On the Use of the Electron Spin Resonance–Flow Technique in the Study of Short-lived Radicals

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The use of double mixing in the study of a mixture of alcohol radicals by means of H_2O_2 + Ti^{III} redox system is shown to be superfluous. The ratio of the concentrations of two such radicals is found to be independent of the order of introduction of the parent alcohols to the system. The ratio of radical concentrations is determined by simple competition of the alcohols for the primary OH radicals but side reactions and differences in recombination rates are shown to influence considerably the ratio of the observed radical concentrations. Limitations on mechanistic conclusions and kinetic studies of such systems are discussed.

THE use of flow systems when studying free radicals is frequently employed in conjunction with e.s.r. detection. With this technique, free radicals, $P^{\cdot}$ are produced by mixing the two reagents A and B [reaction (1)] and

$$A + B \xrightarrow{k_1} P^{\cdot} \qquad (1)$$

rapidly flow into the cavity where their e.s.r. spectra are recorded. Alternatively, secondary free radicals $S^{\cdot}$ can be produced by adding a solute, SH, to the mixture, which then reacts with $P^{\cdot}$ [reaction (2)].

$$P^{\cdot} + SH \longrightarrow S^{\cdot} + \text{products} \qquad (2)$$

This latter method was used in one of two ways:

(a) mixing A, B, and SH in one mixing stage, with reaction (2) following immediately after reaction (1) and (b) using double mixing, where $P^•$ is produced by (1) in the first mixing stage and is then mixed with SH and $S^•$ is formed thereafter through reaction (2).

One of the reactions which is most extensively used to study free radicals by this method is the $Ti^{III} + H_2O_2$ system.[1-7] This system generates $OH^•$ as primary radicals, which in turn react with RH, yielding the secondary radicals $R^•$ [reactions (3) and (4)]. The

$$Ti^{III} + H_2O_2 \longrightarrow Ti^{IV} + OH^• + OH^- \qquad (3)$$

$$RH + OH \longrightarrow H_2O + R^• \qquad (4)$$

assumption made in most of these studies is that reaction (3) is complete immediately after mixing the two reagents. This assumption has been recently challenged[8-10] and it has been shown that in most cases reaction (3) is far from being complete when the mixture reaches the cavity.[11] It was shown that for short-lived radicals, $R^•$, the radicals observed in the cavity are those which are formed there, and their concentration can be calculated assuming the steady state approximation for $OH^•$ and $R^•$.[8,9] Furthermore, this kinetic analysis would imply that double mixing, *i.e.* method (b), is meaningless, as any radical observed in the cavity is as a matter of fact formed there. For radicals with high recombination rate constants ($\geqslant 10^9$ l mol^{-1} s^{-1}), if $R^•$ had been formed immediately after mixing, $[R^•]$ in the cavity would be below the detection limit of most e.s.r. instruments.

Norman and West[12] used the double mixing method, assuming that under their experimental conditions reaction (3) is complete after the first mixing. They formed $R^{1•}$ by mixing Ti^{III}, H_2O_2, and R^1H in the first mixer and then, in a second mixer, R^2H was added. Both $R^{1•}$ and $R^{2•}$ were then observed in the cavity. This result was attributed by them to reaction (5).

$$R^{1•} + R^2H \xrightarrow{k_5} R^{2•} + R^1H \qquad (5)$$

Furthermore, they noticed that the ratio $[R^{1•}]/[R^{2•}]$ was strongly dependent on the mixing order. These results are in apparent contradiction to our hypothesis.[8,9] Since this method is so widely used and since controversial conclusions concerning this system are drawn, we decided to recheck the $Ti^{III} + H_2O_2$ system in the presence of several alcohols using the e.s.r. double mixing flow technique.

EXPERIMENTAL

Materials.—30% Hydrogen peroxide, 70% perchloric acid, t-butyl alcohol (all Merck), propan-2-ol, methanol (Frutarom Laboratory Chemicals), all analytically pure, vanadyl sulphate (Purum, Fluka), and 15% titanous sulphate solutions (technical, B.D.H.) were all used without further purification. Hydrogen peroxide was determined by titration with standard permanganate solutions. Titanium and vanadium were determined spectrophotometrically as peroxy-complexes after treatment with an excess of H_2O_2 (ε_{412} 652 l mol^{-1} cm^{-1} for titanium, ε_{404} 198 l mol^{-1} cm^{-1} for vanadium). The water used was either singly or triply distilled but no difference was observed by replacing triply distilled with singly distilled water. All solutions were deaerated by bubbling dry nitrogen through them for at least 15 min.

Mixing Cells.—Three mixing cells were used, all of which were attached to a Varian 4548 quartz aqueous solution cell. The first was a single mixing cell (Figure 1a) with a ' dead volume ' of 0·14 cm^3 between mixing and the centre of the observation cell (g—h). The second was a double mixing cell (Figure 1b) with ' dead volumes ' of 0·19 cm^3 between first and second mixing points (f—g) and 0·16 cm^3 between second mixing and centre of observation cell (g—h). The third was identical to the second except the first ' dead volume ' (f—g), which was 0·02 cm^3.

