Kinetic–EPR Studies of the Addition of Aliphatic Radicals to Acrylic Acid and Related Alkenes: the Interplay of Steric and Electronic Factors

Bruce C. Gilbert,[a] **John R. Lindsay Smith,**[a] **Elizabeth C. Milne,**[a] **Adrian C. Whitwood**[a] **and Philip Taylor**[b]
[a] *Department of Chemistry, University of York, Heslington, York, UK YO1 5DD*
[b] *Research Department, ICI Paints plc, Wexham Road, Slough, UK SL2 5DS*

A continuous-flow system approach with EPR detection and steady-state analysis has been employed to determine the rate constants for addition of a range of aliphatic radicals to acrylic acid and related alkenes in aqueous solution at room temperature. For acrylic and methacrylic acids the rate constants (in the range 2×10^5–*ca.* 10^8 dm^3 mol^{-1} s^{-1}) are governed largely by polar effects in the transition state, though the deviation from planarity of the attacking species may be important for $\cdot$CHMeOH and related radicals. As expected, steric effects play a prominent role in causing retardation in the reactions of crotonic and 3,3-dimethylacrylic acids, and in addition of $\cdot CMe_2OH$.

EPR spectroscopy finds wide applicability in studies of polymer chemistry—ranging, for example, from continuous-flow studies of the metal-peroxide initiated polymerization of acrylic acid,[1] through investigations of the conformation of the growing polymer chain in methyl methacrylate polymerization,[2] to structural studies of polymer-derived radicals aimed at identifying the mechanisms by which degradation occurs (*e.g.*, by light, thermal, mechanical and chemical processes).[3] Although the technique offers what is often a unique opportunity to confirm the structure and conformation of a given short-lived radical intermediate, examples of its applicability to obtain detailed kinetic and structural information relevant to polymerization are relatively rare.

As part of an investigation into the metal-catalysed decomposition of peroxides and the subsequent initiation of alkene polymerization in aqueous solution, we wished to develop the use of EPR spectroscopy for the direct determination of the rate constants for addition of substituted alkyl radicals ($\cdot CR_2X$; X = OH, CO_2H; R = H, alkyl) to water-soluble alkenes related to acrylic acid ($CH_2{=}CHCO_2H$). A simple method of analysis is reported here, together with an assessment of the relative importance of steric and electronic effects in the addition process[4] and in models for radical propagation reactions in acrylate polymerizations. Our results are discussed in the light of recent results for a range of other substituted radicals and alkenes.

Results

The approach chosen was to study radical addition to alkenes *via* the generation of first-formed radicals by hydrogen-atom abstraction from parent molecules with the hydroxyl radical, itself generated from the Ti^{III}–H_2O_2 couple [see reactions (1) and, for example, (2)]. This initiation reaction was carried out in the presence of the appropriate alkene, with conditions chosen so that the required addition reaction occurs [see, *e.g.*, reaction (3)]: to achieve this it was necessary to adjust the concentration of the organic substrate so that all hydroxyl radicals are scavenged (*via* the abstraction reaction, rather than addition to alkene), with the alkene concentration low enough to prevent propagation.

$$Ti^{III} + H_2O_2 \longrightarrow Ti^{IV} + HO^\bullet + HO^- \quad (1)$$

$$HO^\bullet + CH_3OH \longrightarrow \cdot CH_2OH + H_2O \quad (2)$$

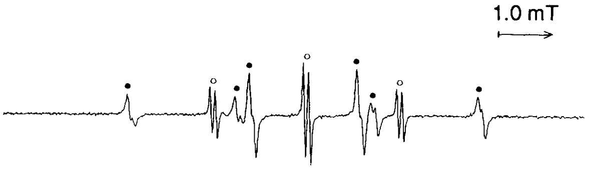

Fig. 1 EPR spectra of $\cdot CH_2OH$ (○) and $HOCH_2CH_2\dot{C}HCO_2H$ (•) produced from the addition of $\cdot CH_2OH$ to acrylic acid at pH 2 ($[Ti^{III}]$ 1.67×10^{-3}, $[H_2O_2]_0$ 1.67×10^{-2}, $[MeOH]_0$ 1.7, [acrylic acid]$_0$ 3×10^{-3} mol dm^{-3}).

$$\cdot CH_2OH + CH_2{=}CHCO_2H \longrightarrow HOCH_2CH_2\dot{C}HCO_2H \quad (3)$$

(*a*) *Addition of* $\cdot CH_2OH$ *and Related Radicals to Acrylic Acid.*—The hydroxyl radical was generated in a three-way continuous-flow system[5] in which the three aqueous streams, containing Ti^{III} (to give a concentration of 1.67×10^{-3} mol dm^{-3}, after mixing),* H_2O_2 (1.67×10^{-2} mol dm^{-3}) and the substrate, were mixed *ca.* 30 ms before passage through the cavity of the EPR spectrometer. Experiments were first carried out at pH *ca.* 2. The concentration of methanol (1.7 mol dm^{-3}) employed as the source of $\cdot CH_2OH$ is believed to be sufficient to scavenge all $\cdot$OH formed [*via* reaction (2)]; thus [RH] was chosen so that $k_{abs}[RH] \gg k_{add}[alkene]$, using typical values[6] of rate constants for reactions of $HO^\bullet$ (k_{abs} *ca.* 10^9 and k_{add} 10^9 dm^3 mol^{-1} s^{-1}) and a value for [alkene] of typically 10^{-3} mol dm^{-3} (see later).

