Kinetic Electron Spin Resonance Spectroscopy. Part IV.† Photoreduction of Triplet Pyruvic Acid and Triplet Biacetyl in Alcoholic Solvents

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The study of the photoreduction of triplet ketones in alcoholic solvents by means of kinetic electron spin resonance spectroscopy has been extended to include the determination of the Arrhenius parameters for the reactions of $^3(n,\pi^*)$ pyruvic acid with methanol, ethanol, propan-2-ol, t-butyl alcohol, and 1-phenylethanol. A competitive quenching method was employed with naphthalene as triplet quencher. Activation energies are between 11 and 22 kJ mol^{-1} and pre-exponential factors between $10^{8\cdot 8}$ and $10^{9\cdot 3}$ l mol^{-1} s^{-1}. Similar studies on the reactions of $^3(n,\pi^*)$ biacetyl provided estimates of the rate constants of the corresponding reactions (ranging from $3\cdot 5 \times 10^3$ l mol^{-1} s^{-1} in ethanol to $6\cdot 5 \times 10^4$ in 1-phenylethanol). Some problems associated with the behaviour of the triplet quencher (acridine) in these systems are discussed.

THE ability of electron spin resonance studies to provide kinetic and mechanistic information on photochemical systems is well known and a number of rate constants for radical–radical and radical–molecule reactions have been obtained from time-resolved [1] and competition [2] experiments. The behavioural similarity of $^3(n,\pi^*)$ ketones and alkoxyl radicals has been demonstrated in several studies,[3] and rate constants for reaction of both t-butoxyl and $^3(n,\pi^*)$ acetone with organoboranes have recently been measured [4] by means of e.s.r. techniques.

We have directed attention towards the photoreduction of carbonyl compounds in alcoholic solvents [5-7] and, in a preliminary communication,[8] we described how kinetic e.s.r. spectroscopy may be used to estimate rate constants for the reaction of $^3(n,\pi^*)$ ketones with alcohols. We now report further results, together with an appraisal of the problems encountered in these and related photochemical studies.

EXPERIMENTAL

The Decca X-3 e.s.r. spectrometer, variable temperature apparatus, and sample preparation have been described previously.[5] For the variable temperature studies the procedure adopted was as follows. A set of solutions containing different concentrations of the chosen triplet quencher was made up and degassed. A reference solution with no added quencher was then examined while undergoing continuous irradiation at a number of different temperatures, the steady-state radical concentration being measured at each temperature. The procedure was repeated for each solution.

Kinetic Scheme.—The basic kinetic scheme previously established [5] for the photoreduction of a carbonyl compound R^1R^2CO by a hydrogen-donor DH is summarised in equations (1)—(8) (the superscript t denotes a triplet excited species and Q is a triplet quencher).

Since our initial communication,[5] the importance of the hydrogen transfer step (5) when $\cdot$D is an α-hydroxyalkyl

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† Part III, P. B. Ayscough and R. C. Sealy, *J.C.S. Perkin II*, 1973, 1620.

[1] *E.g.* J. R. Roberts and K. U. Ingold, *J. Amer. Chem. Soc.*, 1973, **95**, 3228; H. J. Hefter, C-H. S. Wu, and G. S. Hammond, *ibid.*, p. 851, and earlier papers in these series.

[2] A. G. Davies and B. P. Roberts, *Accounts Chem. Res.*, 1972, **5**, 387.

[3] C. Walling and M. J. Gibian, *J. Amer. Chem. Soc.*, 1965, **87**, 3361.

[4] (*a*) A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc.* (*B*), 1971, 1827; (*b*) A. G. Davies, B. P. Roberts, and J. C. Scaiano, *ibid.*, p. 2171.

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

[6] P. B. Ayscough, R. C. Sealy, and D. E. Woods, *J. Phys. Chem.*, 1971, **75**, 3454.

[7] P. B. Ayscough and R. C. Sealy, *J.C.S. Perkin II*, 1973, 543.

