Kinetic Electron Spin Resonance Spectroscopy. Part II.[1] Termination Rates for Ketyl and Semiquinone Radicals in Alcoholic Solvents

By **Peter B. Ayscough** * and **Roger C. Sealy**, School of Chemistry, University of Leeds, Leeds LS2 9JT

An intermittent illumination method using e.s.r. detection has been employed to measure rate constants for the termination reactions of free radicals generated during the photoreduction of pyruvic acid, 2-oxobutyric acid, biacetyl, 1,4-benzoquinone, and 1,4-naphthoquinone in organic solvents. For these ketyl and semiquinone radicals, second-order termination rate constants are in the range 10^8—10^9 l mol^{-1} s^{-1} and show a dependence on solvent viscosity in accord with theories of diffusion-controlled reactions which include rotational diffusion within the solvent cage as a rate-influencing factor. Activation energies were measured for the combination of $Me\dot{C}(OH)CO_2H$ and $Me\dot{C}(OH)COMe$ radicals in alcoholic solvents. Observed values of 10—20 kJ mol^{-1} are in general less than the temperature coefficients for viscous flow in these solvents, again in agreement with this model.

IN Part I [1] we described a study of the photoreduction of biacetyl and pyruvic acid in a number of organic solvents, based on the use of intermittent u.v. irradiation in conjunction with e.s.r. In this paper we consider in some detail the interpretation of termination rates for radicals observed by this method and use the data to make a critical examination of the relationships between combination rate and solvent viscosity predicted by some simple theories of diffusion-controlled reactions. In view of the great paucity of data on the temperature dependence of combination rates of small carbon and oxygen radicals we have determined some activation energies for radical combinations and compared these with the temperature coefficient for viscous flow in a number of solvents.

The systems examined include the photoreduction of pyruvic acid, 2-oxobutyric acid, biacetyl, 1,4-benzoquinone, and 1,4-naphthoquinone in six alcoholic solvents.

EXPERIMENTAL

All chemicals were of the highest commercially available quality. Pyruvic acid, 1,4-benzoquinone, and diphenylpicrylhydrazyl were obtained from B.D.H., 1,4-naphthoquinone from Fluka, biacetyl from Koch-Light, and 2-oxobutyric acid from Emmanuel. Solvents were all AnalaR or AristaR quality. Where alternative sources of solvents were available comparative tests of radical lifetimes showed no significant differences. All samples were degassed by four or more freeze-pump-thaw cycles each to $< 10^{-4}$ mmHg.

Details of the Decca e.s.r. spectrometer, the optical system, and the Biomac computer for averaging transients were given in Part I.[1] Sample tubes used varied according to the system under investigation and the experimental conditions, but wherever possible quartz flat cells with a path length of 0·3 mm and an illuminated area of *ca.* 150 mm^2 were employed. For variable temperature studies the sample tubes were supported in a double-walled outer jacket through which heated or cooled gaseous nitrogen was passed.

In determining the concentration of the absorbing species to be used in any series of experiments it was necessary to compromise between, on the one hand, a good signal-to-noise and negligible depletion of reactants (*i.e.* in terms of the observable radical concentration) and, on the other hand, a non-homogeneous distribution of the photolytically generated radicals. It has been suggested [2] that radical concentrations estimated under such non-uniform conditions should be regarded as a minimum. In most cases it was possible to operate with $<10\%$ of the incident light absorbed in the 0·3 mm path length: on occasions this proportion was allowed to increase to *ca.* 20% but the errors caused by the resulting non-uniform distribution were still less than the errors in measuring the radical concentrations. The procedure for estimating concentrations has been described previously.[1] The experimental problems encountered in rotating sector studies have been discussed elsewhere.[3]

RESULTS

The generalised reaction scheme established for the photoreduction of biacetyl and pyruvic acid [1] serves as a basis for

---

[1] Part I, P. B. Ayscough and M. C. Brice, *J. Chem. Soc.* (*B*), 1971, 491.

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

[3] E. J. Hamilton, jun., D. E. Wood, and G. S. Hammond, *Rev. Sci. Instr.*, 1970, **41**, 452.

the present extended studies. For a carbonyl compound RR′CO the superscripts *s* and *t* refer to the first excited singlet and triplet states respectively, DH and Q are hydrogen donors and triplet quenchers where present. The mechanism may be written as reactions (A)—(I).

