Electron Spin Resonance Studies. Part XLII.[1] The Reactions of Iodine-containing Compounds with Hydroxyl and Carbon Radicals in Aqueous Solution

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E.s.r. spectroscopy and pulse radiolysis with optical detection have been employed to investigate the reactions of some iodine-containing compounds with the hydroxyl radical and with some simple carbon radicals. Competition experiments and direct measurements of the variation of radical concentration with time have afforded absolute rate constants for some of these reactions, including those of iodoacetic acid with $\cdot OH$ [5 (±1) × 10^9], $\cdot CH_2OH$ [2·1 (±0·7) × 10^8], and $\cdot CH_2CMe_2OH$ [1·3 (±0·3) × 10^7 l mol^{-1} s^{-1}]. These data and possible reaction mechanisms are discussed.

THE reaction of the hydroxyl radical with alkyl iodides in aqueous solution has been the subject of few reports.[2-4] Thomas [2,3] suggested that iodine-atom displacement [reaction (1)] occurs in the reaction of hydroxyl with methyl iodide and assigned the optical absorption spectrum obtained in the pulse radiolysis of solutions of methyl iodide saturated with nitrous oxide to a complex of an iodine atom with a molecule of methyl iodide, $I(CH_3I)$. However, a recent investigation [4] has provided evidence that the transient detected in this system is more probably a charge-transfer complex of hydroxyl with the iodide, $HO(CH_3I)$, and that the first-order decay of the signal in aqueous acid is the result of reaction (2).

$$HO\cdot + CH_3I \longrightarrow CH_3OH + I\cdot \qquad (1)$$

$$HO(CH_3I) + H^+ \longrightarrow I(H_2O) + CH_3^+ \qquad (2)$$

The reactions of carbon-centred radicals with iodine-containing compounds in solution have also received some attention. It is known [2,5,6] that alkyl radicals abstract halogen from molecular iodine at essentially the diffusion-controlled limit and that rapid iodine-atom transfer takes place between carbon radicals and alkyl

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[1] (*a*) Part XL, B. C. Gilbert, R. O. C. Norman, and R. C. Sealy, *J.C.S. Perkin II*, 1974, 824; (*b*) Part XLI, B. C. Gilbert, R. O. Norman, and M. Trenwith, *idid.*, p. 1033.

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and aryl iodides,[6-17] but absolute kinetic data for the latter reactions are scarce; apart from a few isolated examples, data are only available for reactions of the methyl radical.[17] (The relative rate constants reported by Szwarc and his co-workers have been placed on an absolute basis by Ingold.[18])

We present evidence adduced from optical and electron spin resonance data for the formation of $\cdot CH_2CO_2H$ from the reaction of hydroxyl with iodoacetic acid; in contrast, reaction of hydroxyl with 3-iodopropionic acid and 2-iodoethanol did not generate organic radicals in sufficient concentration for detection by e.s.r. spectroscopy. We have also investigated the reactions of the radicals $\cdot CH_2CMe_2OH$ and $\cdot CH_2OH$ with some iodine-containing compounds in aqueous solution; absolute rate constants for these reactions have been estimated.

EXPERIMENTAL

The e.s.r. spectrometer, aqueous flow system, and sample preparation have been described previously,[19] as has the equipment for pulse radiolysis with optical detection.[19] Relative radical concentrations were obtained from double integration of the e.s.r. spectra, and estimates of absolute concentration were made by comparison with the signal from a standard solution of vanadyl sulphate.[19]

Of the three reagent streams, stream (i) contained hydrogen peroxide (9—24mM), stream (ii) contained titanium(III) chloride (3—8mM), and stream (iii) contained an iodo-substituted compound, either alone or together with a large molar excess of t-butyl alcohol or methanol. The pH on mixing was adjusted by the addition to stream (ii) of either sulphuric acid or the disodium salt of ethylenediaminetetra-acetic acid in concentration equimolar to that of the Ti^{III} together with ammonia solution (*d* 0·88). The water for the reagent streams was degassed prior to addition of the reagent; iodine-containing compounds were dissolved in the minimum of water and added shortly before starting the flow. Unless otherwise stated, the concentration of the iodine-containing compound or alcohol was sufficient to scavenge essentially all the hydroxyl radicals produced in the reaction between Ti^{III} and H_2O_2. The application of simple kinetic analysis to these systems demands that,[19] of the reagents used, only Ti^{III} undergoes significant depletion along the flow tube; experimental problems associated with this requirement are described in the text.

Chemicals used and not reported previously[1a,19] were iodoacetic acid (B.D.H. Laboratory Reagent), 2-iodoethanol (practical grade, Koch-Light Laboratories), 3-iodopropionic acid and iodoacetonitrile (99 and 95%, respectively, Ralph N. Emanuel Ltd.), and iodine (B.D.H. Analytical Reagent).

RESULTS AND DISCUSSION

The reactions of iodine-containing compounds with hydroxyl and other radicals were investigated with a flow system in conjunction with e.s.r. spectroscopy and, where appropriate, by pulse radiolysis with optical detection. The Ti^{III}–H_2O_2 couple was used to generate hydroxyl for e.s.r. experiments.