[8] P. B. Ayscough and R. C. Sealy, *J. Photochem.*, 1972, **1**, 83.

radical has been demonstrated by other e.s.r.[7,9,10] and flash photolytic [11] investigations for a number of carbonyl compounds. In all our studies involving the photolysis of dicarbonyl compounds in the presence of primary and secondary alcohols we have observed $\cdot CR^1R^2OH$ radicals at concentrations as high as 10^{-6}M but have found no trace of the radical $\cdot D$. Since the bimolecular termination reactions (6)—(8) are unlikely to differ greatly in rate we conclude that under the conditions of our experiments the failure to observe $\cdot D$ is caused by reaction (5), for which we estimate $k_p[R^1R^2CO] > 10^4\ s^{-1}$ (*i.e.* $k_p > 10^4$—$10^6\ l\ mol^{-1}\ s^{-1}$). Such reactions are likely to assume even greater importance in experiments aimed at the measurement of quantum yields since these generally involve much lower light intensities and correspondingly lower radical concentrations.*

$$R^1R^2CO \xrightarrow{\phi I_a} (R^1R^2CO)^t \qquad (1)$$

$$(R^1R^2CO)^t + DH \xrightarrow{k_r} \cdot CR^1R^2OH + \cdot D \qquad (2)$$

$$(R^1R^2CO)^t \xrightarrow{k_d} R^1R^2CO \qquad (3)$$

$$(R^1R^2CO)^t + Q \xrightarrow{k_q} R^1R^2CO + Q^t \qquad (4)$$

$$R^1R^2CO + \cdot D \xrightarrow{k_p} \cdot CR^1R^2OH + D\,(-H) \qquad (5)$$

$$2\ \cdot CR^1R^2OH \xrightarrow{k_1} \text{molecular products} \qquad (6)$$

$$CR^1R^2OH + \cdot D \xrightarrow{k_2} \text{molecular products} \qquad (7)$$

$$2\ \cdot D \xrightarrow{k_3} \text{molecular products} \qquad (8)$$

Steady state analysis of the reaction scheme involving equations (1)—(6) (Scheme A) and (1)—(4) together with (6)—(8) (Scheme B) yields the expression (I) for the stationary concentration of the radical $\cdot CR^1R^2OH$,[7] where

$$[\cdot CR^1R^2OH]^{-2} = (k_t/\phi I_a)\{1 + (k_d + k_q[Q])/k_r[DH]\} \qquad (I)$$

$k_t = k_1$ (Scheme A) or $k_t = 2k_1 + k_2(k_1/k_3)^{\frac{1}{2}}$ (Scheme B). Equation (I) is seen to be the analogue of the Stern–Volmer expression used in the determination of quantum yields and suggests a similar approach to the estimation of k_r, *i.e.* monitoring the radical concentration as a function of [DH] and [Q]. We shall discuss briefly some of the possible problems arising from such an analysis.

Dilution Experiments.—The problem here is how best to change [DH] without varying any other parameters which can effect $[\cdot CR^1R^2OH]$. Some form of dilution must be employed and the additive must be photochemically inert. One may then proceed from either of two standpoints: (*a*) using pure DH as solvent and an inert additive for dilution experiments, or (*b*) using an inert solvent and adding small quantities of DH. Because of the low signal-to-noise ratio apparent in most of our systems, method (*a*) was adopted, with some reservations. Ideally the additive should not only be photochemically inert but should change as few as possible of the physical properties of the system (*e.g.* viscosity and dielectric constant) when added to the hydrogen donor solvent. Of the various additives considered, benzene was found to be most suitable since it is photochemically inert and has a similar viscosity to the alcohols used as hydrogen donors. However, one must recognise that k_r and k_d may well depend to some extent on solvent composition (as does k_t [6]) in such a mixed solvent. The only evidence we have regarding the effect of solvent polarity is that for hydrogen abstraction reactions with low activation energies k_r is little affected by solvent polarity.[13,14] On the other hand if, as is likely, the rate constant k_d corresponds to a diffusion controlled impurity quenching reaction,[15] one may expect a variation of k_d with solvent viscosity: there is also some evidence [16] that radiationless processes have a dependence on viscosity. These effects are minimised in situations in which $k_r[DH]$ and $k_q[Q] \gg k_d$: [17] these conditions apply to our experiments also.

