Mechanism of the Photoinduced Decarboxylation of Carboxylic Acids sensitised by Aromatic Ketones and Quinones

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The rate constants for the decarboxylation of several acids of the type $RXCH_2CO_2H$ (X = O, S, and NH), sensitised by benzophenone and tetrachloro-*p*-benzoquinone have been determined. The reactions are considered as occurring *via* exciplex formation between the carbonyl compound and the acid, and in agreement with this hypothesis, the published values of rate constants for the reaction of triplet benzophenone with substituted hydrocarbons ($RXCH_3$) are very similar to those determined for reaction with the corresponding carboxylic acid. In addition, the rate constants for decarboxylation are in the order expected from a consideration of the ionisation potentials of their corresponding substituted hydrocarbon ($RXCH_3$). The rate constants for reaction with the quinone are higher than those for the corresponding reactions with benzophenone. Decarboxylation of (phenylthio)acetic acid in acetonitrile solution is acid catalysed whereas in benzene solution, acids slightly retard the reaction. This reaction is also quenched by methyl phenyl sulphide. Attention is drawn to the fact that the inefficiency of photoreduction of benzophenone by substituted hydrocarbons ($RXCH_3$) can stem from the hydrogen abstraction reaction being reversible, as well as being due to exciplex formation.

IT has been previously reported that carboxylic acids of the type $RXCH_2CO_2H$ (where X = O, S, or NH) are decarboxylated on irradiation in the presence of biacetyl,[1] aromatic ketones,[2a,b] quinones,[2a] and aromatic nitro-compounds.[3] The mechanistic aspects of these reactions are particularly intriguing since they do not appear to be simple hydrogen-abstraction reactions. If this had been the case, ketones and nitro-compounds

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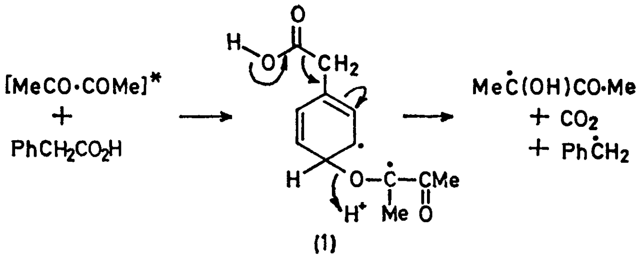
[1] E. J. Baum and R. O. C. Norman, *J. Chem. Soc.* (*B*), 1968, 227.

[2] (*a*) R. S. Davidson and P. R. Steiner, *J. Chem. Soc.* (*C*), 1971, 1682; (*b*) R. S. Davidson, K. Harrison, and P. R. Steiner, *J. Chem. Soc.* (*C*), 1971, 3480.

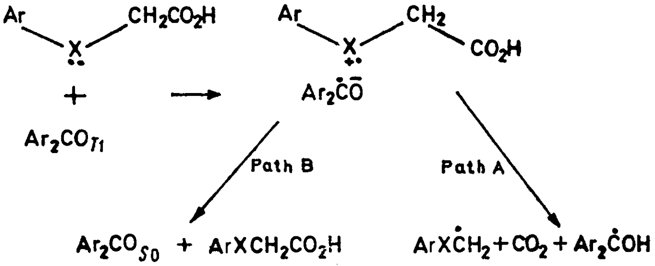
[3] R. S. Davidson, Miss S. Korkut, and P. R. Steiner, *Chem. Comm.*, 1971, 1052.

which have low lying π–π^* triplet states would be expected to be unreactive, and this is not the case.[2b] There appear to be two possible mechanisms. The first is that suggested by Baum and Norman [1] who found that the decarboxylation of phenylacetic acid and phenoxyacetic acid can be photosensitised by biacetyl. They proposed that the excited triplet ketone reacts with the acid to give a biradical (1) which undergoes an acid-catalysed fragmentation reaction to give carbon dioxide and radicals derived from the ketone and acid. This mechanism is particularly appealing because it is known, from e.s.r. studies,[4] that hydroxyl radicals react with such carboxylic acids to give similar biradicals and that the reactions of n–π^* triplet states of ketones are often very similar to those of alkoxyl radicals.[5] Recently, the biradical mechanism has been suggested as operating in the photoreduction of triplet ketones by aromatic hydrocarbons (*e.g.* benzene).[6] A similar mechanism has been proposed to account for the observation that many mono-olefins undergo *cis–trans* isomerisation on reaction with triplet ketones whose energies are lower than the triplet energy of the olefin.[7] At the present time, isomerisation *via* an exciplex intermediate is the favoured view.



