Electron Spin Resonance Studies. Part 61.[1] The Generation and Reactions of the t-Butoxyl Radical in Aqueous Solution

By **Bruce C. Gilbert,*** **P. David R. Marshall, Richard O. C. Norman, Nelson Pineda,** and **Peter S. Williams,** Department of Chemistry, University of York, Heslington, York YO1 5DD

The t-butoxyl radical has been generated in aqueous solution from the reaction between Ti^{III} and Bu^tOOH in a flow system. Evidence is presented which indicates that, although the fragmentation of $Bu^tO\cdot$ to $Me\cdot$ and acetone is rapid under these conditions ($k > 10^6$ dm^3 mol^{-1} s^{-1}), competing addition reactions (*e.g.* to vinyl ethers, furan) and abstraction reactions (with alcohols) can be characterized. $Bu^tO\cdot$ is shown to be electrophilic, like $\cdot OH$, in its reactions, but with prop-2-en-1-ol, unlike $\cdot OH$, it undergoes abstraction rather than addition. Changes in the behaviour of t-butoxyl at very low pH are attributed to the formation and reaction of the protonated counterpart $Bu^tOH^{+\cdot}$.

E.S.R. studies have made a significant contribution [2] to our knowledge of the reactions of the t-butoxyl radical in non-aqueous solvents.[3] These experiments have typically involved [2a,b] the continuous *in situ* photolysis of di-t-butyl peroxide and the direct detection of radicals formed *via* the reaction of $Bu^tO\cdot$ with added substrates [*e.g.* reaction (1) [2a]]. In this way it has been shown that t-butoxyl is a reactive electrophilic radical which is in some respects akin to the more reactive hydroxyl radical. One the other hand one marked difference between $HO\cdot$ and $Bu^tO\cdot$ is that with allylic compounds the former preferentially adds to the double bond whereas the latter reacts predominantly *via* allylic C–H abstraction [2c] [*e.g.* reaction (2)].

By comparison, the chemistry of $Bu^tO\cdot$ in aqueous solution is much less well understood. When this radical was generated in a flow system from the reaction between Ti^{III} and Bu^tOOH [reaction (3)] the methyl radical, evidently formed *via* the fragmentation reaction (4), and, at higher hydroperoxide concentrations, $Bu^tO_2\cdot$ were directly detected;[4] the methyl radical formed in this system can also be 'trapped' *via* its addition to, for example, acrylic acid.[5] The formation of $Me\cdot$ is consistent with the results of a product study of the decomposition of $Bu^tO\cdot$ in which it was found [6] that increasing the polarity of the solvent accelerates fragmentation at the expense of abstraction reactions.

$$Bu^tO\cdot + MeCH_2OH \longrightarrow Bu^tOH + Me\dot{C}HOH \quad (1)$$

$$Bu^tO\cdot + MeCH{=}CH_2 \longrightarrow Bu^tOH + \dot{C}H_2CH{=}CH_2 \quad (2)$$

$$Ti^{III} + Bu^tOOH \longrightarrow Ti^{IV} + Bu^tO\cdot + OH^- \quad (3)$$

$$Bu^tO\cdot \xrightarrow{k_4} Me\cdot + Me_2C{=}O \quad (4)$$

We have previously employed e.s.r. spectroscopy to characterize the reactions of primary [7] and secondary [8] alkoxyl radicals generated in aqueous solution by the one-electron reduction of the corresponding hydroperoxides: fragmentation reactions and 1,n-hydrogen shifts (including unusual examples with $n = 2$) were demonstrated, and it was also possible to intercept alkoxyl radicals with the spin trap $CH_2{=}NO_2^-$ and detect them as the adducts $ROCH_2NO_2^{-\cdot}$. Intermolecular hydrogen-atom abstraction was also observed with reactive substrates that were present at relatively high concentrations.

The aim of the investigation described here was to employ e.s.r. spectroscopy to obtain information about the reactions of $Bu^tO\cdot$ in aqueous solution. In particular we set out to determine whether or not $Bu^tO\cdot$ could similarly be intercepted (*e.g. via* addition to spin traps or reaction *via* abstraction with high concentrations of reactive substrates) and, if possible, to obtain relative rate constants for these competing reactions. It was also hoped to be able to study the selectivity of attack of $Bu^tO\cdot$ at different sites within a given molecule and to learn more about the effect of solvent on its reactivity. Lastly, in view of the suggestion [9] that the photolysis of Bu^tOOBu^t in cyclopropane containing CF_3CO_2H leads to the production of the *protonated* t-butoxyl radical, $Bu^tOH^{+\cdot}$, which apparently shows an enhanced tendency towards addition to alkenes, compared with $Bu^tO\cdot$, we studied avariety of reactions of $Bu^tO\cdot$ in the flow system at low pH.

RESULTS AND DISCUSSION

The experiments were carried out by mixing three solutions, containing titanium(III) (typically *ca.* 0.008 mol dm^{-3}), t-butyl hydroperoxide (*ca.* 0.06 mol dm^{-3}), and the added substrate, just before the entry of the combined stream into the cavity of an e.s.r. spectrometer, with a time between mixing and observation of *ca.* 70 ms.

(a) *Decomposition of t-Butyl Hydroperoxide in the Presence of the* aci-*Anion of Nitromethane.*—Initial experiments over a range of pH values confirmed that mixing Ti^{III} and Bu^tOOH in the absence of added substrates led simply to the detection of the methyl radical. In a typical spin-trapping experiment nitromethane was added to the third stream and the pH was raised to *ca.* 9.5. For a concentration of CH_3NO_2 in the mixed stream † of 0.005 mol dm^{-3}, and hence a concentration of the *aci*-anion of *ca.* 10^{-3} mol dm^{-3} (since the pK_a of nitromethane is 10.2 [10]), the spectrum of $Me\cdot$ was com-

† Concentrations given in the text are those after mixing.

pletely removed and replaced by a signal attributed to a nitro-radical-anion; the parameters [a(N) 2.60, a(2 H) 0.97, a(3 H) 0.05 mT, g 2.0050] confirm that this is from [11] $EtNO_2^{-\bullet}$ (1), evidently formed by the scavenging of Me• with $CH_2{=}NO_2^-$ [reaction (5)]. When the concentration of nitromethane was increased, a second nitro-radical-anion with a(N) 2.53, a(2 H) 1.01 mT, g 2.0050 was also detected; these parameters are typical of an adduct formed by an oxygen-centred radical [*cf.* for [12] $HOCH_2NO_2^{-\bullet}$; a(N) 2.50, a(2 H) 0.90 mT, g 2.0050] and the signal is ascribed to the t-butoxyl adduct $Bu^tOCH_2NO_2^{-\bullet}$ (2) [*cf.* reaction (6)]. As would be expected on this basis, an increase in the concentration of the *aci*-anion of nitromethane led to an increase in the relative intensity of the second signal compared with that of the first, *i.e.* as trapping of $Bu^tO\bullet$ competes more effectively with fragmentation [reaction (4)]. For [CH_3NO_2] 0.025 mol dm^{-3} the concentrations of (1) and (2) were approximately equal. Even at high concentrations of nitromethane (*ca.* 0.08 mol dm^{-3}), at which the signal of the t-butoxyl adduct was predominant, no other adducts were detected.