Experiments with Triplet Quenchers.—A triplet quencher which has a photoreactive triplet state or which may participate in ground state reactions with radicals present in the system may cause considerable deviations from otherwise simple competitive reaction schemes: a thorough test of a proposed mechanism is therefore necessary for each system under investigation. Hitherto unconsidered reactions which would give rise to such complications are (9)—(15).

$$Q^t + DH \xrightarrow{k_{r'}} \cdot QH + \cdot D \qquad (9)$$

$$2\ \cdot QH \longrightarrow \text{molecular products} \qquad (10)$$

$$\cdot QH + \cdot D \longrightarrow \text{molecular products} \qquad (11)$$

$$\cdot QH + \cdot CR^1R^2OH \longrightarrow \text{molecular products} \qquad (12)$$

$$\cdot QH + R^1R^2CO \longrightarrow \cdot CR^1R^2OH + Q \qquad (13)$$

$$\cdot CR^1R^2OH + Q \longrightarrow \cdot QH + R^1R^2CO \qquad (14)$$

$$\cdot D + Q \xrightarrow{k_{p'}} \cdot QH + D\,(-H) \qquad (15)$$

Variable-temperature Experiments.—We may write equation (I) in the form (II), where $[\cdot CR^1R^2OH]_0$ is the

$$([\cdot CR^1R^2OH]_0/[\cdot CR^1R^2OH])^2 = 1 + g[Q] \qquad (II)$$

radical concentration in the absence of a triplet quencher and g is given by $(k_q/k_r)/(k_d/k_r + [DH])$. Now, if k_{r1}, k_{d1}, and k_{q1} are rate constants at temperature T_1, and k_{r2}, k_{d2}, and k_{q2} rate constants at T_2, then we have equation (III),

$$k_{r1}/k_{r2} = (g_2/g_1)\{(k_{q1} - g_1k_{d1})/(k_{q2} - g_2k_{d2})\} \qquad (III)$$

where g_1 and g_2 denote values of g at temperatures T_1 and T_2. Provided that g_1k_{d1} and g_2k_{d2} are small compared with

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* The contention of Kendall and Leermakers [12] that reaction (5) is not important in the photoreduction of pyruvic acid in propan-2-ol is untenable under their experimental conditions. The source of the discrepancy between their limiting quantum yield data in propan-2-ol and in t-butyl alcohol is probably the very high efficiency of reaction (5) in propan-2-ol solution rather than any unusual effect of the t-butyl alcohol.

[9] T. Fujisawa and G. S. Hammond, *J. Amer. Chem. Soc.*, 1972, **94**, 4175.

[10] H. Yoshida and T. Warashira, *Bull. Chem. Soc. Japan*, 1971, **44**, 2950.

[11] K. Tickle and F. Wilkinson, *Trans. Faraday Soc.*, 1965, **61**, 1981.

[12] D. S. Kendall and P. A. Leermakers, *J. Amer. Chem. Soc.*, 1966, **88**, 2766.

[13] G. Porter and M. R. Topp, *Proc. Roy. Soc.*, 1970, *A*, **315**, 163.

[14] S. G. Cohen and A. D. Litt, *Tetrahedron Letters*, 1970, 837.

[15] P. J. Wagner, *Mol. Photochem.*, 1969, **1**, 71.

[16] K. S. Y. Lau, R. O. Campbell, and R. S. H. Liu, *Mol. Photochem.*, 1972, **4**, 315; S. Sharafy and K. A. Muszkat, *J. Amer. Chem. Soc.*, 1971, **93**, 4119; J. Saltiel and E. D. Megarity, *ibid.*, 1972, **94**, 2742.

