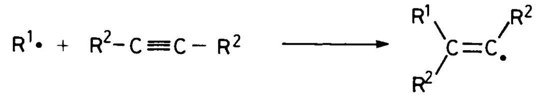
Vinyl-radical Rearrangements. E.S.R. Evidence for the Formation of Enol Radical Cations by the Protonation at Carbon of β-Hydroxyvinyl Radicals and for a 1,4-Hydrogen Shift in some β-Sulphur-substituted Analogues

Bruce C. Gilbert* **and Adrian C. Whitwood**
Department of Chemistry, University of York, Heslington, York YO1 5DD

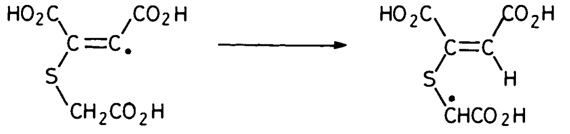
E.s.r. results reveal the occurrence of acid-catalysed conversion of β-hydroxyvinyl radicals (from the reaction of $^{\bullet}OH$ and alkynes) into carbonyl-conjugated radicals in aqueous solution [*e.g.* $RC(OH){=}CR^{\bullet}$ into $RC(O)\dot{C}HR$, R = alkyl, hydroxyalkyl]; it is suggested that the reaction involves the rapid protonation of the vinyl radical at carbon ($k \geqslant 5 \times 10^{6}$ dm^3 mol^{-1} s^{-1}) followed by deprotonation of the intermediate enol radical cation. The ease of hydrogen-atom abstraction by the vinyl radical itself from parent alkyne ($k \geqslant 1.6 \times 10^{7}$ dm^3 mol^{-1} s^{-1} for but-2-yne-1,4-diol) is also noted.

Further examples of 1,4-hydrogen shifts are reported for β-sulphur-substituted vinyl radicals in which a capto-dative stabilized radical can thereby result.

It has been shown that the use of e.s.r. spectroscopy in conjunction with a rapid-flow system provides an excellent method for diagnosing the range of reactions undergone by vinyl radicals derived by addition of first-formed organic radicals to alkynes [reaction (1)].[1–4] Examples of the novel reactions revealed in this way include some 1,4-, 1,5-, and 1,6-hydrogen shifts[1–3] (which may be followed in appropriate examples by fragmentation or cyclization), as well as rapid addition to alkynes and intermolecular hydrogen abstraction[4] [see *e.g.* reactions (2) and (3)]. This range of reactivity appears, at least in part, to reflect the exothermic nature of reactions in which a new C_{sp^2}–H bond is formed.



(1)



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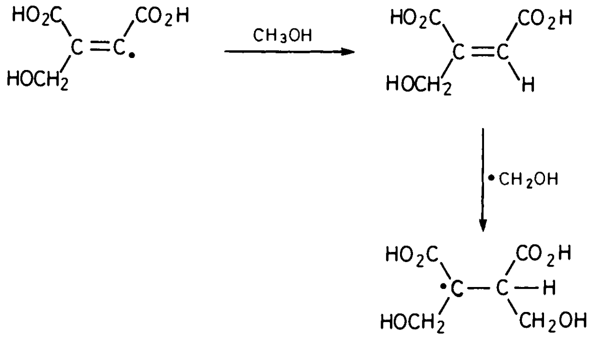

(3)

It has previously been noted that a novel rearrangement, which appears to involve a 1,3-hydrogen shift, occurs during the reaction between $HO^{\bullet}$ and but-2-yne-1,4-diol:[5] thus the detection of (**3**) along with (**1**) (the radical formed by direct hydrogen-atom abstraction) suggests the prior formation of the adduct (**2**), with subsequent transformation [reaction (4)]. We here report an investigation of a number of hydroxyalkyl-substituted alkynes (including but-2-yne-1,4-diol) designed to reveal the nature of this process, as well as to study the competition between addition to the alkyne and C–H abstraction. Since most of our previous studies have involved α,β-dicarboxy-substituted vinyl radicals[1–5] we were also particularly interested to establish which, if any, of the unusual reactions noted above were peculiar to those radicals possessing the carboxyl substituents.

Results and Discussion

E.s.r. experiments typically involved the generation of $^{\bullet}OH$ (from the Ti^{III}–H_2O_2 redox couple) for reaction with the substrate, this being included in the third stream of a three-way continuous flow system in which the three streams are mixed *ca.* 30 ms before entry into the cavity of the spectrometer.[1] Changes in the e.s.r. spectra of the radicals detected under steady-state conditions were studied as a function of the nature and concentrations of substrates over a range of pH.

Reaction of But-2-yne-1,4-diol with $^{\bullet}OH$.—Inclusion of this substrate (at a concentration† of *ca.* 0.007 mol dm^{-3}) in experiments with Ti^{III} and H_2O_2 at pH 1.5, led to the detection of the spectra ascribed to radicls (**1**) and (**3**) (see Figure 1 and Table 1). A variety of subsequent experiments was carried out in order to distinguish between different possible mechanisms to account for the formation of (**3**). These include, in addition to the possibility of a direct 1,3-shift, reaction sequences which involve the appropriate enol (**4**) (formed either *via* hydrogen-atom abstraction or by one-electron reduction of the vinyl radical) and its subsequent reaction with $^{\bullet}OH$ (see Schemes 1(*a*) and 1(*b*): ref. 6 describes analogues of the dehydration reaction

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† Concentrations quoted in the text are those after mixing, except where indicated otherwise.