$$Me\bullet + \bar{C}H_2NO_2 \xrightarrow{k_5} \underset{(1)}{MeCH_2NO_2^{-\bullet}} \quad (5)$$

$$Bu^tO\bullet + \bar{C}H_2NO_2 \xrightarrow{k_6} \underset{(2)}{Bu^tOCH_2NO_2^{-\bullet}} \quad (6)$$

It has previously been shown [7,13] that, for short-lived radicals of the types described here generated by the Ti^{III}–H_2O_2 and Ti^{III}–RO_2H couples, the radicals detected by e.s.r. are those actually formed in the cavity and that a steady-state analysis is applicable. Thus, on the assumptions that methyl radicals are not destroyed to a significant extent other than by reaction with the *aci*-anion of nitromethane (so that $d[Me\bullet]/dt = k_4[Bu^tO\bullet] - k_5[Me\bullet][CH_2{=}NO_2^-] = 0$), that t-butoxyl reacts under these conditions only *via* addition (to $CH_2{=}NO_2^-$) and fragmentation (*e.g.* that no reaction with Ti^{III} occurs) and that the two nitro-radical-anions (1) and (2) are destroyed by processes which involve radical–radical reactions with similar rate constants [*i.e.* $2k_7 = k_8 = 2k_9 = 2k_t$], the steady-state expression (12) may be derived. For the formation and termination of $Bu^tOCH_2NO_2^{-\bullet}$ and $MeCH_2NO_2^{-\bullet}$, we have equations (10) and (11). Combination of (10) and (11) gives equation (12).

$$2Bu^tOCH_2NO_2^{-\bullet} \xrightarrow{k_7} \text{molecular products} \quad (7)$$

$$MeCH_2NO_2^{-\bullet} + Bu^tOCH_2NO_2^{-\bullet} \xrightarrow{k_8} \text{molecular products} \quad (8)$$

$$2MeCH_2NO_2^{-\bullet} \xrightarrow{k_9} \text{molecular products} \quad (9)$$

$$2k_t[Bu^tOCH_2NO_2^{-}]^2 + 2k_t[Bu^tOCH_2NO_2^{-\bullet}][MeCH_2NO_2^{-\bullet}] = k_6[Bu^tO\bullet][CH_2{=}NO_2^-] \quad (10)$$

$$2k_t[MeCH_2NO_2^{-\bullet}]^2 + 2k_t[MeCH_2NO_2^{-\bullet}][Bu^tOCH_2NO_2^{-\bullet}] = k_5[Me\bullet][CH_2{=}NO_2^-] = k_4[Bu^tO\bullet] \quad (11)$$

$$\frac{[(2)]}{[(1)]} = \frac{[Bu^tOCH_2NO_2^{-\bullet}]}{[MeCH_2NO_2^{-\bullet}]} = \frac{k_6[CH_2{=}NO_2^-]}{k_4} \quad (12)$$

Estimates of the relative concentrations of (1) and (2) were obtained at several concentrations of $CH_2{=}NO_2^-$ and the results, when plotted according to equation (12), yielded a reasonable straight line with slope (k_6/k_4) 2×10^2 dm^3 mol^{-1}. As far as we are aware no reliable values for the rate constants for either addition or fragmentation of $Bu^tO\bullet$ (in aqueous solution) have been reported. However, if we assume, by analogy [7] with the reaction between PrO• and $CH_2{=}NO_2^-$, that the lower limit for the rate constant for addition of $Bu^tO\bullet$ to $CH_2{=}NO_2^-$ (k_6) is *ca.* 10^8 dm^3 mol^{-1} s^{-1}, then since the upper limit is likely to be *ca.* 10^9 dm^3 mol^{-1} s^{-1} (close to the diffusion-controlled limit for reactions of this type), it follows that $10^6 < k_4 < 10^7$ s^{-1}. This is to be contrasted with the value of *ca.* 10^2 s^{-1} for the corresponding reaction of $Bu^tO\bullet$ in tetrachloromethane.[14]

(b) *Decomposition of t-Butyl Hydroperoxide in the Presence of Unsaturated Substrates.*—(i) cis-*Butenedioic acid and its anions.* In a series of experiments involving *cis*-butenedioic acid (in both protonated and ionized forms) as a potential spin-trap, in which both pH and substrate concentration were varied over a wide range, no signals were discerned which could be attributed to a t-butoxyl adduct. Instead, signals characteristic of adducts from [15] •OH and Me• [see structures (3)—(5): the states of protonation are discussed later], as well as the methyl radical itself, were detected; the variation with pH of the relative intensities of these (for [substrate] 0.1 mol dm^{-3}) are shown in Figure 1.

	Monoanion from $\bullet CH(CO_2H)CHMeCO_2H$ (3)	$\bullet CH(CO_2^-)CHMeCO_2^-$ (4)
a	α-H 2.08 mT; β-H 1.35 mT	α-H 2.03 mT; β-H 1.03 mT; γ-H 0.07 mT
g	2.0033	2.0032

	$\bullet CH(CO_2^-)CH(OH)CO_2^-$ (5)
a	α-H 2.05 mT; β-H 1.55 mT; OH 0.02
g	2.0032

The important features may be summarized as follows. First, the dominant species, irrespective of pH, is the methyl adduct of the trap. Secondly, a change-over in e.s.r. parameters for the methyl adducts occurs upon going from pH 3.5 to 5, and the γ-proton splitting becomes resolved. Thirdly, the concentration of (4) reaches a well defined maximum at pH *ca.* 6.5. Of further note is the appearance at high pH values not only of the signal from the methyl radical itself but also, rather surprisingly, of that of the hydroxy-radical adduct of the dianion (5). The latter observation would be consistent with the operation of a novel reaction mechanism involving, for example, the one-electron reduction of Bu^tOOH with Ti^{III} to give, in part HO• (and Bu^tO^-) or the hydration of a radical-cation formed by one-electron abstraction from *cis*-butenedioate by $Bu^tO\cdot$. However, the alternative suggestion that adventitious hydrogen peroxide is responsible for these observations is supported by our finding that the addition of Ti^{IV} to the system not only produced immediately the characteristic yellow-orange colour of the Ti^{IV}–H_2O_2 complex but also removed the signal from