(1)

The alternative mechanism for the decarboxylation reactions involves an exciplex intermediate,[2a,b] *i.e.* a step is postulated in which electron transfer from the acid to the excited ketone occurs. In the case of the aryl substituted acids, charge transfer from the conjugated arylheteroatom system will occur whereas with aliphatic carboxylic acids $RXCH_2CO_2H$ ($R =$ alkyl), electron transfer from the hetero-atom occurs. The following factors may be expected to affect the reaction if exciplex intermediates are involved; (*a*) the ionisation potential of the acid, and (*b*) the reduction potential of the excited ketone. As yet, reduction potentials of excited states have not been determined but they can be estimated by a consideration of the reduction potential of the ground-state ketone and the energy available in the excited state of the ketone. This semiqualitative treatment has been shown to work particularly well for estimating the efficiency of exciplex formation between aromatic hydrocarbons and amines.[8] If the exciplex mechanism operates in the decarboxylation reactions, the electron-transfer step is common to these reactions and to the reduction of triplet ketones by substituted hydrocarbons ($RXCH_3$, $X =$ O, S, or NH). Recently, rate constants for the reaction of $RXCH_3$ ($X =$ S or NH) with triplet benzophenone have become available.[9a,b] Thus, if the electron-transfer step is common to both reactions, the rate constants for the primary photochemical steps in the two reactions should be similar.[10]



RESULTS

The following kinetic scheme shows how the rate constants for the decarboxylation reactions can be evaluated from quantum yield measurements.

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\begin{array}{lr}
 & \text{Rate} \\
Ar_2CO_{S_0} \xrightarrow{h\nu} Ar_2CO_{S_1} \xrightarrow{\text{i.-s.c.}} Ar_2CO_{T_1} & I \\
Ar_2CO_{T_1} \xrightarrow{k_d} Ar_2CO_{S_0} & k_d[Ar_2CO_{T_1}] \\
Ar_2CO_{T_1} + A \xrightarrow{k_r} C & k_r[Ar_2CO_{T_1}][A] \\
C \xrightarrow{\text{Path A}} \text{Products} + CO_2 & \\
C \xrightarrow{\text{Path B}} Ar_2CO_{S_0} + A & \\
Ar_2CO_{T_1} + Q \xrightarrow{k_q} Ar_2CO_{S_0} + Q_{T_1} & k_q[Ar_2CO_{T_1}][Q]
\end{array}
$$

A = Acid, C = complex, Q = triplet quencher, $I =$ light intensity, $k =$ rate constant for the reaction.

$$\phi = N\phi_c \qquad (1)$$

$\phi =$ Quantum yield of reaction, $\phi_c =$ quantum yield for complex formation, and $N =$ fraction of 'complex' molecultes which undergo decarboxylation.

Under steady state conditions

$$I = k_r[Ar_2CO_{T_1}][A] + k_d[Ar_2CO_{T_1}] + k_q[Ar_2CO_{T_1}][Q]$$

$$\phi_c = \frac{k_r[Ar_2CO_{T_1}][A]}{I} = \frac{\phi}{N}$$

Therefore for quenched reaction

$$\frac{N}{\phi_q} = 1 + \frac{k_d + k_q[Q]}{k_r[A]} \qquad (2)$$

where $\phi_q =$ quantum yield of quenched reaction.

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[4] R. O. C. Norman and R. J. Pritchett, *J. Chem. Soc.* (*B*), 1967, 926.

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

[6] D. I. Schuster and D. F. Brizzolara, *J. Amer. Chem. Soc.*, 1970, **92**, 4357; K. Maruyama, K. Ono, and J. Osugi, *Bull. Chem. Soc. Japan*, 1969, **42**, 3357; G. Porter and M. R. Topp, *Proc. Roy. Soc.* (*A*), 1970, **315**, 163; J. Saltiel, H. C. Curtis, L. Metts, J. W. Miley, J. Winterle, and M. Wrighton, *J. Amer. Chem. Soc.*, 1970, **92**, 410; J. Saltiel and H. C. Curtiss, *J. Amer. Chem. Soc.*, 1971, **93**, 2056; J. Dedinas, *J. Phys. Chem.*, 1971, **75**, 181; A. V. Buettner and J. Dedinas, *J. Phys. Chem.*, 1971, **75**, 187.

