The Role of Electron Transfer Processes in the Photoinduced Decarboxylation Reaction of α-Oxo-carboxylic Acids

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Irradiation of pyruvic acid in the presence of electron acceptors gives rise to enhanced carbon dioxide production, and in the case of methylviologen, this leads to the formation of reduced methylviologen, which provides further evidence that the photodecarboxylation of pyruvic acid proceeds *via* an electron transfer process. The addition of pyridine to benzene solutions of pyruvic acid enhances decarboxylation. The effect of added triplet quenchers on the decarboxylation of a variety of α-oxo-carboxylic acids is reported. In some cases this led to enhanced carbon dioxide yields, *e.g.* this occurs on the addition of various aromatic hydrocarbons to benzene solutions of pyruvic acid. The fact that the quenchers can enhance or ' sensitise ' carbon dioxide production from α-oxo-carboxylic acids is explained on the basis of an electron transfer mechanism.

Recently there has been considerable interest in ascertaining the mechanism of the photoinduced fragmentation of α-oxo-carboxylic acids [1-3] and their esters.[3,4] It has previously been reported that the photoinduced decarboxylation of pyruvic acid occurs *via* a Type I mechanism [reaction (1)].[1,3]

This decarboxylation process has been shown to be highly solvent dependent and can occur in both non-hydrogen-[2,5,6] and hydrogen-donating solvents.[2,5,6] In the latter solvents photoreduction can occur.[7] The excited state responsible for the photoinduced decarboxylation has been assigned by some to the triplet [1,3,5,6] and by others to the singlet state.[8]

We have previously shown,[2] by a laser flash photolysis study, that the excited triplet state of pyruvic acid is quenched by naphthalene (NpH) giving rise to excited triplet naphthalene [reaction (2)].

The triplet naphthalene so produced is deactivated by electron transfer to pyruvic acid leading to formation of the naphthalene radical cation and the one-electron reduction product of pyruvic acid [reaction (3)].[2]

The photoinduced decarboxylation of pyruvic acid in deoxygenated solution is reported not to involve a Type I cleavage,[1,3] but to occur *via* a bimolecular electron transfer reaction from an excited-to a ground-state molecule [reaction (4)].[2]

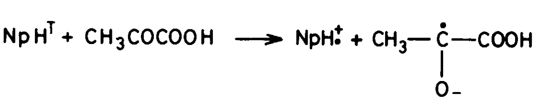
We now report upon further studies aimed at identifying the excited state responsible for the decarboxylation reaction, and provide additional evidence to show that the mechanism involves an electron transfer process [2] rather than the hitherto previously accepted Type I mechanism.[1,3] We also find that the addition of quenchers, in some cases, leads to sensitisation of the decarboxylation reaction and a mechanism involving electron transfer is proposed in order to account for this observation.

Results and Discussion

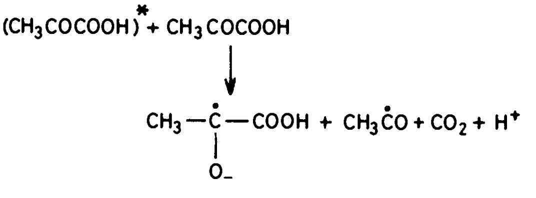
Initial Quenching Studies.—The yields of carbon dioxide from the irradiation of a variety of α-oxo-carboxylic acids in methanol and acetonitrile are shown in Tables 1 and 2 respectively. The addition of the triplet quencher, naphthalene, to these solutions in some cases quenched the carbon dioxide production, and in other cases led to enhanced yields of carbon dioxide (Tables 1 and 2). That the yields of carbon dioxide are solvent dependent is confirmed.[2,5,6] Surprisingly, naphthalene was found to enhance carbon dioxide formation from some of the α-oxo-carboxylic acids, and further experiments were performed on individual acids to ascertain the mechanism by which this occurs.

$$CH_3COCOOH \xrightarrow{h\nu} CH_3\overset{\bullet}{C}O + \overset{\bullet}{C}OOH \qquad (1)$$

$$NpH + CH_3COCOOH^T \longrightarrow CH_3COCOOH + NpH^T \qquad (2)$$



$$NpH^T + CH_3COCOOH \longrightarrow NpH^{\overset{+}{\bullet}} + CH_3{-}\underset{\substack{|\\O^-}}{\overset{\bullet}{C}}{-}COOH \qquad (3)$$



$$(CH_3COCOOH)^* + CH_3COCOOH \\ \downarrow \\ CH_3{-}\underset{\substack{|\\O_-}}{\overset{\bullet}{C}}{-}COOH + CH_3\overset{\bullet}{C}O + CO_2 + H^+ \qquad (4)$$

