Electron Spin Resonance Studies. Part XLIII.[1] Reaction of Dimethyl Sulphoxide with the Hydroxyl Radical

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A kinetic analysis is given of the reaction between the hydroxyl radical (generated from the Ti^{III}–H_2O_2 couple in a continuous flow system) and dimethyl sulphoxide in aqueous acid at ambient temperature; steady-state concentrations of both $Me^{\bullet}$ and $MeSO_2^{\bullet}$ have been monitored. Evidence is presented that the former radical arises from addition of $^{\bullet}OH$ to the sulphoxide followed by rapid decomposition of the intermediate species $Me_2S(O^{\bullet})OH$; this leads to the formation of $MeSO_2H$ which subsequently reacts with $Me^{\bullet}$ to give $MeSO_2^{\bullet}$. There was no evidence for the formation of $^{\bullet}CH_2S(O)Me$. Rate constants for the reaction between hydroxyl and Me_2SO, for that between $Me^{\bullet}$ and $MeSO_2H$, and for the dimerisation of methyl are estimated as 5×10^9, *ca.* 10^6, and $5{\cdot}6 \times 10^9$ l mol^{-1} s^{-1}, respectively.

THE reaction of dimethyl sulphoxide with the hydrogen peroxide–titanium(III) [2] or –iron(II) [3] couple gives the methyl radical; the latter system has been employed as a convenient source of this radical in synthesis.[3] However, the mechanism of its formation is not clear. It was first suggested that the former system yields the methyl radical as in reactions (1)—(3),[2] but other

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

$$^{\bullet}OH + Me_2SO \longrightarrow Me_2S(O^{\bullet})OH \qquad (2)$$

$$Me_2S(O^{\bullet})OH \longrightarrow Me^{\bullet} + MeSO_2H \qquad (3)$$

workers,[3,4] noting that t-butoxyl and methyl radicals react slowly, at best, with dimethyl sulphoxide, concluded that hydroxyl was also likely to do so, and therefore deemed this route, and the analogous one in which Fe^{II} replaces Ti^{III} in reaction (1), unlikely; they suggested instead the sequence in reactions (4), mediate hydroxy-hydroperoxide.

$$Me_2SO + H_2O_2 \longrightarrow Me_2S(OH)O_2H \qquad (4)$$

(5) ($M^{n+} = Fe^{II}$ or Ti^{III}), and (3), involving an inter-

$$Me_2S(OH)O_2H + M^{n+} \longrightarrow Me_2S(O^{\bullet})OH + M^{(n+1)+} + OH^- \qquad (5)$$

However, although methyl and t-butoxyl may react slowly with dimethyl sulphoxide, there is already evidence from pulse radiolysis that the hydroxyl radical reacts at a rate close to the diffusion-controlled limit;[5] the rate constant is 7×10^9 l mol^{-1} s^{-1} when the original value ($4{\cdot}2 \times 10^9$ l mol^{-1} s^{-1}) is revised to the hexacyanoferrate(II) standard.[6] Such a high rate constant is unlikely to correspond to direct † hydrogen atom abstraction from the sulphoxide, but is compatible with addition to the sulphoxide function as in reaction (2).

We have carried out a quantitative investigation of the reaction of dimethyl sulphoxide with the Ti^{III}–H_2O_2 system in order to elucidate the role, if any, of the hydroxyl radical in the oxidation.

EXPERIMENTAL

The spectrometer and flow system have been described in detail.[8] E.s.r. experiments were carried out at room temperature with both Varian E-3 and V-4502 spectrometers. The three-stream mixing device,[8] which we have previously found useful for systems in which reaction of an organic reagent with one of the initiating reagents occurs, was used in all experiments.

Owing to the complex dependence of the lineshape of over-modulated signals on metal ion [titanium(III)] concentration, it was generally not possible to obtain relative radical concentrations from measurements of peak amplitude and linewidth; instead, the more laborious double integration procedure previously employed was used.[8]

The apparatus for pulse radiolysis with optical detection has been described.[9] A 5mM oxygen-saturated solution of potassium hexacyanoferrate(II) was employed as dosimeter.