[7] R. A. Caldwell, *J. Amer. Chem. Soc.*, 1970, **92**, 1439; I. H. Kochevar and P. J. Wagner, *J. Amer. Chem. Soc.*, 1970, **92**, 5742.

[8] D. Riehm and A. Weller, *Israel. J. Chem.*, 1970, **8**, 259.

[9] (*a*) J. Guttenplan and S. G. Cohen, *Chem. Comm.*, 1969, 247; (*b*) S. G. Cohen and A. D. Litt, *Tetrahedron Letters*, 1970, 837.

[10] A preliminary account of this work has been published. R. S. Davidson and P. R. Steiner, *Chem. Comm.*, 1971, 1115.

In the absence of a quencher.

$$\frac{N}{\phi} = 1 + \frac{k_d}{k_r[A]}$$

i.e.

$$\frac{\phi}{\phi_q} = 1 + \frac{k_d[Q]}{k_q + k_r[A]} \qquad (3)$$

It will be noted that the Stern–Volmer equation does not contain terms which refer to the actual decarboxylation step and this serves to emphasise that the efficiency of the primary photochemical step is not directly related to the quantum yield of the reaction.

The decarboxylation of phenoxyacetic acid, (phenylthio)-acetic, (n-butylthio)acetic acid, and *N*-(2-chlorophenyl)-glycine sensitised by benzophenone were studied. Quantum yields for the reductions run in the presence of varying amounts of the triplet quencher naphthalene,[11] were determined and are shown in Table 1. A similar study was made of the decarboxylation of phenoxyacetic acid and (phenylthio)acetic acid sensitised by tetrachloro-*p*-benzoquinone. For these reactions 9-nitroanthracene was used as quencher. This compound was chosen because it did not form a charge-transfer complex with the quinone; it did not absorb the incident radiation and its triplet energy should be below 50 kcal/mol.* A published value of the triplet energy of tetrachloro-*p*-benzoquinone does not appear to be available and we therefore had to guess that it lies above 50 kcal/mol.[12b] The kinetic results show that these assumptions were valid. In all cases, quantum yields were obtained for reactions run to less than 40% completion. The reactions were shown to obey zero-order kinetics to at least 40% completion. Stern–Volmer plots for two of the reactions are shown in Figures 1 and 2. From these plots, values of k_r were evaluated and these are shown in Table 2.

TABLE 1

Quantum yields for the reactions of carboxylic acids ($6{\cdot}25 \times 10^{-2}$M) with benzophenone ($6{\cdot}25 \times 10^{-2}$M) and tetrachloro-*p*-benzoquinone ($6{\cdot}25 \times 10^{-2}$M) run in the presence of naphthalene and 9-nitroanthracene respectively

Reactions with benzophenone

Acid	Solvent	Concn. of naphthalene	ϕ/ϕ_q (±0·03)
Phenoxyacetic acid	Benzene	$1{\cdot}9 \times 10^{-5}$	1·14
,, ,,	,,	$5{\cdot}8 \times 10^{-5}$	1·23
,, ,,	,,	$9{\cdot}7 \times 10^{-5}$	1·37
,, ,,	,,	$15{\cdot}6 \times 10^{-5}$	1·53
(Phenylthio)acetic acid	,,	$3{\cdot}9 \times 10^{-4}$	1·53
,, ,,	,,	$15{\cdot}6 \times 10^{-4}$	2·31
,, ,,	,,	$23{\cdot}4 \times 10^{-4}$	2·70
,, ,,	,,	$31{\cdot}3 \times 10^{-4}$	3·38
,, ,,	Acetonitrile	$7{\cdot}8 \times 10^{-4}$	1·45
,, ,,	,,	$23{\cdot}4 \times 10^{-4}$	2·42
,, ,,	,,	$35{\cdot}2 \times 10^{-4}$	2·93
,, ,,	,,	$46{\cdot}9 \times 10^{-4}$	3·44
(n-Butylthio)acetic acid	Benzene	$1{\cdot}6 \times 10^{-4}$	1·13
,, ,,	,,	$4{\cdot}7 \times 10^{-4}$	1·24
,, ,,	,,	$7{\cdot}8 \times 10^{-4}$	1·43
,, ,,	,,	$11{\cdot}7 \times 10^{-4}$	1·54
N-(2-Chlorophenyl)glycine	Acetonitrile	$23{\cdot}4 \times 10^{-4}$	1·12
,, ,,	,,	$46{\cdot}8 \times 10^{-4}$	1·17
,, ,,	,,	$78{\cdot}1 \times 10^{-4}$	1·28