Pyruvic Acid.—The mechanism proposed [2] for the photodecarboxylation *via* a bimolecular electron transfer process suggests that this reaction should be sensitised by the addition of electron acceptors. Accordingly the carbon dioxide yields from irradiation of pyruvic acid in the presence of electron acceptors were measured and the results shown in Table 3. In each case the electron acceptor absorbed all of the incident light and as can be seen enhanced carbon dioxide yields were obtained. Irradiation of pyruvic acid in the presence of methylviologen, a good electron acceptor, also led to enhanced carbon dioxide production (Table 4), with the formation of reduced methylviologen (identified by its absorption spectrum shown in Figure 1).

These results lend credence to the proposed electron transfer mechanism [2] involved in the photodecarboxylation reaction of pyruvic acid. For example, 9,10-dicyanoanthracene (DCA) has been shown to take part in electron transfer reactions,[9] and could aid carbon dioxide production *via* the mechanism shown in Scheme 1.

To ascertain which excited state of pyruvic acid leads to decarboxylation upon direct irradiation, quenching studies were carried out. In these experiments all the incident light leads to excitation of the n-π^* transition of pyruvic acid.

The photoinduced decomposition of pyruvic acid was monitored by ^1H n.m.r. spectroscopy in deuteriated acetonitrile and deuteriated benzene solutions (Figure 2). Irradiation of pyruvic acid in deuteriated acetonitrile solution led to the rapid consumption of the acid, and the addition of naphthalene was seen to markedly retard the rate of disappearance of pyruvic acid (Figure 2). This suggests that the triplet state of pyruvic acid is being deactivated by naphthalene

Table 1. Yields of carbon dioxide from the direct irradiation of α-oxo-carboxylic acids (A) in methanol under nitrogen, and (B) in methanol containing naphthalene (0.5×10^{-4}M), under nitrogen

	Yield (%) of carbon dioxide			
α-Oxo-carboxylic acid	(A) MeOH		(B) MeOH-NpH	
(10^{-2}M)	6 h	20 h	6 h	20 h
Pyruvic acid	23.6	32.9	23.6	32.9
α-Oxobutyric acid	19.9	26.4	16.2	22.3
α-Oxoglutaric acid	13.2	19.3	18.3	22.3
3,3-Dimethyl-2-oxobutyric acid	12.8	41.3	16.5	52.2
α-Oxovaleric acid	15.0	22.8	19.3	29.2
α-Oxopimelic acid	8.9	33.7	20.7	48.7

Table 2. Yields of carbon dioxide from the direct irradiation of α-oxo-carboxylic acids (A) in acetonitrile under nitrogen, and (B) in acetonitrile containing naphthalene (0.5×10^{-4}M) under nitrogen

	Yield (%) of carbon dioxide			
α-Oxo-carboxylic acid	(A) MeCN		(B) MeCN-NpH	
(10^{-2}M)	6 h	20 h	6 h	20 h
Pyruvic acid	52.8	100	43.1	86.3
α-Oxobutyric acid	69.9	100	50.0	84.5
α-Oxoglutaric acid	76.8	100	53.6	84.1
3,3-Dimethyl-2-oxobutyric acid	40.8	62.7	63.4	98.3
α-Oxovaleric acid	10.0	43.3	29.2	69.0
α-Oxopimelic acid	28.4	66.6	41.4	84.5

Table 3. Yields of carbon dioxide from irradiation [a] of pyruvic acid (10^{-2}M) in the presence of various electron acceptors in acetonitrile solution, under argon

Electron acceptor (10^{-2}M)	Yield (%) of carbon dioxide
None	17.7
Dichlorodicyanobenzoquinone	20.9
1-Cyanonaphthalene	28.0
Tetracyanoethylene	37.6
9,10-Dicyanoanthracene †	43.0

[a] 6 h irradiation.
† OD = 1.0 at 370 nm.

Table 4. Yields of carbon dioxide from irradiation [a] of pyruvic acid (10^{-2}M) in acetonitrile–water–pyridine (8 : 1 : 1) solution under argon in the presence of methylviologen (10^{-2}M)

Conditions	Yield (%) of carbon dioxide
No methylviologen	10.4
Methylviologen present	20.3

[a] 1 h irradiation.

thus slowing down its photodecomposition. However, the rate of photodecomposition in deuteriated benzene was exceedingly slow, and the addition of naphthalene brought about an *increase* in the rate of disappearance of the acid (Figure 2). The photodecomposition of pyruvic acid in benzene has previously been shown to be inefficient [1,2,5,6] and our results confirm this. Obviously the bimolecular electron transfer process [2] will be favoured by the use of polar solvents. The lack of reaction in benzene can be ascribed to the low polarity of the solvent, and to the almost negligible concentration of pyruvic acid anion, which would aid the electron transfer process [reaction (5)].

