Electron Spin Resonance Studies. Part 68.[1] Addition *versus* Overall One-electron Abstraction in the Oxidation of Alkenes and Dienes by $SO_4^{-\cdot}$, $Cl_2^{-\cdot}$, and ·OH in Acidic Aqueous Solution

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E. s. r. spectroscopy has been employed to characterize radicals formed by the reaction of alkenes, dienes, and some substituted derivatives with $SO_4^{-\cdot}$ (generated photolytically), $Cl_2^{-\cdot}$ (from Cl^- and $SO_4^{-\cdot}$ or ·OH, and ·OH (from Ti^{III}–H_2O_2 in a flow system). For some substrates (*e.g.* $HOCH_2CH{=}CH_2$, butadiene) the appropriate $SO_4^{-\cdot}$ and chlorine-atom adducts are detected, whereas for others (*e.g.* cyclopentadiene) only hydroxyl adducts are characterized. It is suggested that the reaction mechanism involves formation of the appropriate chlorine-atom and sulphate adducts, with subsequent rapid hydrolysis: this may involve production and rapid hydration of an incipient radical-cation. It is found that $Cl_2^{-\cdot}$ is more effective than $SO_4^{-\cdot}$ in achieving overall one-electron oxidation. The regioselectivities of ·OH attack on alkenes and of the hydration of alkene radical-cations are contrasted and rationalized. Finally, cyclization reactions of pent-4-en-1-ol (with $Cl_2^{-\cdot}$, ·OH–H^+) and hex-4-en-1-ol ($Cl_2^{-\cdot}$, ·OH–H^+, $SO_4^{-\cdot}$) are rationalized in terms of rapid internal nucleophilic attack on a transient alkene radical-cation.

Evidence has recently been obtained for the existence of alkene radical-cations in the solid state and in solution.

For example, γ-irradiation of alkenes in hydrocarbon matrices has led to the detection of e.s.r. signals of the appropriate radical-cations, formed by positive-charge transfer from ionized solvent molecules,[2] and the optical absorption spectra (and decay kinetics) of radical-cations from conjugated dienes have been obtained *via* pulse-radiolysis.[3] Radical-cations have also been proposed[4] as intermediates in the acid-catalysed rearrangement of β-hydroxyalkyl radicals [reaction (1)], in which a correlation was demonstrated between the rate of interconversion and the ionization potential of the appropriate alkene (though theoretical approaches indicate that an alternative 1,2-migration of OH_2^+ might be involved[5]); the mechanism of related rearrangements of α,β-dioxygen-substituted radicals[6] and some β-phosphate-substituted analogues[7] have been similarly interpreted. Some radical-cations which appear to be particularly stabilized and/or long lived [*e.g.* $\cdot CH_2{-}\overset{+}{C}(OMe)_2$] have been directly detected *via* e.s.r.[8]

E.s.r. studies of the reaction of $SO_4^{-\cdot}$ (from peroxydisulphate) with a variety of aromatic compounds provide[9] evidence for one-electron oxidation to give radical-cations and it has been suggested[10] that $Cl_2^{-\cdot}$ (from ·OH or $SO_4^{-\cdot}$ and Cl^-) may behave similarly. Reactions of both of these radical-anions with electron-rich alkenes (*e.g.* vinyl ethers[11] and vinyl sulphides[12]) and of $SO_4^{-\cdot}$ with some alkenes[13] and substituted styrenes[14] have been similarly interpreted.

We set out to employ e.s.r. spectroscopy first to seek further evidence for the formation of alkene and, particularly, diene radical-cations and, second, to study the factors which encourage one-electron oxidation, rather than addition or hydrogen-atom abstraction reactions, of the intermediates $SO_4^{-\cdot}$ and $Cl_2^{-\cdot}$

Results

Several different approaches were employed to generate radicals within the cavity of an e.s.r. spectrometer. The sulphate radical-anion $SO_4^{-\cdot}$ was generated photolytically from $S_2O_8^{2-}$ in the presence of propanone as a photosensitizer, as described previously.[1] The radical-ion $Cl_2^{-\cdot}$ was generated in two ways: for studies in the pH range 0—2 we employed the reaction of ·OH (from rapid mixing of solutions of Ti^{III} and H_2O_2) with Cl^- (at concentrations > 1 mol dm^{-3}), a system which has been shown[10,15] to proceed in acid solution *via* reactions (2)—(4). For the pH range 3—9 (where the production of $Cl_2^{-\cdot}$ from ·OH and Cl^- is inefficient) we employed reactions (5) (*cf.* ref. 16) and (4), with photolytic generation of $SO_4^{-\cdot}$. The acid-catalysed loss of water [*cf.* reaction (1)] from initially produced ·OH adducts (*via* Ti^{III}–H_2O_2) was also employed for comparative purposes.

$$\cdot CH_2CMe_2OH \xrightarrow[-H_2O]{H^+} \overbrace{CH_2-CMe_2}^{+\cdot} \xrightarrow[-H^+]{H_2O} HOCH_2CMe_2\cdot \quad (1)$$

$$HO\cdot + Cl^- \rightleftharpoons HOCl^{\bar{\cdot}} \quad (2)$$

$$HOCl^{\bar{\cdot}} + H^+ \rightleftharpoons H_2O + Cl\cdot \quad (3)$$

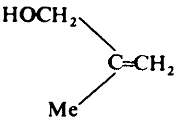
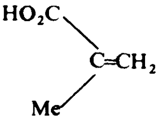
$$Cl\cdot + Cl^- \rightleftharpoons Cl_2^{\bar{\cdot}} \quad (4)$$