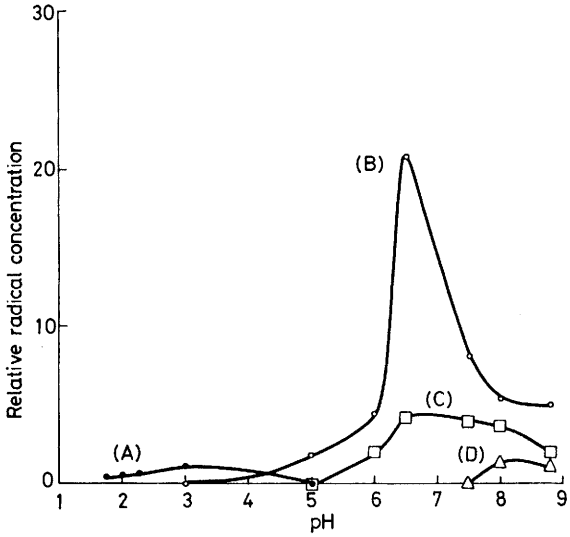


FIGURE 1 Variation with pH of the relative concentrations of radicals detected during the one-electron reduction of Bu^tOOH with Ti^{III} in the presence of *cis*-butenedioic acid (0.1 mol dm^{-3}); (A) $\cdot CH(CO_2^-)CHMeCOH$; (B) $\cdot CH(CO_2^-)CHMeCO_2^-$; (C) $\cdot CH(CO_2^-)CH(OH)CO_2^-$; (D) $\cdot CH_3$

the $\cdot OH$ adduct.* [It was also found that addition of one equivalent of Ti^{IV} to the stream containing H_2O_2 in a flow system experiment involving oxidation of EtOH with $\cdot OH$ (from Ti^{III} and H_2O_2) resulted in the complete removal of the signal from $\cdot CHMeOH$].

The fact that, at all pH values, adducts with the methyl radical, rather than with t-butoxyl, are observed indicates that, under the conditions employed, fragmentation of the latter radical competes effectively with its addition to the double bond of the substrate. Assuming a value of $\geqslant 10^6$ s^{-1} for the fragmentation rate constant, and noting that, even with a substrate concentration of 0.3 mol dm^{-3}, no t-butoxyl adduct was detected, an upper limit for $k(Bu^tO\cdot + XCH{=}CHX,\ X = CO_2^-$ or $CO_2H)$ of *ca.* 3×10^5 dm^3 mol^{-1} s^{-1} may be derived. This value should be compared with the rate constant for the analogous reaction with $\cdot OH$, which is considered to be in excess of 10^9 dm^3 mol^{-1} s^{-1}.[16] The difference, which appears to be a clear demonstration of the reluctance of t-butoxyl radicals to add to C=C, probably reflects the reduced electrophilicity of the alkoxyl radical compared with the hydroxyl radical. Thus, the SOMO of an alkoxyl radical is of much higher energy than that of the hydroxyl radical (−9.0 and −13.1 eV respectively),[17] with the result that, as pointed out previously,[17] the net energy gain from the interaction with the HOMO of the substrate in forming the adduct is reduced.

The changeover in parameters for the methyl adduct in the pH range 3—5 is consistent with a pK_a for the appropriate radical of *ca.* 4.25. This might correspond to either the first or the second ionisation, and, in order to distinguish between these possibilities, the corresponding monomethyl ester was investigated. It was found that even at high pH, the only radical detected, other than methyl, had parameters almost identical to those of the radical detected at low pH from the reaction of the acid. Consequently, we conclude that the radical detected is $\cdot CH(CO_2^-)CHMeCO_2Me$ and that the pK_a characterized for the butenedioic acid-derived radicals corresponds to pK_2 for $\cdot CH(CO_2H)CHMeCO_2H$ (*i.e.* for the monoanion–dianion equilibrium). Notably, the value of 4.25 is significantly lower than pK_2 for *cis*-butenedioic acid itself (6.23).[10]

The maximum in the concentration of $\cdot CH(CO_2^-)CHMeCO_2^-$ at pH *ca.* 6.5 is explained in terms of changes in the rates of its formation and destruction, themselves induced by changes in the degree of ionisation of the substrate and adduct-radical, respectively. For example, since the methyl radical is essentially nucleophilic, it would be expected to add more rapidly to the monoanion of the substrate than to the dianion. Thus, on increasing the pH from 5 to 8, the rate of formation of the methyl adduct is expected to fall as the degree of ionisation of the substrate (pK_2 6.23) increases, and this indeed is reflected in the appearance of methyl radicals at pH > 7.5. In contrast, the doubly ionised methyl-adduct radical is expected to have a much longer lifetime than its singly ionised counterpart, because of the larger adverse coulombic interactions in the transition state leading to the dimerisation (or disproportionation) of the former. Thus, at pH > 4.5, the rate of destruction of the adduct should decrease rapidly with increasing pH. The net result is that, between pH 5 and 7, the adduct is both formed rapidly and destroyed slowly, so that its observed concentration increases accordingly.

In keeping with this interpretation, when the reaction of $\cdot OH$ with dimethyl sulphoxide[18] was employed to generate $Me\cdot$, precisely the same behaviour was observed. Further, when *cis*-butenedioic acid was replaced by its *trans*-isomer (for which $pK_2 = 4.4$ [10]) no well defined concentration maximum was observed in the pH range 6—7. This is as expected on the basis of the foregoing interpretation since, with the *trans*-isomer, in the pH range in which the adduct is destroyed slowly (*i.e.* pH > 5), it is also formed slowly.

(ii) *Alkyl vinyl ethers.* Methyl and vinyl ethyl ethers were chosen as substrates since, in contrast to carboxy-substituted alkenes, they would be expected to be reactive towards the electrophilic t-butoxyl radical but relatively unreactive towards the nucleophilic methyl radical. Further, it was of interest to compare the mode of reaction of $Bu^tO\cdot$ with vinyl ethers with those of $\cdot OH$ (which is known[19] to add at both ends of the double bond) and $Cl_2^{-\cdot}$ (which reacts[19] *via* one-electron

* The corresponding adduct $HOCH_2NO_2^{-\cdot}$ could not be unambiguously characterized in the experiment with $CH_2{=}NO_2^-$ as trap; this is evidently due to the presence of overlapping resonances from other radicals, as well as the lower signal-to-noise ratios obtained with this trap.

abstraction to give a radical-cation, and thence hydroxyl adducts *via* hydration).

When the t-butoxyl radical was generated in the presence of ethyl vinyl ether (present as a saturated solution in one stream) at pH 7, only one radical, other than $\cdot CH_3$, was detected. Its e.s.r. parameters (see Table) were essentially the same, within experimental error, as those for $\cdot CH(OEt)CH_2OH$ [for which [19] a(α-H) 1.72, a(β-H) 0.88, $a(OCH_2)$ 0.175 mT, g 2.0032]; however, as will be explained in the sequel, an alternative structure $\cdot CH(OEt)CH_2OBu^t$ (6) is suggested. When the pH was reduced from 7 to 1, an additional species identified as [19] $\cdot CH_2CH(OH)OEt$ (7) became detectable. Lowering the pH below 1.0 resulted in the detection of traces of the dimeric species [19] $\cdot CH(OEt)CH_2CH_2CH(OH)OEt$ (8). When the pH was reduced to less than 0.7 almost all signals from the vinyl ether-derived species disappeared and a corresponding increase in $[CH_3\cdot]$ occurred. With methyl vinyl ether essentially similar behaviour was noted and signals virtually identical with those from [19] $\cdot CH(OMe)CH_2OH$ [but assigned to $\cdot CH(OMe)CH_2OBu^t$ (9), see below] and, at pH *ca.* 1, $\cdot CH_2CH(OH)OMe$ (10) were detected.