Dimethyl sulphoxide, t-butyl alcohol (Fisons Laboratory Reagents), and t-butyl hydroperoxide (Koch-Light Laboratories) were commercial samples. Sodium ethanesulphinate was prepared from the corresponding magnesium salt,[10] and isolated by the method of Rumpf and Sadet.[11]

RESULTS AND DISCUSSION

Basis of the Study.—For e.s.r. investigations of metal ion–hydrogen peroxide systems in conjunction with flow and mixing techniques, a quasi-steady state radical concentration is attained in the cavity provided that the time interval between the mixing point and the cavity is more than a few ms and that the radicals detected are short-lived (rate constant for bimolecular termination, $2k$, *ca.* 10^9 l mol^{-1} s^{-1}).[12] These conditions were fulfilled in our experiments. To simplify the kinetic analysis, [Ti^{III}] was always substantially less than the concentrations of other reagents; under these conditions, the

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† There is evidence [5,7] from the oxidation of sulphides that *indirect* hydrogen abstraction *via* reaction at sulphur may sometimes be especially rapid.

[1] Part XLII, B. C. Gilbert, R. O. C. Norman, and R. C. Sealy, *J.C.S. Perkin II*, 1974, 1435.

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[3] B.-M. Bertilsson, B. Gustafsson, I. Kühn, and K. Torssell, *Acta Chem. Scand.*, 1970, **24**, 3590.

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

[7] B. C. Gilbert, D. K. C. Hodgeman, and R. O. C. Norman, *J.C.S. Perkin II*, 1973, 1748; B. C. Gilbert, J. P. Larkin, and R. O. C. Norman, *ibid.*, p. 272.

[8] B. C. Gilbert, R. O. C. Norman, and R. C. Sealy, *J.C.S. Perkin II*, 1973, 2174.

[9] D. H. Ellison, G. A. Salmon, and F. Wilkinson, *Proc. Roy. Soc.*, 1972, *A*, **328**, 22.

[10] P. Allen, jun., *J. Org. Chem.*, 1942, **7**, 23.

[11] P. Rumpf and J. Sadet, *Bull. Soc. chim. France*, 1958, 447.

[12] See, *e.g.*, C. E. Burchill and P. W. Jones, *Canad. J. Chem.*, 1971, **49**, 4005.

decay of [Ti^{III}] along the flow-tube is exponential and the depletion of other reagents is negligible.

According to the two mechanistic schemes outlined above, radical initiation may be by reaction (1), or (5), or possibly a combination of both. In addition to these reactions and (2)—(4), we have to consider the possible fates for the methyl radical and for the radical $Me_2S(O^\bullet)OH$ other than its fragmentation (3). These are bimolecular termination, and reactions (6)—(9) [RH = dimethyl sulphoxide, $Me_2S(OH)O_2H$, *etc.*].

$$Me^\bullet + Ti^{III} \longrightarrow Me^- + Ti^{IV} \qquad (6)$$

$$Me^\bullet + RH \longrightarrow MeH + R^\bullet \qquad (7)$$

$$Me_2S(O^\bullet)OH + Ti^{III} \longrightarrow Me_2S(O^-)OH + Ti^{IV} \qquad (8)$$

$$Me_2S(O^\bullet)OH + RH \longrightarrow Me_2S(OH)_2 + R^\bullet \qquad (9)$$

Reaction (6) can be neglected since we have shown previously that, under normal flow-system conditions, the reduction of alkyl radicals by Ti^{III} in acid solution does not contribute significantly to radical termination even when a strongly activating group such as carbonyl is attached to the tervalent carbon.[8] Reaction (7) requires careful consideration, since methyl appears to be more reactive than most other alkyl radicals in hydrogen atom abstraction; for example, $k(Me^\bullet + Me_2CHOH)$ [13] is up to 60 times larger than $k(^\bullet CH_2CHMeOH + Me_2CHOH)$.[14] The possible significance of this reaction and of reactions (8) and (9), and the possible mediation of the radical $^\bullet CH_2S(O)Me$,[15] are examined in the sequel.

The Initiation Step.—The rate of radical initiation can be determined in our experiments by monitoring the concentration of an organic radical as a function of that of hydrogen peroxide.[16] Thus, for the sequence in reactions (10)—(12), [$R^\bullet$] should be maximal for

$$Ti^{III} + H_2O_2 \xrightarrow{k_{in}} Ti^{IV} + {}^\bullet OH + OH^- \qquad (10)$$

$$RH \xrightarrow{^\bullet OH} R^\bullet \qquad (11)$$

$$2R^\bullet \longrightarrow \text{molecular products} \qquad (12)$$

$[H_2O_2]_0$ *ca.* $(k_{in}t)^{-1}$, given that $[H_2O_2]_0 \gg [Ti^{III}]_0$.* The oxidation of t-butyl alcohol provides a system for which this sequence is a satisfactory description since, first, the radical $^\bullet CH_2CMe_2OH$ is formed in almost 100% yield from the hydroxyl radical with an excess of the alcohol[17] and, secondly, this organic radical is neither rapidly oxidised by hydrogen peroxide or Ti^{IV} nor rapidly reduced by Ti^{III}.[8] The profile of the radical's concentration as a function of hydrogen peroxide concentration at pH 1, in experiments with a large excess of the alcohol compared with Ti^{III}, is shown in Figure 1(a); we estimate $k_{in}t$ as *ca.* 25 l mol^{-1}.