$$\mathrm{RR'CO} \longrightarrow (\mathrm{RR'CO})^{s} \qquad\qquad \text{(A)}$$

$$(\mathrm{RR'CO})^{s} \longrightarrow (\mathrm{RR'CO})^{t} \qquad\qquad \text{(B)}$$

$$(\mathrm{RR'CO})^{t} \longrightarrow \mathrm{RR'CO} \qquad k_{\mathrm{d}} \quad \text{(C)}$$

$$(\mathrm{RR'CO})^{t} + \mathrm{Q} \longrightarrow \mathrm{RR'CO} + \mathrm{Q}^{t} \qquad k_{\mathrm{q}} \quad \text{(D)}$$

$$(\mathrm{RR'CO})^{t} + \mathrm{DH} \longrightarrow \mathrm{RR'\dot{C}OH} + \dot{\mathrm{D}} \qquad k_{\mathrm{r}} \quad \text{(E)}$$

$$\dot{\mathrm{D}} + \mathrm{RR'CO} \longrightarrow \mathrm{RR'\dot{C}OH} + \mathrm{D(-H)} \qquad k_{\mathrm{h}} \quad \text{(F)}$$

$$2\mathrm{RR'\dot{C}OH} \longrightarrow \text{products} \qquad k_{1} \quad \text{(G)}$$

$$\mathrm{RR'\dot{C}OH} + \dot{\mathrm{D}} \longrightarrow \text{products} \qquad k_{2} \quad \text{(H)}$$

$$2\dot{\mathrm{D}} \longrightarrow \text{products} \qquad k_{3} \quad \text{(I)}$$

In all the ketones, keto-acids, and quinones we have examined during photolysis in organic solvents we have observed $\mathrm{RR'\dot{C}OH}$ radicals, never the solvent radicals $\dot{\mathrm{D}}$. The hydrogen-transfer reaction with rate constant k_{h} is introduced because it is known from other work that when DH is a primary or secondary alcohol reaction with the ground state ketone [4,5] or quinone [6] can account for a substantial proportion of the $\dot{\mathrm{D}}$ radicals. It is now clear that this reaction is responsible for our failure to observe the solvent radical $\dot{\mathrm{D}}$ in any system in which DH is a primary or secondary alcohol.

If the quantum yield for the production of $(\mathrm{RR'CO})^{t}$ is ϕ, then the rate of formation of $(\mathrm{RR'CO})^{t}$ is given by ϕI, where I is the absorbed light intensity, assumed to be uniform throughout the reaction cell. Because of the precautions described in the experimental section this assumption was justified in all the systems we examined in this series of experiments. The steady-state concentration of $(\mathrm{RR'CO})^{t}$ during continuous illumination can then be written as equation (1). By writing analogous expressions

$$[(\mathrm{RR'CO})^{t}]_{\mathrm{ss}} = I\phi/(k_{\mathrm{d}} + k_{\mathrm{r}}[\mathrm{DH}] + k_{\mathrm{q}}[\mathrm{Q}]) \qquad (1)$$

for $[\mathrm{RR'\dot{C}OH}]_{\mathrm{ss}}$ and $[\dot{\mathrm{D}}]_{\mathrm{ss}}$ we can show that under steady-state conditions equation (2) holds. Thus the steady-

$$k_{1}[\mathrm{RR'\dot{C}OH}]^{2}_{\mathrm{ss}} = k_{3}[\dot{\mathrm{D}}]^{2}_{\mathrm{ss}} + k_{\mathrm{h}}[\mathrm{RR'CO}][\dot{\mathrm{D}}]_{\mathrm{ss}} \qquad (2)$$

state concentration of $\mathrm{RR'\dot{C}OH}$ radicals will be a composite function of the four rate constants k_1, k_2, k_3, and k_{h}. So of course will the rate of decay of these radicals following a period of illumination, but the implications of deviations from steady-state conditions must be considered carefully before the rate of decay can be properly interpreted.

This paper is concerned with the measurement and interpretation of rates of decay of $\mathrm{RR'\dot{C}OH}$ radicals following u.v. irradiation. Our measurements show that the decays are kinetically second order and from these we obtain values of k_{t} defined by equation (3).

$$-\mathrm{d}[\mathrm{RR'\dot{C}OH}]/\mathrm{d}t = k_{\mathrm{t}}[\mathrm{RR'\dot{C}OH}]^{2} \qquad (3)$$

Three important limiting cases can be recognised. In mechanism A the radicals $\dot{\mathrm{D}}$ disappear mainly by geminate combination, *i.e.* $k_{2}[\mathrm{RR'\dot{C}OH}][\dot{\mathrm{D}}] \approx k_{3}[\dot{\mathrm{D}}]^{2} \gg k_{\mathrm{h}}[\mathrm{RR'CO}][\dot{\mathrm{D}}]$. In this case it is readily shown that $[\dot{\mathrm{D}}]_{\mathrm{ss}} \approx (k_1/k_3)^{\frac{1}{2}} [\mathrm{RR'COH}]_{\mathrm{ss}}$ and the observed rate constant for termination $k_{\mathrm{t}} \approx 2k_1 + k_2(k_1/k_3)^{\frac{1}{2}}$ if the ratio $[\dot{\mathrm{D}}]:[\mathrm{RR'\dot{C}OH}]$ remains constant throughout the decay. The assumption that this ratio remains at the steady-state value is probably justified if all the radical reactions are bimolecular and diffusion-controlled, but it has not been proved experimentally.