Reactions with tetrachloro-*p*-benzophenone in benzene solution

Acid	Concn. of 9-nitro-anthracene	ϕ/ϕ_q
Phenoxyacetic acid	$44{\cdot}8 \times 10^{-4}$	1·42
,, ,,	$89{\cdot}7 \times 10^{-4}$	1·86
,, ,,	$134{\cdot}5 \times 10^{-4}$	2·62
(Phenylthio)acetic acid	$44{\cdot}8 \times 10^{-4}$	1·15
,, ,,	$89{\cdot}7 \times 10^{-4}$	1·29
,, ,,	$134{\cdot}5 \times 10^{-4}$	1·49

TABLE 2

Rate constants for the reaction of triplet benzophenone and tetrachloro-*p*-benzoquinone with carboxylic acids as determined by quenching studies

Carbonyl compound	Acid	Solvent	k_r (l mol^{-1} s^{-1})
Benzophenone	Phenoxyacetic acid	Benzene	$1{\cdot}7\ (\pm 0{\cdot}7) \times 10^{7}$
,,	(Phenylthio)acetic acid	Benzene	$1{\cdot}0\ (\pm 0{\cdot}5) \times 10^{8}$
,,	(Phenylthio)acetic acid	Aceto-nitrile	$1{\cdot}45\ (\pm 0{\cdot}15) \times 10^{8}$
,,	(n-Butylthio)acetic acid	Benzene	$1{\cdot}6\ (\pm 0{\cdot}15) \times 10^{8}$
,,	*N*-(2-Chlorophenyl)-glycine	Aceto-nitrile	$2{\cdot}1\ (\pm 0{\cdot}4) \times 10^{9}$
Tetrachloro-*p*-benzoquinone	Phenoxyacetic acid	Benzene	$7{\cdot}7\ (\pm 1{\cdot}0) \times 10^{8}$
Tetrachloro-*p*-benzoquinone	(Phenylthio)acetic acid	Benzene	$2{\cdot}2\ (\pm 0{\cdot}2) \times 10^{9}$

TABLE 3

Rate constants for the quenching of triplet benzophenone by sulphides and amines in benzene solution

Quencher	k_q (l mol^{-1} s^{-1})
Methyl phenyl sulphide [9a]	$7{\cdot}5 \times 10^{7}$
Di-n-butyl sulphide [9a]	$6{\cdot}6 \times 10^{8}$
NN-Dimethylaniline [9a]	$2{\cdot}7 \times 10^{9}$

Table 3 shows the rate constants for the reaction of triplet benzophenone with substituted aromatic hydrocarbons. Quantum yields of decarboxylation and exciplex formation are shown in Table 4.

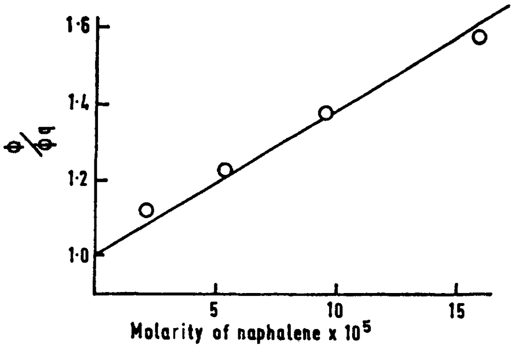

FIGURE 1 Effect of added naphthalene upon the quantum yield for decarboxylation of phenoxyacetic acid in benzene solution sensitised by benzophenone

Table 5 shows the effect of addition of acids to the reactions of (phenylthio)acetic with benzophenone and also the quenching effect of methyl phenyl sulphide and ethyl

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* The triplet energies of reported monosubstituted anthracenes appear to be below 50 kcal/mol.[12a]

[11] A. Terenin and V. Ermolaev, *Trans. Faraday Soc.*, 1952, **52**, 1042; G. Porter and F. Wilkinson, *Trans. Faraday Soc.*, 1961, **57**, 1686.