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

k_{q1} and k_{q2}, respectively, we may write, to a good approximation, equation (IV). The problem is thus reduced to

$$k_{r1}/k_{r2} = (g_2/g_1)(k_{q1}/k_{q2}) \qquad \text{(IV)}$$

measuring the gradient of Stern–Volmer-type plots at a series of temperatures, together with an estimation of the temperature dependence of k_q.

RESULTS AND DISCUSSION

Pyruvic Acid.—Experiments at ambient temperatures have been described earlier.[8] Similar experiments have now been carried out over a range of temperatures in five of the alcoholic solvents studied earlier. For each solvent measurements were made of [$\cdot CR^1R^2OH$] as a function of concentration of added quencher (naphthalene), over a convenient range of temperatures. Some typical plots are shown in Figure 1. Table 1 lists data obtained in these solutions between **294** and **348** K. To be consistent with our previous work we have assumed a modified Debye relationship[18] for k_q (the temperature dependence of which was estimated from viscosity data) in which a correction is made for the probable lowering of k_q below the diffusion-controlled encounter rate in solutions of low viscosity.[17]

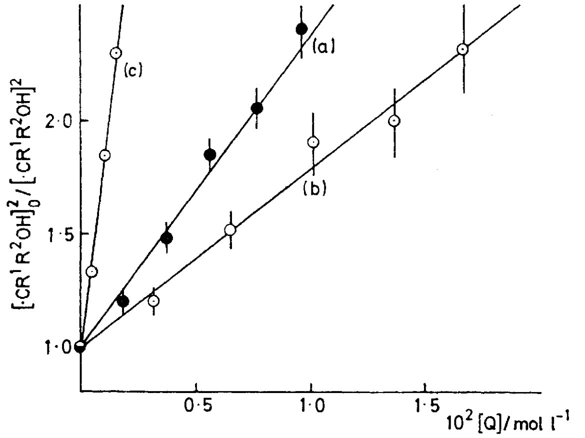

FIGURE 1 Effect of triplet quencher (naphthalene) on the steady state concentration of radicals $\cdot CRR^1OH = \cdot CMe(OH)\text{-}CO_2H$ during the photolysis of pyruvic acid in (a) ethanol, (b) propan-2-ol, and (c) t-butyl alcohol at 298 K

An Arrhenius plot of the data in Table 1 yields the activation parameters for hydrogen abstraction from propan-2-ol by $^3(n,\pi^*)$ pyruvic acid given in Table 2; the Table also lists data for a number of other alcoholic solvents. Estimated *A*-factors are seen not to differ markedly for the alcohols investigated, falling within the range 10^8—10^9 l mol^{-1} s^{-1}, typical of fairly simple radical transfer reactions,[19] and similar to that obtained for the reaction of $^3(n,\pi^*)$ acetophenone with propan-2-ol.[20] They are, however, lower than those predicted by a modified Bond Energy–Bond Order procedure.[21]

Activation parameters obtained by such competitive methods are sensitive to the assumed temperature dependence of k_q; for instance, pre-exponential factors ranging from 10^{11} to $10^{13\cdot7}$ have been obtained[22,23] for the type II fragmentation of valerophenone by procedures assuming different formulations of k_q as a function of temperature.

TABLE 1

Experimental values for the rate constant ratio k_r/k_r^{298} for reaction of $^3(n,\pi^*)$ pyruvic acid with hydrogen donors RH