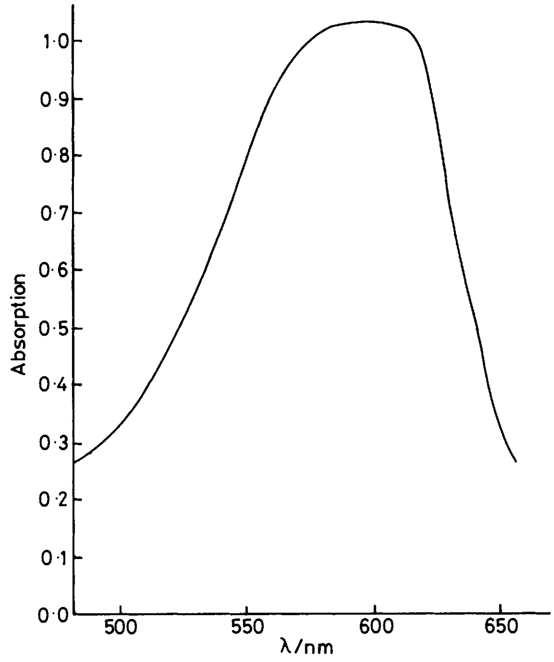
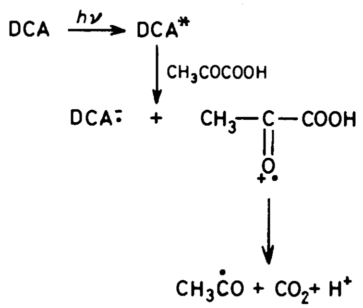


Figure 1. Absorption spectrum of reduced methylviologen produced from 5 min irradiation of pyruvic acid (5×10^{-2}M) in acetonitrile–water–pyridine (8 : 1 : 1) solution containing methylviologen (10^{-2}M) under argon



Scheme 1

The addition of small amounts of pyridine to benzene solutions of pyruvic acid was found to facilitate the decarboxylation process, whereas in acetonitrile solution the addition of pyridine had little effect (Table 5). Thus by forming some pyruvate anion of pyridinium pyruvate the decarboxylation is enhanced.

The effect of added triplet quenchers, naphthalene and myrcene, upon the quantum yield for carbon dioxide production was studied in acetonitrile and benzene solutions and the results are shown in Figure 3. The effect of cyclohexa-1,3-diene upon the reaction was studied in benzene solution and the results are shown in Figure 4. As can be seen quenching occurred with varying efficiency. Since the triplet lifetime of pyruvic acid is known,[2] the slope of the Stern–Volmer plot can be calculated if it is assumed that energy transfer occurs at the diffusional controlled limit of 3×10^{10} l mol^{-1} s^{-1}, and for acetonitrile gives K_{sv} 3 000 and for benzene K_{sv} 2 240. 1-Methylnaphthalene has previously been shown to quench pyruvic acid with a quenching constant of 5.6×10^{9} l mol^{-1} s^{-1} which is close to the diffusional controlled limit.[10] The observed slope of the Stern–Volmer plots (Figures 3 and 4) gives K_{sv} 850 for naphthalene quenching in acetonitrile and K_{sv} 3.3 for cyclohexa-1,3-diene quenching in benzene. From these values it is apparent that the quenchers are not quenching at the diffusional controlled limit or else the quenchers are

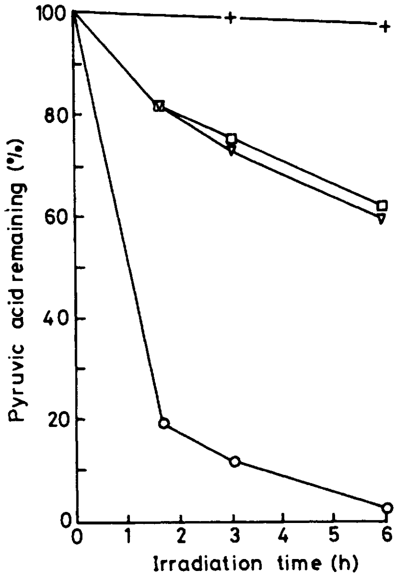
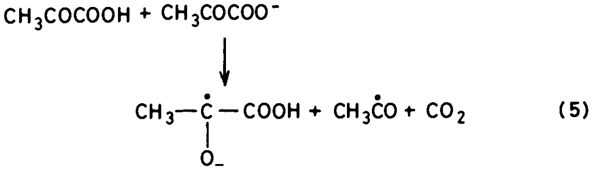