Now the adduct fromed from, for example, ethyl vinyl ether at high pH and with a spectrum typical of the $\cdot OH$ adduct clearly cannot be derived from reaction of $\cdot OH$ with this substrate, since it is known [19] that the latter reaction yields both $\cdot CH(OEt)CH_2OH$ and $\cdot CH_2CH(OH)$-OEt (and likewise for CH_2=CHOMe). Similarly, it cannot be derived from hydration of a first-formed radical-cation, which also yields both radicals. We therefore explored the possibility that the radical in question is in fact $\cdot CH(OEt)CH_2OBu^t$ (6) (formed by direct addition of $Bu^tO\cdot$) for which the splitting constants are fortuitously the same, within experimental error, as those for the corresponding hydroxyl adduct. Such a coincidence appears less surprising than at first sight in view of our earlier finding [20] that radicals with both α- and β-hydroxy- and/or alkoxy-groups have closely similar splittings, which indicates that a 'locked' conformation is adopted in which the β-OR group eclipses the orbital of the unpaired electron. Several further experiments suggest that this is also true for a β-OBu^t group, and therefore that the t-butyl group does *not* exert a steric effect such that the eclipsing conformation is disfavoured. First, reaction of $Bu^tO\cdot$ produced photolytically in non-aqueous conditions in the presence of ethyl vinyl ether led to the production of $\cdot CHMeOCH{=}CH_2$ (formed in relatively low concentrations) and a radical assigned the structure $\cdot CH(OEt)CH_2OBu^t$ (6); the α- and β-splittings in the latter (see Table) are closely similar to those of the related species $\cdot CH(OMe)CH_2OH$ and $\cdot CH(OMe)CH_2OMe$ obtained from saturated precursors under comparable conditions.[21] Evidently a structure with the β-oxygen substituent eclipsing the orbital of the unpaired electron is favoured [and increasingly so at low temperatures as judged by the associated decrease in a(β-H) for (6)]. Secondly, we prepared radicals of the type $\cdot CH(OR)CH_2OBu^t$ (R = Me, Bu^t) in flow experiments with $\cdot OH$ (from Ti^{III}–H_2O_2) and the substrates $MeOCH_2CH_2OBu^t$ and $Bu^tOCH_2CH_2OBu^t$; data on these radicals, and on the other radicals obtained by hydrogen abstraction from these substrates, are collected together in the Table. As judged by the β-proton splittings, the conformational properties of radicals $\cdot CH(OR)CH_2OR'$ appear to be essentially independent of the nature of R′ (H, Me, or Bu^t); in particular the parameters for (9), generated in this way, are identical, within the limits of the experimental error, to those of $\cdot CH(OMe)CH_2OH$, in accord with our claim that it is the former which is formed from $Bu^tO\cdot$ and CH_2=CHOMe. A further observation of mechanistic significance is that, by pH *ca.* 1, the spectrum of (9) from $MeOCH_2CH_2OBu^t$ was joined by that attributed to $\cdot CH_2CH(OH)OMe$ (10), exactly as observed at low pH for the reaction of $Bu^tO\cdot$ with CH_2=CHOMe.

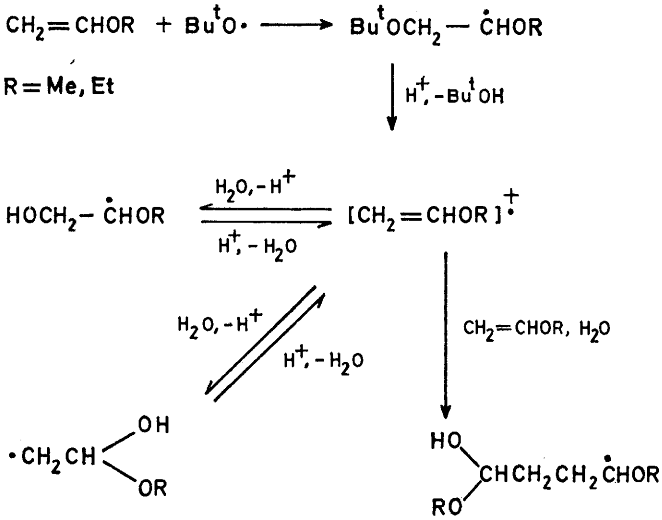
Our observations can be rationalised on the basis of the reactions summarised in the Scheme. That is, the reaction of $Bu^tO\cdot$ with the vinyl ethers produces, at high pH, solely the adduct $\cdot CH(OR)CH_2OBu^t$, with splittings virtually identical to those of $\cdot CH(OR)CH_2OH$. As the pH is lowered, acid-catalysed loss of Bu^tO^- occurs (*cf.*

E.s.r. spectra of radicals derived by reactions of ethers and vinyl ethers

Substrate	Attacking species [a]	Radical	Hyperfine splittings (mT) [b] a(α-H)	a(β-H)	a (other)	g [c]
Ethyl vinyl ether	$Bu^tO\cdot$, flow, pH 7	$EtO\dot{C}HCH_2OBu^t$ (6)	1.73 (1 H)	0.88 (2 H)	0.18 (2γ-H)	2.0032
	$Bu^tO\cdot$, flow, pH *ca.* 1	$EtO\dot{C}HCH_2OH$	1.73 (1 H)	0.88 (2 H)	0.18 (2γ-H)	2.0032
		$\cdot CH_2CH(OH)OEt$ (7)	2.24 (2 H)	1.88 (1 H)		2.0026
		$\cdot CH(OEt)CH_2CH_2CH(OH)OEt$ (8)	1.43 (1 H)	1.94 (1 H), 1.96 (1 H)	0.135 (2 H), 0.06 (2 H)	2.0032
	$Bu^tO\cdot$, u.v., −5°	$\cdot CHMeOCH{=}CH_2$	1.54 (1 H)	2.24 (3 H)	0.12 (1γ-H)	2.0032
		(6)	1.58 (1 H)	1.00 (2 H)	0.20 (2γ-H)	2.0032
	−70°	(6)	1.60	0.85 (2 H)	0.23 (2γ-H)	2.0032
Methyl vinyl ether	$Bu^tO\cdot$, flow, pH 7	$MeO\dot{C}HCH_2OBu^t$ (9)	1.70 (1 H)	0.90 (2 H)	0.18 (3γ-H)	2.0032
	$Bu^tO\cdot$, flow, pH *ca.* 1	$MeO\dot{C}HCH_2OH$	1.72 (1 H)	0.88 (2 H)	0.18 (3γ-H)	2.0032
		$\cdot CH_2CH(OH)OMe$ (10)	2.25 (2 H)	1.89 (1 H)		2.0025
$MeOCH_2CH_2OBu^t$	$HO\cdot$, flow, pH *ca.* 2.5	(9)	1.70 (1 H)	0.89 (2 H)	0.18 (3γ-H)	2.0032
		$Bu^tO\dot{C}HCH_2OMe$	1.78 (1 H)	0.88 (2 H)		2.0033
		$\cdot CH_2OCH_2CH_2OBu^t$	1.70 (2 H)		0.20 (2γ-H)	2.0032
$Bu^tOCH_2CH_2OBu^t$	$HO\cdot$, flow, pH *ca.* 2.5	$Bu^tO\dot{C}HCH_2OBu^t$	1.72 (1 H)	0.92 (2 H)		2.0033

[a] Flow experiments with Ti^{III}–Bu^tOOH; u.v. experiments with *in situ* photolysis of Bu^tOOBu^t. For details, see text. [b] ±0.01 mT. [c] ±0.0001.