For mechanism B, in which the radicals $\dot{\mathrm{D}}$ disappear as a result of hydrogen-transfer to the ketone, $2k_{3}[\dot{\mathrm{D}}]^{2} \ll k_{\mathrm{h}}[\mathrm{RR'CO}][\dot{\mathrm{D}}]$ and then $[\dot{\mathrm{D}}]_{\mathrm{ss}} \approx k_{1}[\mathrm{RR'\dot{C}OH}]^{2}_{\mathrm{ss}}/k_{\mathrm{h}}[\mathrm{RR'CO}]$. In this case k_{t} apparently equals k_1† and indeed in the initial part of the decay when $[\dot{\mathrm{D}}]$ and $[\mathrm{RR'\dot{C}OH}]$ are very close to their steady-state values this is so. However, one can easily demonstrate that in our systems in which the failure to observe the solvent radicals during illumination indicates that $[\dot{\mathrm{D}}]_{\mathrm{ss}}$ is generally $< 0{\cdot}1\ [\mathrm{RR'\dot{C}OH}]_{\mathrm{ss}}$, the rapid depletion of $\dot{\mathrm{D}}$ radicals by the hydrogen-transfer reaction means that they make only a small contribution to the decay kinetics of the $\mathrm{RR'\dot{C}OH}$ radicals, and $k_{\mathrm{t}} \approx 2k_1$ as for mechanism A.†

Mechanism C describes the situation in which the solvent radicals $\dot{\mathrm{D}}$ disappear by a pseudo-first-order process (such as decomposition or addition) which is faster than any of the bimolecular combination processes involved. This is likely to be a fairly common situation and is the mechanism which we believe applies to the photoreduction of biacetyl in cyclohexene. In this case also the rapid depletion of $\dot{\mathrm{D}}$ radicals means that the observed rate of decay of $\mathrm{RR'\dot{C}OH}$ radicals is determined almost entirely by reaction (1) so that $k_{\mathrm{t}} \approx 2k_1$. The photoreduction of acetone in cyclohexene [7] appears to be another example of a complex mechanism to which mechanism C applies.

Pyruvic Acid.—For a propan-2-ol solution $\lambda_{\mathrm{max.}} = 330$ nm for the absorption band corresponding to the $n \longrightarrow \pi^{*}$ transition leading ultimately to the formation of $(\mathrm{MeCOCO_2H})^{t}$. At 330 nm the molar extinction coefficient ε is $15{\cdot}0\ \mathrm{l\ mol^{-1}\ cm^{-1}}$. U.v. irradiation of solutions of pyruvic acid in organic solvents leads to the formation of $\mathrm{Me\dot{C}(OH)CO_2H}$ radicals as reported earlier.[1,8] E.s.r. hyperfine splittings for the methyl and hydroxy-protons are,

---

† This can be illustrated by the following simple calculation. In the steady-state, during illumination, from equation (2) with $k_{3}[\dot{\mathrm{D}}]^{2}_{\mathrm{ss}} \ll k_{\mathrm{h}}[\mathrm{RR'CO}][\dot{\mathrm{D}}]_{\mathrm{ss}}$, we have $k_{1}[\mathrm{RR'\dot{C}OH}]^{2}_{\mathrm{ss}} = k_{\mathrm{h}}[\mathrm{RR'CO}][\dot{\mathrm{D}}]_{\mathrm{ss}}$. Now, the time for the concentration of $\dot{\mathrm{D}}$ radicals to fall from $[\dot{\mathrm{D}}]_{\mathrm{ss}}$ to $[\dot{\mathrm{D}}]$ by the pseudo-first-order reaction with rate constant k_{h} is given by $t = 2{\cdot}303 \log([\dot{\mathrm{D}}]_{\mathrm{ss}}/[\dot{\mathrm{D}}])/k_{\mathrm{h}}[\mathrm{RR'CO}]$. If we define a time $t^{*} = 1/2k_{1}[\mathrm{RR'\dot{C}OH}]^{2}_{\mathrm{ss}}$ (which in the absence of any process for regeneration of RR′COH equals the radical half-life), then after this time $4{\cdot}606 \log([\dot{\mathrm{D}}]_{\mathrm{ss}}/[\dot{\mathrm{D}}]_{t^{*}}) = [\mathrm{RR'\dot{C}OH}]_{\mathrm{ss}}/[\dot{\mathrm{D}}]_{\mathrm{ss}}$. Now, if $[\mathrm{RR'\dot{C}OH}]_{\mathrm{ss}} \geqslant 20[\dot{\mathrm{D}}_{\mathrm{ss}}]$, then $[\dot{\mathrm{D}}]_{t^{*}} < 10^{-4}[\dot{\mathrm{D}}]_{\mathrm{ss}}$. The concentration of $[\dot{\mathrm{D}}]$ is thus negligible, whereas $[\mathrm{RR'\dot{C}OH}]$ will have decreased by *less* than half (since initially the effective rate constant for removal is less than $2k_1$). Alternatively one can show by a similar argument that the concentration of $[\dot{\mathrm{D}}]$ radicals falls to less than 1% of its initial value in *ca.* 0·5 of the half-life of $\mathrm{RR'\dot{C}OH}$ radicals (as defined above).