Figure 2. Irradiation of pyruvic acid (10^{-1}M) in (a) deuteriated acetonitrile solution (○), (b) deuteriated acetonitrile solution containing naphthalene (10^{-2}M) (▽), (c) deuteriated benzene solution (+), and (d) deuteriated benzene solution containing naphthalene (10^{-2}M) (□), under nitrogen



$$\begin{array}{c} CH_3COCOOH + CH_3COCOO^- \\ \downarrow \\ CH_3-\overset{\bullet}{\underset{\underset{O_-}{|}}{C}}-COOH + CH_3\dot{C}O + CO_2 \end{array} \qquad (5)$$

Table 5. Yields of carbon dioxide from the direct irradiation[a] of pyruvic acid (10^{-1}M) under argon in acetonitrile and benzene solutions containing pyridine (10^{-1}M)

Conditions	Yield (%) of carbon dioxide	
Benzene	1.6	17.2 × enhancement
Benzene–pyridine	27.5	
Acetonitrile	25.5	1.3 × enhancement
Acetonitrile–pyridine	33.1	

[a] 9 h irradiation.

quenching triplet production but enhancing carbon dioxide production *via* some other route. The effect of the added quenchers upon the disappearance of α-oxo-carboxylic acids was evaluated by monitoring the decrease in the absorption of the acid at 350 nm, and comparing this to the decrease observed in the absence of quencher. The results are shown in Table 6, and in some cases the quencher retarded, and in others enhanced, the decomposition of pyruvic acid. The ^{1}H n.m.r. observation that naphthalene accelerates the decomposition in benzene (Figure 2) was confirmed in these absorption spectroscopic studies (Table 6).

Naphthalene is not unique in being able to assist the decarboxylation of pyruvic acid, and several other aromatic hydrocarbons were found to behave in a similar manner (Table 7). That these compounds can aid carbon dioxide production is shown by the results utilising benzene as solvent.

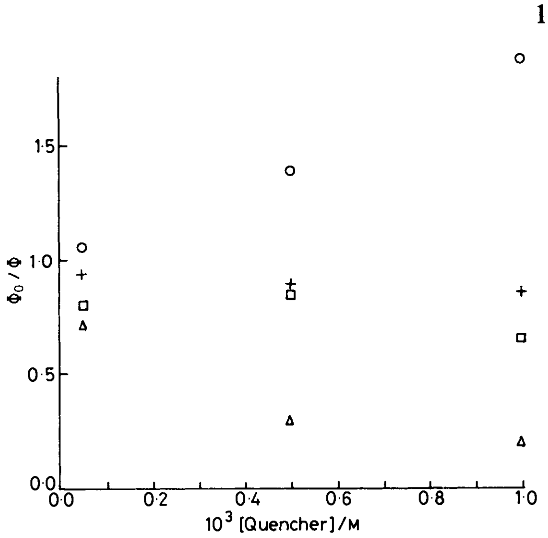


Figure 3. Quantum yields for carbon dioxide production from 9 h irradiation of pyruvic acid (2×10^{-2}M) in the presence of varying amounts of quencher (a) naphthalene in acetonitrile solution (○), (b) naphthalene in benzene solution (△), (c) myrcene in acetonitrile solution (+), and (d) myrcene in benzene solution (□), under nitrogen

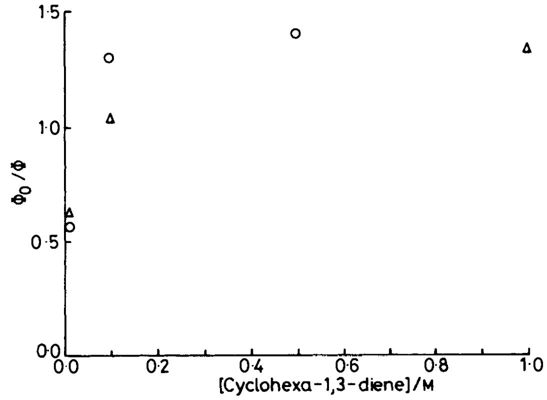


Figure 4. Quantum yields for carbon dioxide production from 9 h irradiation of (A) α-oxo-octanoic acid (2×10^{-2}M) (○) and (B) pyruvic acid (2×10^{-2}M) (△) in benzene solutions containing cyclohexa-1,3-diene under argon

Other α-Oxo-carboxylic Acids.—The effect of added quencher upon the quantum yield for carbon dioxide production was investigated using other α-oxo-carboxylic acids.