As the concentration of acrylic acid added was raised, the steady-state concentration of $\cdot CH_2OH$ detected by EPR (initially *ca.* 3×10^{-6} mol dm^{-3}) decreased, evidently as it reacted with acrylic acid to form an acrylate adduct (see Figs. 1 and 2 and Table 1). The parameters [a(α-H) 2.02, a(β-H) 2.28 mT (two protons), a(OH) 0.10 mT; g 2.0033] confirm that this is the carboxy-conjugated radical $HOCH_2CH_2\dot{C}HCO_2H$ formed by addition of $\cdot CH_2OH$ to the unsubstituted terminus of the double bond [*cf.* $HOCH_2\dot{C}HCO_2H$ which has a(β-H) 2.73 mT]. Close inspection of the spectrum from this radical shows an asymmetry in the two peaks associated with the doublet from the carboxy proton (the doublet, and the asymmetry, disappeared at high pH: see later). This phenomenon, which we have also found[7] in the spectra of the HO$\cdot$ adducts of

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* Here and elsewhere, concentrations are those after mixing.

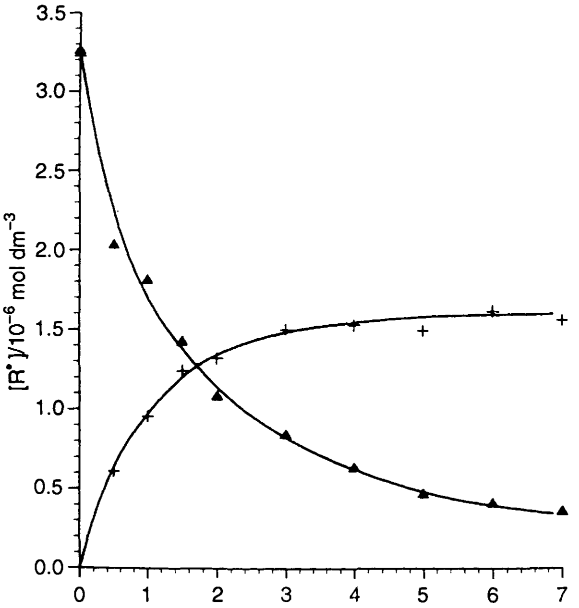


Fig. 2 Variation in the steady-state concentrations of $\cdot CH_2OH$ (▲) and $HOCH_2CH_2\dot{C}HCO_2H$ (+) with initial concentration of acrylic acid in flow-system experiments at pH *ca.* 2: $[Ti^{III}]_0$ 1.67 × 10^{-3}, $[H_2O_2]_0$ 1.67 × 10^{-2}, $[MeOH]_0$ 1.7 mol dm^{-3}

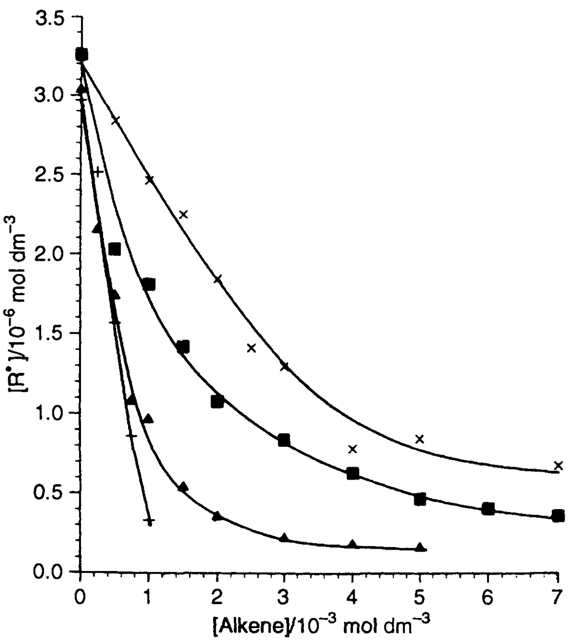
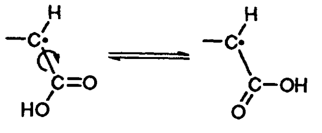


Fig. 3 Variation of the steady-state concentrations of $\cdot CH_3$ (×), $\cdot CH_2OH$ (■), $\cdot CHMeOH$ (▲) and $\cdot CMe_2OH$ (+) with the initial concentration of acrylic acid in a flow system at pH *ca.* 2: $[Ti^{III}]_0$ 1.67 × 10^{-3} mol dm^{-3}, $[H_2O_2]_0$ 1.67 × 10^{-2} mol dm^{-3}, with dimethyl sulfoxide, methanol, ethanol, or propan-2-ol in considerable excess (see the text)

acrylic acid and methacrylic acid ($HOCH_2\dot{C}RCO_2H$) is attributed to the existence of two rotamers of each radical (and two closely similar spectra) which differ in the conformation of the $\dot{C}$–CO_2H group, with hindered rotation about the $\dot{C}$–C(O) bond [(1) ⇌ (2)], for which a barrier of *ca.* 40 kJ mol^{-1} might be expected.[8]