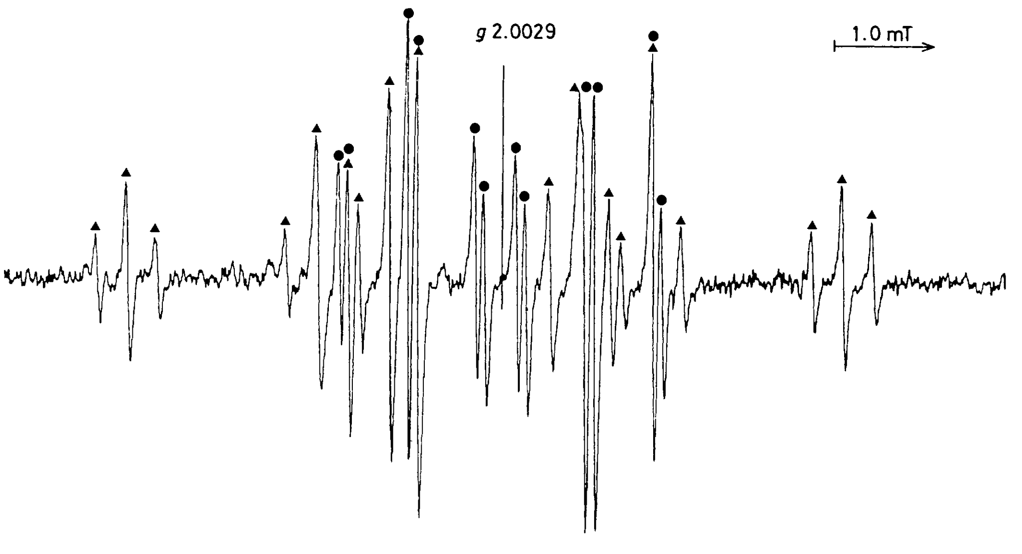
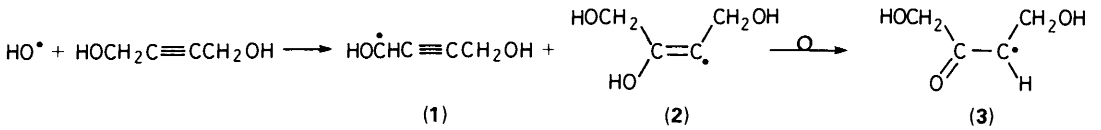
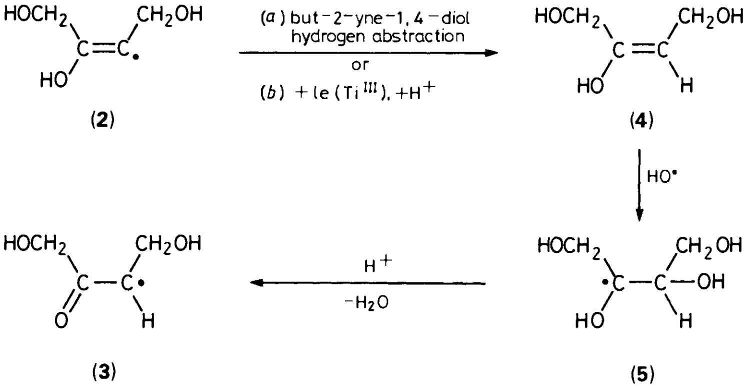


Figure 1. E.s.r. spectra of $HO\dot{C}HC{\equiv}CCH_2OH$ (●) and $HOCH_2CO\dot{C}HCH_2OH$ (▲) obtained from $^{\bullet}OH$ and but-2-yne-1,4-diol at pH 1.45 ([H_2O_2] 0.017 [Ti^{III}] 0.0017 [alkyne] 0.007 mol dm^{-3}).

 (4)

$$HO^{\bullet} + HOCH_2C{\equiv}CCH_2OH \longrightarrow HO\dot{C}HC{\equiv}CCH_2OH + (HOCH_2)(HO)C{=}\dot{C}CH_2OH \xrightarrow{\quad} (HOCH_2)(O{=})C{-}\dot{C}(H)CH_2OH \qquad (4)$$



Scheme 1.

of the α,β-dihydroxyalkyl radical), and a mechanism involving protonation of the intermediate vinyl radical at carbon (Scheme 2).

Initial experiments indicated that the rearrangement involves an acid-catalysed process. Thus, at pH 2, in experiments with [alkyne] 0.007 mol dm^{-3}, only radical (**1**) was detected; the signal due to radical (**3**) grew in intensity when the pH was lowered, as shown in Figure 2. When this experiment was carried out with D_2O as solvent at low pH (*ca.* 0.6) the e.s.r. spectrum observed (Figure 3) confirmed that deuterium had been completely incorporated at the α-position of radical (**3**) [$^{\bullet}C^2H(CH_2OH)COCH_2OH$ has $a(\alpha\text{-}^2H)$ 0.29 mT, $a(\beta\text{-H})$ 2.61 mT and $a(\gamma\text{-H})$ 0.30 mT, exactly as expected from the parameters for (**3**)]. This observation eliminates intermolecular hydrogen-atom abstraction [Scheme 1(*a*)] as the source of radical (**3**).