[4] B. M. Monroe and S. A. Weiner, *J. Amer. Chem. Soc.*, 1969, **91**, 450.

[5] F. D. Lewis, *J. Phys. Chem.*, 1970, **74**, 3332.

[6] J. Nafisi-Movaghar and F. Wilkinson, *Trans. Faraday Soc.*, 1970, **66**, 2268 and references therein.

[7] P. Borrell and J. Sedlar, *Trans. Faraday Soc.*, 1970, **66**, 1670.

[8] N. H. Anderson, A. J. Dobbs, D. J. Edge, R. O. C. Norman, and P. R. West, *J. Chem. Soc. (B)*, 1971, 1004.

respectively, 1·660 ± 0·003 and 0·223 ± 0·003 mT in propan-2-ol at 293 K. There is also a small hyperfine splitting (*ca.* 0·1 mT) arising from the carboxy-proton. This splitting is a function of the acid concentrations and disappears completely at concentrations >0·4M.[9]

In alcoholic solvents the major isolable product is invariably dimethyltartaric acid arising from geminal coupling of $\mathrm{Me\dot{C}(OH)CO_2H}$ radicals.[10] The spectrum of the radical derived from the alcohol is not observed. We therefore conclude that mechanism B applies and that $k_t = 2k_1$. Values of k_t were derived from the usual second-order plots of $[\mathrm{Me\dot{C}(OH)CO_2H}]_{ss}/[\mathrm{Me\dot{C}(OH)CO_2H}]$ as shown in Figure 1. Experimental values of k_t for $\mathrm{Me\dot{C}(OH)CO_2H}$ radicals in a variety of alcoholic solvents and over a range of temperatures are summarised in Table 1 and Figure 2. Observed activation energies for the termination reaction in the solvents propan-2-ol, benzyl alcohol, and ethanol are 15·6 ± 2·0, 9·4 ± 2·0, and 8·5 ± 2·5 kJ mol^{-1} respectively.

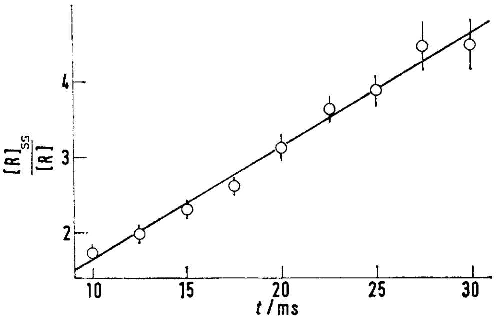


FIGURE 1 Second-order plot for decay of $\mathrm{Me\dot{C}(OH)CO_2H}$ radicals in propan-2-ol at 293 K. R = $\mathrm{Me\dot{C}(OH)CO_2H}$ (the displacement of the line from the origin is a penumbra effect)

TABLE 1

Termination rate constants of radicals derived from pyruvic acid, 2-oxobutyric acid, and biacetyl in various solvents at 293 K

		R = $\mathrm{Me\dot{C}(OH)CO_2H}$		R = $\mathrm{Et\dot{C}(OH)CO_2H}$		R = $\mathrm{Me\dot{C}(OH)COMe}$	
Solvent	Viscosity $10^2\eta$/P *	Radical Concentration $10^7[\mathrm{R}]_{ss}$/M	Termination rate constant $10^{-8}k_t$/l mol^{-1} s^{-1}	Radical concentration $10^7[\mathrm{R}]_{ss}$/M	Termination rate constant $10^{-8}k_t$/l mol^{-1} s^{-1}	Radical concentration $10^7[\mathrm{R}]_{ss}$/M	Termination rate constant $10^{-8}k_t$/l mol^{-1} s^{-1}
Cyclohexene	0·67 ± 0·1					4·00	25 ± 3
Ethanol	1·2 ± 0·1	2·50	6·0 ± 0·7	2·70	5·0 ± 0·6	3·80	12·5 ± 1·4
Propan-2-ol	2·3 ± 0·1	3·75	4·0 ± 0·4	3·82	3·3 ± 0·3	4·75	7·0 ± 0·8
Butan-2-ol	3·9 ± 0·1	5·37	2·4 ± 0·3	5·00	2·4 ± 0·3	9·00	4·2 ± 0·5
2-Methylpropan-1-ol	3·9 ± 0·1	3·75	2·7 ± 0·3	4·28	2·5 ± 0·3	4·75	4·0 ± 0·4
Benzyl alcohol	4·1 ± 0·1	4·82	2·5 ± 0·3	3·64	2·2 ± 0·2	6·00	3·3 ± 0·4
1-Phenylethyl alcohol	10·9 ± 0·2			7·27	1·1 ± 0·1		

* P = Poise = 10^{-1} pascal second.