1 **2**

The regioselectivity of attack of $\cdot CH_2OH$ on acrylic acid is in accord with expectations based on both steric and electronic considerations. Thus $\cdot CH_2OH$ is a relatively nucleophilic radical and might be expected to favour attack as indicated [reaction (4)]; the reaction also yields the more stable (delocalized) radical-adduct.

$$HO\text{–}\dot{C}H_2 \longleftrightarrow H\overset{+\bullet}{O}\text{–}\overset{-}{C}H_2 + \overset{+}{\dot{C}}H_2\text{–}CH\text{=}C(OH)\text{–}O^- \longrightarrow HOCH_2CH_2\dot{C}HCO_2H \quad (4)$$

This approach was repeated in experiments with acrylic acid at pH 2 and the first-formed radicals $\cdot CH_3$ (from the reaction of $HO\cdot$ with Me_2SO) and $\cdot CHMeOH$ and $\cdot CMe_2OH$ (formed as the major radicals from ethanol and propan-2-ol, respectively). In each case, the EPR spectrum of the alkyl or hydroxyalkyl radical was steadily reduced in intensity (see Fig. 3) and ultimately replaced by a signal which characterizes addition at the unsubstituted end of the double bond (see Table 1). The initial rate of decrease in the concentration of the first-formed radical as the concentration of alkene is increased (which would be expected to be a measure of the rate of addition) follows the order

$$\cdot CH_3 < \cdot CH_2OH < \cdot CHMeOH \sim \cdot CMe_2OH$$

which parallels the expected order of nucleophilicity (and, for example, their ease of oxidation).[9] Similar spectra and trends were observed in experiments at pH 9 except that the order for $\cdot CH_3$ and $\cdot CH_2OH$ with increase in $[CH_2\text{=}CHCO_2H]$ was reversed (Table 2). A more detailed kinetic analysis is presented later.

This approach was also employed to study the reactions of $\cdot CHMeOEt$ (from diethyl ether) and other mono- and dioxygen conjugated radicals from dimethoxymethane and 1,3-dioxolane. The former gives $\cdot CH_2OCH_2OMe$ (major) and $\cdot CH(OMe)_2$ (minor); the latter gives predominantly the mono-conjugated radical **3**, together with a small proportion of **4**: for each substrate depletion of both radicals occurred, the relative reduction in intensity of the dioxygen-conjugated radical being more pronounced.

3

4

Experiments were also carried out at pH 2 with acrylic acid in the presence of propanoic acid to scavenge $\cdot OH$ (and whose reaction gives rise to $\cdot CHMeCO_2H$ and $\cdot CH_2CH_2CO_2H$, in the ratio of *ca.* 1.2:1). The observed decline in both α- and β-radicals as acrylic acid was added clearly indicates that radical addition is occurring, and the new spectrum detected (see Table 1) suggests that reactions (5) and (6) are taking place (the separate adducts could not be identified and no clear evidence for the expected non-equivalence in the α-radical adduct[10] could be obtained). The decrease in concentration of the β-radical was more pronounced than that of the α-radical, as expected for the less-substituted and more nucleophilic radical. Similar results were also obtained for radicals derived from $\cdot OH$ and 2-methylpropanoic acid; depletion of the β-radical ($\cdot CH_2CHMeCO_2H$) was significantly greater than the α-isomer ($\cdot CMe_2CO_2H$).

$$\cdot CHMeCO_2H + CH_2\text{=}CHCO_2H \longrightarrow MeCH(CO_2H)CH_2\dot{C}HCO_2H \quad (5)$$

Table 1 EPR parameters for radical-adducts formed by the addition of radicals to acrylic acid and related alkenes at pH *ca.* 2