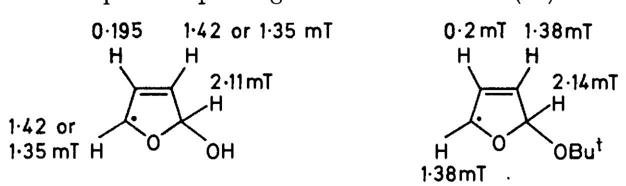
acid-catalysed loss of hydroxide ion from the corresponding hydroxyl adducts), giving a radical-cation $[CH_2{=}CHOR]^{+\cdot}$ which can then be hydrated to give the adducts $\cdot CH_2CH(OH)OR$ and $\cdot CH(OR)CH_2OH$ [for which the resonances are coincident with those of $\cdot CH(OR)CH_2OBu^t$]. For ethyl vinyl ether, where a greater substrate concentration was achieved, reaction of the intermediate radical-cation with the parent alkene results in the formation of the dimer radical (8) (as also



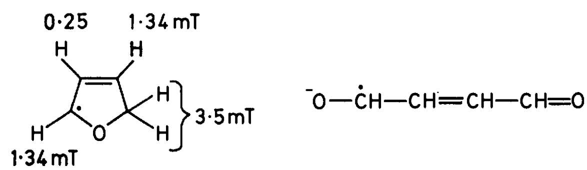
SCHEME

observed in the oxidation of this compound with $Cl_2^{-\cdot}$ and $\cdot OH$). As judged by the pH at which the spectrum of the non-conjugated radical $\cdot CH_2CH(OH)OR$ appears, the ease of loss of a β-OBu^t group is approximately the same as that for β-OH. We shall return later to the enhanced production of Me• at pH < 0.7.

(iii) *Furan*. When the t-butoxyl radical was generated in the presence of furan at either pH 1 or 8, only one species (other than methyl) was detected. On the basis of the similarity between the observed splittings and those of the hydroxyl adduct [19] (11), we assign this spectrum to the t-butoxyl adduct (12); since the (β-type) methine proton splitting is much smaller in (12) than in



(11) (12)



(13) (14)

the unsubstituted analogue (13) we conclude that in (12), as in (11), the β-C–O bond to the t-butoxy-group eclipses the half-filled orbital.[19]

The fact that at pH > 7 no trace of the ring-opened species (14) was detected confirms the requirement, postulated earlier, [19,22] for deprotonation of (11) before its conversion into (14). Furthermore, since at pH 1.0 no trace of (11) was discernible in the reaction of $Bu^tO\cdot$ with furan, the possibility that acid-catalysed elimination of Bu^tO^- from (12) occurs at a significant rate at this pH may be discounted.

Experiments were also conducted at pH < 1.0. However, as the pH approached 0 the ratio $[\cdot CH_3] : [(12)]$ increased considerably until only the former was clearly detectable. This observation parallels those made for the vinyl ethers; the implications are discussed later.

(iv) *Prop-2-en-1-ol*. The addition of a relatively high concentration of this reagent (0.25 mol dm^{-3} in the mixed stream) to the Ti^{III}–Bu^tOOH couple led to the detection of four radicals; the concentration required was much greater than that needed effectively to scavenge •OH from the Ti^{III}—H_2O_2 couple, which presumably reflects the lower reactivity of $Bu^tO\cdot$ than •OH, and it was also greater than that employed for the more reactive vinyl ethers as described earlier. The major species detected were identified as the hydroxyallyl radicals [23] (15) and (16), which were present in approximately equal proportions. In addition weak signals were obtained from Me• and from a radical assigned structure (17) [*cf.* parameters for the related species [24] (18)].

a 1.39(2H), 1.33(1H), 0.32(1H) 0.05(1H) mT

g 2.0030

(15)

a 1.32(2H), 1.42(1H), 0.38(1H) 0.04(1H) mT

g 2.0031

(16)

Bu^tOCH_2—ĊH—CH_2OH

a 2.10(α-H), 2.53(2, β-H), 1.74(2, β-H) mT

g 2.0026

(17)

HO—CH_2—ĊH—CH_2OH

a 2.146(α-H), 2.170(4, β-H) mT

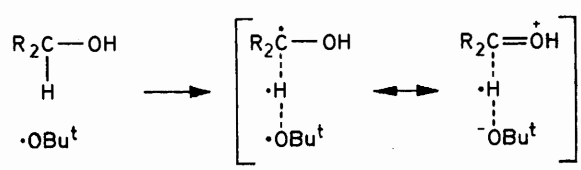
g 2.0024

(18)

These findings are in marked contrast to the results obtained for the reaction of •OH with this substrate, when the major radical detected is (18). This again illustrates the general preference shown by t-butoxyl for abstraction rather than addition.

When in the reaction with t-butoxyl the pH was reduced from 2 to <0, certain changes in the appearance of the spectrum were noted. First, the small doublet splitting arising from the exchangeable hydroxyl protons in the hydroxyallyl radicals (15) and (16) collapsed, presumably owing to the increased rate of exchange in the more acidic medium. Secondly, the concentrations of both (17) and Me• increased significantly, by factors of *ca.* 2 and 1.5, respectively; evidently the rates of both fragmentation and addition relative to abstraction increase in strongly acid solution.

(c) *The Reactions of* $Bu^tO\cdot$ *with Alcohols.*—When methanol, ethanol, or propan-2-ol was introduced into the Bu^tO_2H–Ti^{III} reaction at pH 2, the signal from the methyl radical was replaced by that due to $\cdot CH_2OH$, $\cdot CHMeOH$, or $\cdot CMe_2OH$, respectively. However, it was again noted that, compared with the analogous reaction systems with H_2O_2, considerably higher concentrations of the alcohols were required to effect complete scavenging of the oxygen-centred radical (as judged by the complete removal of signals from $Me\cdot$). Further, with ethanol and propan-2-ol no traces of signals from radicals resulting from hydrogen abstraction at the β-carbon atoms of these substrates ($\cdot CH_2CH_2OH$, $\cdot CH_2CHMeOH$) could be discerned. These differences in behaviour are in accord with the view that the t-butoxyl radical abstracts much more slowly than the hydroxyl radical; the lower rate constant for the former is consistent with its greater selectivity towards abstraction from the α-position [the transition state for which is presumably stabilised by canonical structures such as (19); *cf.* also the greater selectivity of $NH_3^{+\cdot}$ compared with $\cdot OH$ [25]].