2-Oxobutyric Acid.—The absorption spectrum is very similar to that of pyruvic acid and when irradiated with u.v. light in alcoholic solvents the radical observed is $\mathrm{Et\dot{C}(OH)CO_2H}$. The e.s.r. spectrum is interpreted in terms of a triplet splitting of 1·170 ± 0·003 mT from the $\mathrm{CH_2}$ protons, a doublet splitting of 0·230 ± 0·003 mT from the hydroxy-proton, and a doublet splitting of *ca.* 0·1 mT from the carboxy-proton. At acid concentrations much above 0·4M hyperfine interaction is lost because of rapid proton exchange.[9]

Values of k_t for the ketyl radical were obtained using various solvents as for pyruvic acid. On the reasonable assumption that the kinetic scheme for the photoreduction of the two keto-acids is similar we again conclude that $k_t = 2k_1$. The experimental data are included in Table 1.

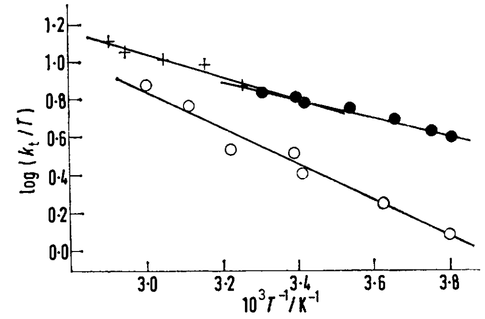


FIGURE 2 Temperature dependence of termination rate constant k_t for $\mathrm{Me\dot{C}(OH)CO_2H}$ radicals in various solvents: +, benzyl alcohol; ●, ethanol; ○, propan-2-ol

Biacetyl.—Product analyses have been performed for photoreduction of biacetyl in several solvents.[11] In alcohols the predominant product is the pinacol which arises from geminal recombination of $\mathrm{Me\dot{C}(OH)COMe}$ radicals. In propan-2-ol the accompanying solvent radicals $\mathrm{Me_2\dot{C}OH}$ are known to give rise almost quantitatively to acetone,[12] so in this system again our experimental values of k_t correspond to $2k_1$.

The u.v. absorption corresponding to the $n \longrightarrow \pi^*$ transition has $\lambda_{\text{max.}}$ 420 nm (ε 15·1 l mol^{-1} cm^{-1}). The e.s.r. spectrum obtained on photolysing biacetyl in various solvents has been described earlier.[1,13] Experimental values for k_t in different solvents are summarised in Table 1 and those for k_t in propan-2-ol over a range of temperature are shown in Figure 3. From these data the observed activation energy for the termination reaction is 19·0 ± 2 kJ mol^{-1} between 261 and 344 K.

1,4-Benzoquinone.—The electronic absorption spectrum in propan-2-ol has $\lambda_{\text{max.}}$ 440 nm (ε 26·3 l mol^{-1} cm^{-1}). U.v. photolysis in ethanol and propan-2-ol gives products which

---

[9] P. B. Ayscough and R. C. Sealy, unpublished observations.

[10] P. A. Leermakers and G. F. Vesley, *J. Amer. Chem. Soc.*, 1963, **85**, 3776.

[11] W. G. Bentrude and K. R. Darnall, *Chem. Comm.*, 1968, 810.

[12] W. H. Urry and D. J. Trecker, *J. Amer. Chem. Soc.*, 1962, **84**, 118.

[13] H. Zeldes and R. Livingston, *J. Chem. Phys.*, 1967, **47**, 1465.

are thought to arise mainly from the disproportionation of the semiquinone radicals $\dot{O}C_6H_4OH$ to give the quinol and quinone.[14]

On photolysis of 1,4-benzoquinone in propan-2-ol we obtain the e.s.r. spectrum shown in Figure 4(a). This was analysed in terms of three hyperfine couplings, 0·181 ± 0·003, 0·035 ± 0·003, and 0·517 ± 0·003 mT. These values compare well with the values 0·179, 0·031, and 0·513 mT obtained by Gough [15] for the radical $C_6H_4(\dot{O})OH$.

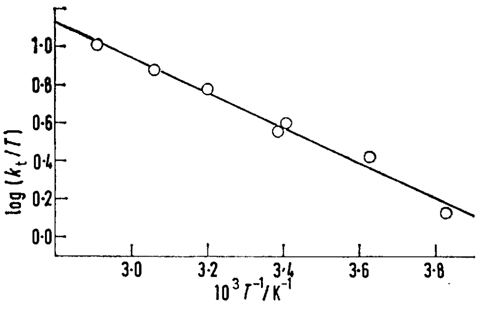


FIGURE 3 Temperature dependence of termination rate constant k_t for $Me\dot{C}(OH)COMe$ radicals in propan-2-ol

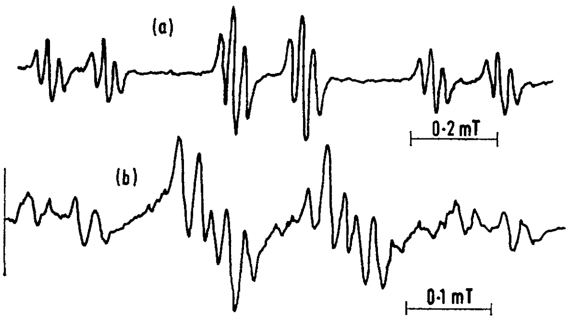
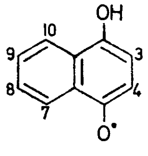