			Hyperfine splitting/mT[a]			
	Radical, $R^\bullet$	Adduct	a(α-H)	a(β-H)	$a(CO_2H)$	g value[b]
Acrylic acid	$\cdot CH_3$	$CH_3CH_2\dot{C}HCO_2H$	2.02	2.35	0.10	2.0031
	$\cdot CH_2OH$	$HOCH_2CH_2\dot{C}HCO_2H$	2.02	2.28	0.10	2.0033
	$\cdot CHMeOH$	$MeCH(OH)CH_2\dot{C}HCO_2H$	2.02	2.27(1) 2.35(1)	0.07	2.0032
	$\cdot CMe_2OH$	$HOCMe_2CH_2\dot{C}HCO_2H$	2.00	2.14	—	2.0032
	3	$\overline{CH_2OCH_2OC}HCH_2\dot{C}HCO_2H$	2.03	2.28	—	2.0032
	$\cdot CHMeOEt$	$MeCH(OEt)CH_2\dot{C}HCO_2H$	2.02	2.23	—	2.0032
	$\cdot CH_2OCH_2OMe$	$MeOCH_2OCH_2CH_2\dot{C}HCO_2H$	2.03	2.33	0.10	2.0033
	$\cdot CHMeCO_2H$	$MeCH(CO_2H)CH_2\dot{C}HCO_2H$	2.02[d]	2.25[d]	—	2.0031
	$\cdot CH_2CH_2CO_2H$	$HO_2CCH_2CH_2CH_2\dot{C}HCO_2H$	2.02[d]	2.25[d]	—	2.0031
	$\cdot CMe_2CO_2H$	$Me_2C(CO_2H)CH_2\dot{C}HCO_2H$	2.03	2.27	—	2.0031
	$\cdot CH_2CHMeCO_2H$	$HO_2CCHMeCH_2CH_2\dot{C}HCO_2H$	2.03	2.27	—	2.0031
Methacrylic acid	$\cdot CH_3$	$CH_3CH_2\dot{C}MeCO_2H$		2.19(3) 1.50(2)	0.10	2.0031
	$\cdot CH_2OH$	$HOCH_2CH_2\dot{C}MeCO_2H$		2.21(3) 1.47(2)	0.10	2.0032
	$\cdot CHMeOH$	$MeCH(OH)CH_2\dot{C}MeCO_2H$		2.22(3) 1.17(1) 1.55(1)	0.10	2.0033
	$\cdot CMe_2OH$	$HOCMe_2CH_2\dot{C}MeCO_2H$		2.23(3) 1.13(2)	—	2.0032
	$\cdot CHMeOEt$	$MeCH(OEt)CH_2\dot{C}MeCO_2H$		2.22(3) 1.26(1) 1.54(1)	—	2.0032
	$\cdot CH_2OCH_2OMe$	$MeOCH_2OCH_2CH_2\dot{C}MeCO_2H$		2.25(3) 1.50(2)	—	2.0032
Dimethylacrylic acid	$\cdot CH_2OH$	$HOCH_2CH(CO_2H)\dot{C}Me_2$	—	2.34(6) 0.84(1)		2.0025
		$HOCH_2CMe_2\dot{C}HCO_2H$	2.08	—	—	2.0032
	$\cdot CHMeOH$	$MeCH(OH)CMe_2\dot{C}HCO_2H$	2.04	—	—	2.0032
	$\cdot CMe_2OH$	$HOCMe_2CH(CO_2H)\dot{C}Me_2$	—	2.36(6) 0.86(1)		2.0026
Crotonic acid	$\cdot CH_3$	$Me_2CH\dot{C}HCO_2H$	2.00	1.32	0.08	2.0031
	$\cdot CH_2OH$	$HOCH_2CHMe\dot{C}HCO_2H$	2.01	1.17	0.08	2.0031
	$\cdot CHMeOH$	$MeCH(OH)CHMe\dot{C}HCO_2H$	2.02	0.99	—	2.0031
	$\cdot CMe_2OH$	$HOCMe_2CHMe\dot{C}HCO_2H$	2.00	0.79	—	2.0031
	$\cdot CHMeOEt$	$MeCH(OEt)CHMe\dot{C}HCO_2H$	2.05	0.99	—	2.0032
	$\cdot CH_2OCH_2OMe$	$MeOCH_2OCH_2CHMe\dot{C}HCO_2H$	2.05	1.09	—	2.0032

[a] ±0.005. [b] ±0.0001. [c] Only the major adduct unambiguously identified, see the text. [d] Separate isomers not distinguished.

Table 2 EPR parameters for radical-adducts formed by the addition of radicals to acrylic acid at pH *ca.* 9

		Hyperfine splitting/mT[a]			
R·	Adduct	a(α-H)	a(β-H)	a(γ-H)	g value[b]
$\cdot CH_3$	$CH_3CH_2\dot{C}HCO_2^-$	2.00	2.36	—	2.0031
$\cdot CH_2OH$	$HOCH_2CH_2\dot{C}HCO_2^-$	2.04	2.34	—	2.0032
$\cdot CHMeOH$	$MeCH(OH)CH_2\dot{C}HCO_2^-$	2.02	2.22(1) 2.33(1)	0.01	2.0032
$\cdot CMe_2OH$	$HOCMe_2CH_2\dot{C}HCO_2^-$	2.02	2.16	—	2.0032

[a] ±0.005. [b] ±0.0001.

$$\cdot CH_2CH_2CO_2H + CH_2{=}CHCO_2H \longrightarrow HO_2CCH_2CH_2CH_2\dot{C}HCO_2H \quad (6)$$

(*b*) *Radical Addition to Methyl-substituted Acrylic Acid Derivatives.*—The approach described above was employed in a series of experiments to investigate the reactivity of $\cdot CH_3$, $\cdot CR^1R^2OH$, and acid-derived radicals with the acrylic monomers methacrylic acid, crotonic acid, and 3,3-dimethylacrylic acid, typically at pH 2.

For methacrylic acid the EPR parameters (see Table 1) confirm that in each case the radical addition is directed solely to the β-position (as expected from steric considerations). For a variety of radicals (see Table 1) the order of reactivity (as judged by the rate of depletion) mirrored that for acrylic acid. The results for $\cdot CH_2OH$ are shown in Fig. 4, together, for comparison, with results for other alkenes. The slower rate of reaction of $\cdot CH_2OH$ with methacrylic acid compared with acrylic acid is notable.