When an excess of dimethyl sulphoxide was used in place of t-butyl alcohol, so as again to ensure essentially complete scavenging of the hydroxyl radical,[5] the organic radicals detected were $Me^\bullet$ and, under some conditions (see later), $MeSO_2^\bullet$ [a(3H) 0·095 mT, g 2·0049; *cf.* ref. 18]; the latter was always present in much the lower concentration of the two. As can be seen [Figure 1(b)], the profile of [$Me^\bullet$] against [H_2O_2] is identical within experimental error with that for [$^\bullet CH_2CMe_2OH$]. This is consistent with removal of $Me^\bullet$ predominantly by dimerisation and with there being a common initiation step in the oxidation of both compounds, namely reaction (10), and renders unlikely the alternative suggestion that radical initiation is by way of reactions (4) and (5); thus, the latter could only be the case if not only was the adduct $Me_2S(OH)O_2H$ formed in a rapidly established equilibrium † or a rapid irreversible reaction, but also $k_5[Me_2S(OH)O_2H]$ was fortuitously equal to $k_{in}[H_2O_2]$. Further, the results of a series of experiments designed to promote formation of the postulated adduct $Me_2S(OH)O_2H$, by employing a high concentration of dimethyl sulphoxide (0·375M), did not differ significantly from those in Figure 1(b). (As expected, premixing of the sulphoxide and hydrogen peroxide gave the same results.)

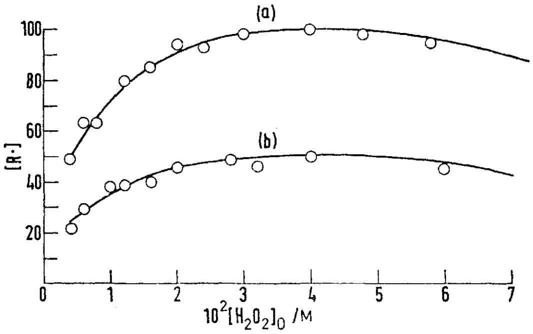

FIGURE 1 Variation of radical concentration [$R^\bullet$] (arbitrary units) with $[H_2O_2]_0$; $[Ti^{III}]_0$ = 2mM: (a) $R^\bullet = {}^\bullet CH_2CMe_2OH$ ($[Bu^tOH]_0$ = 0·33M); (b) $R^\bullet = Me^\bullet$ ($[Me_2SO]_0$ = 33mM)

The inference that the radical initiating step in the oxidation of dimethyl sulphoxide is reaction (10) and not (5) was supported by experiments with mixtures of the sulphoxide and t-butyl alcohol; both $Me^\bullet$ and $^\bullet CH_2CMe_2OH$ were detected, and the results are in the Table. We shall show later that they are entirely consistent with the formation of $^\bullet CH_2CMe_2OH$ by the reaction of the hydroxyl radical with the alcohol; for the moment, we note that they are inconsistent with the reaction of the methyl radical with the alcohol, for the

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* Subscripts 0 and t denote concentrations on mixing and t s after mixing (generally in the cavity), respectively.

† If the equilibrium did not favour the adduct, the rate constant for reaction (5; $M^{n+} = Ti^{III}$) would need to be correspondingly greater than that for reaction (10).

[13] J. K. Thomas, *J. Phys. Chem.*, 1967, **71**, 1919.

[14] C. E. Burchill and G. F. Thompson, *Canad. J. Chem.*, 1971, **49**, 1305.

[15] C. Walling, G. M. El-Taliawi, and R. A. Johnson, *J. Amer. Chem. Soc.*, 1974, **96**, 133.

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

[17] K.-D. Asmus, H. Möckel, and A. Henglein, *J. Phys. Chem.*, 1973, **77**, 1218.