Reaction of Hydroxyl with Iodine-containing Compounds.—(i) *Iodoacetic acid.* Over a range of pH (1·0—9·0), the only carbon radical detected by e.s.r. was $\cdot CH_2CO_2H$ * or its anion. In the absence of hydrogen peroxide no radicals were observed; Ti^{III} reduction of ICH_2CO_2H is presumably slow, as is the corresponding reduction of iodine.[20] When the iodoacetic acid was present in sufficient concentration ($2{\cdot}5 \times 10^{-2}$M),† the singlets from reaction of $\cdot OH$ with Ti^{IV}–H_2O_2 species were not observed in the e.s.r. spectrum and the signal amplitude of $\cdot CH_2CO_2H$ (or $\cdot CH_2CO_2^-$) reached a limiting value. These observations are consistent with a total scavenging of hydroxyl by ICH_2CO_2H under these conditions, and support for this view was obtained as follows. The concentration of $\cdot CH_2CO_2H$ at pH 1 was close to that of $\cdot CH_2CMe_2OH$ from the oxidation of t-butyl alcohol under identical conditions; since the termination rate constants of these radicals are similar (1·8 and 1·4 l mol^{-1} s^{-1}, respectively[21,22]), we conclude that the rates of formation of $\cdot CH_2CO_2H$ and $\cdot CH_2CMe_2OH$ must also be similar and that, just as reaction of hydroxyl with t-butyl alcohol to form $\cdot CH_2CMe_2OH$ is almost 100% efficient,[23] the reaction with iodoacetic acid results in essentially quantitative conversion of hydroxyl into $\cdot CH_2CO_2H$ [reaction (3)].

$$ICH_2CO_2H \xrightarrow{\cdot OH} \cdot CH_2CO_2H \qquad (3)$$

We obtained further evidence for this conclusion from the pulse radiolysis of iodoacetic acid at pH 1. Since under these conditions the hydrated electron is rapidly converted into the hydrogen atom, the formation of $\cdot CH_2CO_2H$ is also expected from reaction (4). The

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* No significant reaction of this radical with hydrogen peroxide or titanium(III) is expected under our reaction conditions; see ref. 19.

† Concentrations given in this section are those on mixing; subscripts 0 and *t*, where used, refer to this moment and *t* s later, respectively.

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transient detected after a 0·6 μs pulse had an absorption spectrum * close to that previously reported for $\cdot CH_2CO_2H$,[21] and it decayed with second-order kinetics, $2k = ca.\ 2 \times 10^9$ l mol^{-1} s^{-1} (*cf.*[21] $1{\cdot}8 \times 10^9$ l mol^{-1} s^{-1}). $G(\cdot CH_2CO_2H)$ (estimated from the optical density at 330 nm immediately after the pulse, assuming[21] $\varepsilon = 5{\cdot}9$ m^2 mol^{-1}) was found to be 6·2, consistent with complete scavenging of both hydrogen atoms and hydroxyl radicals following the pulse.†

$$H + ICH_2CO_2H \longrightarrow HI + \cdot CH_2CO_2H \quad (4)$$

The rate constant for the reaction of hydroxyl with iodoacetic acid was obtained by standard procedures, with hexacyanoferrate(II) as a competitor for scavenging hydroxyl. From the optical density at 420 nm immediately after the pulse, a value of $5(\pm 1) \times 10^9$ l mol^{-1} s^{-1} was obtained for $k(OH + ICH_2CO_2H)$, taking[26] k[OH + hexacyanoferrate(II)] as $9{\cdot}3 \times 10^9$ l mol^{-1} s^{-1}. These experiments indicated an increase in concentration of hexacyanoferrate(III) following the pulse, so that evidently an oxidising species is formed during the pulse; this is probably HOI, which is known to be a powerful oxidant.

(ii) *Iodoacetamide.* The reaction of the hydroxyl radical with iodoacetamide at pH 1 was investigated by e.s.r. spectroscopy. With an iodoacetamide concentration (on mixing) of $2{\cdot}5 \times 10^{-2}$M, $\cdot CH_2CONH_2$[27] was detected in high concentration; no signals from titanium(IV)–peroxy-complexes or any other paramagnetic species were detected. We conclude that under these conditions iodoacetamide reacts rapidly with the hydroxyl radical to form $\cdot CH_2CONH_2$.

(iii) 3-*Iodopropionic acid.* A concentration of 3-iodopropionic acid of 3×10^{-2}M decreased the signal amplitude of S_1 in the e.s.r. spectrum[19] by *ca.* 30% from its value in the absence of this acid; no other paramagnetic species was detected. Since the linewidth of S_1 was unchanged on the addition of $ICH_2CH_2CO_2H$ and since oxygen was rigorously excluded from the solutions (in order to prevent formation of peroxy-species derived from *organic* radicals), this observation may be taken as evidence for fairly slow reaction of the hydroxyl radical with this substrate. Possible reactions are iodine-atom displacement [reaction (5)] or perhaps hydrogen-atom abstraction [reaction (6)] [*cf.* the reaction between hydroxyl and

$$ICH_2CH_2CO_2H \xrightarrow{\cdot OH} HO(ICH_2CH_2CO_2H) \xrightarrow{H^+} I(H_2O) + \overset{+}{C}H_2CH_2CO_2H \quad (5)$$

$$ICH_2CH_2CO_2H \xrightarrow[-H_2O]{\cdot OH} ICH_2\dot{C}HCO_2H \text{ and } I\dot{C}HCH_2CO_2H \quad (6)$$

propionic acid, which is relatively slow—$k = 4{\cdot}6 \times 10^8$ l mol^{-1} s^{-1} if we revise the original value[28] to the hexacyanoferrate(II) standard[26]].