Naphthalene and myrcene led to quenching of carbon dioxide production from α-oxoglutaric acid in acetonitrile solution (Figure 5) and also retarded consumption of the acid (Table 6). This indicates that the triplet state of α-oxoglutaric acid is being deactivated by the quenchers and hence retarding the decarboxylation reaction. Due to solubility problems the effect of these quenchers upon α-oxoglutaric acid in benzene solution could not be assessed.

It is known that α-oxo-carboxylic acids capable of undergoing the Type II fragmentation reaction, *e.g.* α-oxo-octanoic acid, react from the excited singlet state.[4] However, naphthalene and myrcene were found to have a marked effect upon the quantum yield of carbon dioxide production from α-oxo-octanoic acid in acetonitrile and benzene solutions (Figure 6), and little effect upon the decomposition of the acid (Table 6). Cyclohexa-1,3-diene was found to accelerate the decomposition of α-oxo-octanoic acid in benzene solution

Table 6. The effect of added quenchers upon the photodecomposition of α-oxo-carboxylic acids (2×10^{-2}M) monitored by following the decrease in absorption of the acid at 350 nm in the presence and absence of quencher

α-Oxo-carboxylic acid	Solvent	Quencher	Observation
α-Oxoglutaric acid	Acetonitrile	Naphthalene	Retardation
α-Oxoglutaric acid	Acetonitrile	Myrcene	Retardation
Pyruvic acid	Acetonitrile	Naphthalene	Retardation
Pyruvic acid	Acetonitrile	Myrcene	Little effect
Pyruvic acid	Benzene	Naphthalene	Acceleration
Pyruvic acid	Benzene	Myrcene	Acceleration
Pyruvic acid	Benzene	Cyclohexa-1,3-diene	Acceleration
α-Oxo-octanoic acid	Acetonitrile	Naphthalene	Slight retardation
α-Oxo-octanoic acid	Acetonitrile	Myrcene	Slight retardation
α-Oxo-octanoic acid	Benzene	Naphthalene	Little effect
α-Oxo-octanoic acid	Benzene	Myrcene	Little effect
α-Oxo-octanoic acid	Benzene	Cyclohexa-1,3-diene	Acceleration

Table 7. Yields of carbon dioxide from irradiation [a] of pyruvic acid (10^{-1}M) (A) in benzene solution and (B) in acetonitrile solution containing various aromatic hydrocarbons (10^{-2}M) under argon

Aromatic hydrocarbons	Yield (%) of carbon dioxide (A) Benzene	(B) Acetonitrile
None	2.2	16.0
Naphthalene	19.9	1.9
2-Methylnaphthalene	21.9	2.2
2,3-Dimethylnaphthalene	32.3	5.9
2,6-Dimethylnaphthalene	34.5	7.3
Phenanthrene	19.7	6.8

[a] 6 h irradiation.

(Table 6), but the effect on the quantum yield of carbon dioxide production was dependent upon the concentration of the quencher. At high concentrations it led to quenching of the carbon dioxide production (Figure 4). α-Oxo-octanoic acid undergoes the Type II reaction leading to the formation of pent-1-ene and pyruvic acid from the excited singlet state.[4] The enhanced carbon dioxide yields obtained from α-oxo-octanoic acid could arise from the reaction of naphthalene with the triplet state of the acid, or from the reaction of naphthalene with triplet pyruvic acid formed from the Type II fragmentation of α-oxo-octanoic acid. However, if carbon dioxide was arising from the pyruvic acid produced *via* the Type II reaction, one would expect to see a marked quenching of the quantum yield for carbon dioxide production by naphthalene in acetonitrile solutions of α-oxo-octanoic acid, as is observed for pyruvic acid itself (Figure 3). As this is not the case for naphthalene quenching of α-oxo-octanoic acid in acetonitrile solution, it seems that the enhanced carbon dioxide yields are due to the naphthalene interacting with the starting acid and not pyruvic acid that is produced *via* the Type II reaction.