With crotonic acid, addition was also only observed to occur at the β-position, despite the steric effects at the α-and β-position

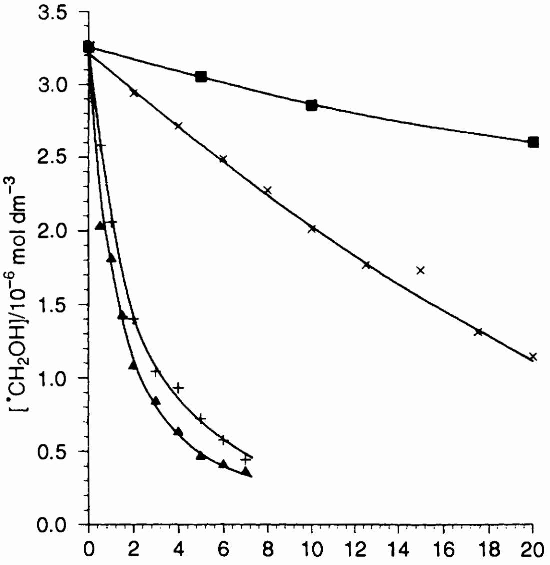


Fig. 4 Variation in the steady-state concentration of $\cdot CH_2OH$ with [alkene] in the addition of $\cdot CH_2OH$ to acrylic acid (▲), methacrylic acid (+), crotonic acid (×) and 3,3-dimethylacrylic acid (■) in flow-system experiments at pH *ca.* 2: $[Ti^{III}]_0$ 1.67×10^{-3}, $[H_2O_2]_0$ 1.67×10^{-2}, [MeOH] 1.7 mol dm^{-3}

being to a certain extent counterbalanced: electronic effects, as outlined above, evidently still control the site of reaction, though, as indicated in Fig. 4 for $\cdot CH_2OH$, reaction is clearly retarded. Other oxygen-conjugated radicals and the methyl radical behaved similarly.

In contrast, the addition of $\cdot CH_2OH$ to 3,3-dimethylacrylic acid led to the formation of both α- and β-adducts, and reaction with $\cdot CMe_2OH$ led solely to the α-adduct; though $\cdot CHMeOH$ gave clearly detectable signals from the β-adduct, resonances from the corresponding α-adduct are believed to lie under those of $\cdot CHMeOH$ itself, ruling out more detailed conclusions. These results suggest that while electronic effects have not been completely overriden, steric effects are now predominant in governing the sites of attack, especially for $\cdot CMe_2OH$ and $Me_2C{=}CHCO_2H$. The relative lack of depletion of a range of initial radicals in experiments with this substrate clearly indicates that the rates of addition are significantly retarded compared with other alkenes.

(*c*) *Kinetic Analysis of Radical Addition.*—The following analysis provides a basis for determining the rate constants for addition of first-formed radicals to alkenes, under certain well-defined conditions. It is based on the steady-state analyses of related flow system studies.[11]

We assume that the reactions which govern the concentration of adduct radicals ($A^\cdot$) detected in the EPR cavity are (1) and (7)–(11) (Scheme 1). We assume that the added organic substrate (RH) scavenges all hydroxyl radicals, that radical oxidation or reduction by H_2O_2 and Ti^{III}, respectively, is slow under these circumstances (and can be neglected) and that no polymerization of $A^\cdot$ occurs under the conditions employed.

$$Ti^{III} + H_2O_2 \longrightarrow Ti^{IV} + HO^\cdot + OH^- \qquad (1)$$

$$HO^\cdot + RH \longrightarrow H_2O + R^\cdot \qquad (7)$$

$$R^\cdot + \text{alkene} \longrightarrow A^\cdot \qquad (8)$$

$$\left.\begin{array}{ll} R^\cdot + R^\cdot & (9) \\ A^\cdot + A^\cdot & (10) \\ R^\cdot + A^\cdot & (11) \end{array}\right\} \xrightarrow{2k_t} \text{non-radical products}$$

Scheme 1

Steady-state analysis for $[R^\cdot]$ and $[A^\cdot]$ leads, under conditions (low alkene concentration) where $[A^\cdot]$ is low (so that terms in $[A^\cdot]^2$ can be ignored) to eqn. (12) as an expression of the predicted variation in $[R^\cdot]$ as a function of [alkene] for a time *t* after mixing.

$$[R^\cdot] = \frac{-k_8[\text{alkene}]}{2k_t} \pm \frac{(4k_8^2[\text{alkene}]^2 + 8k_tk_1[H_2O_2]_t[Ti^{III}]_t)^{\frac{1}{2}}}{4k_t} \qquad (12)$$

When the concentration of alkene is low, the term involving its square can be neglected, to give eqn. (13).

$$[R^\cdot] = \frac{-k_8[\text{alkene}]}{2k_t} \pm \left(\frac{k_1[H_2O_2]_t[Ti^{III}]_t}{2k_t}\right)^{\frac{1}{2}} \qquad (13)$$

It can readily be shown that the square-root term given above is equal to the radical concentration $[R^\cdot]_0$ in the absence of alkene [by applying steady-state equations to reactions (1), (7) and (9)]. It follows that $[R^\cdot]$ can be expressed by eqn. (14) and that a plot of $[R^\cdot]$ *vs.* [alkene] should be linear, with gradient $k_8/2k_t$.

$$[R^\cdot] = [R^\cdot]_0 - \frac{k_8[\text{alkene}]}{2k_t} \qquad (14)$$

As can be seen from Figs. 3 and 4, the expected behaviour appears to be followed, especially at low concentrations of alkene (and most obviously for those alkenes where addition is relatively slow). We believe that, under these circumstances, it is therefore appropriate to derive values of k_8 (Table 3) from the initial gradient of these plots, given the termination rate constants of the added radicals ($2k_t/10^9$ dm^3 mol^{-1} s^{-1}) taken from pulse radiolysis data summarized in ref. 12: ($\cdot CH_3$, 2.5; $\cdot CH_2OH$, 2.4; $\cdot CHMeOH$, 2.3; $\cdot CMe_2OH$, 1.4; $\cdot CH_2CH_2CO_2H$, 2.1; $\cdot CHMeCO_2H$, 2.2; $\cdot CH_2CHMeCO_2H$, 1.4). Results for reaction of all radicals with crotonic and dimethylacrylic and for reaction of $\cdot CH_3$ and $\cdot CH_2OH$ with acrylic and methacrylic acids were obtained in this way.