(19)

An attempt was made to estimate the relative rates of abstraction from propan-2-ol and fragmentation of $Bu^tO\cdot$; in principle, these may be obtained by measuring the ratio $[\cdot CMe_2OH]:[Me\cdot]$ for a known alcohol concentration. However, complications arise from the fact that the methyl radical undergoes bimolecular termination somewhat more rapidly than the α-hydroxyalkyl radicals produced by abstraction.[18] Thus the termination reactions (13)—(15) (R = Me) each have different rate constants.

$$2R_2\dot{C}OH \longrightarrow \text{molecular products} \quad (13)$$

$$R_2\dot{C}OH + Me\cdot \longrightarrow \text{molecular products} \quad (14)$$

$$2Me\cdot \longrightarrow \text{molecular products} \quad (15)$$

In order to minimize such complications without resorting to complex kinetic treatments, the trap *cis*-butenedioate was employed to intercept both $Me\cdot$ and $\cdot CMe_2OH$ (from reaction of $Bu^tO\cdot$ with propan-2-ol) but not $Bu^tO\cdot$, which, as shown earlier, is unreactive towards this substrate. The system is then described by reactions (4) and (16)—(21), where R is CMe_2OH, T represents *cis*-butenedioate, and $MeT\cdot$ and $RT\cdot$ are the adducts formed with the latter.

$$Bu^tO\cdot + RH \longrightarrow Bu^tOH + R\cdot \quad (16)$$

$$\cdot Me + T \longrightarrow MeT\cdot \quad (17)$$

$$R\cdot + T \longrightarrow RT\cdot \quad (18)$$

$$2\,MeT\cdot \longrightarrow \text{molecular products} \quad (19)$$

$$2\,RT\cdot \longrightarrow \text{molecular products} \quad (20)$$

$$MeT\cdot + RT\cdot \longrightarrow \text{molecular products} \quad (21)$$

Equating the rates of formation of the adducts $MeT\cdot$ and $RT\cdot$ to their rates of destruction yields expressions (22) and (23). Dividing equation (22) by (23) gives (24).

$$k_4[Bu^tO\cdot] = 2k_{19}[MeT\cdot]^2 + k_{21}[MeT\cdot][RT\cdot] \quad (22)$$

$$k_{16}[Bu^tO\cdot][RH] = 2k_{20}[RT\cdot]^2 + k_{21}[MeT\cdot][RT\cdot] \quad (23)$$

$$\frac{k_4}{k_{16}[RH]} = \frac{[MeT\cdot](2k_{19}[MeT\cdot] + k_{21}[RT\cdot])}{[RT\cdot](2k_{20}[RT\cdot] + k_{21}[MeT\cdot])} \quad (24)$$

Since the two adducts are of similar molecular weight and would be expected to have similar radical–solvent interactions it is suggested that the assumption that $2k_{19} = 2k_{20} = k_{21}$ may be made without introducing significant errors. Thus equation (24) reduces to (25).

$$\frac{k_4}{k_{16}[RH]} = \frac{[MeT\cdot]}{[RT\cdot]} \quad (25)$$

Expression (25) was employed to determine k_4/k_{16} for propan-2-ol by varying the concentration of the latter and plotting the ratio $[MeT\cdot]/[RT\cdot]$ against $1/[Me_2CHOH]$ (Figure 2). The slope of this plot which, as predicted by

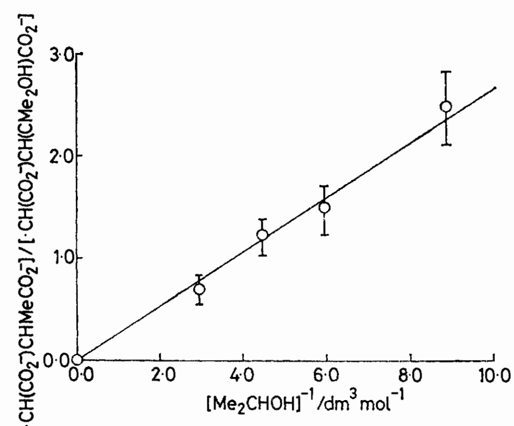


FIGURE 2 Variation of $[\cdot CH(CO_2^-)CHMeCO_2^-]/[\cdot CH(CO_2^-)CH(CMe_2OH)CO_2^-]$ with $[Me_2CHOH]^{-1}$ in the reaction of $Bu^tO\cdot$ (from Bu^tOOH and Ti^{III}) in the presence of propan-2-ol and *cis*-butenedioate (0.03 mol dm^{-3}) at pH 6.3

equation (25), passes through the origin, leads to a value for the ratio of the rate constants for fragmentation and for abstraction from propan-2-ol of $1:3.7 \pm 0.4$. If a value for the fragmentation rate constant in the range 10^6—10^7 s^{-1} is assumed, it follows that $k(Me_3CO\cdot + Me_2CHOH)$ is in the range 4×10^6—4×10^7 dm^3 mol^{-1} s^{-1}. This value is two or three orders of magnitude lower than that of the rate constant for the corresponding reaction with $\cdot OH$ (1.2×10^9 dm^3 mol^{-1} s^{-1}) [26] but is similar to that for abstraction from diphenylmethanol by $Bu^tO\cdot$ of 6.9×10^6 dm^3 mol^{-1} s^{-1} (measured by flash photolysis of a solution containing di-t-butyl peroxide and the substrate).[27]

It should be noted that this method for the determination of the relative rates of fragmentation and abstraction by Bu^{t}O· depends on the fact that the different adducts with *cis*-butenedioate have appreciably different e.s.r. parameters. In the case of propan-2-ol, this criterion is satisfactorily fulfilled (*cf.* the splitting constants collected in ref. 15); however, similar experiments could not be performed with ethanol and methanol owing to the overlap of the resonances from the appropriate adducts with those of the methyl adduct.