[18] W. Damerau, G. Lassman, and K. Lohs, *Z. phys. Chem.* (*Leipzig*), 1969, **9**, 343.

reduction of t-butyl hydroperoxide by Ti^{III} [reaction (13)] gave similar concentrations of $Me^{\bullet}$ [*via* reaction (14)]

$$Ti^{III} + Bu^tO_2H \longrightarrow Ti^{IV} + Bu^tO^{\bullet} + OH^- \quad (13)$$

$$Bu^tO^{\bullet} \longrightarrow Me^{\bullet} + Me_2CO \quad (14)$$

to those above, whereas the inclusion of high concentrations of t-butyl alcohol in this system gave only trace amounts of $^{\bullet}CH_2CMe_2OH$. These results imply also that the t-butoxyl radical abstracts hydrogen from t-butyl alcohol only very slowly compared with the rate at which it fragments; this is in accord with the known propensity of alkoxyl radicals to fragment in polar media.[19]

Concentrations (arbitrary units) of radicals from oxidation of dimethyl sulphoxide–t-butyl alcohol mixtures under identical conditions of radical initiation ($[H_2O_2]_0$ = 6mM; $[Ti^{III}]_0$ = 2mM)

$[Bu^tOH]/[Me_2SO]$	$[Me^{\bullet}]$	$[^{\bullet}CH_2CMe_2OH]$
∞	0	100
25·6	15	79
15·7	20	70
12·7	24	61
8·77	28	55
6·29	35	42·5
3·74	38	35
1·44	45	13
0	50	0

The Radical $Me_2S(O^{\bullet})OH$.—It is reasonable to expect that this radical, if formed, would (like $Bu^tO^{\bullet}$) fragment rapidly in aqueous solution as compared with the rates at which it would abstract a hydrogen atom or undergo bimolecular termination. Some evidence that reaction (3) is indeed rapid was derived from the pulse radiolysis of a nitrous oxide-saturated 10^{-2}M solution of dimethyl sulphoxide at neutral pH. Very weak optical absorption was detected in the wavelength range 240—300 nm (other workers [5] were unable to detect a transient in the range 270—800 nm). The absorption spectrum (Figure 2) decayed rapidly, with $t_{\frac{1}{2}}$ *ca.* 5 μs, with the corresponding build-up of a permanent product. The methyl radical does not absorb significantly above 240 nm,[20] but we would expect other transient species such as $Me_2S(O^{\bullet})OH$ to absorb weakly above this wavelength; moreover, we found that the sodium salt of ethanesulphinic acid has ε 36 l mol^{-1} cm^{-1} at 240 nm, so we suggest that the permanent product, which had ε *ca.* 40 l mol^{-1} cm^{-1} at 240 nm [assuming $G = G(^{\bullet}OH + e^-_{aq}) = 5{\cdot}6$] is $MeSO_2^-$ ($MeSO_2H$ has [21] pK_a 2·28) and that the transient is indeed $Me_2S(O^{\bullet})OH$. It follows that any other weakly absorbing intermediate must have at least as transient an existence as $Me_2S(O^{\bullet})OH$. Since the product is formed within 10 μs, we can put a lower limit on the rate constant for reaction (3) of 10^5 s^{-1}; it is extremely unlikely that a hydrogen atom abstraction can compete effectively with so rapid a first-order process (*cf.* $Bu^tO^{\bullet} + Me_2CH{\cdot}CHMe_2$, for which [19] $k = 6 \times 10^4$ l mol^{-1} s^{-1} in CCl_4 at 40°). This would be the case also for reduction of the radical by Ti^{III} under our conditions.

The Methyl Radical.—Additional evidence for predominantly second-order termination of the methyl radical was obtained from experiments in which the rate of radical initiation was varied. For initiation by reaction (10), complete scavenging of hydroxyl by dimethyl sulphoxide to yield methyl, and bimolecular termination, the concentration of the methyl radical in the cavity is given by equation (15); for $[H_2O_2]_0 \gg$

$$2k[R^{\bullet}]^2 = k_{in}[H_2O_2]_t[Ti^{III}]_t \quad (15)$$

$[Ti^{III}]_0$, this can be written as equation (16). Thus, for

$$2k[R^{\bullet}]^2 = k_{in}[H_2O_2]_0[Ti^{III}]_0 exp(-k_{in}[H_2O_2]_0 t) \quad (16)$$

constant $[H_2O_2]_0$ and t, $[R^{\bullet}]$ should be a linear function of $[Ti^{III}]_0^{\frac{1}{2}}$. The variation of $[Me^{\bullet}]$ with $[Ti^{III}]_0^{\frac{1}{2}}$ is in accord with this prediction over a twenty-fold change in $[Ti^{III}]_0$ (Figure 3). Since reactions (6)—(9) would each correspond to a $[Ti^{III}]_0^{<0.5}$ dependence and would