Line-broadening from anisotropy in the iodine splitting (or possibly quadrupolar relaxation) would probably prevent the detection of α- and β-iodine-substituted radicals in solution by e.s.r. [*cf.* solid-state spectra[29] of iodine-substituted radicals].

(iv) 2-*Iodoethanol.* Results similar to those for 3-iodopropionic acid were obtained for this compound, *i.e.* some scavenging of hydroxyl was detected, but no e.s.r. spectrum of an organic radical product was observed. It seems likely that iodine atoms are produced in solution, either *via* hydroxyl–iodoethanol complexes or *via* fragmentation of a first-formed hydroxyalkyl radical [reactions (7) and (8)], as we have previously[30] suggested.

$$HO\cdot + ICH_2CH_2OH \longrightarrow ICH_2\dot{C}HOH + H_2O \quad (7)$$

$$ICH_2\dot{C}HOH \longrightarrow \cdot I + CH_3CHO \quad (8)$$

The rate constant for reaction (7) might be expected to be *ca.* 10^9 l mol^{-1} s^{-1}, at least by comparison with that for the reaction of hydroxyl with ethanol ($1{\cdot}85 \times 10^9$ l mol^{-1} s^{-1}).[26] The diminution in signal intensity of S_1 in the presence of ICH_2CH_2OH (>90% for $1{\cdot}8 \times 10^{-2}$M-2-iodoethanol) indicated that this substrate is substantially more reactive than $ICH_2CH_2CO_2H$ towards $\cdot OH$. If this suggestion is correct then the reaction sequence expressed in (7) and (8) would seem to be more probable than a rather slow formation of a charge-transfer complex followed by a diffusion-controlled[4] reaction with acid.

Reaction of Carbon-centred Radicals with Iodine-containing Compounds.—(i) *Reaction of* $\cdot CH_2CMe_2OH$ *with* ICH_2CO_2H. Oxidation of a mixture of t-butyl alcohol (0·25M) and iodoacetic acid (5×10^{-3}M) under typical flow-system conditions (pH 1, $[Ti^{III}]_0 = 2{\cdot}67$mM, $[H_2O_2]_0 = 8$mM, $t = ca.$ 50 ms) gave only the spectrum of the radical $\cdot CH_2CO_2H$, in concentration equal to that from the corresponding oxidation of iodoacetic acid alone (see earlier). From the concentrations of the organic substrates employed and the rate constants for reaction of hydroxyl with t-butyl alcohol[23] and iodoacetic acid (see earlier), we calculate that scavenging of hydroxyl is mainly (>90%) by t-butyl alcohol; the detection of $\cdot CH_2CO_2H$ in such a concentration therefore indicates essentially complete conversion from $\cdot CH_2CMe_2OH$ under our conditions. Since the possibility of electron-transfer reactions involving $\cdot CH_2CMe_2OH$ appears slight, we infer the occurrence of iodine-atom abstraction [reaction (9)].

$$\cdot CH_2CMe_2OH + ICH_2CO_2H \longrightarrow ICH_2CMe_2OH + \cdot CH_2CO_2H \quad (9)$$

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* Repeated pulsing gave increased absorption at longer wavelengths, probably due to the formation of I_2^-.[24] The spectrum of HOI is expected to be very weak (*cf.*[25] IO^-).

† Neither the radiolysis nor the e.s.r. method would reveal a precursor if this were to break down to give $\cdot CH_2CO_2H$ with a rate constant (first order or pseudo-first order) > *ca.* 10^7 s^{-1}.

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When the concentration of iodoacetic acid was reduced further, both $\cdot CH_2CO_2H$ and $\cdot CH_2CMe_2OH$ were detected. Under these conditions, we would expect the system to be described for kinetic analysis by equations (10)—(15) (RI = organic iodide):

$$\mathrm{Ti^{III}} + H_2O_2 \xrightarrow{k_{in}} \mathrm{Ti^{IV}} + OH^- + \cdot OH \quad (10)$$

$$\cdot OH + Bu^tOH \longrightarrow \cdot CH_2CMe_2OH + H_2O \quad (11)$$

$$\cdot CH_2CMe_2OH + RI \xrightarrow{k_{12}} ICH_2CMe_2OH + \cdot R \quad (12)$$

$$2\cdot CH_2CMe_2OH \xrightarrow{k_{13}} \text{molecular products} \quad (13)$$

$$\cdot CH_2CMe_2OH + \cdot R \xrightarrow{k_{14}} \text{molecular products} \quad (14)$$