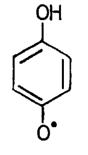
FIGURE 4 E.s.r. spectra of radicals produced by photolysis of (a) 1,4-benzoquinone, (b) 1,4-naphthoquinone in propan-2-ol (half spectrum on expanded scale)

We have measured the rate constants for the decay of these radicals in a number of solvents. Second-order kinetics are observed; values of k_t are summarised in Table 2.

1,4-*Naphthoquinone*.—The $n \longrightarrow \pi^*$ transition for this compound in propan-2-ol is centred at *ca.* 400 nm (ε 68·5 l mol⁻¹ cm⁻¹). In chloroform [16] the corresponding value is $\lambda_{max.}$ 400 nm (ε 63·1 l mol⁻¹ cm⁻¹). Photolysis of the quinone in the presence of a hydrogen donor solvent gave rise to a radical with the e.s.r. spectrum shown in Figure 4(b). By analogy with 1,4-benzoquinone we assign this spectrum to the radical (I) having the following hyperfine splittings:



(I)



(II)

$a_1 = 0{\cdot}155$, $a_3 = 0{\cdot}027$, $a_4 = 0{\cdot}718$, $a_7 = 0{\cdot}023$, $a_8 = 0{\cdot}177$, $a_9 = 0{\cdot}023$, and $a_{10} = 0{\cdot}177$ mT (all ±0·005 mT). Termination rate constants k_t obtained in the same manner as for the other systems are summarised in Table 2.

TABLE 2

Termination rate constants of radicals derived from 1,4-benzoquinone and 1,4-naphthoquinone in various solvents at 293 K

Solvent	Viscosity $10^2\eta$/P *	Radical concentration $10^6[R]_{ss}$/M	Termin- rate constant $10^{-8}k_t$/l mol⁻¹ s⁻¹	Radical concentration $10^7[R]_{ss}$/M	Termin- rate constant $10^{-8}k_t$/l mol⁻¹ s⁻¹
Ethanol	1·2 ± 0·1	1·11	2·7 ± 0·3	1·90	2·6 ± 0·3
Propan-2-ol	2·3 ± 0·1	1·21	1·9 ± 0·2	2·18	2·2 ± 0·2
Butan-2-ol	3·9 ± 0·1	1·18	1·7 ± 0·2	4·08	1·2 ± 0·1
2-Methylpropan-1-ol	3·9 ± 0·1	1·62	1·6 ± 0·2	2·21	1·4 ± 0·2
Benzyl alcohol	4·1 ± 0·1	1·18	1·7 ± 0·2	2·17	1·2 ± 0·1

* See note to Table 1.

9,10-*Anthraquinone*.—Photolysis of this compound in propan-2-ol did not give rise to an observable e.s.r. signal. Other workers have reported their failure to observe this radical in a similar system.[17] We attributed this failure to a reduced rate constant for hydrogen-abstraction from propan-2-ol (relative to 1,4-benzoquinone and 1,4-naphthoquinone) and to the likely complexity of the spectrum of the radical produced on photolysis.

DISCUSSION

For all the systems which we have examined the rate constants for combination of the radicals are in the range 10^8—10^9 l mol⁻¹ s⁻¹; the rates are higher in solvents of low viscosity and increase with temperature with activation energies similar in magnitude to the temperature coefficient of viscosity.

Diffusion coefficients for radicals are experimentally rather inaccessible and a common simplification is to use the Stokes–Einstein relationship for the diffusion coefficient, which, for molecules diffusing through a solvent of comparable molecular diameter takes the form $D = kT/\pi\eta d$, where D = diffusion coefficient, η is the coefficient of viscosity and d = hydrodynamic diameter.[18] When substituted into the Smoluchowski equation [19] the expression for the rate of diffusion is (4).

$$k_{\text{diff}} = 8RT/2000\eta \ \text{l mol}^{-1}\,\text{s}^{-1} \qquad (4)$$

Thus, for diffusion controlled reactions, k_t should be a linear function of η^{-1} with slope = $8RT/2000$. Since η is a function of temperature which can generally be written in the form $\eta = \eta_0 \exp(E_d/RT)$ where E_d is the temperature coefficient for viscous flow, it follows that k_{diff} should also be a function of temperature, given by equation (5) where $C = 8R/20000$.

$$\ln(k_{\text{diff}}/T) = \ln(C/\eta_0) - E_d/RT \qquad (5)$$

Our data for k_t for the four radicals studied are

---

[14] J. M. Bruce, *Quart. Rev.*, 1967, **21**, 405.

[15] T. E. Gough, *Trans. Faraday Soc.*, 1966, **62**, 2321.