The quantum yields for disappearance of α-oxovaleric acid in acetonitrile solution, as shown in Figure 7, were obtained by following the decrease in absorption of the acid at 350 nm in the presence of varying amounts of naphthalene. The carbon dioxide yield was found to be highly dependent on the naphthalene concentration, and in each case gave a higher yield than in the absence of naphthalene, the enhancement being most prominent at low naphthalene concentrations (Figure 7). It would appear that α-oxovaleric acid can react by processes other than the Type II reaction from its singlet state, and the addition of naphthalene to the solutions of this acid quenches some of the former processes. The carbon dioxide yields will be perturbed by pyruvic acid which is formed *via* the Type II reaction of α-oxovaleric acid.

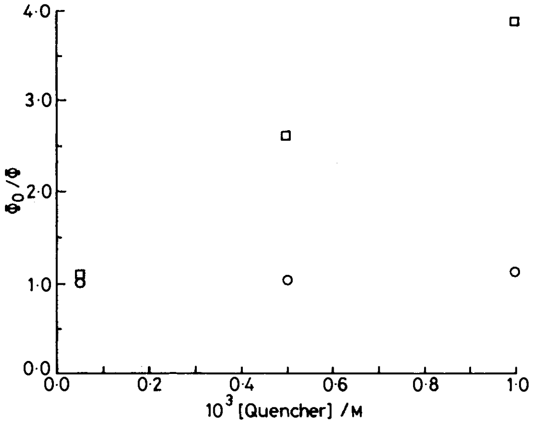


Figure 5. Quantum yields for carbon dioxide production from 9 h irradiation of α-oxoglutaric acid (2×10^{-2}M) (a) in acetonitrile solution containing naphthalene (□) and (b) in acetonitrile solution containing myrcene (○), under nitrogen

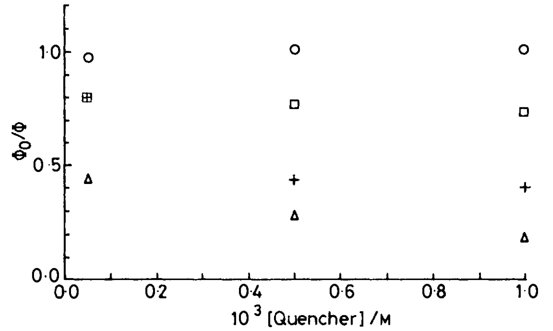


Figure 6. Quantum yields for carbon dioxide production from 15 h irradiation of α-oxo-octanoic acid (2×10^{-2}M) in the presence of varying amounts of quencher (a) naphthalene in acetonitrile solution (○), (b) naphthalene in benzene solution (△), (c) myrcene in acetonitrile solution (+), and (d) myrcene in benzene solution (□), under nitrogen

The Mechanism of Decarboxylation.—Our previous results [2] show that triplet pyruvic acid is quenched by naphthalene forming triplet naphthalene which reacts with pyruvic acid to give the naphthalene radical cation. It is conceivable that the naphthalene radical cations could react with pyruvic acid to produce carbon dioxide (Scheme 2).

In order to rationalise the effect of solvent upon the sensitisation of carbon dioxide production and the rate of photodecomposition of pyruvic acid by quenchers such as naphthalene, the mechanism in Scheme 3 is proposed.

In acetonitrile solution photodecomposition of pyruvic acid leading to carbon dioxide production *via* route 1 is relatively efficient. In the presence of naphthalene the triplet pyruvic acid can be physically quenched *via* route 2 which will reduce the carbon dioxide yield. There is also the pos-

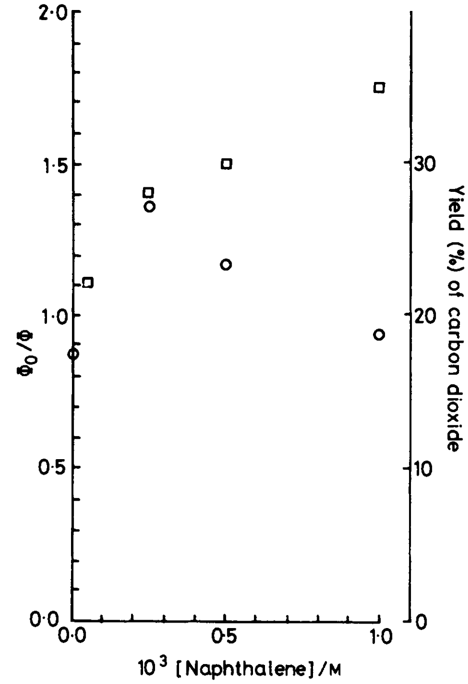
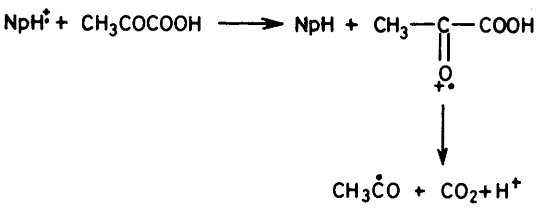