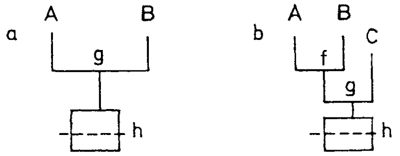

FIGURE 1 Mixing cells: a, single mixing cell; b, double mixing cell

Flow Systems.—Two types of flow systems were used. In the first, the solutions were stored in 2 l flasks and forced through the system by the pressure of N_2 (2·0 cm^3 s^{-1} total flow rate). In the second method solutions were stored in syringes and were driven by motor (2·8 cm^3 s^{-1} total flow rate). The latter method had the advantage that flow ratios of the various solutions were fixed at a constant 1 : 1 : 1 ratio, while in the gas-pressure method flow ratios changed somewhat during a set of experiments, probably due to changes in the heights of the solutions in the containers. This effect was more pronounced when the double mixing cells were used.

E.s.r. Apparatus.—E.s.r. spectra were recorded on a Varian X-band 4502 spectrometer with 100 kHz modulation. Relative intensities of the e.s.r. signals were calibrated with $VOSO_4$ solutions without removing the cell in order to eliminate misalignment problems when comparing VO^{2+} with the radicals. Signal areas were calculated as $\Delta H^2 \times h$ where ΔH is the peak-to-peak line width of the first derivative signal and h is its peak-to-peak height. Each spectrum was taken at least three times and

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[1] R. O. C. Norman and B. C. Gilbert, *Adv. Phys. Org. Chem.*, 1967, **5**, 53.

[2] T. Shiga, A. Boukhors, and P. Douzou, ' Recent Developments in Magnetic Resonance in Biological Systems,' eds. S. Fujiwara and L. H. Piette, Hirokawa, Tokyo, 1968.

[3] R. E. Florin, F. Sicilio, and L. A. Wall, *J. Res. Nat. Bur. Stand. Sect. A*, 1968, 49.

[4] W. T. Dixon and R. O. C. Norman, *J. Chem. Soc.*, 1963, 3119.

[5] D. J. Edge, B. C. Gilbert, R. O. C. Norman, and P. R. West, *J. Chem. Soc.* (*B*), 1971, 189.

[6] R. E. James and F. Sicilio, *J. Phys. Chem.*, 1970, **74**, 1166.

[7] T. Shiga, *J. Phys. Chem.*, 1965, **69**, 3805.

[8] G. Czapski, *J. Phys. Chem.*, 1971, **75**, 2957.

[9] G. Czapski, A. Samuni, and D. Meisel, *J. Phys. Chem.*, 1971, **75**, 3271.

[10] C. E. Burchill, *J. Phys. Chem.*, 1971, **75**, 168.

[11] A. Samuni, D. Meisel, and G. Czapski, *J.C.S. Dalton*, 1972, 1273.

[12] R. O. C. Norman and P. R. West, *J. Chem. Soc.* (*B*), 1969, 389.

each experiment was repeated at least twice with freshly prepared solutions.

RESULTS AND DISCUSSION

We produced, using the syringe technique, mixtures of $\dot{C}H_2OH$ and $Me_2\dot{C}OH$ or $\dot{C}H_2OH$ and CH_2CMe_2OH radicals by first mixing $H_2O_2 + R^1H$ with Ti^{III}. The solution leaving the first mixer was then mixed with the other alcohol, R^2H, and flowed through the e.s.r. cavity. The spectra and ratios of concentrations of these radicals were recorded, changing the order of introduction of the various reactants. Results are presented in Table 1. The spectrum observed for $\dot{C}H_2OH$ was a triplet of doublets (attributed to the OH hydrogen atom), for $\dot{C}H_2CMe_2OH$ a triplet of septets (with the expected 1,6,15,20,15,6,1 ratio of intensities) and for $Me_2\dot{C}OH$ a septet of singlets with the above ratio of intensities in accordance with previous results.[4,13] No splitting due to the OH hydrogen atoms was observed for $Me_2\dot{C}OH$, probably due to fast H^+ exchange at the low pH (*ca.* 1), as suggested previously.[13] In experiments with Pr^iOH the β-radical $\dot{C}H_2MeCHOH$ was also observed, but its concentration never exceeded 10% of the α-isomer; thus this radical was neglected in our calculations. When a mixture of two radicals was recorded, some of the lines overlapped. In order to achieve better resolution when the spectrum of the $\dot{C}H_2OH$ radical was taken simultaneously with another, the lower intensity higher-field line of its triplet was recorded; the same procedure was carried out for the $\dot{C}H_2CMe_2OH$ radical. For the $Me_2\dot{C}OH$ radical, the higher-field ' 15 intensity line ' was recorded. Figure 2 shows such spectra for mixtures of $\dot{C}H_2OH + \dot{C}H_2CMe_2OH$ and $\dot{C}H_2OH + Me_2\dot{C}OH$ radicals. This procedure enabled us to determine each radical in the mixture without interference. When calculating the concentrations of radicals, the appropriate intensity factors were taken into account. No difficulties were encountered on estimating ΔH for the Bu^tOH or Pr^iOH radicals, but ΔH for the MeOH radical was liable to a larger experimental error since the two splittings attributed to the OH hydrogen atom somewhat overlapped each other. Thus ΔH for the MeOH radical was calibrated against the Bu^tOH radical when each of the alcohols was introduced separately to the system, assuming that the same concentration of radicals was present. This assumption will be justified later. It should be stressed, however, that this method of calibration should have no effect on relative intensities and only absolute concentrations of the $\dot{C}H_2OH$ radical will be affected.