$$2\cdot R \xrightarrow{k_{15}} \text{molecular products} \quad (15)$$

We assume that all the hydroxyl radicals are scavenged by t-butyl alcohol and that both oxidation and reduction of the organic radicals produced are negligible under our reaction conditions. For $[H_2O_2]_0 \gg [\mathrm{Ti^{III}}]_0$, an exponential decrease in the concentration of $\mathrm{Ti^{III}}$ along the flow tube occurs, and a quasi-steady-state is attained,[19,31,32] so that the following relationships hold:

$$\begin{aligned} R_{in} &= k_{in}[H_2O_2]_0[\mathrm{Ti^{III}}]_0 \exp(-k_{in}[H_2O_2]_0 t) \\ &= 2k_{13}[\cdot CH_2CMe_2OH]^2 + 2k_{14}[\cdot CH_2CMe_2OH][\cdot R] + 2k_{15}[\cdot R]^2 \quad (16) \end{aligned}$$

where R_{in} denotes the rate of radical initiation;

and $$[\cdot R]/[\cdot CH_2CMe_2OH] = k_{12}[RI]/(2k_{15}[\cdot R] + k_{14}[\cdot CH_2CMe_2OH]) \quad (17)$$

Equation (17) forms a basis for the analysis of our e.s.r. data.

Preliminary experiments indicated that the reaction of the radical $\cdot CH_2CMe_2OH$ with iodoacetic acid is rapid. For example, under our initial conditions a concentration of iodoacetic acid of *ca.* $7{\cdot}5 \times 10^{-4}$M was sufficient to halve the concentration of $\cdot CH_2CMe_2OH$ from its value in the absence of this acid. Since some depletion of iodoacetic acid along the flow tube was expected under these conditions, a modification of the experimental conditions was required. The depletion of organic iodide along the flow tube is related to the depletion of titanium(III),* which may be reduced by reducing $[\mathrm{Ti^{III}}]_0$, $[H_2O_2]_0$, and t. A decrease in $[\mathrm{Ti^{III}}]_0$ ($[ICH_2CO_2H]$ constant) has the effect of linearly reducing its depletion along the flow tube, but at the same time it increases the efficiency of scavenging of $\cdot CH_2CMe_2OH$ by iodoacetic acid, since the rate of radical initiation is thereby also lowered ($R_{in} \propto [\mathrm{Ti^{III}}]_0^{\frac{1}{2}}$). One effect of a reduction in $[H_2O_2]_0$ will similarly be a reduction in the depletion of titanium(III); the rate of radical initiation in the cavity may also be changed.[31,32] For this system and others in which low concentrations of organic iodide were necessary, experimental conditions were therefore modified as follows. (*a*) The flow rate was approximately doubled (t *ca.* 30 ms); (*b*) $[H_2O_2]_0$ was reduced to 5·3 mM; (*c*) $[\mathrm{Ti^{III}}]_0$ was reduced to 1 mM. Under these conditions we calculate that the depletion of $\mathrm{Ti^{III}}$ along the flow tube to the cavity is $<10^{-4}$M (less than 10% of $[\mathrm{Ti^{III}}]_0$). Data obtained for the concentrations of the two radicals $\cdot CH_2CMe_2OH$ and $\cdot CH_2CO_2H$ under these conditions are collected in Table 1.

We would expect on purely statistical grounds that $k_{14} = 2k_{13} = 2k_{15}$; equation (17) then predicts that a plot of $[\cdot CH_2CO_2H]/[\cdot CH_2CMe_2OH]$ against $[ICH_2CO_2H]/\{[\cdot CH_2CO_2H] + [\cdot CH_2CMe_2OH]\}$ should be linear, with gradient $k_{12}/2k_{15}$. Figure 1 shows that the expected behaviour is observed, and we obtain $k_{12} = [7{\cdot}3\ (\pm\ 1{\cdot}5) \times 10^{-3}]2k_{15}$; taking[21] $2k_{15}$ as $1{\cdot}8 \times 10^9$ l mol^{-1} s^{-1} we calculate k_{12} as $1{\cdot}3\ (\pm 0{\cdot}3) \times 10^7$ l mol^{-1} s^{-1}.

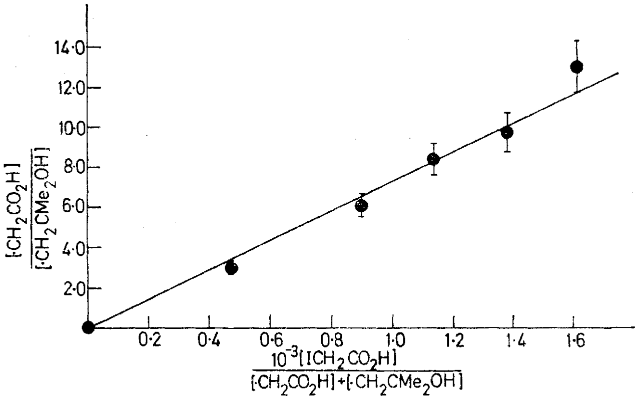

FIGURE 1 Variation in $[\cdot CH_2CO_2H]/[\cdot CH_2CMe_2OH]$, plotted according to equation (17) (see text)