$$SO_4^{\bar{\cdot}} + Cl^- \longrightarrow Cl\cdot + SO_4^{2-} \quad (5)$$

(i) *Oxidation of Alkenes.*—Photolysis of a solution in aqueous propanone of sodium peroxydisulphate (0.01 mol dm^{-3}) and ethene (saturated) at room temperature in the pH range 1—9 led to the detection of an e.s.r. signal assigned[17] to $\cdot CH_2CH_2OSO_3^-$ (see Table 1); the spectrum is quite distinct from that of $\cdot CH_2CH_2OH$ generated by attack of ·OH, having a different β-proton splitting. Generation of $Cl_2^{-\cdot}$ both by the reaction of ·OH with Cl^- at low pH and by the reaction between $SO_4^{-\cdot}$ and Cl^- failed to give detectable signals with ethene. Our failure to detect either ·OH or $SO_4^{-\cdot}$ adducts in this case implies that the chloride ion is successfully scavenging the initially formed radicals; the lack of observation of $\cdot CH_2CH_2Cl$ (which can be detected under similar conditions when generated[17] *via* oxidative decarboxylation of $ClCH_2CH_2CO_2^-$ with $SO_4^{-\cdot}$) suggests that, unlike the reaction of ·OH and $SO_4^{-\cdot}$ with this substrate, neither Cl· nor $Cl_2^{-\cdot}$ reacts rapidly.

Reaction of propene with $SO_4^{-\cdot}$ led to the detection of only $\cdot CHMeCH_2OSO_3^-$ (*cf.* ref. 18), whereas the less selective radical ·OH adds at both ends of the double bond to give[19] $\cdot CHMeCH_2OH$ and $\cdot CH_2CH(OH)Me$ in the ratio *ca.* 5:1,

Table 1. E.s.r. parameters of radicals detected in the reaction of $Cl_2^{-\bullet}$, $SO_4^{-\bullet}$, and $^\bullet OH$ with alkenes, dienes, and their derivatives

Substrate	Method of generation[a]	Radical	Hyperfine splittings (mT)[b]			g[c]
			α-H	β-H	Other	
$CH_2{=}CH_2$	A	$^\bullet CH_2CH_2OSO_3^-$	2.21(2)	2.47(2)		2.0025
	C	$^\bullet CH_2CH_2OH$	2.20(2)	2.76(2)		2.0025
Me–CH=CH_2	A	$^\bullet CHMeCH_2OSO_3^-$	2.20(1)	2.52(3) 1.62(2)		2.0025
	B	$^\bullet CHMeCH_2Cl$	2.00(1)	2.32(3) 0.82(2)	2.12(^{35}Cl)	*f*
	C	$^\bullet CHMeCH_2OH$	2.16(1)	2.54(3) 1.98(2)		2.0025
	C	$^\bullet CH_2CH(OH)Me$	2.21(1)	2.44(1)	0.073(3)	2.0024
$HOCH_2$–CH=CH_2	A	$^\bullet CH(CH_2OH)CH_2OSO_3^-$	2.17(1)	2.38(2) 1.79(2)		2.0025
	A	$^\bullet CH_2CH(OSO_3^-)CH_2OH$	2.22(2)	2.06(1)		2.0025
	B	$^\bullet CH(CH_2OH)CH_2Cl$	2.07(1)	2.40(2) 0.92(2)	1.90(^{35}Cl)	*f*
HO_2C–CH=CH_2	A	$^\bullet CH(CO_2H)CH_2OSO_3^-$	2.05(1)	2.475(2)		2.0031
Me–CH=CH–Me	A	$^\bullet CHMeCHMeOSO_3^-$	2.06(1)[d]	1.47(1)[d] 2.47(3)[d]		2.0025
	B,C	$^\bullet CHMeCHMeOH$	2.12(1)	1.70(1) 2.50(3)		2.0025
$Me_2C{=}CH_2$	A	$^\bullet CMe_2CH_2OSO_3^-$		2.31(6) 1.17(1)		2.0025
	B,C	$^\bullet CMe_2CH_2OH$		2.32(6) 1.45(1)		2.0025
$HOCH_2$–CH=CH–Me	A	$^\bullet CHMeCH(OSO_3^-)CH_2OH$	2.15(1)	1.35(1) 2.57(3)		2.0025
	B,C	$^\bullet CH(CH_2OH)CH(OH)Me$	2.17(1)	1.75(1) 2.15(2)	0.075(3)	2.0025
	B,C	$^\bullet CMe(CH_2OH)CH_2OH$	2.13(1)	1.71(1) 2.51(3)		2.0025
	A	$^\bullet CMe(CH_2OH)CH_2OSO_3^-$		2.35(3) 1.79(2) 1.30(2)		2.0025
	B,C	$^\bullet CMe(CH_2OH)CH_2OH$		1.61(4) 2.36(3)		2.0025
HO_2C–CH=CH–Me	A	$^\bullet CHMeCH(OSO_3^-)CO_2H$	2.18(1)	1.42(1) 2.56(3)		2.0025
	A	$^\bullet CH(CO_2H)CH(OSO_3^-)Me$	2.05(1)[d]	1.35(1)[d]	0.14(3)[d]	2.0031
	C	$^\bullet CHMeCH(OH)CO_2H$	2.16(1)	2.55(3) 1.60(1)		2.0025
	C	$^\bullet CH(CO_2H)CH(OH)Me$	2.05(1)	1.56(1)	0.14(3)	2.0031
	A	$^\bullet CMe(CO_2H)CH_2OSO_3^\bullet$		2.31(3) 1.75(2)		2.0031
	C	$^\bullet CMe(CO_2H)CH_2OH$		2.30(3) 1.99(2)		2.0031
	C	$^\bullet CH_2CMe(OH)CO_2H$	2.32(2)			2.0025
Cyclopentene	B,C	(**1**)	1.43(2)	2.26(4) 0.28(1)		2.0029
$Me_2C{=}CH$–CH_2OH	A,B,C	$^\bullet CMe_2CH(OH)CH_2OH$		2.34(6) 1.00(1)		2.0026
$Me_2C{=}CH$–CO_2H	A,B,C	(**3**)		2.36(6) 0.85(1)		2.0026
		(**4**)	2.08(1)		0.12(6)	2.0031
MeCH=$CMeCO_2H$	A	$^\bullet CMe(CO_2H)CH(OSO_3^-)Me$		2.27(3) 0.82(1)	0.16(3)	2.0031
	B,C	$^\bullet CMe(CO_2H)CH(OH)Me$		2.27(3) 1.00(1)	0.12(3)	2.0032
	B,C	$^\bullet CHMeCMe(OH)CO_2H$	2.15(1)	2.52(3)	*e*	2.0027
Cyclopentadiene	A,B,C	(**7**)	1.40(2), 1.45(1), 1.55(1), 1.75(1), 0.28(1)			*f*
$CH_2{=}CHCH{=}CH_2$	A	$^\bullet CH_2CH{=}CHCH_2OSO_3^-$	1.47(1), 1.35(2), 1.10(2), 0.40(1)[g]			*f*
	B	$^\bullet CH_2CH{=}CHCH_2Cl$	1.40(1), 1.18(1), 0.39(1), 0.78(2), 1.06(1)[g]		1.33(^{35}Cl)[g]	*f*
	C	$^\bullet CH_2CH{=}CHCH_2OH$	1.44(1), 1.34(2), 0.40(1), 1.24(2)[g]			