TABLE 1

Effect of the order of introduction of alcohols on radical concentrations [a]

Exp. no.	First mixer A	First mixer B	Second mixer	t_{f-g}/ms [b]	t_{g-h}/ms [c]	$\dot{C}H_2OH$: $Me_2\dot{C}OH$	$[\dot{C}H_2OH] + [Me_2\dot{C}OH]$/μM	$[\bar{R}$ calc]/μM [d]
1	8mM-Ti^{III}	25mM-H_2O_2 + 1M-MeOH	1M-Bu^tOH	70	60	$1{\cdot}5_8$	2·0	1·15
2	1M-Bu^tOH	25mM-H_2O_2 + 1M-MeOH	8mM-Ti^{III}	70	60	$1{\cdot}5_9$	2·2	1·47
3	8mM-Ti^{III}	1M-Bu^tOH	25mM-H_2O_2 + 1M-MeOH	70	60	$1{\cdot}5_9$	2·2	1·47
4	8mM-Ti^{III}	25mM-H_2O_2 + 1M-Bu^tOH	1M-MeOH	70	60	$1{\cdot}5_2$	2·0	1·15
5	1M-MeOH	25mM-H_2O_2 + 1M-Bu^tOH	8mM-Ti^{III}	70	60	$1{\cdot}5_0$	2·2	1·47
6	1M-MeOH	8mM-Ti^{III}	25mM-H_2O_2 + 1M-Bu^tOH	70	60	$1{\cdot}4_5$	2·3	1·47
7	1M-MeOH	8mM-Ti^{III}	25mM-H_2O_2 + 1M-Bu^tOH	7	60	$1{\cdot}5_2$	2·2	1·47
8	8mM-Ti^{III}	25mM-H_2O_2 + 1M-Bu^tOH	1M-MeOH	7	60	$1{\cdot}5_0$	2·2	1·18
						$\dot{C}H_2OH$: $\dot{C}H_2CMe_2OH$	$[\dot{C}H_2OH] + [\dot{C}H_2CMe_2OH$/μM	
9	8mM-Ti^{III}	25mM-H_2O_2 + 1M-MeOH	1M-Pr^iOH	70	60	$0{\cdot}7_0$	1·5	1·15
10	1M-Pr^iOH	25mM-H_2O_2 + 1M-MeOH	8mM-Ti^{III}	70	60	$0{\cdot}6_7$	1·7	1·47
11	8mM-Ti^{III}	25mM-H_2O_2 + 1M-Pr^iOH	1M-MeOH	70	60	$0{\cdot}6_7$	1·6	1·15

[a] Motor-driven syringe flow system, double-mixing cell, all solutions at 0·1M-$HC1O_4$. [b] t_{i-g} = time interval between first and second mixing points. [c] t_{g-h} = time interval between second mixer and the centre of the observation cell (the time between second mixer and the entrance to the observation cell is 16 ms). [d] $\bar{R}$ = average total radical concentration calculated according to equation (8).

The first point to stress is that the relative intensities of the alcohol radical signals are entirely independent of the order of mixing of the reactants. Furthermore $[R^{1\cdot}] : [R^{2\cdot}]$ turns out to be independent of the time lag between the initiating reaction (3) and entry into the observation cell (*e.g.* results of experiment 1 as compared with experiments 2 or 8 in Table 1). Our results (experi-

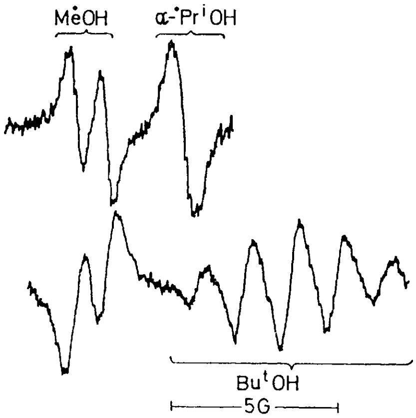

FIGURE 2 Simultaneously recorded partial spectra of mixtures of two alcohol radicals taken for estimation of $[R^{1\cdot}]$ and $[R^{2\cdot}]$: upper $\dot{C}H_2OH + Me_2\dot{C}OH$; lower $\dot{C}H_2OH + \dot{C}H_2CMe_2OH$

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[13] R. Livingston and H. Zeldes, *J. Chem. Phys.*, 1966, **44**, 1245.