An alternative analysis is possible for experiments in which significant concentrations of two initial radicals are formed from the substrates (*e.g.*, the acids). Consider a radical $R^{i\cdot}$, one of a number of radicals formed in the reaction of $\cdot OH$ with the substrate, which adds to the alkene with a rate constant k_{R^i}. Steady-state analysis for this radical yields eqn. (15) where $[R^{i\cdot}]$ is the steady-state concentration of $R^{i\cdot}$ in the presence of a given concentration of alkene, $[R^{i\cdot}]_0$ is the steady-state concentration in the absence of alkene and $[R^\cdot]_T$ in the total radical concentration in the cavity (independent of the concentration of alkene if we make the assumption that the rate constant for all radical–radical reactions is the same, $2k_t$).

$$\frac{1}{[R^{i\cdot}]} - \frac{1}{[R^{i\cdot}]_0} = \frac{k_{R^i}[\text{alkene}]}{2k_t[R^\cdot]_T[R^{i\cdot}]_0} \qquad (15)$$

This analysis was applied to the results of experiments in which two initial radicals were generated in each case from the substrates propanoic acid, 2-methylpropanoic acid, dimethoxymethane and 1,3-dioxolane, in reactions with alkenes. As

Table 3 Rate constants ($k_{add}/10^6$ dm^3 mol^{-1} s^{-1}) for the addition of carbon-centred radicals to acrylic acid and related alkenes at pH *ca.* 2[a]

Alkene	$Me_2\dot{C}OH$	$Me\dot{C}HOEt$	$Me\dot{C}HOH$	$\cdot CH_2OCH_2OMe$	$(MeO)_2\dot{C}H$	**3**	**4**
$CH_2{=}CHCO_2H$	*ca.* 10[b]	*ca.* 15[b]	*ca.* 15[b]	*ca.* 10[b]	15.0	*ca.* 10[b]	*ca.* 100[b]
$CH_2{=}CMeCO_2H$	*ca.* 10[b]	*ca.* 15[b]	*ca.* 10[b]	*ca.* 10[b]	22.0	—	—
$MeCH{=}CHCO_2H$	2.0	2.0	1.8	0.6	0.8	—	—
$Me_2CH{=}CHCO_2H$	0.01	—	0.02	—	—	—	—

Alkene	$\cdot CH_2OH$	$\cdot CH_3$	$\cdot CH_2MeCHCO_2H$	$\cdot CH_2CH_2CO_2H$	$Me_2\dot{C}CO_2H$	$Me\dot{C}HCO_2H$
$CH_2{=}CHCO_2H$	9.5	3.0	2.5	3.0	0.5	0.3
$CH_2{=}CMeCO_2H$	6.0	5.8	2.5	3.5	0.7	0.5
$MeCH{=}CHCO_2H$	0.4	0.1	—	—	—	—
$Me_2CH{=}CHCO_2H$	0.09	—	—	—	—	—

[a] Unless otherwise stated, rates were determined from plots using eqns. (14) or (15) and confirmed by computer simulation; $k \pm 20\%$. [b] Estimated from simulations; $k \pm 20\%$.

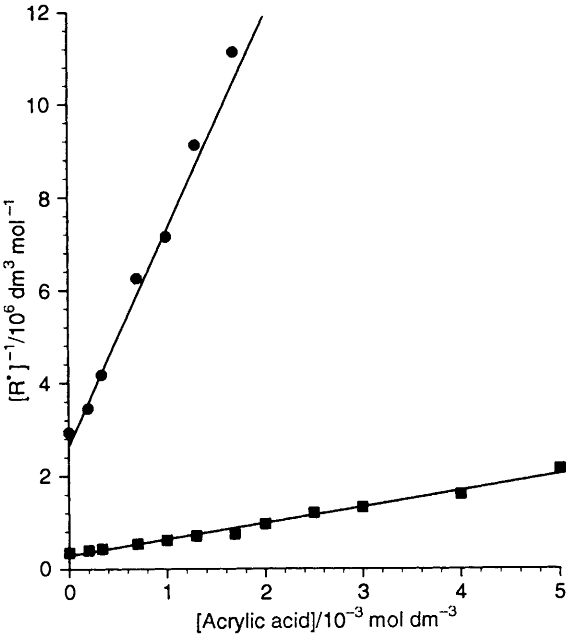


Fig. 5 Variation in $[R^{\bullet}]^{-1}$ [R = $(MeO)_2CH^{\bullet}$ (●) and $\cdot CH_2OCH_2OMe$ (■)] with concentration of acrylic acid in experiments with the first-formed radicals from dimethoxymethane reacting with the alkene. For conditions, see the text.