RH	T/K	$10^9\ k$/ l mol^{-1} s^{-1} (calc.) †	g/l mol^{-1}	k_r/k_r^{298}	log (k_r/k_r^{298})
MeOH	294	8·70	595	0·90	−0·05 ± 0·02
	303	9·40	361	1·13	0·05 ± 0·02
	312	10·07	273	1·60	0·20 ± 0·04
	321	10·69	271	1·71	0·23 ± 0·04
	328	11·14	240	2·02	0·30 ± 0·05
	337	11·67	178	2·84	0·45 ± 0·06
EtOH	297	6·06	135	0·96	−0·02 ± 0·02
	307	6·96	112	1·32	0·12 ± 0·04
	316	7·77	114	1·44	0·16 ± 0·04
	325	8·55	110	1·67	0·22 ± 0·04
	334	9·31	83	1·92	0·28 ± 0·05
	343	9·99	85	2·52	0·40 ± 0·05
Pr^{i}OH	298	3·81	70	1·00	0·00
	308	4·85	77	1·15	0·06 ± 0·02
	318	5·97	71	1·55	0·19 ± 0·04
	328	7·14	87	1·51	0·18 ± 0·04
	338	8·28	50	2·00	0·30 ± 0·05
	348	9·41	58	2·00	0·30 ± 0·05
PhMe-CHOH	298	1·08	5·9	1·00	0·00
	308	1·67	8·1	1·12	0·05 ± 0·02
	318	2·41	10·2	1·29	0·11 ± 0·04
	328	3·43	10·9	1·70	0·23 ± 0·04
	338	3·83	11·5	1·82	0·26 ± 0·05
	348	4·75	12·7	2·04	0·31 ± 0·05
Bu^{t}OH	297	3·37	404	0·96	−0·02 ± 0·02
	308	3·25	487	1·32	0·12 ± 0·04
	317	3·16	372	2·00	0·30 ± 0·05
	328	3·05	520	2·00	0·30 ± 0·05
	338	2·96	452	2·96	0·47 ± 0·06
	348	2·87	431	3·82	0·58 ± 0·07

† Calculated from $k_q = \gamma k_{diff}$, where k_{diff} is the diffusion-controlled rate constant and $(1 - \gamma)/\gamma = 0\cdot56\ k_{diff} \times 10^{-10}$ (see ref. 18).

TABLE 2

Rate constants and Arrhenius parameters for reaction of $^3(n,\pi^*)$ pyruvic acid with hydrogen donors RH

RH	Activation energy E_a/kJ mol^{-1}	Pre-exponential factor log (A/ l mol^{-1} s^{-1})	Rate constant at 298 K $10^{-5}\ k_r$/ l mol^{-1} s^{-1}
Bu^{t}OH	22·2 ± 2·2	9·1 ± 0·4	1·7 ± 0·2
MeOH	20·9 ± 1·7	9·3 ± 0·4	4·5 ± 0·5
Bu^{i}OH			18 ± 2 †
EtOH	15·8 ± 1·4	9·3 ± 0·3	35 ± 4
Bu^{s}OH			36 ± 4 †
Pr^{i}OH	12·5 ± 1·6	8·8 ± 0·3	42 ± 5
PhCH$_2$OH			140 ± 15 †
PhMeCHOH	10·8 ± 1·0	9·1 ± 0·3	170 ± 20

† From ref. 8.

Biacetyl.—The photoreduction of biacetyl is a more difficult subject for investigation since a low rate constant for hydrogen abstraction by $^3(n,\pi^*)$ biacetyl and a relatively high value of k_d/k_r are expected.[24] As

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[18] P. J. Wagner and I. Kochevar, *J. Amer. Chem. Soc.*, 1968, **90**, 2232.

[19] *E.g.* K. U. Ingold, *J.C.S. Perkin II*, 1973, 420.

[20] H. Lutz, personal communication quoted in ref. 21*b*.

[21] C. M. Previtali and J. C. Scaiano, *J.C.S. Perkin II*, 1972, (*a*) 1667; (*b*) 1672.

[22] F. D. Lewis, *Mol. Photochem.*, 1972, **4**, 501.

[23] J. C. Scaiano, J. Grotewold, and C. M. Previtali, *J.C.S. Chem. Comm.*, 1972, 390.

[24] H. L. J. Bäckström and K. Sandros, *Acta Chem. Scand.*, 1958, **12**, 823.

pointed out earlier, dilution studies may therefore be subject to error if small amounts of quenching impurity are present.[17] Furthermore, a dependence of k_r on solvent polarity [25] is possible.

