Mechanism of the Benzophenone Photosensitised Decarboxylation of Carboxylic Acids

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Summary Kinetic measurements of the naphthalene quenching of the photoinduced decarboxylation of acids ($RXCH_2{\cdot}CO_2H$, X = O, S, NH) sensitised by benzophenone show that the decarboxylation reactions involve an exciplex intermediate.

IT has been shown that biacetyl[1] and a number of aromatic ketones[2] and quinones[2] photosensitise the decarboxylation of acids of the type $RXCH_2{\cdot}CO_2H$ (X = O, S, NH). A kinetic study has been made of the naphthalene quenching of the reactions sensitised by benzophenone [equations (1)—(5)] in order to elucidate the mechanism of the reaction.

Quantum yields for the decarboxylation of acids, sensitised by benzophenones, were measured for reactions run in the presence of varying amounts of the triplet quencher,

Rate

$$Ph_2CO \rightarrow Ph_2CO(S_1) \rightarrow Ph_2CO(T_1) \qquad I \tag{1}$$

$$Ph_2CO(T_1) + \text{Acid} \xrightarrow{k_r} \text{Complex} \qquad k_r[Ph_2CO(T_1)][\text{Acid}] \tag{2}$$

$$Ph_2CO(T) \xrightarrow{k_d} Ph_2CO(S_0) \qquad k_d[Ph_2CO(T_1)] \tag{3}$$

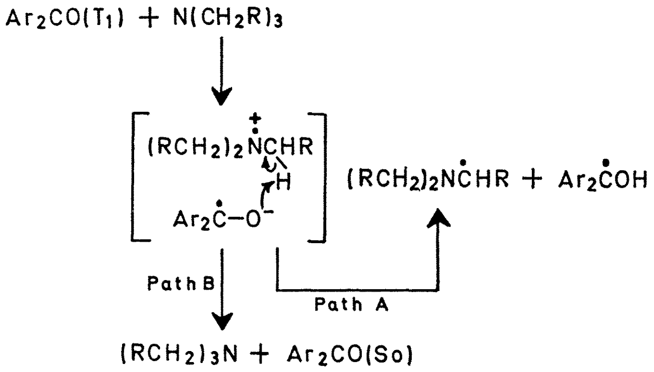
$$Ph_2CO(T_1) + Q \xrightarrow{k_q} Ph_2CO(S_0) + Q(T_1) \qquad k_q[Ph_2CO(T_1)][Q] \tag{4}$$

$$\text{Complex} \rightarrow CO_2 + \text{Radicals} \tag{5}$$

$$\phi/\phi_q = 1 + k_q[Q]/(k_d + k_r[\text{Acid}]) \tag{6}$$

k = Rate constants for processes shown.
[Q] = Naphthalene concentration.
[Acid] = Carboxylic acid concentration.
ϕ_q and ϕ = Quantum yield for quenched and unquenched reactions.

naphthalene. A plot of the reciprocal of the quantum yield *versus* the naphthalene concentration gave a straight line for each acid and from the Stern–Volmer equation [equation (6)] the slopes of the lines gave values of $k_q/k_d + k_r$[Acid]. Since k_q and k_d are 5×10^9 M^{-1} s^{-1} (ref. 3) and 3×10^5 s^{-1} (ref. 4) respectively, values of k_r could be obtained (see Table). Values of the rate constants for quenching of triplet benzophenone by sulphides[5] and amines[6] are also shown in the Table. The values of these rate constants are very similar to those for the corresponding decarboxylations. We conclude that this agreement is a result of a common mechanism for the two deactivation processes. It has been previously proposed,[7] and in certain cases demonstrated[6,8] that electron transfer from sulphides[5] and amines[6,8] to triplet ketones can occur. The exciplexes so formed can either undergo intramolecular proton transfer to give radicals (Scheme 1, Path A) or else undergo electron transfer to give neutral molecules which results in quenching of the excited ketone (Scheme 1, Path B).



SCHEME 1

The acids should be able to interact in a similar way, but in these cases, proton transfer should readily occur because (a) the acidity of the proton of the carboxy-group and (b) the flexibility of the acetic acid residue will facilitate interaction of the oxygen atom of the anion radical with the proton of the carboxy-group (Scheme 2). These factors account for the fact that the thio-acids, n-butylthioacetic acid and phenylthioacetic acid, readily decarboxylate whereas the corresponding sulphides, n-butyl methyl sulphide and methyl phenyl sulphide, are ineffective as reductants for triplet benzophenone.

The order of reactivity of the acids: amino acids > sulphur acids > phenoxyacetic acid, is that expected from a consideration of the ionisation potential of the related compounds: anisole 8·2 eV,[9] methyl phenyl sulphide 7·9 eV,[9] *N*-methylaniline 7·58 eV.[10]

TABLE

Rate constants for benzophenone sensitised decarboxylation of carboxylic acids and for the quenching of triplet benzophenone by sulphides and amines

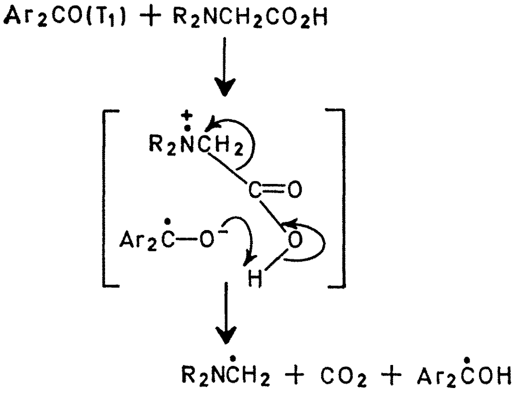
Rate constants for the benzophenone sensitised decarboxylation of carboxylic acids

Acid	Solvent	k_r/M^{-1} s^{-1}
Phenoxyacetic acid ..	.. Benzene	$1{\cdot}7 \times 10^7$
Phenylthioacetic acid	.. Benzene	$1{\cdot}0 \times 10^8$
" "	.. Acetonitrile	$1{\cdot}45 \times 10^8$
n-Butylthioacetic acid	.. Benzene	$1{\cdot}6 \times 10^8$
N-(*o*-Chlorophenyl)glycine ..	Acetonitrile	$2{\cdot}1 \times 10^9$

Rate constants for the quenching of triplet benzophenone by sulphides and amides

Quencher	Solvent	k_q/M^{-1} s^{-1}
Methyl phenyl[5] sulphide ..	Benzene	$7{\cdot}5 \times 10^7$
Di-n-butylsulphide[5]	Benzene	$6{\cdot}6 \times 10^8$
NN-Dimethylaniline[6] ..	Benzene	$2{\cdot}7 \times 10^9$

α-Amino-acids which have a primary or secondary aliphatic amino group, and α-alkoxyacetic acids are unreactive and this is undoubtedly due to their high ionisation potentials (all are > 9 eV).



SCHEME 2

The kinetic data rule out some alternative mechanisms, *e.g.* direct hydrogen abstraction from the strong O–H bond of the carboxy-group (the k_r values are too high) and protonation of the triplet ketone followed by electron transfer (this mechanism requires the k_r values for the acids to be the same). The similarity in the k_r values for reaction with n-butylthioacetic acid and phenylthioacetic acid, unless it is fortuitous, points to a common mechanism for the two acids which precludes the operation of the mechanism suggested by Baum and Norman.[1]

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