Finally, in view of the significant changes noted in the reactivity of Bu^{t}O· with unsaturated substrates in strongly acid media, the effect of increased acid concentration on the relative proportions of the methyl radical and the α-hydroxyalkyl radicals formed in its reactions with methanol, ethanol, and propan-2-ol were investigated. It was found that the ratio [Me·] : [$R_2\dot{C}OH$] increased with increasing acidity in the region pH *ca.* 0. The results for Me· and ·CHMeOH (from ethanol) are shown in Figure 3, in which the concentration

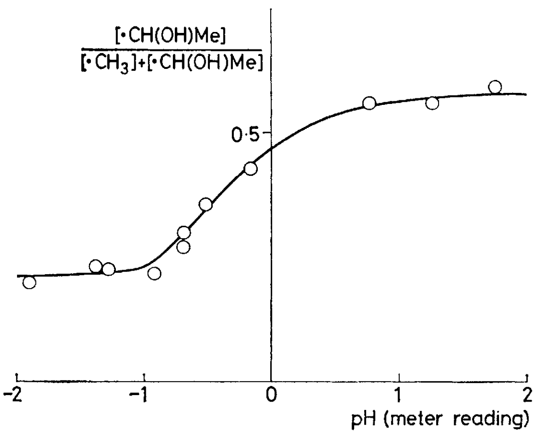


FIGURE 3 Variation of [·CHMeOH]/([·CH_3] + [·CHMeOH]) with pH (meter reading) in the reaction of Bu^{t}O· (generated from Ti^{III} and Bu^{t}OOH) with EtOH ([EtOH] 1.4 mol dm^{-3})

of ·CHMeOH, expressed as a fraction of the total detected radical concentration, is plotted against the pH meter reading; a point of inflexion occurs for a meter reading of *ca.* −0.3. Similar plots were obtained for methanol and propan-2-ol with inflexions at *ca.* −0.5 and 0.1, respectively. The *order* of the inflexions appears to follow the basicity of the three substrates, though the magnitudes of the measured values do not correspond to either measured [28] or calculated [29] values of pK_b. Further evidence that the changes in selectivity are not due to protonation of the substrates is provided by our finding that in the reaction of ·OH with CH_3CH_2OH, the ratio [·CH_2CH_2OH] : [·CHMeOH] shows no comparable changes in this acidity range. An alternative explanation must therefore by sought, and in this respect it is useful to summarise the observations made concerning the behaviour of t-butoxyl at high acidities: (i) as judged from the results with ethyl vinyl ether and furan, the rate of fragmentation of t-butoxyl increases relative to its rate of addition; (ii) as judged from the results with alcohols, the rate of fragmentation also increases relative to the rate of abstraction; (iii) as judged from the results with prop-2-en-1-ol, the rate of addition increases relative to the rate of abstraction.

These observations closely resemble those made by Davies and his co-workers following low-temperature photolysis of solutions of di-t-butyl peroxide and trifluoroacetic acid in cyclopropane in the presence of alkenes and alkanes.[9] Thus, whereas in the absence of the acid photolysis in the presence of propene yielded the allyl radical as the only detectable species, in its presence the adduct (20) was detected. These results were interpreted in terms of the formation, under acid conditions, of the t-butyl alcohol radical-cation (21). It was pointed out that, since such a species should be more electrophilic than the t-butoxyl radical, addition should be favoured over abstraction (*cf.* the behaviour of ·OH with alkenes).

$Me\dot{C}HCH_2\overset{+}{O}(H)Bu^t$ (20) $\qquad$ $Bu^tOH^{+\bullet}$ (21)

Now strictly, a pH meter may only be employed to estimate acidities down to pH *ca.* 0. For aqueous strong acid systems, pH is replaced by H_0,[20] the value for which is empirically derived by, for example, studying the ionisation of a series of indicators as the acid concentration is varied. However, it has been shown [30,31] that the acidity functions derived by these methods vary with the nature of the bases employed; further, it is also clear that the H_0 function must be redefined when high concentrations of solutes such as alcohols are employed.[31,32] As far as we are aware, reliable acidity functions are not available for the systems employed here. However, our finding that the pH meter reading for a given concentration of sulphuric acid depends not only on the concentration but also the nature of the alcohol added suggests that the difference in the points of inflexion found for Bu^{t}O· in methanol, ethanol, and propan-2-ol reflects differences in the acidity functions appropriate for each solvent. Accordingly we suggest that the change in reactivity observed is due to the protonation of Bu^{t}O·, to give $Bu^tOH^{+\bullet}$ (with pK_a *ca.* −0.3) and that further speculation on the precise nature of the solvent effect is unjustified.

EXPERIMENTAL

E.s.r. spectra were recorded on Varian E-4 and E-104 spectrometers, each equipped with 100 kHz modulation and an *X*-band klystron. Splitting constants were measured directly from the spectrometer field-scan, which was periodically recalibrated with an aqueous solution of Fremy's salt [*a*(N) 1.309 mT [33]]. All the *g* values reported were measured by comparison with that from ·CHMeOH [*g* 2.0033, itself checked by comparison with Fremy's salt (*g* 2.0055) [34]]. Where the spectra were complex, assignments were confirmed by simulation carried out on a DEC KL-10 computer with a program (kindly supplied by Dr M. F. Chiu) incorporating Lorentzian line-shapes and second-order effects. Relative radical concentrations were determined from measurements of peak heights (where the appropriate line-widths were the same), by numerical double integration of selected peaks,[35] or (especially where spectra were complex with many overlapping resonances) by spectrum simulation.

The flow system comprised a modified Varian three-way perspex mixing chamber in conjunction with an aqueous sample cell. In most of the experiments the flow was driven by a Watson-Marlowe HR flow inducer positioned on the tubings leading to the entry ports of the mixing chamber. This was adjusted to give an overall flow rate of *ca.* 1.5—2.5 ml s^{-1}, which corresponds to a mixing time of *ca.* 50—80 ms. In some experiments employing a flow inducer, the associated pulsing of the flow led to regular fluctuations in the signal intensity as a signal was scanned (although the peak envelope remained the same). These were especially noticeable for long lived radicals (*e.g.* the hydroxyl adduct of *cis*-butenedioate) or when slow flow rates and low time constants were employed (though the fluctuations could be almost completely eliminated by employing high flow rates, or by positioning the pump on the exit tubing rather than on the entry tubings). However, in experiments with *cis*-butenedioic acid gravity feed was also employed (with *ca.* 2 m head of solution); the flow rate was then adjusted to give an overall rate of *ca.* 5 ml s^{-1}. No significant differences were observed in the results obtained under the different sets of conditions.

pH Measurements were achieved by inserting a Russell pH Ltd. glass electrode (coupled to a Pye–Unicam PW 9410 pH meter) into a small chamber positioned immediately above the cavity of the spectrometer, and through which the effluant stream passed. The small dead volume between mixing and pH measurement (*ca.* 10—15 ml) allowed relatively rapid response to pH fluctuations during a given flow experiment. The error in pH measurements is estimated as $\pm$ 0.05 pH units, except in the pH range 4—7, when estimates to no better than $\pm$ 0.1 of a pH unit could be made. These errors stem, at least in part, from pH changes accompanying the initiation reaction down the flow tube. The greater error between pH 4 and 7 presumably reflects the poorer buffering properties of the solution in that range. The pH meter was calibrated using commercially available buffer solutions.

The compositions of the three streams of the flow system were typically as follows. Stream (i) contained titanium(III) sulphate (0.003—0.01 mol dm^{-3}), stream (ii) contained t-butyl hydroperoxide (0.01—0.1 mol dm^{-3}), with the organic substrate at the required concentration in stream (iii). For reactions at pH < 2.5, stream (i) [and in some cases stream (ii)] contained sufficient concentrated sulphuric acid to yield a solution after mixing of the required pH. For pH > 2.5, stream (i) also contained EDTA (6 g dm^{-3}), and the pH was adjusted with concentrated ammonia solution (*d* 0.880). In the experiment with the *aci*-anion of nitromethane, ammonia was also added to the third stream (to give a pH of *ca.* 9). In each case solutions were made up in water deoxygenated with a nitrogen purge and were held under a nitrogen atmosphere during use.