[12] (*a*) S. P. McGlynn, T. Azumi, and M. Kasha, *J. Chem. Phys.*, 1964, **40**, 507; (*b*) J. M. Bruce, *Quart. Rev.*, 1967, **21**, 405.

TABLE 4

Quantum yields for the decarboxylation of carboxylic acids ($6{\cdot}25 \times 10^{-2}$M) sensitised by benzophenone ($6{\cdot}25 \times 10^{-2}$M)

Acid	Solvent	ϕ ($\pm 0{\cdot}03$)	N [a]	ϕ_c [a]
Phenoxyacetic acid	Benzene	0·11	0·14	0·78
(Phenylthio)acetic acid	Benzene	0·37	0·39	0·95
(Phenylthio)acetic acid	Acetonitrile	0·15	0·15 [b]	0·97 [b]
(n-Butylthio)acetic acid	Benzene	0·29	0·30	0·97
N-(2-Chlorophenyl)glycine	Acetonitrile	0·28	0·28 [b]	1 [b]

[a] Calculated from equation (2) using k_r values from Table 2. [b] To obtain these values it has been necessary to assume that k_d for triplet benzophenone is of the same order in benzene and acetonitrile solution. The value of k_d will only make a significant calculation if it is $> 7 \times 10^6$ s^{-1}.

TABLE 5

The effect of solvent and added acid upon the yield of carbon dioxide from the decarboxylation of carboxylic acids sensitised by carbonyl compounds [a]

Acid	Solvent	Compound added (M)	Irradiation time (min)	% Yield of carbon dioxide (±2%)
(Phenylthio) acetic acid	Benzene		25	45
	,,	Acetic acid ($6{\cdot}25 \times 10^{-2}$)	25	40
	,,	Acetic acid (0·83)	25	36
	,,	Phenylacetic acid ($6{\cdot}25 \times 10^{-2}$)	25	44
	,,	Phenylacetic acid (0·38)	25	39
	Acetonitrile		60	45
	,,	Acetic acid ($6{\cdot}25 \times 10^{-2}$)	60	51
	,,	Acetic acid (0·83)	60	75
	,,	Phenylacetic acid ($6{\cdot}25 \times 10^{-2}$)	60	54
	,,	Phenylacetic acid (0·38)	60	70
	Benzene	Methyl phenyl sulphide ($6{\cdot}25 \times 10^{-2}$)	30	30
	,,	Methyl phenyl sulphide (0·4)	30	23
	,,	Ethyl (phenylthio)acetate ($6{\cdot}25 \times 10^{-2}$)	30	43
	,,	t-Butanol (0·675)	30	24
Phenoxyacetic acid	Benzene		60	52
	Acetonitrile		60	13
	t-Butanol		60	41
Tetrachloro-*p*-benzoquinone as sensitiser				
Phenoxyacetic acid	Benzene		60	85
Phenoxyacetic acid	Acetonitrile		60	23

[a] Irradiation procedure (ref. 2*a*).

(phenylthio)acetate. Table 5 also shows the effect of solvent upon the decarboxylation of phenoxyacetic acid sensitised by benzophenone.*

DISCUSSION

A comparison of the k_r values for the decarboxylation reactions sensitised by benzophenone (Table 2), with the rate constants for deactivation of triplet benzophenone by various electron donors (Table 3) shows that there is a striking similarity between the two sets of results. Furthermore, the order of reactivity of the acids is that expected from a consideration of the ionisation potentials of the parent substituted hydrocarbons $ArXCH_3$, *i.e.* *N*-(2-chlorophenyl)glycine > (phenylthio)acetic acid > phenoxyacetic acid (ionisation potentials of either parent substituted hydrocarbons or closely related compound; *N*-methylaniline, 7·58 eV,[14] methyl phenyl sulphide 7·9 eV,[15] and methyl phenyl ether [15] 8·2 eV). Furthermore, the fact that the rate constants for reactions sensitised by tetrachloro-*p*-benzoquinone are higher than those for the corresponding reactions with benzophenone is to be expected because of the greater electron affinity of the quinone.† The slightly higher rate constant for the decarboxylation of (phenylthio)acetic acid, sensitised by benzophenone in acetonitrile, compared with benzene solution is in accordance with predictions, if the exciplex mechanism holds.[17] It is not surprising that carboxylic acids such as α-amino-acids, and alkoxyacetic acids ($ROCH_2CO_2H$) are unreactive because they have very high ionisation potentials (>9 eV).