ments 9—11 in Table 1) contradict those obtained by Norman and West[12] who found a change of about an order of magnitude in $[\mathrm{R}^{1\cdot}]/[\mathrm{R}^{2\cdot}]$ on executing similar experiments. When we used the gas-driven flow system we obtained similar results to those given in Table 1, but these results were much more scattered, probably due to variations in mixing ratios. The constancy of the ratio $[\mathrm{R}^{1\cdot}]/[\mathrm{R}^{2\cdot}]$ rules out any contribution of the conversions (6) or (7) under our (and Norman and West's) experimental conditions. After discussing this matter with Professor Norman, we both believe that their results may be due to inefficient mixing.

$$\dot{\mathrm{C}}\mathrm{H_2OH} + \mathrm{Me_2CHOH} \longrightarrow \mathrm{MeOH} + \mathrm{Me_2}\dot{\mathrm{C}}\mathrm{OH} \qquad (6)$$

$$\dot{\mathrm{C}}\mathrm{H_2CMe_2OH} + \mathrm{MeOH} \longrightarrow \mathrm{Bu^tOH} + \dot{\mathrm{C}}\mathrm{H_2OH} \qquad (7)$$

This does not rule out the possibility of reactions (6) and (7) as long as $k_5 \leqslant 10^3$ l mol^{-1} s^{-1} as found by Burchill *et al.* for the conversion of β- to α-radicals of $\mathrm{Pr^iOH}$ or EtOH.[14,15]

Another feature seen from Table 1 is the approximate constancy of $[\mathrm{R}^{1\cdot}] + [\mathrm{R}^{2\cdot}]$ at a given time after initiation in spite of variation in order of introduction of the various substrates; thus the method of calibration of the methanol radical is considered justified. The variation in the time interval between initiation and observation by a factor of 2 did change $[\mathrm{R}^{1\cdot}] + [\mathrm{R}^{2\cdot}]$ by *ca.* 10—15% only. This result is in agreement with the suggestion that almost all the radicals detected in the cavity are produced therein. The average total radical concentration ($\bar{\mathrm{R}}$) present in the observation cell, is given by equation (8),[8] provided the initial concentrations satisfy $A_0 > B_0$, where $\mathrm{R_{ss}}$ is the steady

$$\bar{\mathrm{R}} = \frac{\int_{t_1}^{t_2} \mathrm{R_{ss}}\,\mathrm{d}t}{\int_{t_1}^{t_2} \mathrm{d}t} = \frac{1}{t_2 - t_1}\left(\frac{2B_0}{k_1 k_{10} A_0}\right)^{\frac{1}{2}} [\exp(-\tfrac{1}{2}k_1 A_0 t_1) - \exp(-\tfrac{1}{2}k_1 A_0 t_2)] \qquad (8)$$

state concentration of R at time t after initiation given by equation (9) where t_1 is the time between the initiation

$$\mathrm{R_{ss}} = \left(\frac{k_1 A_0 B_0 \mathrm{e}^{-k_1 A_0 t}}{2k_{10}}\right)^{\frac{1}{2}} \qquad (9)$$

of reaction (1) and the entrance to the observation cell while t_2 is the time between initiation and the exit from the observation cell, and k_{10} is the second-order rate constant of the recombination reaction (10). It

$$\mathrm{R}^{\cdot} + \mathrm{R}^{\cdot} \xrightarrow{k_{10}} \text{products} \qquad (10)$$

should be noted that under the experimental conditions generally used, the reactions $\mathrm{OH^{\cdot}} + \mathrm{OH^{\cdot}}$ and $\mathrm{OH^{\cdot}} + \mathrm{H_2O_2}$ are negligible as compared to (4). This calculation assumes only one radical is formed through (4). If several different radicals are produced through this reaction, then $\bar{\mathrm{R}}$ and $\mathrm{R_{ss}}$ refer to the sum of the radicals, provided that the recombination reaction (10) for all radicals has about the same rate constant.

Results of this calculation are shown in the final column of Table 1 where it can be seen that variations are $<\pm 15\%$ of the average value which is less than the experimental error of the calibration of the absolute concentrations. No perfect agreement is expected upon comparing the computed $\bar{\mathrm{R}}$ with the experimental values for the sum of the radicals mainly because of uncertainty in the effective volume of the cell and inaccuracy of calibration. A factor of 2 between these two values is considered satisfactory.

If our assumptions above are correct we can show that equation (11) holds where k_{12} and k_{13} are the corre-

$$[\mathrm{R}^{1\cdot}]/[\mathrm{R}^{2\cdot}] = k_{12}[\mathrm{R^1H}]/k_{13}[\mathrm{R^2H}] \qquad (11)$$

sponding rates of the hydrogen abstractions (12) and (13). Equation (11) will hold provided that $2k_{14} \simeq k_{15} \simeq 2k_{16}$,

$$\mathrm{OH} + \mathrm{R^1H} \longrightarrow \mathrm{R}^{1\cdot} + \mathrm{H_2O} \qquad (12)$$

$$\mathrm{OH} + \mathrm{R^2H} \longrightarrow \mathrm{R}^{2\cdot} + \mathrm{H_2O} \qquad (13)$$

$$\mathrm{R}^{1\cdot} + \mathrm{R}^{1\cdot} \longrightarrow \text{products} \qquad (14)$$