[a] A = $SO_4^{-\bullet}$, B = $Cl_2^{-\bullet}$, C = $^\bullet OH$. [b] ±0.01 except where stated. [c] ±0.0001. [d] ±0.02. [e] Further unresolved small splittings. [f] 2.0027 ± 0.0002. Signals from different stereoisomers could not be distinguished.

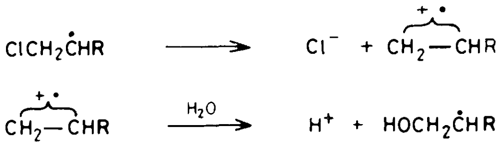
Table 1. (*continued*)

Substrate	Method of generation[a]	Radical	Hyperfine splittings (mT)[b] α-H	β-H	Other	g[c]
$HO_2CCH=CHCH=CHCO_2H$	A,B,C	(**10**)	1.35(1), 1.31(1), 1.23(1), 0.37(1)[g]			*f*
	A	(**12**)	1.31(1), 1.23(1), 1.04(1), 0.37(1)[g]			*f*
	B,C	(**11**)	1.32(1), 1.25(2), 0.37(1), 0.06(1)[g]			*f*
$MeCH=CHCH=CHCO_2H$	C	(**13**)	1.62(3), 1.35(2), 0.62(1), 0.38(1)[g]			*f*
	A,B,C	(**14**)	1.31(1), 1.24(1), 0.87(1), 0.37(1)		0.07(3)[g]	*f*

$$SO_4^{-\bullet} + CH_2{=}CHR \longrightarrow {}^{-}O_3SOCH_2\dot{C}HR \qquad (6)$$

$$Cl_2^{-\bullet} + CH_2{=}CHR \longrightarrow Cl^- + ClCH_2\dot{C}HR \qquad (7)$$

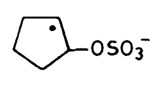
$$ClCH_2\dot{C}HR \longrightarrow Cl^{\bullet} + CH_2{=}CHR \qquad (8)$$



$$ClCH_2\dot{C}HR \longrightarrow Cl^- + \overset{+\,\bullet}{CH_2{-}CHR} \qquad (9)$$

$$\overset{+\,\bullet}{CH_2{-}CHR} \xrightarrow{H_2O} H^+ + HOCH_2\dot{C}HR \qquad (10)$$

(**1**)



(**2**)

$$\bullet CMe_2CH(OH)CO_2H$$

(**3**)

$$\bullet CH(CO_2H)CMe_2OH$$

(**4**)

respectively. With allyl alcohol and $SO_4^{-\bullet}$ signals were detected from $^{\bullet}CH(CH_2OH)CH_2OSO_3^-$ and, in trace quantities, $^{\bullet}CH_2CH(OSO_3^-)CH_2OH$ (see also ref. 9*a*); with $^{\bullet}OH$ the corresponding ratio of [$^{\bullet}CH(CH_2OH)_2$] to [$^{\bullet}CH_2CH(OH)CH_2OH$] is *ca.* 3.3:1 [with some hydrogen-abstraction to give $^{\bullet}CH(OH)CH{=}CH_2$[20]]. Acrylic acid was investigated at pH *ca.* 2 (below its pK_a[21]); it reacted with $SO_4^{-\bullet}$ to give solely[9a] $^{\bullet}CH(CO_2H)CH_2OSO_3^-$ (in contrast to the observation of both adducts in the corresponding reaction of $^{\bullet}OH$): as with ethene, propene, and allyl alcohol, only addition [reaction (6)] rather than electron- or hydrogen-abstraction, was characterized.

Attempts to observe e.s.r. signals from the reaction of $Cl_2^{-\bullet}$ with acrylic acid were thwarted, evidently by the lack of reactivity of this radical or the low concentration of substrate employed (to avoid polymerization in the cell). However, with allyl alcohol (at *ca.* 0.05 mol dm^{-3}) and propene (as a saturated solution) complex but weak signals with many lines are assigned to chlorine-adducts $^{\bullet}CH(CH_2Cl)CH_2OH$ and $^{\bullet}CHMeCH_2Cl$ (see Table 1) formed as in reaction (7) (the complexity results from the overlap of signals from radicals containing each of the two chlorine isotopes, with splittings from the halogen's nuclei, each with $I = 3/2$). Further, the radical's concentrations may be lowered by the occurrence of relatively rapid fragmentation [reaction (8)] as previously demonstrated[17] for related species.