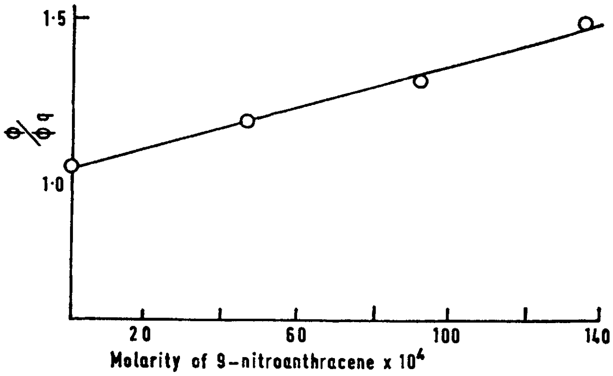

FIGURE 2 Effect of added 9-nitroanthracene upon the quantum yield for decarboxylation of (phenylthio)acetic acid in benzene solution, sensitised by tetrachloro-*p*-benzoquinone

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* A value of 3×10^5 s^{-1} was used for k_d of benzophenone.[13a] A value of 5×10^9 l mol^{-1} s^{-1} was used for k_q.[13b] A value for k_d of triplet chloranil in benzene solution does not appear to be available. It is likely to be similar to that determined for triplet chloranil in ethanol,[13c] *i.e.* between 10^5 and 10^6 s^{-1}.

† $E_{\frac{1}{2}}$ for benzophenone = $-1{\cdot}14$ V.[16a] $E_{\frac{1}{2}}$ for chloranil = $+0{\cdot}01$ V.[16b]

[13] (*a*) P. J. Wagner, *Mol. Photochem.*, 1969, **1**, 71; (*b*) P. J. Wagner and I. Kochevar, *J. Amer. Chem. Soc.*, 1968, **90**, 2232; (*c*) D. R. Kemp and G. Porter, *Chem. Comm.*, 1969, 1029.

[14] P. G. Farrell and J. Newton, *J. Phys. Chem.*, 1965, **69**, 3506.

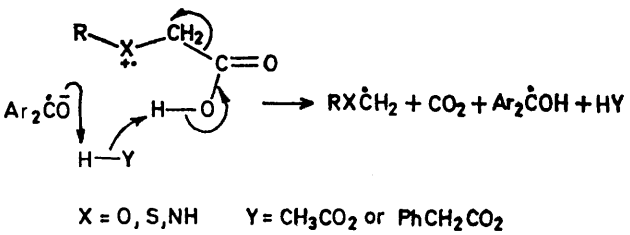
[15] E. M. Voigt and C. Reid, *J. Amer. Chem. Soc.*, 1964, **86**, 3930.

[16] (*a*) R. W. Brockman and D. E. Pearson, *J. Amer. Chem. Soc.*, 1952, **74**, 4128; (*b*) M. Peover, *J. Chem. Soc.*, 1962, 4540.

[17] A. Weller in 'Luminescence of Organic and Inorganic Materials,' ed. by H. P. Kallman and G. M. Spruch, J. Wiley, New York, 1962.

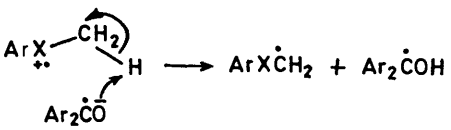
It will be noted that the k_r values for the decarboxylation reactions are high and yet the quantum yields for decarboxylation are relatively low. This indicates that although exciplex formation is efficient, its decomposition to give carbon dioxide is relatively inefficient. One source of inefficiency is the decomposition of the exciplex to give ground-state ketone and acid (Path B). The relative efficiency of the two modes of decay will depend upon the degree of charge transfer in the exciplex and the solvating properties of the solvent. The most startling solvent effect was that of t-butyl alcohol which completely suppressed the decarboxylation of phenoxyacetic acid sensitised by benzophenone. It is not likely that the lack of reaction is due to the non-formation of exciplex since it is known that amines can quench triplet benzophenone in the presence of alcohols.[18b] Furthermore, it is also known that the singlet state of biacetyl undergoes electron-transfer reactions with amines in ethanolic solution.[19] The lack of decarboxylation in t-butyl alcohol must be due to quenching pathway (Path B) becoming much more favoured relative to the decarboxylation reaction. It is quite conceivable that the decarboxylation reaction will have a higher energy of activation in protic solvents than in non-protic solvents since reaction in protic solvents requires disruption of the hydrogen bonds formed between the carboxy-group and solvent. This factor may well alter the favourabilities of pathways A and B.

