis are considered accurate to ±2 K.

Sample Preparation.—Static samples (total volume *ca.* 0.7 cm^3) were used when the concentration of DEVP was $\geqslant 0.3$M. The DEVP was transferred by calibrated microsyringe to a nitrogen-filled sample tube (4 mm o.d. Suprasil), followed by the primary (Bu^tOOBu^t, Bu^t_2CO, or RN=NR; *ca.* 15% v/v) and secondary [$(EtO)_3P$, R_3P, R_3B, or RH; *ca.* 15% v/v] sources of radical addenda and the mixture was degassed on a vacuum line. The solvent (cyclopropane or cyclopentane) was added and the tubes were sealed under vacuum. The total sample volume at 233 K was determined by removing the tube from the spectrometer and affixing a label to mark the liquid level. The tube was emptied and refilled with mercury to the mark; the sample volume was calculated from the weight of mercury. To compensate for changes in sample composition during photolysis, spectra were monitored as a function of time and radical concentrations were extrapolated to zero photolysis time.

When [DEVP] was *ca.* 0.16M the sample was flowed slowly (*ca.* 1 cm^3 min^{-1}) through the microwave cavity to avoid the effects of reagent consumption.[36] The cyclopentane solutions were made up by weight under nitrogen and driven through Teflon tubes to the sample cell (4 mm o.d. Suprasil) using a motor-operated syringe pump (Sage Instruments).

The rate constants for self-reaction of (1; R = Me or Bu^t) were determined by the rotating sector kinetic e.s.r. technique as described previously.[14,15]

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* This equation differs somewhat from that given in ref. 34 and obtained from the data given by Fessenden.[35] The present equation is considered more correct.

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