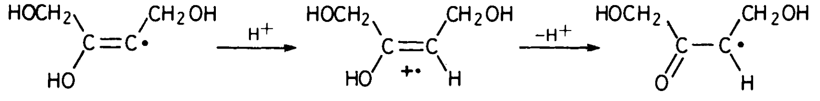
Several observations appear to rule out Scheme 1(*b*) [and the formation of the enol (**4**)] as the source of (**3**). Firstly the ratio of [(**1**)]:[(**3**)] (*ca.* 1:1.75) did not decrease significantly when the concentration of Ti^{III} was increased from 1.5×10^{-3} to 5×10^{-3} mol dm^{-3} in experiments with [H_2O_2] 1.7×10^{-2} mol dm^{-3} and [alkyne] 7×10^{-3} mol dm^{-3} at pH 1.3 (contrast the dramatic effect of increase in Ti^{III} on the concentration of enol-derived radicals formed *via* reduction of α-carbonyl-substituted radicals[7]); in addition the observation of (**3**) at *low* pH contrasts with the finding[7] that Ti^{III} is a less effective reductant for organic radicals as the pH is lowered. Secondly, no evidence was obtained for the radical (**5**), even under conditions (pH > 4) where this radical does not undergo acid-catalysed dehydration. [In addition it should be noted that when the radical (**5**) is generated as one of the species formed by reaction of $^{\bullet}OH$ with erythritol, addition of acid (to give pH 2.5) leads[6] mainly to the formation of the radical $^{\bullet}CH_2COCH(OH)CH_2OH$ by loss of hydroxide from the methylene carbon of (**5**): no trace of this species was detected in experiments with but-2-yne-1,4-diol].

Although Scheme 1(*a*) is ruled out as a source of detectable concentrations of (**3**), we investigated the possibility that intermolecular hydrogen-atom abstraction by the first-formed vinyl radical can occur *via* reaction with the parent alkyne-diol. Experiments in which [$HOCH_2C{\equiv}CCH_2OH$] was varied at a given pH [in the range where rearrangement to (**3**) occurs] demonstrate that the ratio of [(**1**)]:[(**3**)] does indeed increase with increase in substrate concentration as would be anticipated on this basis (Figure 4). Extrapolation of these results to zero

Table 1. E.s.r. parameters of radicals formed by reaction of $^{\bullet}OH$ with a variety of alkynols.[a]

		Hyperfine splittings[b]			
Substrate	Radical	a(α-H)	a(β-H)	a(other)	g[c]
$HOCH_2C\equiv CCH_2OH$	$HO\dot{C}HC\equiv CCH_2OH$ (**1**)	1.76	0.68(2,β′-H)	0.09(OH)	2.002 90
	$HOCH_2C(O)\dot{C}HCH_2OH$ (**3**)	1.89	2.61(2 H)	0.30(2 H)	2.003 90
$HOCH_2C\equiv CH$	$HO\dot{C}HC\equiv CH$	1.785 0.98(α′)		0.09(OH)	2.002 90
	$HOCH_2C(O)\dot{C}H_2$	1.97		0.225(2 H)	2.003 90
	$HOCH_2\dot{C}HCHO$[d]	1.76	2.76(2 H) 0.13(CHO)		2.004 50
	$HOCH_2\dot{C}HCHO$[e]	1.85	2.54(2 H) 0.15(CHO)		2.004 30
$MeCH(OH)C\equiv CCH(OH)Me$	$Me\dot{C}(OH)C\equiv CCH(OH)Me$		1.67(3 H) 0.675(β′-H)		2.003 00
	$MeCH(OH)C(O)\dot{C}HCH(OH)Me$	1.88	1.40	0.13	2.004 05
$HOCH_2C\equiv CMe$[f]	$HO\dot{C}HC\equiv CMe$	1.79	1.12(3,β′-H)	0.06(OH)	2.003 10
	$HOCH_2\dot{C}HC(O)Me$	1.89	2.585(2 H)	0.17(3 H)	2.004 00
	$HOCH_2C(O)\dot{C}HMe$	1.89	2.245(3 H)	0.13(2 H)	2.003 90
$HOCH_2CH_2C\equiv CH$	$HO\dot{C}HCH_2C\equiv CH$	1.47	1.955		2.003 10
	$HOCH_2\dot{C}HC\equiv CH$	1.86 1.18(α′)	1.96		2.002 60
	$HOCH_2CH_2\dot{C}HCHO$[d]	1.74	2.04(2 H) 0.165(CHO)		2.004 50
	$HOCH_2CH_2\dot{C}HCHO$[e]	1.80	1.975(2 H) 0.17(CHO)		2.004 30
	$HOCH_2CH_2C(O)\dot{C}H_2$	1.96		0.105(2 H)	2.004 10
$HOCH_2CH_2C\equiv CMe$	$HOCH_2CH_2C(O)\dot{C}HMe$	1.85	2.22(3 H)	0.185(2 H)	2.004 00
	$HOCH_2CH_2\dot{C}HC(O)Me$	1.88	2.055(2 H)	0.19(3 H)	2.004 05
$MeCH(OH)CH_2C\equiv CH$	$MeCH(OH)CH_2\dot{C}HCHO$	1.85	2.01(2 H) 0.185(CHO)		2.004 30