We have already reported our results showing the diminution in concentration of the protonated biacetyl semidione radicals on dilution of various hydrogen donor solvents with an inert solvent. The plots of $[\cdot CR^1R^2OH]^{-2}$ against $[DH]^{-1}$ were linear within experimental error and no significant variation of k_d/k_r with solvent composition was detected. However, other factors may be involved and this particular set of results may show a deceptive simplicity. For example, values of k_d are likely to increase because of the decrease in viscosity which occurs on dilution with benzene or they may decrease because of the decreasing concentration of any quenching impurity present in the alcohol. Values of k_r may well decrease because of the decreasing polarity of the medium. Since k_d is likely to be subject to opposing influences which may be of comparable magnitude but k_r is more likely to be overestimated, the values of k_d/k_r obtained from these experiments may yield upper limits for rates of hydrogen abstraction from the pure hydrogen donor solvent. We shall return to this point later.

Acridine was chosen as a suitable acceptor for $^3(n,\pi^*)$ biacetyl for our investigation. The triplet state $^3(n,\pi^*)$ acridine lies 188 kJ mol^{-1} above its ground state, whereas $^3(n,\pi^*)$ biacetyl lies 230 kJ mol^{-1} above its ground state. The corresponding singlet energies are 342 and 272 kJ mol^{-1} above the respective ground states. A suitable optical filter (Corning OGr3) with a frequency cut-off between the two singlet states was employed so that direct excitation of the $^3(n,\pi^*)$ acridine did not occur. Although the photochemistry of acridine is not well understood it has been concluded that $^3(n,\pi^*)$ biacetyl is quenched by $^3(n,\pi^*)$ acridine [26] and that the quenching is diffusion-controlled.[25]

In our experiments some depletion of acridine during irradiation was evident, pointing to the occurrence of one or more of reactions (9), (14), and (15). Koizumi and his collaborators concluded on the basis of quantum yield measurements [26] that at least 60% of the $^3(n,\pi^*)$ acridine formed in a photosensitised experiment with biacetyl reacts by way of hydrogen abstraction from solvent. One would therefore expect that in alcoholic solvents, which are well known to be excellent hydrogen donors, practically all the triplet acridine molecules will be deactivated chemically by reaction (9). This suggestion is not borne out by our observations, which show that the observed rate of depletion is at least tenfold less than that predicted by calculating the rate of depletion of acridine assuming 100% efficiency for hydrogen abstraction by triplet acridine.*

The importance of reaction (14), which must compete with dimerisation for the removal of $\cdot C(OH)MeCOMe$, was assessed from a rotating sector experiment on a solution containing sufficient acridine to reduce the concentration of $\cdot C(OH)MeCOMe$ to half its value in neat propan-2-ol. (The total irradiation time was kept as short as possible in order to minimise the depletion of acridine.) Under these conditions the decay of $\cdot C(OH)MeCOMe$ was closely second-order and we conclude that reaction (14) is not of major importance under these experimental conditions.

For the removal of D·, reaction (15) must compete with the hydrogen transfer reaction (5); the relative contributions of these alternative routes will depend on the ratio of the concentrations of acridine and biacetyl ($[Q]/[B]$). For $D\cdot = \cdot CPh_2OH$ the rate constant for reaction (15) is known to be high,[27] and this reaction cannot be ruled out, particularly if $[Q]/[B]$ is relatively high.

The effect of reactions (9) and (15) on studies based on competitive quenching can be seen by a steady state analysis of a kinetic scheme consisting of reactions (1)—(6) together with (9), (10), (12), and (15). Reaction (13) has been disregarded since it has been shown in some flash photolysis experiments [28] that the decay of ·QH is not affected by the presence of 10^{-2}M-biacetyl, and our experimental conditions are not sufficiently different to invalidate this assumption. To simplify the procedure, reactions (6), (10), and (12) are assumed to have the same rate coefficient k_1 (k_{10} has been estimated [28] as 4×10^8 l mol^{-1} s^{-1} in ethanol), and physical deactivation of Q^t is neglected. The ketyl radical concentration is given by an expression of the form (V), where $f_1[Q] = (k_q[Q])/(k_r[DH])$, $f_2[Q] =$

$$\frac{[\cdot CR^1R^2OH]_0{}^2}{[\cdot CR^1R^2OH]^2} = 4(1 + g)\{1 + f_1[Q]\}\{1 + (f_1 + f_2[Q])\}^{-2} \quad (V)$$