$$\mathrm{R}^{1\cdot} + \mathrm{R}^{2\cdot} \longrightarrow \text{products} \qquad (15)$$

$$\mathrm{R}^{2\cdot} + \mathrm{R}^{2\cdot} \longrightarrow \text{products} \qquad (16)$$

which is nearly the case with the alcohols studied here, as was found by Hayon *et al.*[16] from pulse radiolysis studies ($2k_{10,\mathrm{MeOH}} = 2{\cdot}4 \times 10^9$, $2k_{10,\mathrm{Pr^iOH}} = 1{\cdot}4 \times 10^9$, $2k_{10,\mathrm{Bu^tOH}} = 1{\cdot}4 \times 10^9$ l mol^{-1} s^{-1}). Effects of differences in the values of k_{10} will be discussed later. We measured the ratio $[\mathrm{R}^{1\cdot}]/[\mathrm{R}^{2\cdot}]$ as a function of $[\mathrm{R^1H}]/[\mathrm{R^2H}]$ by changing $[\mathrm{R^1H}]$ and keeping $[\mathrm{R^2H}]$ constant and *vice versa* ($\mathrm{R^1H} = \mathrm{MeOH}$; $\mathrm{R^2H}$ either $\mathrm{Bu^tOH}$ or $\mathrm{Pr^iOH}$), using the single mixing cell. The ratio $[\mathrm{R}^{1\cdot}]/[\mathrm{R}^{2\cdot}]$ is plotted against $[\mathrm{R^1H}]/[\mathrm{R^2H}]$ in Figure 3 yielding a straight line as expected from equation (11). Any serious contribution due to reaction (5) should cause pronounced deviation from linearity and/or observable intercept. From the slope of the corresponding line we derive $k_{\mathrm{OH+MeOH}}/k_{\mathrm{OH+Bu^tOH}} = 1{\cdot}60$ slightly lower but in excellent agreement with previous, most accurate data obtained by pulse radiolysis (1·73).[17] Chemical competition in the Fenton reagent[18] gave a somewhat higher value (2·2). The sum $[\dot{\mathrm{C}}\mathrm{H_2OH}] + [\dot{\mathrm{C}}\mathrm{H_2CMe_2OH}]$ plotted in Figure 3 is constant within ±10% on changing the alcohol concentration by a factor of *ca.* 10, as expected. This constancy provides further confirmation for the validity of our method for the calibration of $\dot{\mathrm{C}}\mathrm{H_2OH}$ concentration. The slope of the corresponding line in Figure 3 for MeOH–$\mathrm{Pr^iOH}$ competition is 0·67, which is appreciably higher than the value $k_{\mathrm{OH+MeOH}}/$

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[14] C. E. Burchill and I. S. Ginns, *Canad. J. Chem.*, 1970, **48**, 1232.

[15] C. E. Burchill and I. S. Ginns, *Canad. J. Chem.*, 1970, **48**, 2628.

[16] M. Simic, P. Neta, and E. Hayon, *J. Phys. Chem.*, 1969, **73**, 3794.

[17] R. L. Willson, C. L. Greenstock, G. E. Adams, R. Wagman, and L. M. Dorfman, *Internat. J. Radiation Phys. Chem.*, 1971, **3**, 211.

[18] C. Walling and S. Kato, *J. Amer. Chem. Soc.*, 1971, **93**, 4275.

$k_{OH + Pr^iOH} = 0{\cdot}42$ given in the literature.[17] Since we neglected the β-radical throughout our treatment, our value should be lowered by *ca.* 10% to ∼0·61, which is still significantly higher than the previously determined value. Several factors might cause this discrepancy.

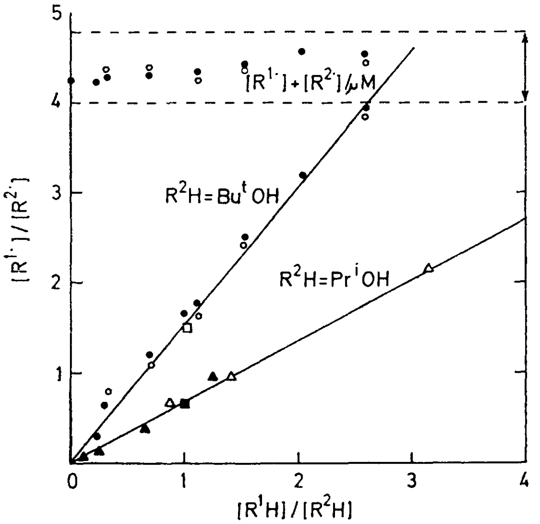

FIGURE 3 The dependence of the ratio $[R^{1\cdot}]/[R^{2\cdot}]$ and the sum $[R^{1\cdot}] + [R^{2\cdot}]$ on $[R^1H]/[R^2H]$ (R^1H = MeOH, R^2H = Bu^tOH or Pr^iOH): △ [MeOH] = 0·42M; ▲ [Pr^iOH] = 0·57M; ○ [MeOH] = 0·55M; ● [Bu^tOH] = 0·55M; □, ■ values from Table 1. $[H_2O_2]_0$ = 12mM, $[Ti^{III}]_0$ = 4mM, t_{g-h} = 70 ms, single mixing cell