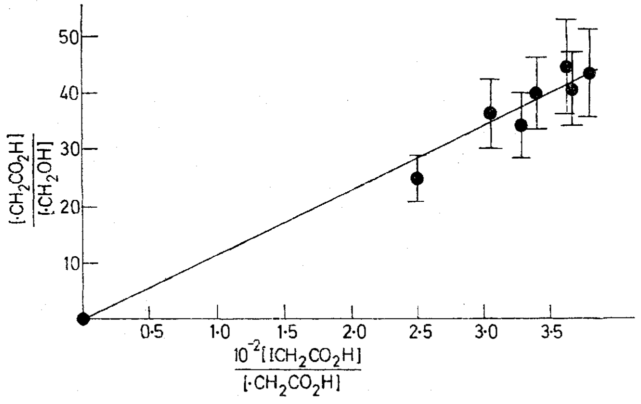

FIGURE 2 Variation in the ratio $[\cdot CH_2CO_2H]/[\cdot CH_2OH]$, plotted according to equation (22) (see text)

It is possible that cross-termination of the radicals $\cdot CH_2CO_2H$ and $\cdot CH_2CMe_2OH$ is favoured (*i.e.* that $k_{14} > 2k_{15}$). This type of behaviour is characteristic[33] of the combination of radicals of opposite polarity (electron-donor and electron-acceptor type) but may not be marked in this case since, although $\cdot CH_2CO_2H$ is

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* Assuming complete scavenging of hydroxyl by t-butyl alcohol, removal of one mole of titanium(III) will lead to the formation of one mole of $\cdot CH_2CMe_2OH$ and thus to the removal of up to one mole of RI; the extent of removal of the latter of course depends on the efficiency of scavenging of $\cdot CH_2CMe_2OH$ by RI.

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

[33] W. A. Pryor, 'Free Radicals,' McGraw-Hill, New York, 1966, p. 16.

electrophilic, $\cdot CH_2CMe_2OH$ should be hardly more than weakly nucleophilic.* However, even if the cross-termination was favoured (with k_{14} approaching, say, a limiting value expected for diffusion-control, *ca.* 10^{10} l mol^{-1} s^{-1}), the highest values of $\{2k_{15}[\cdot CH_2CO_2H] + k_{14}[\cdot CH_2CMe_2OH]\}$ should be in error (too low) by only *ca.* 20%, although the lowest value could be *ca.* 40% in error. Since no significant deviations from linearity are apparent in Figure 1 and calculations of the rate of radical initiation [equation (16)] on the basis of $k_{14} = 2k_{15}$ give reasonably constant results, we believe that this assumption is appropriate.

In an attempt to obtain some indication of the correctness of our analysis and the accuracy of our data, we investigated the same reaction with pulse radiolysis. Solutions were adjusted to pH 1 by addition of sulphuric acid and deoxygenated by bubbling with argon. Unfortunately under conditions ($[Bu^tOH] = 1$M, $[ICH_2CO_2H] = 1\cdot 6 \times 10^{-3}$M) such that removal of $\cdot CH_2CMe_2OH$ from the system was by iodine-atom abstraction from ICH_2CO_2H rather than by bimolecular termination, the hydrogen atoms formed from the hydrated electron at this pH react during the pulse with iodoacetic acid rather than with t-butyl alcohol; some $\cdot CH_2CO_2H$ ($G = 3\cdot 4$) was therefore detected immediately following the pulse. The concentration of this radical (monitored *via* the optical density at 330 nm) increased after the pulse, consistent with the occurrence of reaction (12). The time-dependence of the absorption at 330 nm was complex (a combination of second-order removal and first-order build-up is expected), and it was impossible to estimate k_{12} with any degree of accuracy; however, from the concentration of ICH_2CO_2H necessary to give a net increase in $\cdot CH_2CO_2H$ after the pulse, our estimate of k_{12} appears to be of the correct order, *i.e. ca.* 10^7 l mol^{-1} s^{-1}.

(ii) *Reactions of* $\cdot CH_2CMe_2OH$ *with other iodine-containing compounds*. The reactions of the radical $\cdot CH_2CMe_2OH$ with iodoacetonitrile, 3-iodopropionic acid, and 2-iodoethanol were studied by e.s.r. spectroscopy. The procedure adopted was essentially that described previously, *viz.* the concentrations of $\cdot CH_2CMe_2OH$ and the radical derived from iodine-atom abstraction from the organic iodide were monitored as a function of organic iodide concentration; a substantial excess of t-butyl alcohol was used ($[Bu^tOH]/[RI] \geqslant 250$) in order to ensure scavenging of hydroxyl by t-butyl alcohol. Analysis of the experimental data was determined by a consideration of each experimental system, and will therefore be briefly described for each case.