Chemicals employed were commercially available (and used without further purification) except for the following. The monomethyl ester of *cis*-butenedioic acid was prepared from the reaction between methanol and maleic anhydride.[36] 1-Methoxy-2-t-butoxyethane was prepared by a modification of a reported method [37] in which 2-methylpropene (prepared [38] by dehydration of 2-methylpropan-2-ol using oxalic acid) was bubbled through a solution of concentrated sulphuric acid in 2-methoxyethanol and the resulting solution was stirred for 24 h. 1,2-Di-t-butoxyethane was prepared similarly by the dropwise addition of 2-methylpropan-2-ol to a stirred solution of concentrated sulphuric acid and ethane-1,2-diol; the mixture was again stirred for 24 h. In both cases the original purification procedure was followed.[37]

We thank the S.R.C. for a studentship (for P. D. R. M.) and the British Petroleum Company Ltd. for a studentship (for P. S. W.).

[1/576 *Received*, 10*th April*, 1981]

REFERENCES

[1] Part 60, B. C. Gilbert, R. O. C. Norman, and P. S. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1981, 207.
[2] (*a*) J. Q. Adams, *J. Am. Chem. Soc.*, 1968, **90**, 5363; (*b*) P. J. Krusic and J. K. Kochi, *ibid.*, p. 7154; (*c*) J. K. Kochi and P. J. Krusic, *ibid.*, p. 7157.
[3] For general reviews of the chemistry of t-butoxyl in non-aqueous solvents see J. K. Kochi, ' Free Radicals ', ed. J. K. Kochi, Wiley Interscience, New York, 1973, vol. 2, p. 665; J. A. Howard, *Adv. Free-Radical Chem.*, 1972, **4**, 49; E. S. Huyser, *ibid.*, 1975, **1**, 77.
[4] M. F. R. Mulcahy, J. R. Steven, and J. C. Ward, *Aust. J. Chem.*, 1965, **18**, 1177.
[5] H. Fischer and G. Giacometti, *J. Polym. Sci. C*, 1967, **16**, 2763.
[6] C. Walling and P. J. Wagner, *J. Am. Chem. Soc.*, 1964, **86**, 3368.
[7] B. C. Gilbert, R. G. G. Holmes, H. A. H. Laue, and R. O. C. Norman, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1047.
[8] B. C. Gilbert, R. G. G. Holmes, and R. O. C. Norman, *J. Chem. Res.*, 1977; (*S*) 1, (*M*) 0101.
[9] P. G. Cookson, A. G. Davies, B. P. Roberts, and M.-W. Tse, *J. Chem. Soc., Chem. Commun.*, 1976, 937.
[10] A. Albert and E. P. Serjeant, ' Ionisation Constants of Acids and Bases ', Methuen, London, 1962.
[11] M. McMillan and R. O. C. Norman, *J. Chem. Soc. B*, 1968, 590.
[12] D. J. Edge and R. O. C. Norman, *J. Chem. Soc. B*, 1969, 182.
[13] See also, *e.g.* G. Czapski, *J. Phys. Chem.*, 1971, **75**, 2957; B. C. Gilbert, R. O. C. Norman, and R. C. Sealy, *J. Chem. Soc., Perkin Trans. 2*, 1973, 2174.
[14] D. J. Carlsson and K. U. Ingold, *J. Am. Chem. Soc.*, 1967, **89**, 4891.
[15] W. T. Dixon, J. Foxall, and G. H. Williams, *J. Chem. Soc., Faraday Trans. 2*, 1974, **70**, 1614.
[16] P. Neta, *J. Phys. Chem.*, 1971, **75**, 2570.
[17] M. P. Bertrand and J.-M. Surzur, *Tetrahedron Lett.*, 1976, 3451.
[18] B. C. Gilbert, R. O. C. Norman, and R. C. Sealy, *J. Chem. Soc., Perkin Trans. 2*, 1975, 303.
[19] B. C. Gilbert, R. O. C. Norman, and P. S. Williams, *J. Chem. Soc., Perkin Trans. 2*, 1980, 647.
[20] A. J. Dobbs, B. C. Gilbert, and R. O. C. Norman, *J. Chem. Soc., Perkin Trans. 2*, 1972, 786; B. C. Gilbert, R. O. C. Norman, and A. J. Dobbs, *J. Magn. Reson.*, 1973, **11**, 100.
[21] A. Hudson and K. D. J. Root, *Tetrahedron*, 1969, **21**, 5311.
[22] R. H. Schuler, G. P. Laroff, and R. W. Fessenden, *J. Phys. Chem.*, 1973, **77**, 456.
[23] A. J. Dobbs, B. C. Gilbert, H. A. H. Laue, and R. O. C. Norman, *J. Chem. Soc., Perkin Trans. 2*, 1976, 1044; R. Livingston and H. Zeldes, *J. Chem. Phys.*, 1966, **44**, 1245.
[24] P. Smith, R. A. Kaba, and P. B. Wood, *J. Phys. Chem.*, 1974, **78**, 117.
[25] B. C. Gilbert and P. R. Marriott, *J. Chem. Soc., Perkin Trans. 2*, 1977, 987.
[26] P. Neta, *Adv. Phys. Org. Chem.*, 1976, **12**, 223.
[27] R. D. Small and J. C. Scaiano, *J. Am. Chem. Soc.*, 1978, **100**, 296.
[28] D. G. Lee and R. Cameron, *J. Am. Chem. Soc.*, 1971, **93**, 4724; P. D. Bartlett and J. D. McCollum, *ibid.*, 1956, **78**, 1441.
[29] L. S. Levitt and B. W. Levitt, *Tetrahedron*, 1971, **27**, 3777.
[30] M. A. Paul and F. A. Long, *Chem. Rev.*, 1957, **57**, 1.
[31] D. Dolman and R. Stewart, *Can. J. Chem.*, 1967, **45**, 903.

[32] B. Gutbezahl and E. Grunwald, *J. Am. Chem. Soc.*, 1953, **75**, 565.
[33] R. J. Faber and G. K. Fraenkel, *J. Chem. Phys.*, 1967, **47**, 2462.
[34] J. Q. Adams, S. W. Nicksic, and J. R. Thomas, *J. Chem. Phys.*, 1966, **45**, 654.
[35] P. B. Ayscough, 'Electron Spin Resonance in Chemistry', Methuen, London, 1967, p. 442.
[36] S. M. Spatz and H. Stone, *J. Org. Chem.*, 1958, **23**, 1559.
[37] J. W. Evans and K. R. Edlund, *Ind. Eng. Chem.*, 1936, **28**, 1186.
[38] H. S. Davis, *J. Am. Chem. Soc.*, 1928, **50**, 2769.