The effect of added acids upon the decarboxylation reactions was a little surprising. Acetic acid slightly retarded the decarboxylation of phenylthioacetic acid sensitised by benzophenone and this is probably due to the quenching of the triplet ketone by the acid.* In contrast, the acid catalysed the reaction run in acetonitrile solution. The solvent dependence of the effect of added acid is believed to stem from the fact that in benzene solution the exciplexes remain intact whereas in acetonitrile they probably dissociate to give radical ions.[18a] The acids will have little chance to affect the intact complexes whereas they should be able to react with the radical ions.



The observation that the decarboxylation reactions in acetonitrile solution can be catalysed by acids is nicely paralleled by the finding of Baum and Norman that the biacetyl-sensitised decarboxylation reactions run in aqueous solution can also be catalysed by acids.[1]

Whilst the reported results are seen to be consistent with the exciplex mechanism, their relevance to the ‘ biradical ’ mechanism must also be considered. The most striking result is that (n-butylthio)acetic acid and (phenylthio)acetic acid have similar rate constants for reaction with triplet benzophenone and this suggests that reaction occurs *via* similar mechanisms. This, of course, rules out the biradical mechanism. However, the similarity in the rate constants may be fortuitous and this criticism may therefore be invalid. Presumably, if the ‘ biradical ’ mechanism operates in the decarboxylation reactions, it should also operate in the reaction of triplet benzophenone with the substituted aromatic hydrocarbons $ArXCH_3$. In the case of *N*-methylanilines [18b] and sulphides,[9a] it is known that the interaction also leads to hydrogen abstraction for the *N*-methyl and *S*-methyl groups respectively. There seems little driving force for the biradical intermediates to collapse to give such radicals.



On the other hand, collapse of the exciplex intermediate should occur relatively easily. Collapse of the exciplex formed in the reactions with carboxylic acid should be more favoured than in the case of reactions with the substituted hydrocarbons because (*a*) of the acidity of the carboxy-group proton (*b*) collapse is *via* a 6-membered as opposed to a 4-membered transition state. It is on these grounds that we favour the exciplex mechanism for the reaction of triplet carbonyl compounds with the carboxylic acids and substituted aromatic hydrocarbons.

The results on the decarboxylation reactions also have a bearing upon the photoreduction of benzophenone by substituted aromatic hydrocarbons. The reduction of benzophenone by methyl phenyl ether [21] and methyl phenyl sulphide [9a,21] is, as judged by product yields, very inefficient. Whilst quenching *via* exciplex formation is undoubtedly important, the fact that the radicals generated in the hydrogen abstraction reaction can undergo hydrogen-atom transfer in the reverse direction must also be important.

$$Ph_2CO_{T_1} + PhOMe \longrightarrow Ph_2\dot{C}OH + PhO\dot{C}H_2$$
$$PhO\dot{C}H_2 + Ph_2\dot{C}OH \longrightarrow PhOMe + Ph_2CO$$

That this latter reaction can occur is attested by the

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* Acetic acid has been found to act as a relatively inefficient quencher of benzophenone triplets.[20]

[18a] H. Knibbe, Ph.D. Thesis, Vrihe University, Amsterdam, 1969; [b] R. S. Davidson and P. F. Lambeth, *Chem. Comm.*, 1968, 511.

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

[20] R. S. Davidson and S. Korkut, unpublished results.

[21] R. S. Davidson, *Chem. Comm.*, 1966, 575.

fact that it occurs with moderate efficiency in the decarboxylation reactions.[2a] *E.g.*

$$Ph_2CO_{T_1} + PhOCH_2CO_2H \longrightarrow Ph_2\dot{C}OH + PhO\dot{C}H_2 + CO_2$$

$$Ph_2\dot{C}OH + PhO\dot{C}H_2 \longrightarrow Ph_2CO + PhOMe$$

Thus in kinetic schemes for photoreduction it is not only necessary to account for exciplex formation if this occurs,[22] but also to account for hydrogen-atom transfer reactions between the radicals.