(a) *Iodoacetonitrile.* It is possible that, as we considered for the iodoacetic acid system, combination of radicals of different electronic characteristics is favoured. However, under conditions such that depletion of iodoacetonitrile along the flow tube could be neglected, values of $[\cdot CH_2CN]/[\cdot CH_2CMe_2OH]$ were high (>10). Under these conditions, $2k_{15}[\cdot CH_2CN]$ should be considerably greater than $k_{14}[\cdot CH_2CMe_2OH]$ and equation (17) reduces to equation (18). The radical ratio was therefore plotted

$$[\cdot R]/[\cdot CH_2CMe_2OH] = k_{12}[RI]/2k_{15}[\cdot R] \quad (18)$$

against [RI] ([·R] was essentially constant over the range of radical ratios studied). From the gradient of this plot, together with a radical concentration calibration, and assuming $2k_{15} = 2 \times 10^9$ l mol^{-1} s^{-1} (the value of $2k$ for $\cdot CMe_2CN$ in benzene has been estimated [34] as $1\cdot 9 \times 10^9$ l mol^{-1} s^{-1}), we obtain $k_{12} = 2\cdot 0\ (\pm 0\cdot 5) \times 10^7$ l mol^{-1} s^{-1}.

(b) 2-*Iodoethanol and* 3-*iodopropionic acid.* Little preference for radical cross-combination is expected in these systems. We have therefore assumed that $k_{14} = 2k_{15} = 1\cdot 9 \times 10^9$ l mol^{-1} s^{-1} [from ref. 19, $2k(\cdot CH_2CMe_2OH) = 1\cdot 4 \times 10^9$ l mol^{-1} s^{-1}; $2k(\cdot CH_2CH_2OH) = 2\cdot 3 \times 10^9$ l mol^{-1} s^{-1}; $2k(\cdot CH_2CH_2CO_2H)$ is probably similar to $2k(\cdot CH_2CH_2OH)$]; the sum of the concentrations of the two radicals was found to be essentially constant for a range of radical ratios and is consistent with this assumption. Values of k_{12} were estimated from equation (17) and are reported in Table 2 together with values from other systems and with other relevant data.

TABLE 1

Variation of radical ratio with concentration of iodoacetic acid

10^3 $[ICH_2CO_2H]$/M	10^6 $[\cdot CH_2CMe_2OH]$/M	10^6 $[\cdot CH_2CO_2H]$/M	$[\cdot CH_2CO_2H]/[\cdot CH_2CMe_2OH]$
0	1·50	0	0
0·54	0·31	0·91	2·9
1·20	0·19	1·14	6·1
1·60	0·15	1·26	8·4
2·00	0·13	1·32	9·8
2·40	0·11	1·38	13·1

TABLE 2

Rate constants for reactions of radicals ($R^1\cdot$) with organic iodides (R^2I)

R^1	R^2I	k/l mol^{-1} s^{-1}	Conditions	Ref.
CH_3	ICH_2CH_3	$5\cdot 4 \times 10^4$	Toluene, 65°	15
	$ICH(CH_3)_2$	$2\cdot 5 \times 10^5$		
	ICH_2Cl	$1\cdot 9 \times 10^7$		
	(I_2)	(6×10^9)	(H_2O, 25°)	(2)
CH_2OH	$ICH_2CH_2CO_2H$	$1\cdot 0 \times 10^5$	H_2O, 20°	This work
	ICH_2CO_2H	$2\cdot 1 \times 10^8$		
CH_2CMe_2OH	ICH_2CH_2OH	$1\cdot 5 \times 10^5$	H_2O, 20°	This work
	$ICH_2CH_2CO_2H$	$1\cdot 8 \times 10^5$		
	ICH_2CO_2H	$1\cdot 3 \times 10^7$		
	ICH_2CN	$2\cdot 0 \times 10^7$		

(iii) *Reaction of* $\cdot CH_2CMe_2OH$ *with iodine.* Oxidation of an aqueous solution of t-butyl alcohol saturated with iodine did not give rise to a detectable spectrum of the radical $\cdot CH_2CMe_2OH$ or any other paramagnetic species. Reduction of the iodine concentration gave qualitatively the expected behaviour, *i.e.* the spectrum of $\cdot CH_2CMe_2OH$ appeared and increased in intensity to a limiting value as $[I_2]$ was reduced. However, values of $[\cdot CH_2CMe_2OH]$ were generally higher than expected if we assume that

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* For example, pulse-radiolysis data [22] indicate that the combination of $\cdot CH_2CMe_2OH$ with $\cdot CO_2^-$ or $\cdot CH_2CO_2^-$ is no faster than anticipated on statistical grounds by comparison with the dimerisation of CO_2^- or $\cdot CH_2CO_2^-$ when allowance is made for the effect of charge repulsion on the latter. In contrast, the rates for cross-termination of the more strongly nucleophilic radicals CH_2OH and $\cdot CHMeOH$ with these anionic radicals appear to be slightly greater than so predicted.

[34] S. A. Weiner and G. S. Hammond, *J. Amer. Chem. Soc.*, 1969, **91**, 986.

reaction of $\cdot CH_2CMe_2OH$ with iodine is diffusion-controlled and that the concentration of iodine in the cavity is that immediately after mixing (iodine-containing solutions were prepared by dilution of a saturated solution in water, taking [35] the concentration of iodine in this solution to be $1\cdot3 \times 10^{-3}$ M). This discrepancy almost certainly arises from a depletion of iodine along the flow tube (the concentration of iodine on mixing was at the most *ca.* 4×10^{-4} M).