[a] Typically pH 1.5: in each case (except where indicated otherwise) the carbonyl-conjugated radical was only detected below pH 2. [b] ±0.01 mT: hyperfine splitting from one proton unless indicated otherwise. [c] ±0.000 05. [d] Attributed to the *Z*-isomer (see ref. 8). [e] Attributed to the *E*-isomer (see ref. 8). [f] Carbonyl-conjugated radicals detected below pH 1.8.



(**2**) (**3**)

Scheme 2.

alkyne concentration (which gives an estimated value of 0.29 for [(**1**)]:[(**3**)]) suggests that attack of $^{\bullet}OH$ on the alkynol itself proceeds *via* both C-H abstraction and addition in the ratio *ca.* 1:3. A full kinetic analysis (see below) supports this interpretation.

Experiments at very low alkyne concentrations (to avoid intermolecular abstraction) and at higher pH (>2.5, to avoid acid-catalysed rearrangement) gave weak signals which could not be analysed, though traces of (**1**) were clearly present: we were unable to detect signals unambiguously associated with the vinyl radical (**2**) itself.

Reactions of Other Alkynes with $^{\bullet}OH$.—Table 1 also contains details of the e.s.r. spectra of radicals obtained by reaction of $^{\bullet}OH$ with other alkynols in the pH range 1–2.5: in each case the detection of α-keto-alkyl radicals (in some cases in *cis* and *trans* forms)[8] at low pH is believed to reflect the occurrence of acid-catalysed conversion of initial hydroxyl adducts, as for but-2-yne-1,4-diol. In each case, the predominance of the α-keto radical at low pH indicates the marked preference for attack by $^{\bullet}OH$ on the triple bond rather than hydrogen abstraction. For several substrates, including $HOCH_2C\equiv CH$, $HOCH_2CH_2C\equiv CH$, and $MeC\equiv CCH_2OH$, radicals resulting from rearrangement of both possible hydroxyl adducts were detected (below pH 1.5 in these cases); for $MeC\equiv CCH_2CH_2OH$ the corresponding adducts were first detected at somewhat higher pH (*ca.* 2.2), which perhaps reflects the relative ease of formation of a cation radical (see later) in alkenes containing α,β-dialkyl substituents. This substrate, as with $MeCH(OH)CH_2C\equiv CH$, showed no evidence for hydrogen-atom abstraction in competition with addition (and rearrangement): of those substrates for which C–H abstraction was noted at higher pH, all (except $HOCH_2CH_2C\equiv CH$) possess both an hydroxyl and a vinyl substituent at the radical centre, an observation which presumably reflects the combined radical-stabilizing ability of both groups (see ref. 9 and references cited therein). For each of these substrates the marked increase in the concentration of the abstraction radical with pH (in the range 1.0–2.0) indicates that

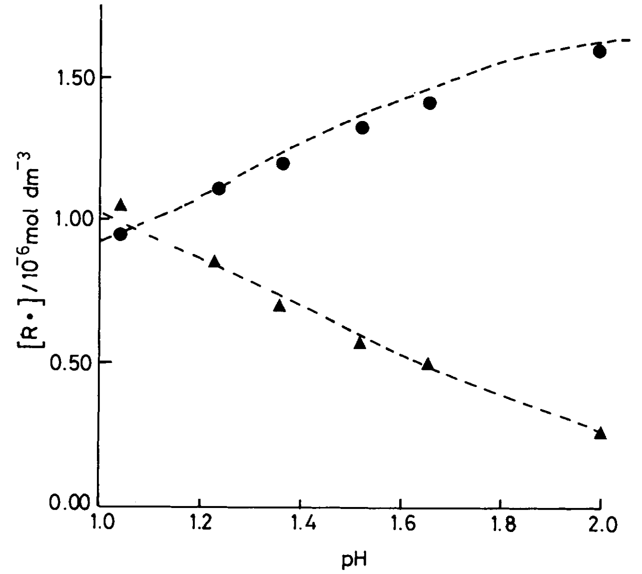


Figure 2. Variation with pH of the concentrations of $HO\dot{C}HC{\equiv}C\text{-}CH_2OH$ (●) and $HOCH_2CO\dot{C}HCH_2OH$ (▲) in experiments with but-2-yne-1,4-diol (conditions as in Figure 1). Dotted lines show the simulated behaviour (for reaction mechanism and kinetic parameters, see text).