For a variety of alkenes with two substituents (alkyl, carboxy) on the double bond, reaction with $SO_4^{-\bullet}$ led to the detection of adducts in each case (see Table 1). Thus but-2-ene and 2-methylpropene gave $^{\bullet}CHMeCHMeOSO_3^-$ and $^{\bullet}CMe_2CH_2OSO_3^-$, respectively, and crotyl alcohol [which gave predominantly $^{\bullet}CHMeCH(OSO_3^-)CH_2OH$ and weak lines from $^{\bullet}CH(CH_2OH)CHMeOSO_3^-$], methallyl alcohol [$^{\bullet}CMe(CH_2OH)CH_2OSO_3^-$], methacrylic acid [$^{\bullet}CMe(CO_2H)CH_2OSO_3^-$], and crotonic acid [which gave mainly $^{\bullet}CHMeCH(OSO_3^-)CO_2H$ and also $^{\bullet}CH(CO_2H)CHMeOSO_3^-$, *cf.* ref. 9*a*], reacted similarly. Very weak and unanalysable signals were obtained from both cyclohexene and cyclopentene; at least in the latter case the signals were different from those obtained from $^{\bullet}OH$[22] [which are attributed to the allyl radical (**1**)*] and it seems likely that adducts [*e.g.* (**2**)] are again formed (see also ref. 16).

The behaviour of $Cl_2^{-\bullet}$ with the same set of substrates was found to be markedly different. For but-2-ene, 2-methylpropene, crotyl alcohol, and methallyl alcohol spectra were obtained which were dominated by signals (see Table 1) with parameters identical to those of the corresponding $^{\bullet}OH$ adducts (as confirmed in separate experiments in which $^{\bullet}OH$ was generated from Ti^{III} and H_2O_2 in the absence of chloride ion). For crotyl and methallyl alcohol traces of signals from allyl radicals[23] were also obtained. Although, as with $^{\bullet}OH$, only one of the two possible $^{\bullet}OH$ adducts was clearly detected for both $Me_2C{=}CH_2$ and $HOCH_2CMe{=}CH_2$ with each of $Cl_2^{-\bullet}$ and $^{\bullet}OH$, both possible adducts were obtained in the reactions of crotyl alcohol with each of $Cl_2^{-\bullet}$ and $^{\bullet}OH$ (with a *ca.* 1:1 ratio in each case). On the other hand, no signals were obtained from the reaction between $Cl_2^{-\bullet}$ and either crotonic and methacrylic acids, and cyclohexene also failed to react. Cyclopentene gave a weak spectrum from (**1**).

The e.s.r. results for $Cl_2^{-\bullet}$ with but-2-ene, 2-methylpropene, and both crotyl and methallyl alcohol are consistent with the intitial formation of adducts of $^{\bullet}Cl$ (*cf.* behaviour of $Cl_2^{-\bullet}$ with, *e.g.* propene, and the reaction of these substrates with $SO_4^{-\bullet}$) which are then readily hydrolysed (*cf.* evidence from pulse-radiolysis studies[18] that some β-chloroalkyl radicals, including $^{\bullet}CHMeCHMeCl$ and $^{\bullet}CMe_2CH_2Cl$, undergo ready hydrolysis to give H^+, Cl^-, and, in the latter case, $^{\bullet}CMe_2CH_2OH$). Although direct (S_N2-type) hydrolysis of the β-chloro radicals may be envisaged, it is also possible that reaction proceeds *via* the formation [see *e.g.* reaction (9)] of the corresponding radical-cation followed by rapid hydration [reaction (10)]. If the latter is the correct interpretation then the formation of (**1**) from cyclopentene and $Cl_2^{-\bullet}$ may well proceed *via* a radical-cation which preferentially undergoes loss of a β-proton (a

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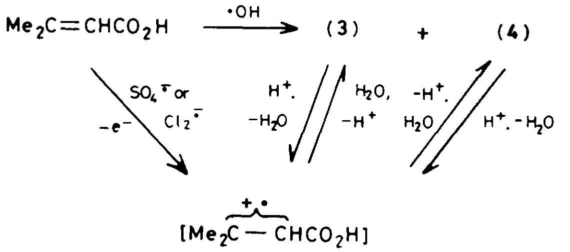
* The reasons for the apparent preponderance of *abstraction* rather than *addition* by $^{\bullet}OH$ (contrast *e.g.* allyl alcohol) remain to be established.

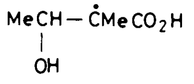


Scheme 1

process which may be facilitated by the geometry of the intermediate and the expected ease of loss of a pseudo-axial β-proton). Analogous reactions of $Cl_2^{-\bullet}$ with crotonic and methacrylic acids are presumably retarded by the electron-withdrawing nature of the carboxy substituent.