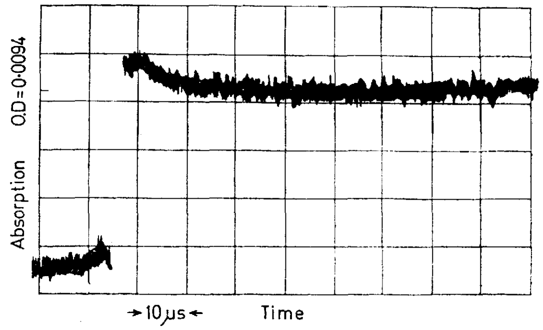

FIGURE 2 Decay of optical absorption at 240 nm after pulse radiolysis of a neutral aqueous solution of dimethyl sulphoxide (10mM) (5 cm cell; 7·5 krad dose)

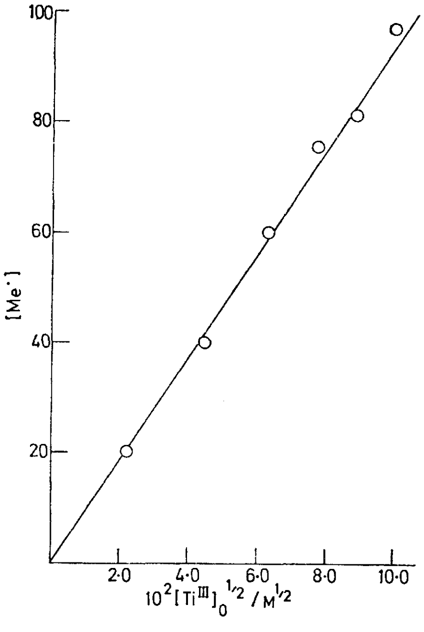

FIGURE 3 Methyl radical concentration $[Me^{\bullet}]$ (arbitrary units) as a function of $[Ti^{III}]_0^{\frac{1}{2}}$

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[19] J. A. Howard, *Adv. Free Radical Chem.*, 1972, **4**, 49.

[20] G. Herzberg and J. Shoosmith, *Canad. J. Phys.*, 1956, **34**, 523.

[21] F. Wudl, D. A. Lightner, and D. J. Cram, *J. Amer. Chem. Soc.*, 1967, **89**, 4099.

manifest themselves as deviations from linearity in Figure 3 if they were to make more than a *ca.* 20% contribution to methyl radical termination, we infer that these reactions have pseudo-first-order rate constants $<0{\cdot}2 \times 2k[\text{Me}^\bullet]$. Further, since $[\text{Me}^\bullet]$ was unaffected by a ten-fold variation in the concentration of dimethyl sulphoxide, the reaction of the methyl radical with dimethyl sulphoxide must also be relatively slow, unless the resulting species is rapidly converted into methyl.

The Methylsulphonyl Radical.—This species was detected in the experiments with dimethyl sulphoxide described above except when low concentrations of one or both of the initiating reagents were employed or the pH was raised much above 2. These observations suggest that $\text{MeSO}_2^\bullet$ is a secondary radical, most probably formed by reaction of the molecular product of reaction (3); the pH effect would follow if, as we should expect, hydrogen atom abstraction as in reaction (17)

$$\text{R}^\bullet + \text{MeSO}_2\text{H} \longrightarrow \text{MeSO}_2^\bullet + \text{RH} \qquad (17)$$

were faster than electron abstraction from the corresponding anion.

The concentration of $\text{MeSO}_2^\bullet$ was found to be independent of $[\text{Me}_2\text{SO}]$ (30—375mM); the possibility that the radical arises from an impurity in the dimethyl sulphoxide is thus eliminated. This finding also appears to preclude an earlier suggestion [18] that, under similar conditions to those employed in this study, $\text{MeSO}_2^\bullet$ is formed by reaction of the hydroxyl radical with the sulphinic acid, for the following reason. For $[\text{Me}_2\text{SO}] =$ 375mM, the proportion of hydroxyl radicals which react with MeSO_2H must be less than one-hundredth of the proportion that react with dimethyl sulphoxide, even if the maximum possible amount of MeSO_2H is formed (in these experiments, *ca.* 2mM) and if the reaction of hydroxyl with MeSO_2H is diffusion controlled. This predicted low rate of formation of $\text{MeSO}_2^\bullet$ is incompatible with the values obtained for $[\text{MeSO}_2^\bullet]/[\text{Me}^\bullet]$ even if the rate constant for recombination of $\text{MeSO}_2^\bullet$ radicals is 100 times smaller than that for recombination of methyl; available evidence suggests that this is unlikely to be so ($2k$ for $\text{MeSO}_2^\bullet$ in cyclopropane at $-110°$ is [22] of the order of 10^9 l mol^{-1} s^{-1}), and in any case cross-combination of $\text{MeSO}_2^\bullet$ with $\text{Me}^\bullet$, which is present in large excess, is likely to be the predominant mode of disappearance of the species (*cf.* gas-phase reactions [23]) and should be extremely rapid. We infer that the radical $\text{R}^\bullet$ in reaction (17) is not hydroxyl.