$(k_p[B])/(k_p[B] + k_{p'}[Q])$, and g has the form given earlier. These functions represent the contributions from reaction (9) and reactions (5) and (15), respectively. Reaction (9) confers a downward curvature to the plot, although kinetic data for small degrees of quenching should not be subject to serious error (the error in $[\cdot CR^1R^2OH]_0{}^2/[\cdot CR^1R^2OH]^2$ would be *ca.* 20% if hydrogen abstraction by triplet acridine were 100% efficient and considerably less if, as we submit, it is much less efficient). If reaction (15) competes effectively with reaction (5) for removal of D· from the system, then upward curvature of the plot would result.

Data for biacetyl in propan-2-ol and in benzyl alcohol are plotted in Figure 2. Whereas no appreciable curvature is evident in the propan-2-ol system, deviation

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* The calculation involves estimating the rate of initiation in a typical system; this estimate was made from the concentration of protonated biacetyl semidione radical in neat propan-2-ol, together with the appropriate termination rate constant.[7]

[25] N. J. Turro and R. Engel, *J. Amer. Chem. Soc.*, 1969, **91**, 7113.

[26] Y. Miyashita, S. Niizuma, H. Kokobun, and M. Koizumi, *Bull. Chem. Soc. Japan*, 1970, **43**, 3435.

[27] E. Van der Donckt and G. Porter, *J. Chem. Phys.*, 1967, **46**, 1173.

[28] P. W. Jooly and P. de Mayo, *Canad. J. Chem.*, 1964, **42**, 170.

from linearity is apparent at high quencher concentrations for benzyl alcohol solvent. On the basis of the previous discussion we believe that the latter is attributable to the increasing effectiveness of the quencher in removing ·CHPhOH radicals as its concentration is increased. From the gradient of the plot for ketyl radical concentrations in propan-2-ol and the limiting gradient at low quencher concentrations in benzyl alcohol we estimate the rate constants for abstraction by $^3(n,\pi^*)$ biacetyl in these solvents as $1{\cdot}1 \times 10^4$ and $2{\cdot}8 \times 10^4$ l mol^{-1} s^{-1}, respectively. These values are to be compared with $1{\cdot}3 \times 10^4$ for abstraction from propan-2-ol in acetonitrile solvent [25] and $6{\cdot}9 \times 10^3$ for abstraction from benzyl alcohol in benzene solvent.[24] The agreement is reasonable in view of the known effect of solvent polarity on hydrogen abstraction reactions. Experimental values of k_r for abstraction from other solvents are summarised in Table 3.

TABLE 3

Rate constants for the reaction of $^3(n,\pi^*)$ biacetyl with various hydrogen donors

Donor	10^{-9} k_q/ l mol^{-1} s^{-1}	10^{-3} g/ l mol^{-1}	10^4 k_q/k_r	k_r/l mol^{-1} s^{-1}
EtOH	5·58	70 ± 7	16 ± 3	(3·5 ± 0·6) × 10^3
Pr^{i}OH	3·48	20 ± 2	32 ± 5	(1·1 ± 0·2) × 10^4
PhCH$_2$OH	2·08	6·9 ± 0·8	7·3 ± 1	(2·8 ± 0·4) × 10^4
PhMeCHOH	0·85	1·6 ± 0·3	1·3 ± 0·3	(6·5 ± 1·5) × 10^4
Cyclohexene	8·10	3·0 ± 0·5	3·0 ± 0·5	(2·7 ± 0·5) × 10^5

† Calculated from $k_q = \gamma k_{diff}$ where k_{diff} is the diffusion-controlled rate constant and $(1 - \gamma)\gamma = 0{\cdot}56\, k_{diff} \times 10^{-10}$ (see ref. 18).