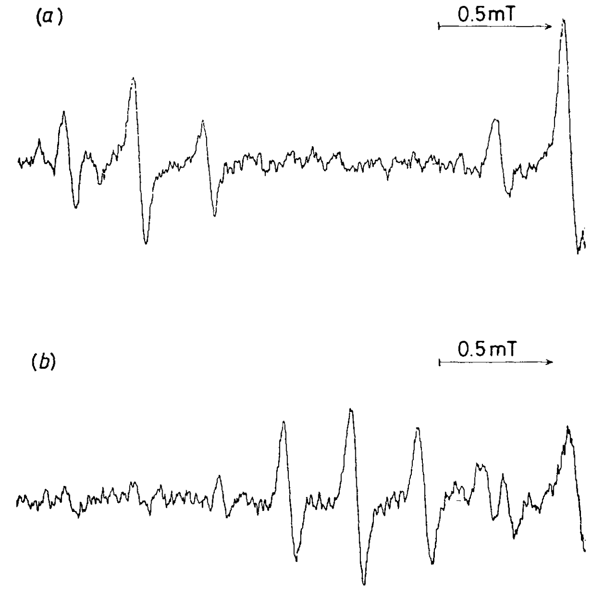


Figure 3. (*a*) Extreme low-field portion of the e.s.r. spectrum of the radical $HOCH_2CO\dot{C}HCH_2OH$. (*b*) Corresponding portion of the e.s.r. spectrum attributed to $HOCH_2CO\dot{C}{}^2HCH_2OH$, obtained from $^{\bullet}OH$ and but-2-yne-1,4-diol in D_2O at pH 0.63.

it is the first-formed vinyl radical (rather than $^{\bullet}OH$) which is responsible for hydrogen removal.

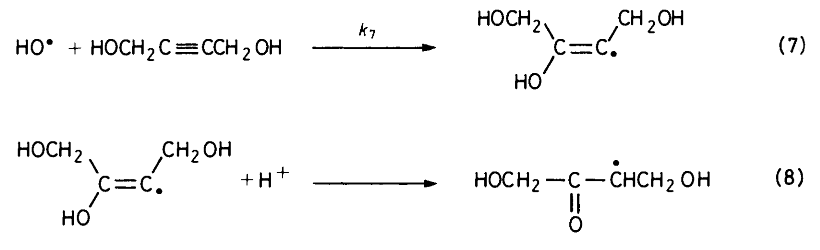
Kinetic Analysis.—We set out first to determine the rate of reaction of $HO^{\bullet}$ with but-2-yne-1,4-diol (as a model alkyne) by use of competition experiments involving methanol (whose rate of reaction with the hydroxyl radical is known).[10] At low pH (*ca.* 0.6) and with low but-2-yne-1,4-diol concentrations (1.5×10^{-3} mol dm^{-3}), the vinyl radicals formed by addition of $^{\bullet}OH$ to the triple bond would be expected solely to rearrange to carbonyl-conjugated radicals, as described above. We therefore carried out experiments under these conditions in the presence of low concentrations of added methanol, and monitored concentrations of $^{\bullet}CH_2OH$ and both $HOCH_2\dot{C}HCOCH_2OH$ and $HO\dot{C}HC{\equiv}CCH_2OH$ formed by direct competition for $^{\bullet}OH$ between the two substrates. On the assumptions that termination rates between these three radicals (self- and cross-termination) are identical and that the (stabilized) radical $^{\bullet}CH_2OH$ does not react with the alkynol under these conditions, it follows that the ratio of radical concentrations detected at low pH is related to the rates of $^{\bullet}OH$ attack as indicated by equation (9).

The predicted behaviour was verified in experiments with varying substrate concentrations in which the concentrations of the three radicals were monitored. The overall rate of attack on the alkyne was determined as 7.2×10^9 dm^3 mol^{-1} s^{-1} and the absolute rate constants for the individual reactions k_6 and k_7 were calculated as 1.6×10^9 and 5.6×10^9 dm^3 mol^{-1} s^{-1} respectively.

At higher pH, where no acid-catalysed rearrangement occurs, we were unable to detect e.s.r. signals from the intermediate vinyl radicals which we nevertheless conclude are formed in the initial reaction. We suggest that, in the absence of rearrangement, the steady-state concentration of the vinyl radicals (which must be $< ca.$ 10^{-7} mol dm^{-3}, unless unforeseen line-broadening occurs) is governed not only by radical–radical reaction ($2k_t$ *ca.* 2×10^9 dm^3 mol^{-1} s^{-1})[11] but also, largely, by reaction of the radical with parent compound

$$HO^{\bullet} + CH_3OH \xrightarrow{k_5} H_2O + {}^{\bullet}CH_2OH \qquad (5)$$

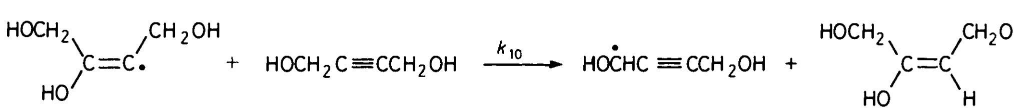
$$HO^{\bullet} + HOCH_2C{\equiv}CCH_2OH \xrightarrow{k_6} H_2O + HO\dot{C}HC{\equiv}CCH_2OH \qquad (6)$$