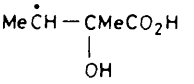
The simplest trisubstituted alkene (2-methylbut-2-ene) was too insoluble for reaction with $SO_4^{-\bullet}$, $Cl_2^{-\bullet}$, or $^{\bullet}OH$ to be investigated, but 3-methylbut-2-en-1-ol ($Me_2C{=}CHCH_2OH$) reacted in each case to give $^{\bullet}CMe_2CH(OH)CH_2OH$. Reaction of 3,3-dimethylacrylic acid with both $SO_4^{-\bullet}$ (see also ref. 9*a*) and $Cl_2^{-\bullet}$ at low pH led to the detection of adducts (**3**) and (**4**) [together with weak signals from the allyl radical $^{\bullet}CH(CO_2H)$-$CMe{=}CH_2$[23]], whose parameters and assignment were confirmed by generating them from reaction with $^{\bullet}OH$ (see Scheme 1). However, whereas the ratio [(**3**)]:[(**4**)] in the experiments with $SO_4^{-\bullet}$ and $Cl_2^{-\bullet}$ (*ca.* 3:1, in the pH range 2.0—0.5) was different from that obtained with $^{\bullet}OH$ at pH *ca.* 2 (ratio *ca.* 9:1) the ratio for hydroxyl addition changed as the pH was lowered until, at pH *ca.* 0, it was similar to that observed for $SO_4^{-\bullet}$ and $Cl_2^{-\bullet}$. The fact that the same two hydroxy adducts are formed from the latter two reagents (and in the same relative proportions) supports the suggestion that this reaction proceeds *via* a unique radical-cation (rather than *via* S_N2-type hydrolysis of first-formed adducts); the *ratio* of the concentration of the adducts observed presumably then reflects the kinetic control of *hydration*. With $^{\bullet}OH$ attack, the high-pH ratio evidently reflects the *kinetic* control of *hydroxyl addition*, whereas as the pH is lowered acid-catalysed loss of OH^- provides a route to the interconversion of isomers *via* a radical-cation and its subsequent hydration (with $^{\bullet}OH$ at *very* low pH, equilibration of the adducts should eventually be established and the thermodynamic ratio of the products observed: it is not clear whether this point has been reached but, if so, the kinetic and thermodynamic control of hydration must lead to similar ratios: in either case, hydration appears to be less selective than $^{\bullet}OH$ attack).

Reaction of 2,3-dimethylacrylic acid with $SO_4^{-\bullet}$ at pH *ca.* 2 led, in contrast, to the detection of the adduct $^{\bullet}CMe(CO_2H)CHMeOSO_3^-$; no sign of the isomeric adduct or of $^{\bullet}OH$ adducts could be discerned. As with 3,3-dimethylacrylic acid, reaction with $Cl_2^{-\bullet}$ in the pH range 2.0—0.5 led to the detection of the hydroxy adducts (**5**) (present as the dominant species) and (**6**) (together with weak unanalysable signals from one or both possible allyl radicals): again, (**5**) and (**6**) are evidently formed *via* overall one-electron abstraction and hydration. With $^{\bullet}OH$ itself, the ratio of (**5**):(**6**) was 1.2:1 at pH 3 whereas by pH 0 the ratio had become 2.4:1. We again interpret this change in terms of acid-catalysed interconversion of $^{\bullet}OH$-adducts and the hydration of the intermediate radical cation (*cf.* Scheme 1); the predominance of (**5**) presumably reflects thermodynamic control of isomerization as well as a kinetic preference in the hydration of the radical-cation. We return later to the possible reasons for the difference between the reaction mechanisms of $SO_4^{-\bullet}$ with the isomeric dimethylacrylic acids.



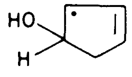
$\underset{\text{OH}}{\text{MeCH}}-\dot{\text{C}}\text{MeCO}_2\text{H}$

(5)



$\text{Me}\dot{\text{C}}\text{H}-\underset{\text{OH}}{\text{CMeCO}_2\text{H}}$

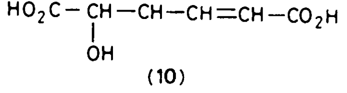
(6)



(7)

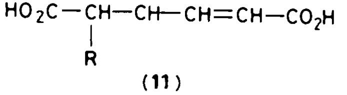
(8)

(9)



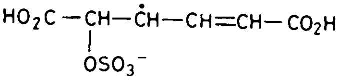
$\text{HO}_2\text{C}-\underset{\text{OH}}{\text{CH}}-\dot{\text{C}}\text{H}-\text{CH}{=}\text{CH}-\text{CO}_2\text{H}$

(10)



$\text{HO}_2\text{C}-\underset{\text{R}}{\text{CH}}-\dot{\text{C}}\text{H}-\text{CH}{=}\text{CH}-\text{CO}_2\text{H}$

(11)



$\text{HO}_2\text{C}-\underset{\text{OSO}_3^-}{\text{CH}}-\dot{\text{C}}\text{H}-\text{CH}{=}\text{CH}-\text{CO}_2\text{H}$

(12)

(ii) *Reaction of Dienes.*—Reaction of buta-1,3-diene with $^{\bullet}OH$, $SO_4^{-\bullet}$, and $Cl_2^{-\bullet}$ gave in each case the e.s.r. signals from the respective adduct $^{\bullet}CH(CH_2X)CH{=}CH_2$ (see Table 1):* no evidence for radical-cation formation was obtained. On the other hand oxidation of cyclopentadiene with both $SO_4^{-\bullet}$ and $Cl_2^{-\bullet}$ led to the detection solely of radical (**7**); the identical e.s.r. spectrum was the only radical detected in the reaction with $^{\bullet}OH$ (in the pH range 0—9). No trace of (**8**) was discerned (though this radical is formed[24] in the reaction of this substrate with $Bu^tO^{\bullet}$). Our results imply that with $SO_4^{-\bullet}$ and $Cl_2^{-\bullet}$ a radical-cation (**9**) (whose formation may of course involve the appropriate adducts) is rapidly hydrated to give (**7**); this intermediate would also be expected to be formed *via* acid-catalysed loss of OH^- from (**7**) (*e.g.* in the reaction with $^{\bullet}OH$ at low pH) and our failure to detect (**8**) may imply either that hydration is much faster than deprotonation or that (**8**) is readily removed by, *e.g.*, reduction by Ti^{III}.

Only very weak and unanalysable signals were obtained from cyclohexa-1,3-diene but muconic acid ($HO_2CCH{=}CHCH{=}CHCO_2H$) gave characteristic signals in all three systems. For example, with $^{\bullet}OH$ at pH 2, and with [substrate] 0.01 mol dm^{-3}, the strong signal obtained is attributed to the carboxy-conjugated allyl radical (**10**) formed by addition at the 2-position. As the pH was lowered to *ca.* 0, this signal was joined by another with parameters which were similar, except for an extra small splitting. This spectrum is assigned to a 'dimeric' species (**11**) (where R has a single proton in the position formally γ to the site of the unpaired electron). When higher concentrations of substrate were employed, polymerization in the flow cell occurred. $Cl_2^{-\bullet}$ reacted to give the same two adducts and $SO_4^{-\bullet}$ gave (**10**) and the adduct (**12**).