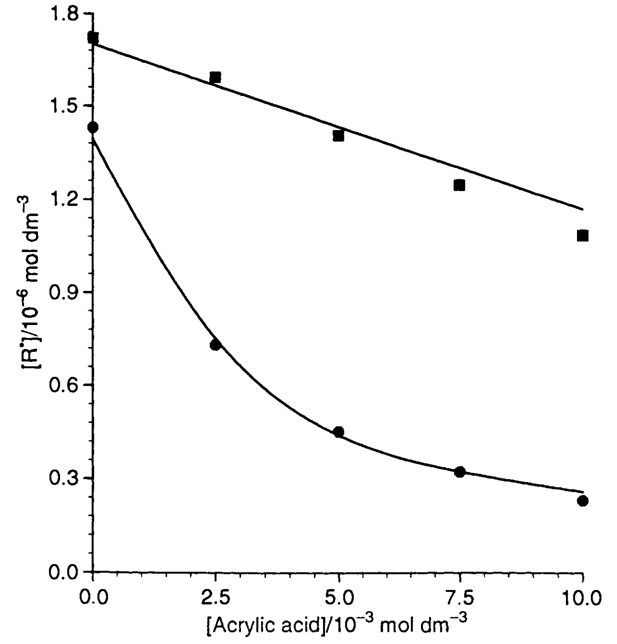


Fig. 6 Variation in $[R^{\bullet}]$ [R = $Me\dot{C}HCO_2H$ (■) and $\cdot CH_2CH_2CO_2H$ (●)] with concentration of acrylic acid in experiments with radicals from propanoic acid reacting with the alkene (for conditions, see the text). Solid lines indicate simulated behaviour with $k_8 = 3 \times 10^5$ dm^3 mol^{-1} s^{-1} and 3×10^6 dm^3 mol^{-1} s^{-1} for $Me\dot{C}HCO_2H$ and $\cdot CH_2CH_2CO_2H$, respectively.

expected from eqn. (15), plots of $[R^{i\bullet}]^{-1}$ *vs.* [alkene] give good straight lines (see Fig. 5): values of $k_{R'}$ were obtained from the slope ($k_{R'}/2k_t[R^{\bullet}]_T$) and are shown in Table 3. It can readily be shown that for a substrate which essentially gives a single radical and at low alkene concentrations this equation reduces to eqn. (14), since $[R^{\bullet}]_T$ approximates to $[R^{\bullet}]_0$. Plotting the data for $\cdot CH_2OH$ according to eqn. (15) rather than (14) gives the expected straight line, with value of k_8 in excellent agreement with those obtained by the earlier method.

To check the validity of our analysis and the derived rate-constants (k_8) we have used a kinetic simulation approach (see, *e.g.*, ref. 13) to match plots of $[R^{\bullet}]$ *vs.* [alkene] (see Fig. 6) as well as plots according to eqn. (15). The observed behaviour is matched, as expected, and the corresponding value of k_8 confirmed for those radicals from single substrates which add to the alkene with $k < ca.\ 5 \times 10^6$ dm^3 mol^{-1} s^{-1}. For more rapid addition ($> 10^7$ dm^3 mol^{-1} s^{-1}) of major or sole radicals from alcohols, this analysis shows that reliable estimates of k_8 cannot be obtained, because the very rapid addition causes significant depletion of the alkene (at low concentrations of the latter). For this reason, values of the rates of addition for $\cdot CHMeOH$ and $\cdot CMe_2OH$ to acrylic acid and methacrylic acid (both $> 10^7$ dm^3 mol^{-1} s^{-1}) must remain estimates (see Table 3).

Discussion

The rate constants for addition of a variety of small aliphatic radicals to acrylic acid and some simple derivatives in aqueous solution at room temperature are found to be in the range 10^4–10^8 dm^3 mol^{-1} s^{-1} (see Table 3).

The results for acrylic acid and methacrylic acid are broadly as expected if polar effects are dominant in governing the stability of a (relatively early) transition state: since the reactions are exothermic the reaction enthalpies and/or radical stabilization evidently play a very minor role (see refs. 4, 14 and refs. therein). Thus the increase in rate constant (*e.g.*, for acrylic acid) as the radical becomes more nucleophilic (electron rich), *i.e.*, $\cdot CH_3 < \cdot CH_2OH < \cdot CHMeOH$ can be understood both in terms of the polar canonical structures which can be drawn for both reagents [see reaction (4)] and, in frontier orbital terminology, in terms of the increasingly effective overlap which will occur in the transition state as the radical SOMO is raised

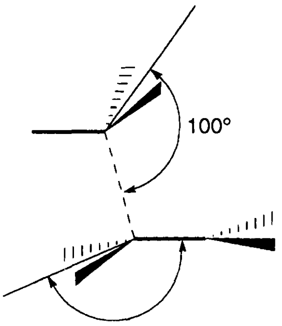


Fig. 7 Calculated transition-state structure for the addition of ·CH_3 to ethene (see ref. 17).

closer to the LUMO of the alkene (which itself is lowered by the electron-withdrawing carboxy group: see ref. 15).