$$HO^{\bullet} + HOCH_2C{\equiv}CCH_2OH \xrightarrow{k_7} (HOCH_2)(HO)C{=}\dot{C}CH_2OH \qquad (7)$$

$$(HOCH_2)(HO)C{=}\dot{C}CH_2OH + H^+ \longrightarrow HOCH_2{-}C({=}O){-}\dot{C}HCH_2OH \qquad (8)$$

$$\frac{[{}^{\bullet}CH_2OH]}{[HO\dot{C}HC{\equiv}CCH_2OH] + [HOCH_2C(O)\dot{C}HCH_2OH]} = \frac{k_5[MeOH]}{(k_6 + k_7)[HOCH_2C{\equiv}CCH_2OH]} \qquad (9)$$



$$(HOCH_2)(HO)C{=}\dot{C}(CH_2OH) + HOCH_2C\equiv CCH_2OH \xrightarrow{k_{10}} HO\dot{C}HC\equiv CCH_2OH + (HOCH_2)(HO)C{=}C(CH_2OH)H \qquad (10)$$

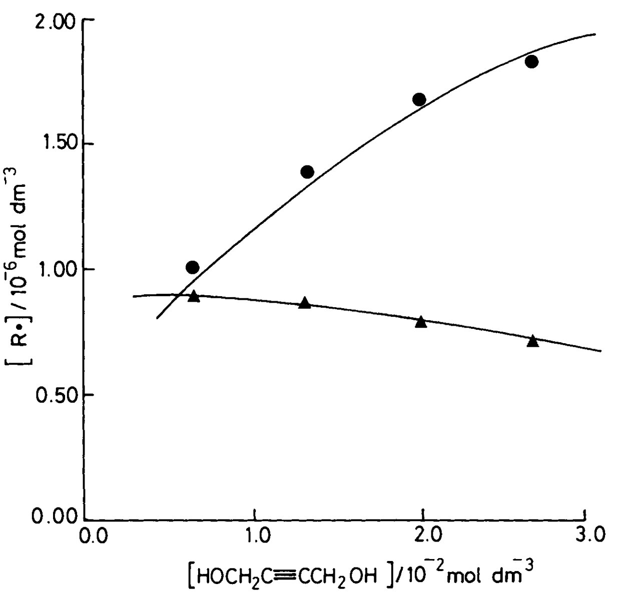


Figure 4. Variation of the concentrations of $HO\dot{C}HC\equiv CCH_2OH$ (●) and $HOCH_2CO\dot{C}HCH_2OH$ (▲) with $[HOCH_2C\equiv CCH_2OH]$ in experiments at pH 1.15.

[presumably mainly by C–H abstraction, reaction (10), as noted earlier].

Now if an initial radical ($R_1^{\bullet}$) largely decays by conversion into a secondary radical ($R_2^{\bullet}$) *via* reaction with substrate S (as in this case) then steady-state analysis for $[R_2^{\bullet}]$ leads, when $[R_1^{\bullet}] \ll [R_2^{\bullet}]$ to the following relationship (see *e.g.* ref. 12).

$$k_r[R_1^{\bullet}][S] = 2k_t[R_2^{\bullet}]^2 \qquad (11)$$

Applying this relation to reaction (10), with $2k_t$ 2×10^9 dm^3 mol^{-1} s^{-1} $[HO\dot{C}HC\equiv CCH_2OH]$ 2×10^{-6} mol dm^{-3} (as observed), $[HOCH_2C\equiv CCH_2OH]$ 5×10^{-3} mol dm^{-3} (the lower limit employed) and $HOCH_2C(OH){=}C(CH_2OH)^{\bullet} \leqslant 10^{-7}$ mol dm^{-3} (above which it should have been detected) we conclude that k_{10} is $\geqslant 1.6 \times 10^7$ dm^3 mol^{-1} s^{-1}.

From the results of experiments at lower pH (1.65), in which both rearranged and abstraction radicals are detected, we calculate the ratio of rate constants for abstraction and rearrangement ($k_{10}:k_8$) as 3.4: it follows that k_8, the rate constant for the acid-catalysed rearrangement is $\geqslant 5 \times 10^6$ dm^3 mol^{-1} s^{-1}. Use of these two lower limits in a kinetic simulation program [incorporating the initiation reactions between Ti^{III} and H_2O_2, reactions (6)–(8) and (10), and both self- and cross-termination, $2k_t$ 2×10^9 dm^3 mol^{-1} s^{-1}] led to a satisfactory agreement between observed and predicted behaviour in experiments in which pH and [alkyne] were varied (see *e.g.* Figure 2).