(iv) *Reactions of* $\cdot CH_2OH$ *with iodine-containing compounds.* The radical $\cdot CH_2OH$ is an efficient electron donor, and it has previously been suggested [7] that the reaction of the related radical $\cdot CMe_2OH$ with alkyl iodides involves electron transfer, according to reaction (19).

$$\cdot CMe_2OH + RI \longrightarrow \cdot R + Me_2CO + H^+ + I^- \qquad (19)$$

When mixtures of iodoacetic acid and methanol were oxidised, with $[ICH_2CO_2H] \geqslant 5 \times 10^{-4}$ M in order to be able to rule out significant depletion of this compound along the flow tube, high ratios of $[\cdot CH_2CO_2H]$ to $[\cdot CH_2OH]$ were apparent; these observations indicate a high rate constant for reaction (20) [we expect the radical ratio to be described by equation (21) where k' is the rate constant for the reaction of $\cdot R$ with $\cdot CH_2OH$], one that is certainly higher than that for the corresponding reaction involving $\cdot CH_2CMe_2OH$.* Owing to the high ratios involved, the data are of lower accuracy than those previously reported. From the data plotted in Figure 2 [analysis according to equation (22), the reduced form of equation (21); again, although cross-combination of $\cdot CH_2OH$ with $\cdot CH_2CO_2H$ may well be favoured, this should make only a small contribution to the estimated rate constant] we calculate k_{20} as $2\cdot1\ (\pm0\cdot7) \times 10^{8}$ l mol^{-1} s^{-1}.

$$\cdot CH_2OH + RI \xrightarrow{k_{20}} \cdot R + \text{products} \qquad (20)$$

$$[\cdot R]/[\cdot CH_2OH] = k_{20}[RI]/(2k_{15}[\cdot R] + k'[\cdot CH_2OH]) \qquad (21)$$

$$[\cdot R]/[\cdot CH_2OH] \simeq k_{20}[RI]/2k_{15}[\cdot R] \qquad (22)$$

Pulse radiolysis of aqueous solutions of methanol containing low concentrations of iodoacetic acid was complicated, as in the experiments with t-butyl alcohol, by reaction of the hydrogen atom with iodoacetic acid rather than with the alcohol. However, the increase in optical density at 330 nm following the pulse was consistent with the occurrence of reaction (20), with $k_{20} < 3\cdot5 \times 10^{8}$ l mol^{-1} s^{-1}.

We also investigated the reaction of the hydroxymethyl radical with 3-iodopropionic acid. Possible termination reactions in this system are:

$$2\cdot CH_2OH \xrightarrow{k_{23}} \text{molecular products} \qquad (23)$$

$$\cdot CH_2OH + \cdot CH_2CH_2CO_2H \xrightarrow{k_{24}} \text{molecular products} \qquad (24)$$

$$2\cdot CH_2CH_2CO_2H \xrightarrow{k_{25}} \text{molecular products} \qquad (25)$$

If we assume that $k_{24} = 2k_{23} = 2k_{25} = 2\cdot4 \times 10^{9}$ l mol^{-1} s^{-1} (from ref. 22, $2k_{23} = 2\cdot4 \times 10^{9}$ l mol^{-1} s^{-1}; as before, we take $2k_{25}$ to be *ca.* $2k$ for the self-reaction of $\cdot CH_2CH_2OH$,[22] *i.e.* $2\cdot3 \times 10^{9}$ l mol^{-1} s^{-1}) then from the radical ratios over a range of $[ICH_2CH_2CO_2H]$ we calculate that $k_{20} = 1\cdot5\ (\pm0\cdot5) \times 10^{5}$ l mol^{-1} s^{-1}.

Reactivity of Carbon Radicals towards Organic Iodides.—The reactions of $\cdot CH_2OH$ and $\cdot CH_2CMe_2OH$ with iodoacetic acid are much faster than those with iodopropionic acid (see Table 2); this is understandable in terms of the more exothermic nature of the reactions leading to the formation of the delocalised species $\cdot CH_2CO_2H$. The behaviour of ICH_2CN and ICH_2CH_2OH towards $\cdot CH_2CMe_2OH$ can also be rationalised on this basis. Similarly, the slower reaction of $\cdot CH_2OH$ with $ICH_2CH_2CO_2H$ than of $\cdot CH_2CMe_2OH$ with the same substrate presumably reflects the more endothermic nature of the former reaction ($\cdot CH_2OH$ is stabilised by delocalisation). In contrast, the radical $\cdot CH_2OH$ reacts faster with ICH_2CO_2H than does $\cdot CH_2CMe_2OH$. We infer that polar factors must dominate in this case and therefore that the transition state for the iodine-atom abstraction is stabilised by the contribution of charged structures, with incipient positive and negative charges developing on the attacking radical and the substrate, respectively, so that the effect is marked for $\cdot CH_2OH$ and iodoacetic acid:

$$HOCH_2\cdot + ICH_2CO_2H \longrightarrow HOCH_2{}^{+}\cdots\dot{I}\cdots{}^{-}CH_2CO_2H$$

We note that the relative reactivities of both aryl and alkyl iodides (RI) towards phenyl radicals (Ph·) can be correlated with the Hammett equation with $\rho = 0\cdot57$ for the aromatic series and $0\cdot18$ for the aliphatic series [12] (*i.e.* structures of the form $Ph^{+}\cdots I\cdots R^{-}$ contribute significantly to the transition state).