Separate experiments in which reaction with $^{\bullet}OH$ was conducted at pH *ca.* 2 but with increasing concentrations of muconic acid failed to reveal any trace of (**11**), which suggests

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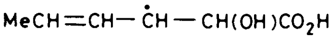
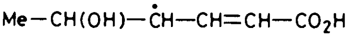
* With these allyl radicals and those from the other dienes studied, signals from different stereoisomers could not be distinguished. This probably reflects the complex, overlapping nature of the spectra.



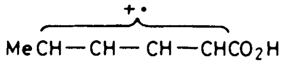
$MeCH{=}CH{-}\dot{C}H{-}CH(OH)CO_2H$

(13)



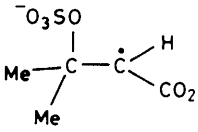
$Me{-}CH(OH){-}\dot{C}H{-}CH{=}CH{-}CO_2H$

(14)



$\overbrace{MeCH{-}CH{-}CH{-}CH}^{+\bullet}CO_2H$

(15)



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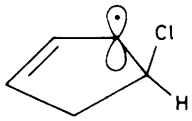

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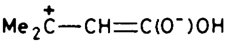
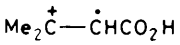


$Me_2\overset{+}{C}{-}CH{=}C(O^-)OH$

(18)



$Me_2\overset{+}{C}{-}\dot{C}HCO_2H$

(19)

that it does not arise *via* addition of (**10**) to the parent molecule (*cf.* the behaviour of acrylic acid and related monomers). The behaviour resembles instead the reaction of certain electron-rich monomers (*e.g.* $CH_2{=}CHOR$, R_2S) to give dimeric species at very low pH[11,12] [*e.g.* $HO(RO)CHCH_2CH_2\dot{C}HOR$ and $R_2SSR_2^{+\bullet}$ respectively] *via* the reaction of first-formed radical-cations with the parent molecules. On this basis it seems likely that radical (**11**) is similarly derived.

Reaction of $^{\bullet}OH$ with sorbic acid ($MeCH{=}CHCH{=}CHCO_2H$) at pH 2 gave a complex spectrum, the main signal from which is attributed to the allyl radical (**13**) formed by attack at the 2-position. No sign of the isomeric adduct (**14**) was detected (see later) and no lines which could be attributed to the appropriate pentadienyl radical ($^{\bullet}CH_2CH{=}CHCH{=}CHCO_2H$) could be discerned. As the pH was lowered the signal from (**13**) disappeared, to be replaced by that assigned to (**14**) on the basis of its hyperfine splittings (see Table 1); this spectrum was also obtained from reaction of sorbic acid with either $SO_4^{-\bullet}$ or $Cl_2^{-\bullet}$ at pH *ca.* 2. These results are consistent with the formation of a radical-cation (**15**) either by overall one-electron oxidation with $SO_4^{-\bullet}$ or $Cl_2^{-\bullet}$ or *via* acid-catalysed loss of OH^- from an initially formed $^{\bullet}OH$ adduct. The regioselectivity of both $^{\bullet}OH$ attack and hydration of the incipient radical-cation are discussed in the next section.

Discussion

Our results suggest that both $SO_4^{-\bullet}$ and $Cl_2^{-\bullet}$ are capable of effecting overall one-electron oxidation of certain alkenes, dienes, hydroxy and carboxylic acid-substituted counterparts, and that the latter oxidant is apparently the more effective of the two. Thus whereas electron abstraction (and subsequent hydration), rather than addition, is the major process detected for reaction of $SO_4^{-\bullet}$ with highly substituted alkenes (*e.g.* 3,3-dimethylacrylic acid, 3-methylbut-2-en-1-ol) and the dienes cyclopentadiene, muconic acid, and sorbic acid, reaction of $Cl_2^{-\bullet}$ with, in addition, but-2-ene, 2-methylpropene, methallyl alcohol, and crotyl alcohol (as well as 2,3-dimethylacrylic acid) evidently proceeds *via* radical-cations whose subsequent hydration can be monitored.

Our results also provide clear evidence for the formation of adducts from $SO_4^{-\bullet}$ and $Cl_2^{-\bullet}$ (*e.g.* with the simpler alkenes and with butadiene). The lack of evidence for hydration of a radical-cation from, *e.g.*, propene and but-2-ene with $SO_4^{-\bullet}$ is in contrast with the claim[13] that alkenic radical-cations are generated by reaction of $SO_4^{-\bullet}$ in certain metal-catalysed oxidations of *e.g.* oct-1-ene and -2-ene with $S_2O_8^{2-}$ (*e.g.* with Ag^+, Cu^+, or Fe^{2+}). Such an apparent discrepancy could be accommodated if in these systems the initial oxidant is actually a metal ion (*e.g.* Ag^{2+}) or if a first formed sulphate adduct undergoes relatively slow fragmentation or direct hydrolysis (see later).

We are unable to distinguish unambiguously between production of radical-cations by $SO_4^{-\bullet}$ and $Cl_2^{-\bullet}$ by direct electron-transfer or *via* initial adduct formation (as observed for simpler alkenes) followed by rapid fragmentation. As anticipated for either mechanism, the reaction would be facilitated by incorporation of electron-donating groups into the molecule: the lowering of the ionization potential would clearly assist direct electron-transfer but would also assist heterolytic fragmentation of an adduct by stabilization of the resulting cation-radical (a process which may also be aided by steric effects on the conformation of the intermediate).