The marked reactivity of $^{\bullet}OH$ towards addition to but-2-yne-1,4-diol (k 5.6×10^9 dm^3 mol^{-1} s^{-1}) is not surprising in view of the radical's extremely electrophilic character, and its enhanced reactivity in C–H abstraction (k 1.6×10^9 dm^3 mol^{-1} s^{-1}), to give $HO\dot{C}HC\equiv CCH_2OH$, is understandable in terms of the weakening of this bond (see earlier) and the electronic effect ($+M$) of the hydroxy group. The inherent reactivity of the intermediate vinyl radical and the relative ease of abstraction to produce the stabilized radical (**1**) (and a C_{sp^2}–H bond) presumably also explains the rapidity of intramolecular reaction ($k \geqslant 1.6 \times 10^7$ dm^3 mol^{-1} s^{-1}). We believe that the facility of acid-catalysed transformation [reaction (8)] reflects the ease of protonation of a (vinylic) carbon atom in which negative-charge density is enhanced by the presence of the β-oxygen atom as illustrated by the contribution of canonical form (**6**) to the structure of the vinyl radical (**2**) (itself expected to be of σ-type, as illustrated). We note that the lower limit estimated for the rate constant for protonation is of the same order of magnitude reported[13] for the protonation at carbon of some 1-oxyallyl radical anions and pyrimidine $^{\bullet}OH$-adducts by water (and for which increase in electron density correlates with increase in rate).

In order to obtain further corroboration of this interpretation we examined the effect of added phosphate (0.08 mol dm^{-3}) on the ratio of concentrations of rearranged and abstraction radicals [(**3**) and (**1**)] at pH *ca.* 2 (it has been noted[13] that phosphate can bring about catalysis of related proton-transfer reactions in both acidic and basic conditions). In accord with expectation on this basis, signals from (**3**) were considerably enhanced [with a corresponding reduction in the concentration of (**1**)] under these conditions, evidently on account of the rapid protonation of (**2**) by H_3PO_4 and/or $H_2PO_4^-$.

Reaction of Alkynols with other Radicals.—We also carried out a variety of experiments to determine whether other radicals (including $Me^{\bullet}$, $Bu^tO^{\bullet}$, and $RS^{\bullet}$) react readily with alkynols to give spectra from adducts, or derived radicals.

There was no direct evidence that $Me^{\bullet}$ (from $^{\bullet}OH$ and excess of DMSO) adds to but-2-yne-1,4-diol (since no vinyl radical is detected) but enhanced signals from $HO\dot{C}HC\equiv CCH_2OH$ in the presence of $Me^{\bullet}$ suggest that intermolecular C–H abstraction occurs [involving either $Me^{\bullet}$, reaction (12), or an intermediate

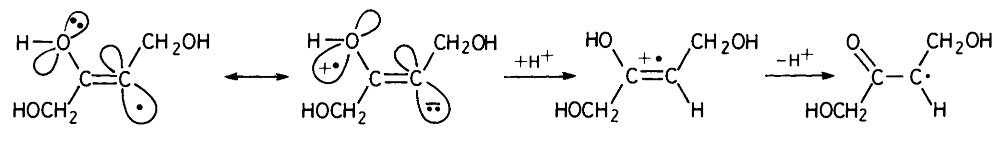
$$Me^{\bullet} + HOCH_2C\equiv CCH_2OH \longrightarrow MeH + HO\dot{C}HC\equiv CCH_2OH \qquad (12)$$

vinyl adduct]. In related experiments we were unable to obtain evidence that either $^{\bullet}CH_2OH$ or the α- and β-radicals from tetrahydrofuran (from methanol and THF, respectively, present in excess) react readily with but-2-yne-1,4-diol: in contrast, oxygen-conjugated radicals react readily by addition to butynedioic acid (to give vinyl radicals which subsequently react to give detectable secondary radicals). We calculate that k_{add} is $\leqslant 10^6$ dm^3 mol^{-1} s^{-1} for the alkynol, in contrast to *ca.* 10^7 dm^3 mol^{-1} s^{-1} for addition to alkynoic acids,[4] which presumably reflects the electron-withdrawing effect of the carboxyl groups in accelerating a reaction with nucleophilic oxygen-conjugated radicals.

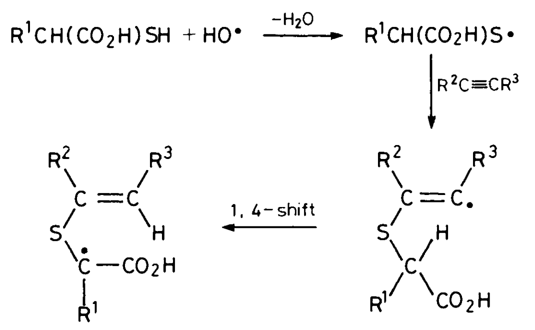
Generation of $Bu^tO^{\bullet}$ from Ti^{III} and Bu^tOOH led to the detection of $Me^{\bullet}$ (from $Bu^tO^{\bullet}$) as well as $HO\dot{C}HC\equiv CCH_2OH$ in significant concentrations: the ratio of the concentration of the two radicals was *ca.* 1:1 for [alkyne] *ca.* 0.033 mol dm^3. As a steady-state approach and computer simulations show, the observed increase in the latter with [alkyne] is compatible with either or both reactions (12) and (14) being the source of this

$$Bu^tO^{\bullet} \longrightarrow Me^{\bullet} + Me_2CO \qquad (13)$$

$$^tBuO^{\bullet} + HOCH_2C\equiv CCH_2OH \longrightarrow {}^tBuOH + HO\dot{C}HC\equiv CCH_2OH \qquad (14)$$



(2) (6) (7) (3)



(8)

Scheme 3.

species. Given that k_{13} is 1.4×10^6 dm^3 mol^{-1} s^{-1} under these circumstances[14] we calculate that a value for k_{12} of 5×10^4 dm^3 mol^{-1} s^{-1} or for k_{14} of 5×10^7 dm^3 mol^{-1} s^{-1} would account for the observed behaviour.