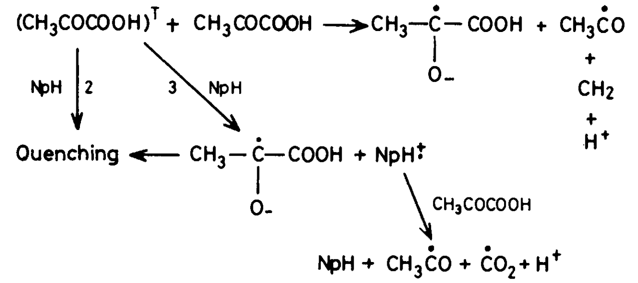
Figure 7. Yields of carbon dioxide (○) production and quantum yields for decomposition of α-oxovaleric acid (10^{-2}M) (□) from 4.5 h irradiation in acetonitrile solutions containing varying amounts of naphthalene under nitrogen



Scheme 2

sibility that quenching of triplet pyruvic acid by naphthalene will lead to the formation of radical ions *via* route 3 and this could lead to an enhancement in carbon dioxide production. However no overall enhancement of carbon dioxide will be observed due to the fact that reaction *via* route 1 is efficient and the addition of naphthalene to acetonitrile solution simply suppresses this reaction by the combined effects of routes 2 and 3.

In benzene solution the photodecomposition of pyruvic acid leading to carbon dioxide production *via* route 1 is very inefficient and gives rise to very low yields of carbon dioxide. In the presence of naphthalene, quenching of triplet pyruvic acid can occur *via* route 2 and could lead to reduced carbon dioxide yields. As the carbon dioxide yields are enhanced by naphthalene, the contribution of route 2 may be small, and quenching of triplet pyruvic acid leading to the formation of radicals *via* route 3 important. This could result in increased yields of carbon dioxide by the subsequent reaction of naphthalene radical cations with pyruvic acid molecules. Thus in benzene solution the addition of naphthalene enhances the carbon dioxide by route 3, as reactions by route 1 (and/or route 2) are unfavourable for carbon dioxide production.



Scheme 3

$$CH_3COCOOH^T + NpH \longrightarrow NpH^T + CH_3COCOOH \quad (6)$$

$$CH_3COCOOH + NpH^T \longrightarrow \text{radicals} \longrightarrow CO_2 \quad (7)$$

The balance between quenching of triplet pyruvic acid by naphthalene leading to triplet naphthalene, and the subsequent reaction of triplet naphthalene with pyruvic acid to give radical formation and hence carbon dioxide production, will determine the quantum yield of carbon dioxide [reactions (6) and (7)].

Therefore in retrospect the carbon dioxide yields, and rate of photodecomposition, are not particularly good guides as to the efficiency of quenching, since a number of triplet aromatic hydrocarbons sensitise carbon dioxide formation.

The mechanism described in Scheme 3 can be used to account for the quenching effects noted with other α-oxo-carboxylic acids and quenchers.

That the triplet state of the α-oxo-carboxylic acids is involved is shown by the ability of naphthalene to quench triplet pyruvic acid and α-oxoglutaric acid.

The ability of myrcene to quench the decomposition and decarboxylation of the α-oxo-carboxylic acids will be dependent upon the relative efficiency with which this quencher deactivates triplet production giving rise to radical formation, *i.e.* a partitioning effect between the two reactions will be operative.

Cyclohexa-1,3-diene undergoes [2 + 2] cycloaddition reactions with pyruvic acid and α-oxo-octanoic acid [11,12] and the occurrence of this reaction would account for the observed quenching of carbon dioxide production and the accelerating effect that this compound exerts on the disappearance of the acids. At high concentrations of cyclohexa-1,3-diene, photoaddition can occur by reaction of the diene with the excited singlet state of the acids,[13] which accounts for the difference in the K_{sv} value observed for reaction with pyruvic acid. A further consequence of the occurrence of the cycloaddition reaction of the excited singlet state of the acid is that the triplet yield of the acid will be reduced, and consequently the carbon dioxide yield also. At low concentrations of cyclohexa-1,3-diene, carbon dioxide production is enhanced by reaction of the diene triplet with the acid, giving rise to radical formation (*via* route 3). This explains the results obtained with pyruvic and α-oxo-octanoic acids in the presence of cyclohexa-1,3-diene.