Since g, the slope of the plots shown in the Figure, is a reciprocal function of k_d/k_r + [DH], the uncertainty in the estimated values of k_d/k_r is most serious if $k_d/k_r \geqslant$ [DH]. For propan-2-ol we estimate that $k_d/k_r < 0{\cdot}2$[DH], but for ethanol $k_d/k_r \approx 0{\cdot}5$[DH] and we have assumed the same value for 1-phenylethanol solutions. Thus the uncertainties in our estimates of k_r for $^3(n,\pi^*)$ biacetyl reacting with ethanol and 1-phenylethanol ($3{\cdot}5 \times 10^3$ and $6{\cdot}5 \times 10^4$ l mol^{-1} s^{-1}, respectively) are greater. Furthermore these values are likely to be lower limits because, as explained earlier, our estimates of k_d/k_r are probably overestimates and both plots show upward curvature at high quencher concentrations. In the case of hydrogen abstraction from cyclohexene the fate of the radicals derived from solvent is uncertain in view of the complexity of the molecular products,[28] but our estimate of k_r ($2{\cdot}7 \times 10^5$ l mol^{-1} s^{-1}) is in reasonable agreement with a value determined from pulse radiolysis experiments [29] for cyclohexene in predominantly benzene solution ($1{\cdot}2 \times 10^5$ l mol^{-1} s^{-1}).

A disturbing inconsistency appears when we calculate rates of self-quenching (k_d) from our values of k_r and k_d/k_r and compare these with earlier estimates. For example, in propan-2-ol we estimate k_d as $(2{\cdot}6 \pm 1{\cdot}3) \times 10^4$ l mol^{-1} s^{-1}, which is considerably higher than estimates in benzene [24] (*ca.* 10^3 l mol^{-1} s^{-1}) and methanol [30] ($<5 \times 10^3$ l mol^{-1} s^{-1}). Rather higher values have been estimated from pulse radiolysis experiments [29,31] in benzene and attributed to quenching of the triplet state of biacetyl by the high concentration of radicals present in the system. Although this suggestion offers a partial explanation of our anomalously high values for self-quenching, the radical concentrations obtained in our experiments (*ca.* 5×10^{-7}M) are not high enough for this explanation to be fully satisfactory and the data given in Table 3 must be treated with some reservation.

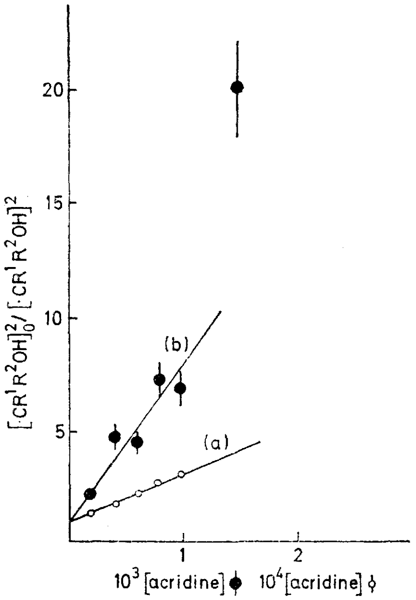

FIGURE 2 Effect of triplet quencher (acridine) on the steady state concentration of radicals $\cdot CRR^1OH = \cdot CMe(OH)COMe$ during the photolysis of biacetyl in (a) propan-2-ol and (b) benzyl alcohol at 298 K

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[29] R. B. Cundall, G. B. Evans, and E. J. Land, *J. Phys. Chem.*, 1969, **73**, 3982.

[30] M. Koizumi, Y. Ikeda, and H. Yamashita, *Bull. Chem. Soc. Japan*, 1968, **41**, 1056.

[31] R. B. Cundall, G. B. Evans, P. A. Griffiths, and J. P. Keene, *J. Phys. Chem.*, 1968, **72**, 3877.