Quantitative analysis of the dependence of $[\text{MeSO}_2^\bullet]$ on $[\text{Ti}^{\text{III}}]_0$ and $[\text{H}_2\text{O}_2]_0$ suggests that methyl is the radical involved in this reaction. Thus, $[\text{MeSO}_2^\bullet]$ varies linearly with $[\text{Ti}^{\text{III}}]_0$ for constant $[\text{H}_2\text{O}_2]_0$, and its dependence, for constant $[\text{Ti}^{\text{III}}]_0$, on $[\text{H}_2\text{O}_2]_0$, at least up to 40mM-peroxide,* mirrors the expected depletion in $[\text{Ti}^{\text{III}}]$; Figure 4 shows the concentration of $\text{MeSO}_2^\bullet$ as a function of $[\text{H}_2\text{O}_2]_0$ together with the predicted depletion in $[\text{Ti}^{\text{III}}]$. Thus, $[\text{MeSO}_2^\bullet]$ is evidently proportional to the concentration of MeSO_2H in the cavity, a concentration which should be equal to the concentration of Ti^{III} removed, providing that depletion of MeSO_2H along the flow-tube owing to reaction (17) is small. We have previously argued that $\text{MeSO}_2^\bullet$ should be removed mainly by reaction with $\text{Me}^\bullet$; combination of this destruction mode [reaction (18)] with reaction (17; R = Me) for the generation of the species yields equation (19) for the stationary state. Since the concentration of MeSO_2H is given (neglecting any slight removal along the flow-tube) by equation (20), then the observed dependence of $[\text{MeSO}_2^\bullet]$ on $[\text{Ti}^{\text{III}}]_0$ and $[\text{H}_2\text{O}_2]_0$ is accounted for.

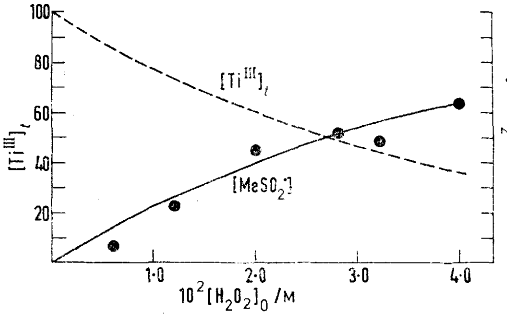

FIGURE 4 Variation with $[\text{H}_2\text{O}_2]_0$ of $[\text{MeSO}_2^\bullet]$ (arbitrary units) and $[\text{Ti}^{\text{III}}]_t$ {calculated from $[\text{Ti}^{\text{III}}]_t = [\text{Ti}^{\text{III}}]_0 \exp(-k_{\text{in}}[\text{H}_2\text{O}_2]_0 t)$ taking $k_{\text{in}}t = 25$ l mol^{-1} (see text) and expressed as a percentage of $[\text{Ti}^{\text{III}}]_0$}

$$\text{MeSO}_2^\bullet + \text{Me}^\bullet \longrightarrow \text{Me}_2\text{SO}_2 \qquad (18)$$

$$[\text{MeSO}_2^\bullet] = k_{17}[\text{MeSO}_2\text{H}]_t/k_{18} \qquad (19)$$

$$[\text{MeSO}_2\text{H}]_t = [\text{Ti}^{\text{III}}]_0\{1 - \exp(-k_{\text{in}}[\text{H}_2\text{O}_2]_0 t)\} \qquad (20)$$

Our conclusion that reaction (18) represents the main destruction path for $\text{MeSO}_2^\bullet$ implies that the sulphone Me_2SO_2 should be a reaction product. It is notable that radicals from sulphones are reported to have been trapped by nitroso-compounds when sulphoxide–hydrogen peroxide mixtures are photolysed; [24] it seems likely that they are formed by reaction of the hydroxyl radical with R_2SO_2 which is itself formed *via* reaction (18) or its analogue for other sulphoxides.