For the above discussion we neglected the chain initiating reaction (17). Such reactions have been

$$\dot{R} + H_2O_2 \longrightarrow OH + \text{products} \qquad (17)$$

shown to occur during alcohol oxidation in the Ti^{III} + H_2O_2 system at high H_2O_2 concentrations[12] and during radiolytic[9,14,15,19] and photolytic[20] oxidation of alcohols in the presence of H_2O_2. By means of the latter two methods, Burchill *et al.* determined a value of k_{17} of 5×10^4 l mol^{-1} s^{-1} [15] for the MeOH radical and 5×10^5 l mol^{-1} s^{-1} [20] for the α-radical of Pr^iOH. Quantitatively as a result of this reaction our observed value for $k_{OH + MeOH}/k_{OH + Bu^tOH}$ should be somewhat lower than the true one since the β-Bu^tOH radical is expected to reduce H_2O_2 by reaction (17) much more slowly than the $\dot{C}H_2OH$ radical, while the contrary holds for the observed $k_{OH + MeOH}/k_{OH + Pr^iOH}$ value. We examined quantitatively this effect by numerically integrating the rate equations for reactions (3), (10), (12), (13), and (17) on a CDC 6400 computer. Under our experimental conditions ($[Ti^{III}]_0$ = 4mM, $[H_2O_2]_0$ = 10mM, t = 50 ms) and taking $2k_{10} = 2 \times 10^9$ l mol^{-1} s^{-1},[16] $k_{17} = 5 \times 10^4$ l mol^{-1} s^{-1} [15] for the MeOH radical and zero for the Bu^tOH radical, no deviation from linearity was observed (see Figure 4) upon changing the ratio [MeOH]/[Bu^tOH] from 0·1 to 10, and less than 5% reduction in the slope could be detected (Figure 4). The value of $[R^{1\cdot}]/[R^{2\cdot}]$ for this system changed by <3% with time from 5 up to 100 ms. Thus we may conclude that the chain length is very short in this system under our experimental conditions. If we had taken $k_{17} = 5 \times 10^5$ l mol^{-1} s^{-1}, which corresponds to the Pr^iOH–Bu^tOH system (which we have not studied experimentally) or, alternatively, if we had taken higher H_2O_2 concentrations such a system would have shown similar but much more pronounced effects (Figure 4). The MeOH–Pr^iOH system is somewhat more complicated since both α-radicals react with H_2O_2 with the above mentioned rate constants. Numerical integration along with some experimental results of this system are shown in Figure 5. Even in the cases where reaction (17) is not negligible, the curves in Figure 5 yield straight lines but their slopes differ from k_{12}/k_{13}. Reduction in both $[H_2O_2]_0$ and $[Ti^{III}]_0$ by an order of magnitude had no effect on the slope (computed and experimental). This seemingly surprising result is readily explained by visualizing that the reduction in both $[H_2O_2]_0$ and $[Ti^{III}]_0$ results in a corresponding reduction in radical concentration and thus in the rate of reaction (10), along with a reduction in the rate of reaction (17). The slope, for such experimental conditions, is therefore higher than the ratio k_{12}/k_{13}. On the contrary, lowering $[H_2O_2]_0$ to 1mM and increasing $[Ti^{III}]_0$ to 10mM resulted in a value of 0·45 which is nearly equal to k_{12}/k_{13}. In the latter case, reaction (17) is evidently slow compared with reaction (10) and the chain length is negligibly small. The experimental results yielding straight lines and the slopes of these lines, for both the MeOH–Bu^tOH and MeOH–Pr^iOH systems are in full agreement with the computed values, taking into account reactions (3), (10), (12), (13), and (17). (The rate constants used for these reactions are the literature values, but assume $2k_{14} = k_{15} = 2k_{16} = 2 \times 10^9$ l mol^{-1} s^{-1}.) It might be argued that

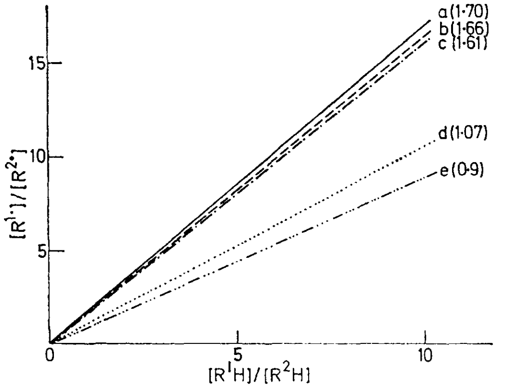

FIGURE 4 Computed effect of the reaction $R^{1\cdot} + H_2O_2$ on the ratio $[R^{1\cdot}]/[R^{2\cdot}]$: a, $k_{17} = 0$; b, $k_{17} = 5 \times 10^4$ l mol^{-1} s^{-1}, $[H_2O_2]_0$ = 10mM; c, $k_{17} = 5 \times 10^4$ l mol^{-1} s^{-1}, $[H_2O_2]_0$ = 20mM; d, $k_{17} = 5 \times 10^5$ l mol^{-1} s^{-1}, $[H_2O_2]_0$ = 10mM; e, $k_{17} = 5 \times 10^5$ l mol^{-1} s^{-1}, $[H_2O_2]_0$ = 20mM. Numbers in parentheses indicate slopes. $[Ti^{III}]_0$ = 4mM, t = 50 ms, $2k_{14} = k_{15} = 2k_{16} = 2 \times 10^9$ l mol^{-1} s^{-1}

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[19] W. A. Seddon and A. O. Allen, *J. Phys. Chem.*, 1967, **71**, 1914.