[16] S. Nagakura and A. Kuboyama, *J. Amer. Chem. Soc.*, 1954, **76**, 1004.

[17] J. H. Sharp, T. Kuwana, A. Osborne, and J. N. Pitts, jun., *Chem. and Ind.*, 1962, **1**. 508.

[18] M. J. V. Tyrell, 'Diffusion and Heat Flow in Liquids,' Butterworths, London, 1961.

[19] For a discussion of the approximations involved see R. M. Noyes, *Progr. Reaction Kinetics*, 1961, **1**, 130.

plotted against η^{-1} in Figure 5. Some deviation from linearity is apparent in solvents of low viscosity. This kind of observation may be accounted for in terms of the effects of ' caging ' of the radicals by molecules of solvent. In our systems the radicals $RR'\dot{C}OH$, some of which are produced by abstraction from solvent by triplet ketone and some by hydrogen-transfer from solvent radicals $\dot{D}$, are initially separated by solvent molecules and must diffuse together before reaction. If we represent the rate of diffusion in and out of the solvent ' cage ' by k_{diff} and $k_{-\text{diff}}$, and the pair of caged radicals (*i.e.* not separated by solvent) by X, then the overall process for recombination may be represented by steps (6) and (7).

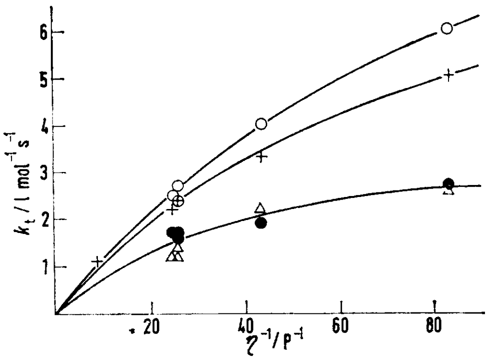


FIGURE 5 Viscosity dependence of termination rate constants for ketyl and semiquinone radicals in alcoholic solvents: ○, $Me\dot{C}(OH)CO_2H$; +, $Et\dot{C}(OH)CO_2H$; ●, radical (II); △, radical (I)

$$2RR'\dot{C}OH \underset{k_{-\text{diff}}}{\overset{k_{\text{diff}}}{\rightleftharpoons}} X \qquad (6)$$

$$X \xrightarrow{k} \text{products} \qquad (7)$$

The rate constant k in this formulation is that for chemical reaction in the cage and is supposed to be independent of the properties of the solvent. (A similar scheme has been used by Porter *et al.*[20] in an attempt to estimate extinction coefficients from the viscosity dependence of k_t for some ketyl radicals.)

In the stationary state for caged and uncaged species we have equation (8) so that the rate of disappearance of

$$[X] = \frac{k_{\text{diff}}}{(k + k_{-\text{diff}})}[RR'\dot{C}OH]^2 \qquad (8)$$

$$-d[RR'\dot{C}OH]/dt = 2k_{\text{diff}}[RR'\dot{C}OH]^2 - 2k_{-\text{diff}}[X] \qquad (9)$$

$RR'\dot{C}OH$ radicals is given by (9) and the equations (10) hold. If the ratio $k_{\text{diff}} : k_{-\text{diff}}$ is viscosity independent

$$k_t = 2k \times k_{\text{diff}}/(k + k_{-\text{diff}});$$
$$(\tfrac{1}{2}k_t)^{-1} = (k_{\text{diff}})^{-1} + k_{-\text{diff}}/k \times k_{\text{diff}} \qquad (10)$$

then k_t must depend on viscosity to an extent determined by the relative magnitude of the terms in equations (10). If we further assume that k_{diff} may be expressed by a modified Debye equation (*i.e.* $= 8RT/2000\eta$) we have equation (11) and plots of data in the

$$(\tfrac{1}{2}k_t)^{-1} = 2000\eta/8RT + k_{-\text{diff}}/k \times k_{\text{diff}} \qquad (11)$$

form $(k_t)^{-1}$ against η should then be linear.

Our results for the radicals derived from pyruvic acid and 2-oxobutyric acid are shown in Figure 6. Within experimental error a straight line is obtained in each case. However, the gradient of each line is greater than that calculated from $4000/8RT$ (*ca.* 10^{-6} kg mol m^{-4}) by a factor of *ca.* 20. Table 3 lists the values of k_1 ($=\tfrac{1}{2}k_t$) and calculated values of k_{diff}.

TABLE 3

Comparison of measured termination rate constants (k_1) for $Me\dot{C}(OH)CO_2H$ with those predicted by diffusion theory (k_{diff})

Solvent	$10^{-8}k_1$/l mol^{-1} s^{-1}	$10^{-9}k_{\text{diff}}$/l mol^{-1} s^{-1}
Ethanol	3·0	8·1
Propan-2-ol	2·0	4·3
Butan-2-ol	1·2	2·5
2-Methylpropan-1-ol	1·3	2·5
Benzyl alcohol	1·2	2·4

We believe that this discrepancy is most probably due to the necessity for correct orientation of the radicals within the solvent cage before reaction can take place.