The Radical $^\bullet\text{CH}_2\text{S(O)CH}_3$.—There was no detectable signal from this radical in any of our experiments on the oxidation of dimethyl sulphoxide with hydroxyl. We considered the possibility that it might nevertheless be formed in significant amounts but that it is either undetectable owing, for example, to a line broadening phenomenon or that it does not reach detectable concentrations owing to rapid destruction steps through

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* For concentrations much above this, some diminution of the $\text{MeSO}_2^\bullet$ signal was found and the singlet S_1 (g 2·0132) [24] was detected. The latter, whose origin is thought to be the reaction of an oxygen-centred radical with Ti^{IV}–H_2O_2, [24] could not be quenched by increasing $[\text{Me}_2\text{SO}]$ and is therefore unlikely to be formed by inefficient scavenging of the hydroxyl radical under our conditions.

[22] A. G. Davies and B. P. Roberts, personal communication.

[23] A. Good and J. C. J. Thynne, *Trans. Faraday Soc.*, 1967, **63**, 2708, 2720.

[24] H. Fischer, *Ber. Bunsengesellschaft Phys. Chem.*, 1967, **71**, 685.

reaction with Ti^{III} or dimethyl sulphoxide. However, we were able to observe the spectrum of $^{\bullet}CH_2S(O)Me$, prepared by the reduction of $MeSOCH_2Br$ with the Ti^{III}–H_2O_2–HPO_2^{2-} system [25] (details of the e.s.r. spectra of this and other α-sulphinyl radicals will be discussed subsequently). There was no evidence that this radical was destroyed by rapid reaction with either Ti^{III} or dimethyl sulphoxide, and we conclude that our failure to detect it in the Ti^{III}–H_2O_2–dimethyl sulphoxide system signifies that it only plays a minor role, if any, in this oxidation.

Kinetics of Methyl Radical Reactions.—We have established that methyl is formed by a reaction of the hydroxyl radical with dimethyl sulphoxide and that, over a range of experimental conditions, the ratio of the concentration of this radical to that of the radical from the oxidation of t-butyl alcohol, $^{\bullet}CH_2CMe_2OH$ (generated in a separate experiment) is constant. Since $Me^{\bullet}$ and $^{\bullet}CH_2CMe_2OH$ are the only radicals formed in quantity in the dimethyl sulphoxide and t-butyl alcohol systems respectively, we assume that their rates of formation are the same and are given by $k_{in}[H_2O_2]_t[Ti^{III}]_t$. The relative concentrations of the two radicals are then governed by their respective rate constants for recombination, *i.e.* for reactions (21) and (22), and for

$$2Me^{\bullet} \longrightarrow \text{molecular products} \quad (21)$$

$$2\ ^{\bullet}CH_2CMe_2OH \longrightarrow \text{molecular products} \quad (22)$$

these conditions equations (23) and (24) apply. For a

$$2k_{21}[Me^{\bullet}]^2 = k_{in}[H_2O_2]_t[Ti^{III}]_t = 2k_{22}[^{\bullet}CH_2CMe_2OH]^2 \quad (23)$$

$$2k_{21} = 2k_{22}([^{\bullet}CH_2CMe_2OH]/[Me^{\bullet}])^2 \quad (24)$$

series of paired experiments, the average value of the ratio $[^{\bullet}CH_2CMe_2OH]/[Me^{\bullet}]$ was $2{\cdot}0 \pm 0{\cdot}2$; taking $2k_{22}$ as $1{\cdot}4 \times 10^9$ l mol^{-1} s^{-1},[26] we obtain $2k_{21} = 5{\cdot}6 \times 10^9$ l mol^{-1} s^{-1}.

From our data for dimethyl sulphoxide–t-butyl alcohol mixtures (see Table) it is possible to estimate an approximate rate constant for the cross-combination reaction (27), provided that the methyl and $^{\bullet}CH_2CMe_2OH$ radicals, formed *via* reactions (25) and (26) respectively, disappear through the bimolecular reactions (21), (22), and (27) only. Then equation (28) applies. For

$$^{\bullet}OH + Me_2SO \longrightarrow Me^{\bullet} + MeSO_2H \quad (25)$$

$$^{\bullet}OH + Bu^tOH \longrightarrow {}^{\bullet}CH_2CMe_2OH + H_2O \quad (26)$$

$$Me^{\bullet} + {}^{\bullet}CH_2CMe_2OH \longrightarrow \text{molecular products} \quad (27)$$