[20] C. E. Burchill and P. W. Jones, *Canad. J. Chem.*, 1971, **49**, 4005.

the value (0·64) obtained by chemical competition in the Fenton system [18] is higher than the one obtained by pulse radiolysis [17] (0·42) as a result of similar interfering reactions, but since the experimental conditions of ref. 18 are less well defined, we could not check this effect there.

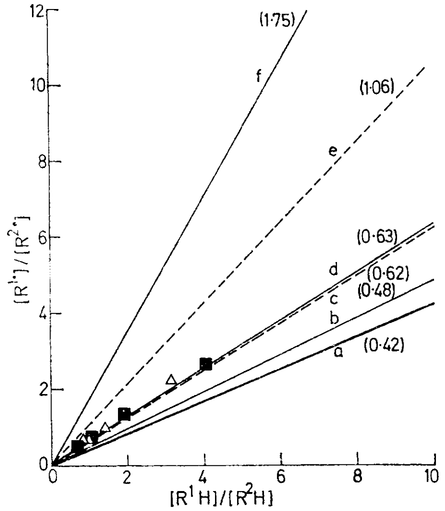

FIGURE 5 The effect of the reactions $R^{1\cdot} + H_2O_2$ and $R^{2\cdot} + H_2O_2$ on the ratio $[R^{1\cdot}]/[R^{2\cdot}]$: ■ experimental results, $[R^1H] = [MeOH] = 0{\cdot}52\text{M}$, $[R^2H] = [Pr^iOH]$ = variable, $[Ti^{III}]_0 = 0{\cdot}4\text{mM}$, $[H_2O_2]_0 = 1{\cdot}2\text{mM}$; △ experimental results as in Figure 3. Lines are computed: solid lines $[Ti^{III}]_0 = 4\text{mM}$; dashed lines $[Ti^{III}]_0 = 0{\cdot}4\text{mM}$. a, $k_{R^{1\cdot}+H_2O_2} = k_{R^{1\cdot}+H_2O_2} = 0$; b—f, $k_{R^{1\cdot}+O_2H_2} = 5 \times 10^4$ l mol^{-1} s^{-1} and $k_{R^{1\cdot}+H_2O_2} = 5 \times 10^5$ l mol^{-1} s^{-1}; b, c, $[H_2O_2]_0 = 1\text{mM}$; a, d, e, $[H_2O_2]_0 = 10\text{mM}$; f, $[H_2O_2]_0 = 0{\cdot}1\text{M}$. $2k_{14} = k_{15} = 2k_{16} = 2 \times 10^9$ l mol^{-1} s^{-1}, $t = 50$ ms. Numbers in parentheses indicate slopes

Another factor which should be considered is the oxidation of the alcohol radical by Ti^{IV} formed through reaction (3) [reaction (18)]. Similar reactions have

$$R^{1\cdot} + Ti^{IV} \longrightarrow Ti^{III} + \text{products} \qquad (18)$$

been suggested by Norman and West [12] and confirmed by us.[9] From our previous results [8,9] we could estimate $k_{18} \sim 10^5$—10^6 l mol^{-1} s^{-1} for the α-Pr^{i}OH radical and in the low concentrations of Ti^{IV} produced in our experiments no appreciable contribution of this reaction is to be expected under any of our experimental conditions. This latter expectation has been verified by including reaction (18) in our computations.

The last factor to be considered is the sensitivity of these systems to variations in the recombination rates, *i.e.* in $k_{14} : k_{15} : k_{16}$. The dependence of the ratio $[R^{1\cdot}]/[R^{2\cdot}]$ computed by integrating the rate equations of reactions (3) and (12)—(16) on the relative values of the recombination reactions (14)—(16) is shown in Figure 6 and Table 2. It can be seen that $[R^{1\cdot}]/[R^{2\cdot}]$ as a function of $[R^1H]/[R^2H]$ may have a pronounced curvature, yet the best fit lines for such results (computed by the least mean square method) would leave experimental points within the range of the normal experimental error of the e.s.r. technique, for most cases displayed in Figure 6 and Table 2. The slopes of such 'best fit lines' might differ considerably from k_{12}/k_{13} as seen in Table 2. It can be seen in Figure 6 that when considering reactions (3), (10), (12), and (13) alone, we can get a slope of 0·67 if $k_{14} : k_{15} : k_{16}$ are taken to be in the ratio of 1 : 2 : 2 respectively, which differs appreciably from the known values for the MeOH–Pr^{i}OH system (k_{15} has never been determined but a plausible estimation would be to take it as somewhat higher than both k_{14} and k_{16}). The ratio of 2 : 2 : 1 (approximately the ratio determined experimentally [18]) yields a slope which is lower by *ca.* 25% than the theoretical k_{12}/k_{13}. This implies that the value of k_{17} for the reaction of α-Pr^{i}OH with H_2O_2 is slightly higher than the value determined by Burchill,[20] assuming that the values for k_{10} [16] are accurate. Since the value of k_{17} for this reaction was obtained by assuming $2k_{14} = k_{15} = 2k_{16}$,[20] such minor deviations might cause slight inaccuracy in the value determined for k_{17}. A ratio of 4 : 6 : 1 is sufficient to reduce the slope by >50% of the theoretical one. This effect of non-linearity is obviously dependent on the range of $[R^1H]/[R^2H]$ studied. It should be mentioned that the conversions, such as