The slightly lower rate constants for reaction with methacrylic acid can be understood in terms of a slight increase in the LUMO of the alkene, which clearly plays a more important role than the extra stabilization afforded in the product radical by the α-methyl substituent. The lower rate constants for addition of ·$CHRCO_2H$ become immediately understandable in terms of their reduced SOMO. The slightly lower values for addition of ·CMe_2OH compared with ·CHMeOH may reflect a small steric retardation of addition, though it should be noted that the value of $2k_t$ reported and used for ·CMe_2OH (from ref. 12) is significantly smaller than those employed for the smaller alkyl radicals, which may be a source of error.

It is particularly instructive to compare the rate constants for addition to acrylic acid of ·Me (E_i = 9.73 eV), ·CH_2OH and ·CHMeOH with those of the reactions of CH_2=$CHCO_2Me$ with the nucleophilic *tert*-butyl radical [k (in methylbenzene) 10^6 dm^3 mol^{-1} s^{-1}, E_i = 6.7 eV], the benzyl radical [k (in methylbenzene) 4.5 × 10^2 dm^3 mol^{-1} s^{-1}, E_i = 7.2 eV] and the (ambiphilic) radical ·CH_2CO_2Me [k (in acetonitrile) 4.5 × 10^5 dm^3 mol^{-1} s^{-1}, E_i > 10 eV].[14,16] Whilst the order ·CR^1R^2-OH > Bu^t > ·Me > ·CH_2CO_2Me can be readily understood in terms of SOMO/LUMO overlap (as judged by the corresponding E_i values), the very low value for $PhCH_2$· (despite a high overall exothermicity) may, as pointed out by Fischer, reflect the relatively high resistance to bending of the planar delocalized radical. Given the proposed transition-state structure (see Fig. 7) for the addition of an alkyl radical to an alkene,[14,17] then the enhanced values for k_{add} for ·CH_2OH, ·CHMeOH and related radicals may also reflect, at least in part, the *pyramidal* nature of these oxygen-conjugated radicals (a feature established through the use of EPR spectroscopy);[18] it is particularly notable that the 1,3-dioxolanyl radical, which as shown by EPR spectroscopy has the greatest degree of bending at the trigonal carbon,[19] has the highest rate constant for addition to acrylic acid (*ca.* 1 × 10^8 dm^3 mol^{-1} s^{-1}).

The reduction of the rate constants for addition of ·CH_3 and oxygen-conjugated radicals to crotonic acid, compared with acrylic and methylacrylic acid, is clearly understandable in terms of the extra steric hindrance introduced at the non-carboxy-substituted end of the double bond (though the order for different attacking radicals still reflects the operation of electronic and, possible, geometrical effects, as noted earlier). The retardation is even more pronounced for dimethylacrylic acid, though ·CH_2OH adds faster than its alkylated counterparts, as would be expected on steric grounds.

The limited results obtained at high pH, involving the addition of small aliphatic radicals to the acrylate anion (see Table 4), establish that the rate of reaction is reduced on ionization; this is believed to reflect the higher LUMO energy expected for the carboxylate anion compared with the corresponding acid (*i.e.*, CO_2^- is, overall, much less electron-withdrawing than CO_2H). Our observation that ·CH_3 adds *faster* than ·CH_2OH may also indicate that with the more ambiphilic alkyl radical, favourable interaction in the transition state now occurs with the (higher) HOMO in the carboxylate ion. This would not be unexpected in terms of the finding that both SOMO–LUMO and SOMO–HOMO interactions govern the addition of the ambiphilic radical ·$CH_2CO_2Bu^t$ to a range of alkenes.[20]

Table 4 Rate constants for the addition of carbon-centred radicals to acrylic acid at pH *ca.* 9[a]

Radical, R·	k/10^6 dm^3 mol^{-1} s^{-1}
·CH_3	0.7
·CH_2OH	0.5
·CHMeOH	1.6
·CMe_2OH	3.2

[a] ±20%.

Experimental

EPR spectra were recorded on a Bruker ESP 300 spectrometer equipped with an X-band microwave bridge and 100 kHz modulation. Hyperfine splittings and g-values were determined directly from the spectrometer's field scan, this having been calibrated with the signal from Fremy's salt [a_N = 1.3091 mT,[21] g = 2.0055].[22] Radical concentrations were determined by comparison with spectra obtained from standard solutions of vanadyl sulfate by use of double integration. A mixing chamber was employed which allowed simultaneous mixing of three reagent streams *ca.* 30 ms before passage through the cavity of the spectrometer: flow was maintained using a Watson–Marlow 502S peristaltic pump placed on the inlet tubing. pH Measurements were made using a Pye-Unicam PW9410 pH meter with the electrode inserted into the effluent stream. The three solutions typically contained (*i*) titanium(III) chloride (0.005 mol dm^{-3}), (*ii*) hydrogen peroxide (0.05 mol dm^{-3}) and (*iii*) the substrate (0.05–1.0 mol dm^{-3}) and the alkene (0.0005–0.01 mol dm^{-3}); pH was varied by addition of sulfuric acid (18 mol dm^{-3}) or ammonia solution (15 mol dm^{-3}) to the first stream and all solutions were deoxygenated by nitrogen purge both before and during use.

The kinetic simulation program was originally written by Dr. T. M. F. Salmon and modified by Dr. M. J. Brown to run on a VAX computer and by us to run on an IBM-PC 486DX clone.

All chemicals employed were commercial samples and were used as supplied.

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