For a variety of carboxy-substituted thiols of the structure $R^1CH(CO_2H)SH$, reaction with $^{\bullet}OH$ [which is believed[1] to give $R^1CH(CO_2H)S^{\bullet}$] in the presence of a series of alkynols (with typical concentrations of thiol and alkyne 0.01 and 0.05 mol dm^3, respectively) led to the detection of radicals whose parameters in each case establish the presence of thioalkyl and carboxy substituents at the radical centre (the structures are shown in Table 2). The reaction mechanism (see Scheme 3) is believed to involve addition of thiyl radicals to the triple bond, followed by 1,4-shift of hydrogen, assisted (we presume) by the strength of the C–H bond formed and the stabilizing (captodative) effect[15] of the $+M$ and $-M$ substituents at the new radical centre (the resultant exothermicity is expected[1] to be *ca.* 80 kJ mol^{-1}). The rearrangement, which is estimated to have k *ca.* 10^5 s^{-1} (see ref. 1), is presumably favoured by the ease of achieving a transition state in which the long C–S bonds (*ca.* 0.18 nm) and small $C\hat{S}C$ (*ca.* 100°) allow close approach of the radical centre and δ-hydrogen.

Conclusions

Although alkynols appear to be somewhat less reactive than butynedioic acid to alkyl and hydroxyalkyl radicals (but not $HO^{\bullet}$ or sulphur-centred radicals), the vinyl radicals which result from radical addition (and which presumably share the σ-structure of the vinyl radical itself[16]) are particularly reactive in inter- and intra-molecular reactions. Examples studied include intermolecular abstraction of hydrogen from a C–H bond in alkynols ($k \geqslant 10^7$ dm^3 mol^{-1} s^{-1}) and a 1,4-shift (k *ca.* 10^5 s^{-1}) in β-sulphur-substituted radicals in which the resultant radical is stabilized by conjugation to sulphur and a carboxyl group. Evidence for rapid protonation (of the α-carbon atom) of β-hydroxyvinyl radicals, and its catalysis by phosphate, has also been obtained, a result which is believed to reflect the importance of negative charge density in governing the rate of protonation.

Experimental

E.s.r. spectra were recorded on Bruker ESP 300 and Varian E-104 spectrometers each equipped with X-band microwave bridges and 100 KHz modulation. Hyperfine splittings and g-values were determined directly from the spectrometer's field scans, these having been calibrated with the signal from Fremy's salt [a_N = 1.3091 mT,[17] g 2.0055[18]]. Radical concentrations were determined by comparison with spectra obtained from standard solutions of vanadyl sulphate by use of double integration with the Bruker ESP 300. A mixing chamber was employed which allowed simultaneous mixing of three reagent streams *ca.* 30 ms before passage through the cavity of the spectrometer: the 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 (0.025 mol dm^{-3}) and (*iii*) the alkyne (0.02 mol dm^{-3}); pH was varied by addition of sulphuric acid (18 mol dm^{-3}) or sodium hydroxide (10 mol dm^{-3}) to the first stream and all solutions were deoxygenated by a nitrogen purge both before, and during use. In some experiments, sodium dihydrogenphosphate (0.25 mol dm^{-3}) was added to the first stream.

Spectrum simulations were carried out using a program originally written by Dr. M. F. Chiu modified to run on a VAX mainframe computer. The kinetic simulation program, executed on the VAX computer, was originally written by Dr. T. M. F. Salmon and modified by Dr. M. J. Brown.

All chemicals employed were commercial samples used as supplied.

Table 2. E.s.r. parameters[a] of α-thioalkyl-α-carboxyl radicals[b] derived from addition of $R^1CH(CO_2H)S^{\bullet}$ to $R^2C{\equiv}CR^3$.

Thiyl radical	Alkynol		Hyperfine splittings/mT		
R^1	R^2	R^3	$a(R^1)$	a (other)	g
H	$HOCH_2$	$HOCH_2$	1.36(1 H)	0.14(1 H, 2 H)	2.0057
Me	$HOCH_2$	$HOCH_2$	1.59(3 H)		2.0052
CH_2CO_2H	$HOCH_2$	$HOCH_2$	0.93(2 H)		2.0050
H	HOCHMe	HOCHMe	1.36(1 H)	0.14(1 H)	2.0057
Me	HOCHMe	HOCHMe	1.59(3 H)		2.0053
CH_2CO_2H	HOCHMe	HOCHMe	0.86(2 H)		2.0057
H	H	$HOCHMeCH_2$	1.35(1 H)	0.18(2 H)	2.0047

[a] h.f.s. ±0.05 mT, g ±0.0001. [b] Proposed structure, (8) (Scheme 3).

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