Our results showing that addition of what should be a quencher for a reaction can lead to enhanced product formation *via* a sensitisation process are not unique. It has previously been reported [14] that if interaction of an excited state with ' quencher ' leads to product formation, rather than to other modes of decay, then ' negative ' Stern–Volmer plots will be obtained. Such Stern–Volmer plots have been observed for piperylene quenching of acetone-sensitised reactions of *trans*-crotyl chloride,[14] and for piperylene quenching of acetone-sensitised rearrangement of norbornadiene to quadricyclene.[15] These results [14,15] are discussed in terms of the 'quencher' in effect acting as 'sensitiser' of product formation.

The proposed mechanism (Scheme 3) is similar to that proposed to account for the acceleration by azulene of reduction of dyes by allylthiourea.[16] Irradiation of thionine in the presence of allylthiourea produces the reduced form of thionine, leucothionine. The addition of the quencher azulene was found to dramatically increase the rate of the reduction process. Azulene was found to react with thionine to produce radicals, *via* an electron transfer process, which subsequently undergo reaction with the allylthiourea and give rise to increased amounts of leucothionine.[16]

Conclusions.—The photoinduced decarboxylation of α-oxo-carboxylic acids such as pyruvic acid involves a bimolecular electron transfer process from the excited triplet state to a ground state molecule, in accord with the previously reported observations.[2] This reaction can be sensitised by known electron acceptors. The addition of triplet quenchers can enhance the decarboxylation reaction, and this is proposed to occur *via* interaction of quencher and triplet acid leading to radical formation and the subsequent interaction of quencher radical cation with another molecule of α-oxo-carboxylic acid.

Our results show that the previously held idea that the addition of a quencher should retard product formation does not hold in all cases, as other processes may be operative which can lead to an actual sensitisation of product formation.

Experimental

Materials.—The following chemicals were used as supplied: pyruvic acid, α-oxobutyric acid, α-oxoglutaric acid, methylviologen hydrate, dichlorodicyanobenzoquinone, cyclohexa-1,3-diene, 2,6-dimethylnaphthalene (all Aldrich); α-oxovaleric acid (Fluka): α-oxopimelic acid (Koch–Light); α-oxooctanoic acid (Sigma); 9-10-dicyanoanthracene (Eastman-Kodak); tetracyanoethylene, myrcene, 2,3-dimethylnaphthalene, 1-cyanonaphthalene (all Ralph N. Emmanuel); naphthalene, 2-methylnaphthalene, phenanthrene, pyridine (all B.D.H.); methanol (AnalaR), benzene (AnalaR) (both Fisons); acetonitrile (AnalaR) (Cambrian); deuteriated acetonitrile, deuteriated benzene (both Goss).

Irradiation Procedure and Determination of Carbon Dioxide Yields.—The prepared solutions were flushed with a stream of dry carbon dioxide and oxygen-free nitrogen or argon for 45 min in Pyrex photolysis tubes. The stoppered tubes were irradiated by rotating the tubes within a circular array of fluorescent lamps having a maximum emission at 350 nm (16 × 8 W; Sylvania F8T5/BLB). After irradiation the yield of carbon dioxide was determined from the weight of barium carbonate precipitated by flushing each reaction mixture with nitrogen gas for 2 h, and passing the exit gases through two Dreschel bottles in series, each containing a saturated solution of aqueous barium hydroxide (*ca.* 100 ml). The yields were calculated on the basis of one mole of carbon dioxide being generated per mole of α-oxo-carboxylic acid.

The above procedure was used for each of the reported reactions. Where the concentration of α-oxo-carboxylic acid was 10^{-2}M, 25 ml solutions were used, and for 2×10^{-2}M solutions, 45 ml were used.

In the case of the Stern–Volmer quenching experiments the absorption of α-oxo-carboxylic acid at 350 nm was recorded prior to, and upon cessation of, illumination in order to evaluate the effect of quencher upon the rate of α-oxo-carboxylic acid photodecomposition.

^{1}H N.m.r. Studies of Pyruvic Acid.—N.m.r. tubes containing pyruvic acid solution (10^{-1}M) and tetramethylsilane as internal standard were degassed with a stream of dry argon, stoppered, and irradiated. Quenching experiments were performed by the addition of naphthalene (10^{-2}M) to the pyruvic acid solutions. 100 MHz ^{1}H N.m.r. spectra (JEOL JMN-NH-100 n.m.r. spectrometer) were recorded prior to and after irradiation. The amount of pyruvic acid remaining was evaluated by reference to the ratio of peak heights of the pyruvic acid methyl singlet and the residual proton peaks of the deuteriated benzene and deuteriated acetonitrile in each case.

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