It would be anticipated that 3,3- and 2,3-dimethylacrylic acid would have similar ionization potentials (*cf.* values[25] of 9.13 and 9.23 eV for but-2-ene and 2-methylpropene, respectively): the marked difference in their mode of oxidation by $SO_4^{-\bullet}$ could, however, be explained in terms of the steric acceleration of fragmentation by the *gem* dimethyl groups in the adduct (**16**) of the former (the preferred conformation would be expected to exhibit an eclipsing geometry of the β-C–O bond and the unpaired electron, which would facilitate overlap and hence fragmentation). The difference in reactivity between butadiene (which undergoes addition with both $Cl_2^{-\bullet}$ and $SO_4^{-\bullet}$) and cyclopentadiene (which is oxidised *via* electron transfer) may reflect the relative ease of oxidation of the latter (*cf.* ionization potentials of 9.07 and 8.58 eV respectively), and, at least in part, the adoption by transient adducts from the latter of conformations which favour fragmentation [*i.e.* with the β-CX bond pseudo-axial, *e.g.* (**17**)].

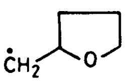
We can contrast the regioselectivity of addition of $SO_4^{-\bullet}$ to simple alkenes with that of $^{\bullet}OH$ (the increased selectivity of the former presumably largely reflects steric factors) and note the difference between the regioselectivity of hydroxyl attack *versus* hydration of a radical-cation intermediate. For example, $^{\bullet}OH$ attack on 3,3-dimethylacrylic acid clearly favours the 2-position, to give (**3**) rather than (**4**) (ratio 9:1); this presumably reflects the electrophilic nature of $^{\bullet}OH$ [and the contribution to the structure of the substrate of canonical structure (**18**)] as well as the importance of the stability of the radical produced. Attack of water on the appropriate radical-cation gives an increased amount of (**4**) which may be explained if an important feature is now the preferential localization of charge at C(3) in the radical-cation [*cf.* contributing structure (**19**)]. A similar explanation may underlie the observation of (**13**) (from sorbic acid) with $^{\bullet}OH$ but (**14**) from hydration of the appropriate radical-cation.

Experiments with Pent-4-en-1-ol and Hex-4-en-1-ol.—Finally, we have employed the approach described above to study the reactivity of unsaturated alcohols in which the hydroxy group is γ to the double bond, in an attempt to obtain evidence about the mechanism of oxidation of such species and, in particular, to explain the relevance of the formation of cyclized products. For example, oxidation of pent-4-en-1-ol with[26] Ag^+–$S_2O_8^{2-}$ in the presence of aromatic bases leads to products whose ratio

Table 2. E.s.r. parameters of radicals detected in the reactions of $Cl_2^{-\cdot}$, $SO_4^{-\cdot}$, and $^{\cdot}OH$ with pent-4-en-1-ol and hex-4-en-1-ol

Substrate	Method of generation[a]	Radical	Hyperfine splittings (mT)[b] α-H	β-H	Other	g[c]
$CH_2{=}CHCH_2CH_2CH_2OH$	C	$^{\cdot}CH(CH_2OH)CH_2CH_2CH_2OH$	2.12(1)	2.27(2) 2.47(2)	0.05(OH)	2.0026
	A	$^{\cdot}CH(CH_2OSO_3^-)CH_2CH_2CH_2OH$	2.12(1)	1.60(2) 2.49(2)		2.0026
	B,C	**(20)**	2.17(2)	1.81(1)	*d*	2.0025
$CH_3CH{=}CHCH_2CH_2CH_2OH$	C	$^{\cdot}CH(CHMeOH)CH_2CH_2CH_2OH$	2.07(1)	2.54(2) 1.72(1)	0.07(3)	2.0026
	C	$^{\cdot}CHMeCH(OH)CH_2CH_2CH_2OH$	2.15(1)	2.54(3) 1.57(1)	*d*	2.0026
	A,B,C	**(22)**	2.14(1)	2.54(3) 1.37(1)	*d*	2.0027

[a] A = $SO_4^{-\cdot}$, B = $Cl_2^{-\cdot}$, C = $^{\cdot}OH$. [b] ±0.01. [c] ±0.0001. [d] Further unresolved splittings.



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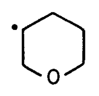

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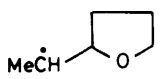

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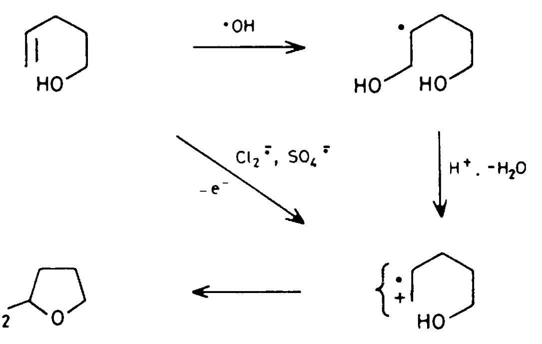


Scheme 2.

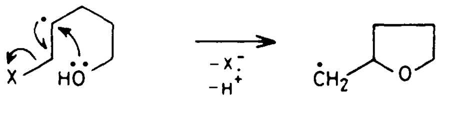
suggests that ring cyclization occurs to give **(20)** and **(21)** in the ratio 9:1. Some controversy surrounds the mechanism of such ring closure;[26] both formation of an alkoxyl radical (followed by intramolecular addition) and electron-transfer from the double bond (followed by intramolecular 'solvation' of the radical-cation) have been suggested. It has been recently claimed[27] that Ag^+–$S_2O_8^{2-}$ reacts with alcohols to give alkoxyl radicals and it is known from e.s.r. experiments[28] that $CH_2{=}CH{-}(CH_2)_3O^{\cdot}$ cyclizes rapidly under similar conditions to give **(20)** [a reaction whose regioselectivity has been satisfactorily rationalized[29] in terms of kinetic control reflecting the ease of attaining a transition-state geometry with effective overlap between the SOMO of the radical and the π-bond (HOMO) of the alkene].