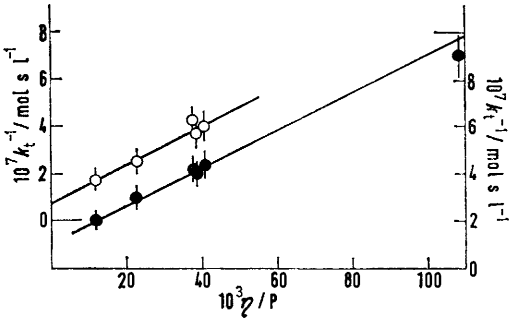


FIGURE 6 Viscosity dependence of termination rate constants for ketyl radicals in alcoholic solvents: ○, $Me\dot{C}(CH)CO_2H$; ●, $Et\dot{C}(OH)CO_2H$

From experiments on the cage recombination of CH and CF_3 radicals Szwarc *et al.*[21] has suggested that a critical orientation requirement for reaction may introduce rotational diffusion as a rate-influencing factor. For the radicals we have studied this orientation requirement may be quite strict so that the radicals may spend relatively long periods of time within the solvent cage without reaction, thus reducing the overall termination rate by a large factor. The scheme we suggest is essentially a simplified version of that proposed by North[22] for polymeric species which also predicts a linear relationship between $(k_t)^{-1}$ and η, though with slightly different values for gradient and intercept. For gas-phase reactions a spin correction factor has been introduced to take into account the fact that only one

---

[20] A. Beckett, A. D. Osborne and G. Porter, *Trans. Faraday Soc.*, 1964, **60**, 873.

[21] O. Dobis, J. M. Pearson, and M. Szwarc, *J. Amer. Chem. Soc.*, 1968, **90**, 278.

[22] A. M. North, ' The Collision Theory of Chemical Reactions in Liquids,' Methuen, London, 1964.

collison in four leads to the required singlet state, but this factor is usually neglected in solution because of the much longer duration of collisions. It is assumed that spin flipping is rapid compared with diffusion from the solvent cage.

The effect of temperature on the termination rate is also in general accord with the predictions of this modified theory for diffusion-controlled reactions. As can be seen from Table 4 $E_{\mathrm{obs}} \leqslant E_{\mathrm{d}}$ in all three solvents. This follows from the form of Figure 5. At high viscosities k_{t} is proportional to η^{-1} and a close correlation between E_{obs} and E_{d} is expected (*e.g.* for benzyl alcohol). However, at low viscosities k_{t} does not increase as rapidly as η^{-1} and $E_{\mathrm{obs}} < E_{\mathrm{d}}$. This relationship between E_{obs} and E_{d} has also been observed by Weiner[23] in his study of the combination of $\mathrm{Ph_2\dot{C}OH}$ radicals.

TABLE 4

Activation energy data for the combination reactions of $\mathrm{Me\dot{C}(OH)CO_2H}$ and $\mathrm{Me\dot{C}(OH)COMe}$ radicals

Radical	Solvent	E_{obs}/kJ mol^{-1}	E_{d}/ kJ mol^{-1}
$\mathrm{Me\dot{C}(OH)CO_2H}$	Propan-2-ol	15·6 ± 2·0	21·8
	Benzyl alcohol	9·4 ± 2·0	10·0
	Ethanol	8·5 ± 2·5	14·1
$\mathrm{Me\dot{C}(OH)COMe}$	Propan-2-ol	19·0 ± 2·0	21·8

E_{obs} = Observed activation energy. E_{d} = Activation energy for viscous flow (from ' Handbook of Chemistry,' McGraw-Hill, New York, 10th edn., 1967).

As we have noted earlier the rate constants for combination of chemically similar radicals in any one solvent do not differ markedly, though such differences as there are in the expected direction if rearrangement of the encounter pair is a rate-influencing factor. Thus, k_{t} for $\mathrm{Et\dot{C}(OH)CO_2H}$ radicals in propan-2-ol is less than that for $\mathrm{Me\dot{C}(OH)CO_2H}$ radicals in the same solvent. Similar considerations apply to the decay of the radicals derived from 1,4-naphthoquinone and 1,4-benzoquinone in, say, propan-2-ol. These observations are in accord with the general observation that the higher the molecular weight of chemically similar radicals the slower is the recombination rate.[24] Somewhat surprisingly the semiquinone radicals combine as rapidly as the smaller open chain ketyl radicals. Our limited data do not justify much speculation, but the explanation is likely to be found in a less stringent orientation requirement for reaction since it is known that disproportionation is the predominant mode of reaction of the semiquinones whereas the open-chain ketyls mainly dimerise.

[2/2219 *Received, 25th September, 1972*]

---

[23] S. A. Weiner, *J. Amer. Chem. Soc.*, 1971, **93**, 6978.

[24] G. B. Watts and K. U. Ingold, *J. Amer. Chem. Soc.*, 1972, **94**, 491.