The rate constants for iodine-atom abstraction from organic compounds of general type ICH_2CH_2X are in the range 1—2×10^{5} l mol^{-1} s^{-1} for both $\cdot CH_2OH$ and $\cdot CH_2CMe_2OH$. No data are available for the reaction of methyl with, for example, $ICH_2CH_2CH_3$, but we would expect the rate constant to be similar to that for reaction with ethyl iodide and therefore *ca.* 10^{5} l mol^{-1} s^{-1} (in toluene solution at 65°; see Table 2). If we assume a 'normal' pre-exponential factor [18] of *ca.* $10^{8\cdot5}$ l mol^{-1} s^{-1} for the reaction, then the rate constant in toluene at 20 °C should be *ca.* 4×10^{4} l mol^{-1} s^{-1}. This is somewhat lower than the rate constants for reaction of the other radicals although we should expect reactions of the methyl radical to be thermodynamically favoured; solvent effects on the reactions of carbon-centred radicals are

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* With experimental conditions (low $[ICH_2CO_2H]$, slow flow) for which significant depletion of ICH_2CO_2H along the flow tube was expected, $\cdot CH_2OH$ appeared to be *less* reactive than $\cdot CH_2CMe_2OH$ towards this substrate, as judged from the respective radical ratios in the two systems for the same value of $[ICH_2CO_2H]$. This may be explained by the fact that under these conditions depletion of ICH_2CO_2H was *greater* in the presence of $\cdot CH_2OH$ than in the presence of $\cdot CH_2CMe_2OH$ (*i.e.* $\cdot CH_2OH$ is a more efficient scavenger of ICH_2CO_2H than is $\cdot CH_2CMe_2OH$). This observation illustrates the importance of a correct choice of experimental conditions in rapid-flow experiments.

[35] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 2nd edn., Interscience, London, 1966.

usually expected to be small,[36] although a polar medium such as water would be expected to facilitate a reaction involving a polar transition state.

These data on halogen abstractions should be relevant to the e.s.r. experiments concerning the reaction of organolithium reagents with alkyl halides described by Russell and Lamson [8] and by Fischer.[9] We assume that a quasi-steady state is attained and that only a small amount of conversion occurs during the period between mixing and observation. The following reaction scheme [equations (26)—(31)] has been suggested.

$$\mathrm{R^1Li + R^2I \xrightarrow{k_{26}} R^{1\cdot} + R^{2\cdot} + LiI} \qquad (26)$$

$$\mathrm{R^{1\cdot} + R^2I \xrightarrow{k_{27}} R^1I + R^{2\cdot}} \qquad (27)$$

$$\mathrm{R^{2\cdot} + R^1Li \xrightarrow{k_{28}} R^2Li + R^{1\cdot}} \qquad (28)$$

$$\mathrm{2R^{1\cdot} \xrightarrow{k_{29}}} \text{ molecular products} \qquad (29)$$

$$\mathrm{R^{1\cdot} + R^{2\cdot} \xrightarrow{k_{30}}} \text{ molecular products} \qquad (30)$$

$$\mathrm{2R^{2\cdot} \xrightarrow{k_{31}}} \text{ molecular products} \qquad (31)$$

If we assume that reactions (29)—(31) can be described by a single rate coefficient ($2k$), then steady-state analysis of the above yields

$$\frac{[\mathrm{R^{1\cdot}}]}{[\mathrm{R^{2\cdot}}]} = \frac{2k_{27}[\mathrm{R^2I}]_t + 2k([\mathrm{R^{1\cdot}}] + [\mathrm{R^{2\cdot}}])}{2k_{28}[\mathrm{R^1Li}]_t + 2k([\mathrm{R^{1\cdot}}] + [\mathrm{R^{2\cdot}}])} \qquad (34)$$

where $[\mathrm{R^2I}]_t$ and $[\mathrm{R^1I}]_t$ are reagent concentrations in the cavity.

From the data of Russell and Lamson (conversion of starting materials should be lower in their system than in that of Fischer), $[\mathrm{R^{1\cdot}}]/[\mathrm{R^{2\cdot}}] > 20$ for $\mathrm{R^2} \neq \mathrm{Me}$. Typically, $2k = 2 \times 10^9\ \mathrm{l\ mol^{-1}\ s^{-1}}$, $[\mathrm{R^{1\cdot}}] + [\mathrm{R^{2\cdot}}] = 10^{-6}\mathrm{M}$ and $[\mathrm{R^2I}]_t \leqslant [\mathrm{R^2I}]_0 = 0{\cdot}2\mathrm{M}$. Thus, $k_{27} > \{100k_{28}[\mathrm{R^1Li}]_t + (9 \times 10^4)\}\ \mathrm{l\ mol^{-1}\ s^{-1}}$, *i.e.* $k_{27} > 9 \times 10^4\ \mathrm{l\ mol^{-1}\ s^{-1}}$, in agreement with our previous estimates.

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[36] E. S. Huyser, *Adv. Free Radical Chem.*, 1965, **1**, 77.