Reaction of $^{\cdot}OH$ with pent-4-en-1-ol in the pH range 2—9 gave rise to signals assignable to the adduct-radical $^{\cdot}CH(CH_2OH)(CH_2)_3OH$ (see Table 2); no signals from the radical arising from addition at the other end of the double bond were observed, though a small amount of this species would be expected (*cf.* reaction of propene described earlier). As the pH was lowered below 2, the signals were replaced by those assigned[28] to radical **(20)**, together with much weaker signals which may well be from **(21)**, though this could not be unambiguously established. This changeover, which is complete by pH *ca.* 0.5, is believed to be due to the acid-catalysed loss of HO^-, to give a radical-cation, followed by internal nucleophilic attack. Support for this proposed mode of reaction derives from the observation that reaction of $Cl_2^{-\cdot}$ (in the pH range 0.5—1) gave the same mixture of radicals, with **(20)** again dominant. In contrast, reaction of $SO_4^{-\cdot}$ led to the detection of a different radical, assigned the adduct structure $^{\cdot}CH(CH_2OSO_3^-)(CH_2)_3OH$ (see Table 2), as would be expected by comparison with propene (see earlier).

With hex-4-en-1-ol, $^{\cdot}OH$ reacted in the pH range 2.5—9 to give $^{\cdot}CH(CHMeOH)(CH_2)_3OH$ and $^{\cdot}CHMeCH(OH)(CH_2)_3OH$ but below pH 2 the spectra were increasingly dominated by the signal from **(22)** (which was the only signal obtained with $Cl_2^{-\cdot}$ and $SO_4^{-\cdot}$).

It is known[10,19,26] that none of the radicals $^{\cdot}\bar{O}H$, $Cl_2^{-\cdot}$, and $SO_4^{-\cdot}$ react significantly with aliphatic alcohols *via* O–H abstraction (α-H abstraction is preferred) so a mechanism other than direct addition of an alkoxyl radical to the double bond must be occurring. Our results suggest instead that a radical-cation is first formed (*via* acid-catalysed loss of OH^-, or *via* effective overall electron transfer by $Cl_2^{-\cdot}$ or, for hex-4-en-1-ol, $Cl_2^{-\cdot}$, and $SO_4^{-\cdot}$) followed either by internal electron-transfer from oxygen to the $\overset{+}{C}$–$\dot{C}$ function *or* by internal nucleophilic attack. Consideration of ionization potentials of alkenes and alcohols indicates that the former are too high for rapid electron-transfer to occur[25] and we favour a mechanistic interpretation involving internal nucleophilic attack and proton loss (see *e.g.* Scheme 2). If this is so then it appears that the regioselectivity of attack by the hydroxyl group on the radical-cation resembles that for attack of the alkoxyl radical on the double bond [to give **(20)**].[29] This would not be unexpected: in both cases it would reflect the achievement of good overlap between the (incipient) unpaired electron on the radical centre and the developing β-C–O bond.

However, it should be noted that the behaviour of pent-4-en-1-ol with $Cl_2^{-\cdot}$ and hex-4-en-1-ol with $SO_4^{-\cdot}$ is different to what would have been predicted on the basis of our results for related simple alkenes (propene, but-2-ene, respectively) where *adducts* were observed; further in the acid-catalysed hydroxyl reaction, ring closure occurs at a higher pH than would have been predicted on the basis of the inductive effect of the substituent and the results for simpler alkenes (see above). This may indicate that there is neighbouring-group participation in the departure of the leaving group [reaction (11; X = OH_2^+, Cl^-, OSO_3^-)] and that the incipient radical-cation may not even have become a discrete species. This would be consistent with pulse radiolysis–scavenger studies[18] of the heterolysis of substituted β-chloro radicals in which it was suggested that



(11)

alkene radical-cations, if formed, must have very short life-times ($\leqslant 10^{-10}$ s^{-1}).

Experimental

E.s.r. spectra were recorded on a Varian E-104 spectrometer equipped with an X-band klystron and 100 kHz modulation. Splitting constants were measured to within ±0.005 mT and g factors to within ±0.0001 by comparison with an aqueous solution of Fremy's salt [a(N) 1.3091 mT,[30] g 2.0055[31]]. Relative radical concentrations were determined by spectrum simulation using a program kindly supplied by Dr. M. F. Chiu.

For the rapid-flow experiments a mixing chamber was employed which allowed simultaneous mixing of three reagent streams *ca.* 50 ms before passage through the cavity of the spectrometer. The flow was maintained using a Watson–Marlow 502S flow-inducer positioned on the inlet tubing. For experiments with $HO^{\bullet}$ the solutions used were as follows: stream (i) contained titanium(III) chloride (0.008 mol dm^{-3}), stream (ii) contained hydrogen peroxide (0.0134 mol dm^{-3}), and the third stream contained the substrate at a concentration up to 0.1M. For experiments above pH 2.5, EDTA (3 g dm^{-3}) was added to stream (i) together with sufficient NaOH to give the desired pH. For experiments at pH <2.5 concentrated sulphuric or perchloric acid was added to stream (i). For experiments with $Cl_2^{-\bullet}$, the above reagent streams were used except that NaCl was added to stream (i) to give $[Cl^{-}] > 1$ mol dm^{-3} after mixing.

The flow photolysis experiments were carried out as described previously.[1] pH Measurements in both systems were made using a Pye–Unicam PW9410 pH meter with the electrode inserted into the effluent stream. All solutions were deoxygenated both before and during use by purging with oxygen-free nitrogen. The chemicals were all commercial samples and used as supplied.

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