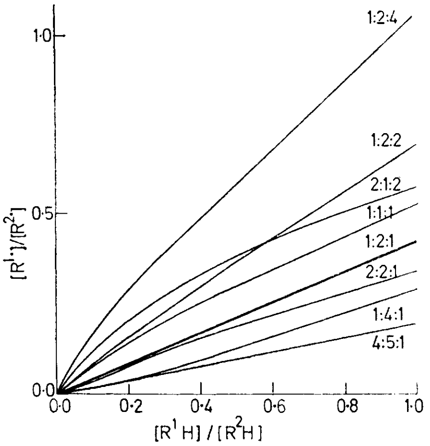

FIGURE 6 The effect of differences in recombination efficiency on $[R^{1\cdot}]/[R^{2\cdot}]$. Numbers indicate $k_{14} : k_{15} : k_{16}$, respectively. The bold line is the 1 : 2 : 1 line resulting in the theoretical $k_{12}/k_{13} = 0{\cdot}42$ slope. $[H_2O_2]_0 = 10\text{mM}$, $[Ti^{III}]_0 = 4\text{mM}$, $t = 50$ ms

TABLE 2

Effect of differences in recombination ratios on $[R^{1\cdot}]/[R^{2\cdot}]$ *vs.* $[R^1H]/[R^2H]$ plots [a]

k_{14}	k_{15}	k_{16}	a_1 (l.m.s. slope)	a_0 (l.m.s. intercept)	r (correlation coefficient)
1	1	1	0·487	0·049	0·9973
1	2	1	0·420	0·000	1·0000
			Theoretical		
1	3	1	0·352	−0·014	0·9987
1	4	1	0·299	−0·020	0·9965
2	1	1	0·352	0·053	0·9954
2	2	1	0·325	0·015	0·9992
2	3	1	0·291	−0·002	0·9998
2	4	1	0·259	−0·105	0·9992
4	3	1	0·227	0·008	0·9995
4	4	1	0·209	0·001	0·9998
4	6	1	0·177	−0·072	0·9983

[a] Computed by changing $[R^1H]/[R^2H]$ from 0·1 to 1·0 taking $k_3 = 500$ l mol^{-1} s^{-1}, $[Ti]_0 = 4\text{mM}$, $[H_2O_2]_0 = 10\text{mM}$, $t = 50$ ms.

reaction (5), have a similar, but much more pronounced, effect in cases where $k_5 \geqslant 10^4$ l mol^{-1} s^{-1}.

Observations of k_{12}/k_{13} from experimental measurements of the dependence of the ratio $[R^{1\cdot}]/[R^{2\cdot}]$ on $[R^1H]/[R^2H]$ by this method are thus liable to yield errors. Although plots of $[R^{1\cdot}]/[R^{2\cdot}]$ *vs.* $[R^1H]/[R^2H]$ may yield straight lines the slopes may differ considerably from k_{12}/k_{13}. This is due either to differences in the efficiency of recombination of the radicals and/or to secondary reactions such as reactions (5), (17), and (18). A straight line in such plots with the correct slope of k_{12}/k_{13} may accidentally be due to cancellation of opposite effects of reactions (5), (10), (17), or (18).

Conclusions.—The results lead to the following conclusions. (a) Almost none of the short-lived radicals observed in the cavity using this flow method are those produced at the mixing point. Most of them are produced in the observation cell. (b) As a consequence, no advantage is gained by using double mixing cells when $Ti^{III} + H_2O_2$ and similar systems are the source of the short-lived radicals. (c) For short-lived radicals, studied by this method, secondary reactions of the radicals which have rate constants $\leqslant 10^3$ l mol^{-1} s^{-1} may be neglected. (d) Side reactions with higher rate constants might have a pronounced influence on the kinetics of the system and on the ratio of the radicals concentration. (e) This method is severely limited for both kinetic and mechanistic studies. In any case where such studies are attempted one has to know the rate of the initiating reaction as well as the contribution of side reactions and of the various recombination reactions.

Conclusions (c)—(e) are relevant for experiments using any steady-state technique, such as *in situ* photolysis or radiolysis. The point which we have tried to stress in this study is that the e.s.r. flow method falls into the same category of steady-state techniques. Unless these factors are taken into consideration, erroneous conclusions may be reached.

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