EXPERIMENTAL

The details of purification of reagents, the instruments used to record spectra and the method employed for determination of carbon dioxide have been previously described.[2a] Irradiation procedures A and B have been previously described.[2a]

Irradiation Procedure C: for the Determination of the Yields of Carbon Dioxide from Decarboxylation Reactions run in the Presence of Triplet Quenchers.—' Pyrex ' tubes equipped with a gas inlet and gas outlet tube were used. The reaction mixture (12 ml) was placed in the tube and the solution purged with ' oxygen and carbon-dioxide free ' nitrogen for 1 h after which time the volume was reduced to (10 ml). The reaction mixture was made up so that after this reduction in volume, the solutions were 6·25 × 10^{-2}M in the acid and carbonyl compound. Similarly, when quenchers were added to the reaction mixture, the molarity of quencher employed in the reactions was that for 10 ml of the reaction mixture. The Pyrex tubes were mounted on a turntable which fitted into a Rayonet Reactor (Southern New England Ultraviolet) equipped with lamps having maximum emission at 350 nm for the reactions with benzophenone and with lamps having maximum emission at 310 nm for the reactions with tetrachloro-*p*-benzoquinone. After irradiation, the solutions were purged with nitrogen for 1 h, the exit gases being passed through baryta solution so that the yield of carbon dioxide could be estimated. The reaction mixtures were not purged with nitrogen during irradiation.

Kinetic Studies.—Irradiation procedure C was used. For each of the reactions, the yield of carbon dioxide as a function of time was measured so that the ' optimum ' time for irradiation for reactions run in the presence of quenchers could be determined. The optimum time was taken as being the time required for the formation of a measurable amount of barium carbonate whilst the reaction still obeyed zero-order kinetics.

Reaction mixtures, containing varying amounts of the appropriate quencher were irradiated for the optimum time and the yield of carbon dioxide was determined. The values of ϕ/ϕ_q were obtained by dividing the amount of barium carbonate precipitated from the unquenched reaction by the amount of barium carbonate from the quenched reaction.

Actinometry.—The benzophenone–diphenylmethanol actinometer was used.[23] Benzene solutions (10 ml) of benzophenone (6·25 × 10^{-2}M) containing diphenylmethanol (6·25 × 10^{-2}M) were irradiated for varying lengths of time using irradiation procedure C. The rate of disappearance of benzophenone was found to be 1·695 × 10^{19} molecules l^{-1} s^{-1}. Benzene solutions (10 ml) of benzophenone (6·25 × 10^{-2}M) containing varying amounts of diphenylmethanol were then irradiated for a known period of time. Taking the reaction containing 6·25 × 10^{-2}M of benzophenone and diphenylmethanol as the actinometer solution, a plot of the reciprocal of the diphenylmethanol concentration *versus* ϕ_{act}/ϕ_{react} was made (Figure 3). The intercept gives the quantum yield of the actinometer solution as 0·56. Since

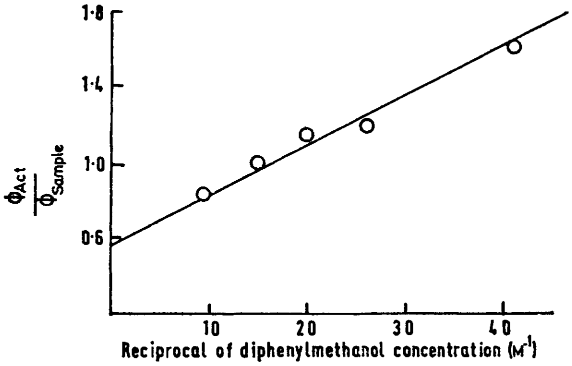

FIGURE 3 Effect upon the quantum yield for photoreduction of benzophenone by diphenylmethanol caused by varying the diphenylmethanol concentration

$$\text{Quantum yield for } \phi_2(C{=}O) \text{ disappearance} = \frac{\text{Rate of } \phi_2(C{=}O) \text{ disappearance}}{\text{Light intensity}}$$

$$I = \text{Light intensity} = \frac{1{\cdot}695 \times 10^{19}}{0{\cdot}56} = 3{\cdot}0 \times 10^{19} \text{ quanta } l^{-1}\, s^{-1}$$

Quantum yields for carbon dioxide formation were calculated from the rate of the evolution of the gas and the light intensity.

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