$$k_{in}[H_2O_2]_t[Ti^{III}]_t = 2k_{21}[Me^{\bullet}]^2 + 2k_{22}[^{\bullet}CH_2CMe_2OH]^2 + k_{27}[Me^{\bullet}][^{\bullet}CH_2CMe_2OH] \quad (28)$$

constant $[H_2O_2]_t$ and $[Ti^{III}]_t$, a plot of $2k_{21}[Me^{\bullet}]^2 + 2k_{22}[^{\bullet}CH_2CMe_2OH]^2$ *versus* $[Me^{\bullet}][^{\bullet}CH_2CMe_2OH]$ should have gradient $-k_{27}$ and from Figure 5 we estimate k_{27} as $3{\cdot}2 \times 10^9$ l mol^{-1} s^{-1}. Although the errors involved in the procedure are large (squares of radical concentrations are required), this value is in reasonable accord with the statistical expectation [27] $[k_{27} = (2k_{21} \times 2k_{22})^{\frac{1}{2}}]$.

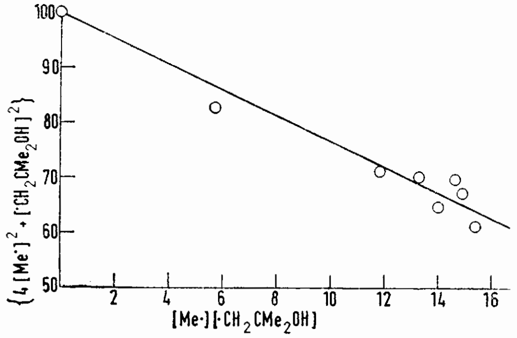

FIGURE 5 Concentrations of $Me^{\bullet}$ and $^{\bullet}CH_2CMe_2OH$ plotted according to equation (28). Ordinate values have been divided by a factor of $1{\cdot}4 \times 10^9$

For a system described by reactions (1), (21), (22), and (25)—(27), the ratio $[Me^{\bullet}]/[^{\bullet}CH_2CMe_2OH] = r$ is given by equation (29), where $R = k_{25}[Me_2SO]/k_{26}[Bu^tOH]$.

$$r = R(k_{27}r + 2k_{22})/(2k_{21}r + k_{27}) \quad (29)$$

Analysis of our data for a number of values of $[Bu^tOH]/[Me_2SO]$ gives $k_{25} = (10 \pm 2)k_{26}$. Since $k_{26} = 5 \times 10^8$ l mol^{-1} s^{-1},[6] we obtain $k_{25} = (5 \pm 1) \times 10^9$ l mol^{-1} s^{-1}, close to the value from pulse radiolysis experiments of 7×10^9 l mol^{-1} s^{-1}.

Finally, we return to the formation of $MeSO_2^{\bullet}$ from methanesulphinic acid. If we make the assumption that $MeSO_2^{\bullet}$ behaves as a typical small radical, then its rate constant for reaction with methyl, k_{18}, should be similar to that for the corresponding reaction of $^{\bullet}CH_2CMe_2OH$, k_{27}, *viz. ca.* $3{\cdot}2 \times 10^9$ l mol^{-1} s^{-1}. For $[H_2O_2]_0 = 28$mM and $[Ti^{III}]_0 = 2$mM, $[MeSO_2H]_t$ is *ca.* 9×10^{-4}M and $[MeSO_2^{\bullet}]$ (from an absolute concentration calibration with a standard solution of Fremy's salt [28]) $= 2{\cdot}5 \times 10^{-7}$M. Then, from equation (19), $k_{17} = ca.$ 10^6 l mol^{-1} s^{-1} for R = Me $\{k_{17}[MeSO_2H]_t$ is then *ca.* $0{\cdot}08$ $(2k[Me^{\bullet}])$, inside our previous limit for the rate constant of a pseudo-first-order reaction$\}$. This value appears high for a hydrogen atom abstraction by methyl at ambient temperature, at least when compared with data for abstraction from C–H bonds [*e.g.*[13] $k(Me^{\bullet} + Me_2CHOH) = 3{\cdot}4 \times 10^3$ l mol^{-1} s^{-1}]. However, the rapid reaction of t-butoxyl with alkanesulphinic acids has also been noted;[29] as was previously proposed to account for that observation, the magnitude of k_{17} may stem from either the weakness of the sulphinic acid O–H bond or the occurrence of abstraction from a

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proportion of the S–H tautomer that may be present [*cf.*[30] $k(\mathrm{Me}^{\bullet} + \mathrm{MeSH}) = 7{\cdot}4 \times 10^{7}\ \mathrm{l\ mol^{-1}\ s^{-1}}$].

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