The Role of Electron Transfer Processes in the Photoinduced Decarboxylation of Alkyl Pyruvates

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Irradiation of degassed solutions of alkyl pyruvates leads to the production of carbon dioxide, the yield of which is enhanced by the presence of electron acceptors, and in the case of methylviologen, the formation of reduced methylviologen is observed. A mechanism involving an electron transfer process is proposed in order to account for the decarboxylation reaction. The effect of added aromatic hydrocarbons, which act as triplet quenchers, upon the decarboxylation of methyl pyruvate is reported and was found to give enhanced carbon dioxide yields. The fact that the quenchers can enhance or 'sensitise' carbon dioxide production from methyl pyruvate is explained on the basis of an electron transfer mechanism.

We have recently reported[1] that in degassed solution alkyl pyruvates undergo a photoinduced fragmentation reaction *via* a Type II mechanism [reaction (1)] and not a Type I mechanism as previously supposed.[2]

It has previously been noted by Hammond and his co-workers,[3] in the only report pertaining to the decarboxylation of alkyl pyruvates, that ethyl pyruvate upon irradiation in degassed benzene solution gives rise to small amounts of carbon dioxide. Since alkyl pyruvates undergo fragmentation *via* a Type II process the possibility of carbon dioxide production from esters of this type is particularly intriguing. We now report upon investigations of the decarboxylation reaction and the mechanism by which this process occurs.

Direct Photoinduced Decarboxylation.—Carbon dioxide production was found to occur for several alkyl pyruvates in degassed solution, albeit to a small extent (Table 1). That ethyl pyruvate undergoes decarboxylation[3] is confirmed. The yields of carbon dioxide and hexanal from the 3 h irradiation of n-hexyl pyruvate in degassed acetonitrile solution (5×10^{-2}M) were found to be 7 and 30%, respectively.

Table 1. Yields of carbon dioxide from the direct irradiation[a] of alkyl pyruvates (10^{-2}M) in degassed solution

Alkyl pyruvate	Solvent	Yield (%) of carbon dioxide
Methyl pyruvate	Benzene	5.3
Methyl pyruvate	Acetonitrile	7
Methyl pyruvate	Acetonitrile–water[b]	12
Ethyl pyruvate	Acetonitrile	9
Isopropyl pyruvate	Acetonitrile	11
t-Butyl pyruvate	Acetonitrile	0
t-Butyl pyruvate	Benzene	0
t-Butyl pyruvate	Acetonitrile–pyridine–water[c]	0

[a] 6 h irradiation. [b] 9 : 1 v/v. [c] 8 : 1 : 1 v/v.

Irradiation in the presence of methylviologen (MV^{2+}). It has previously been reported that α-oxocarboxylic acids undergo decarboxylation *via* an electron transfer mechanism.[4,5] Therefore the possibility exists that α-oxocarboxylic esters, such as alkyl pyruvates, may undergo analogous reactions. In order to ascertain whether alkyl pyruvates are capable of undergoing photoinduced electron transfer reactions, irradiations of several esters were performed in the presence of MV^{2+}. In each case the blue species, reduced methylviologen ($MV^{+\cdot}$), characterised by its absorption spectrum, was rapidly produced. The yield of $MV^{+\cdot}$ was shown to increase with increasing irradiation time. On cessation of illumination the intensity of the absorption band due to $MV^{+\cdot}$ was observed to decline with time. Since the colour due to $MV^{+\cdot}$ was subject to fading, the absorption values obtained cannot be used quantitatively, but clearly indicate the production of $MV^{+\cdot}$ in the reactions.

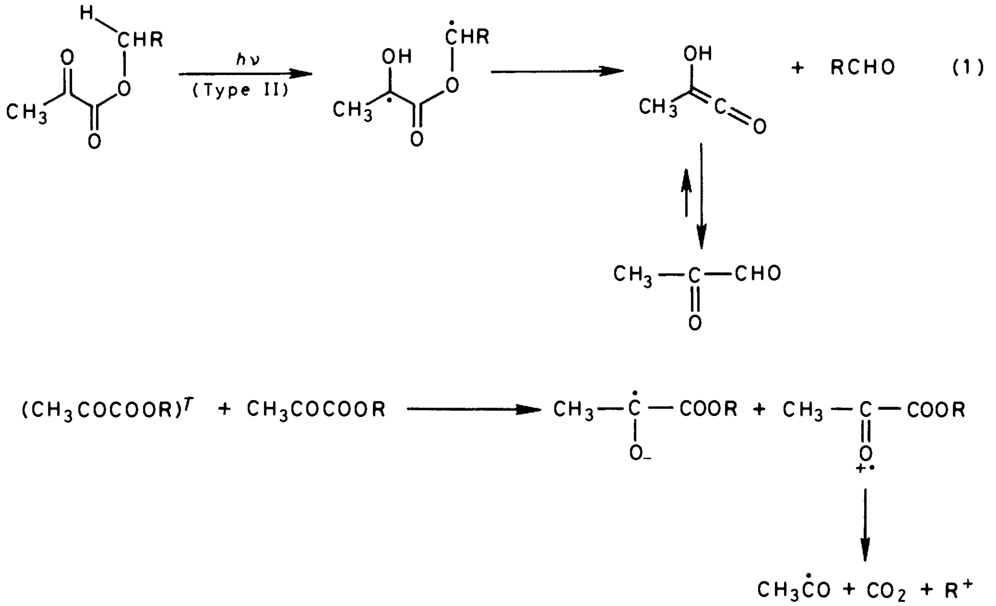
It is interesting to note that t-butyl pyruvate, which has previously been shown to be photostable[1] and did not lead to carbon dioxide production upon direct irradiation (Table 1), was capable of reducing MV^{2+} to $MV^{+\cdot}$.

Control experiments in the absence of alkyl pyruvate did not give rise to $MV^{+\cdot}$ and confirm that the $MV^{+\cdot}$ is produced *via* an electron transfer reaction from the alkyl pyruvate to MV^{2+}

Laser flash photolysis. Methyl pyruvate has previously been shown,[6] by laser flash photolysis, to have a triplet–triplet absorption spectrum similar to that of pyruvic acid.[4,7] That the transient produced is triplet methyl pyruvate is illustrated by the observation that the triplet quenchers naphthalene and oxygen reduced the lifetime of the transient.[6,7] The triplet lifetime of methyl pyruvate was found to be concentration dependent, having a self-quenching rate constant of 2×10^7 l mol^{-1} s^{-1}, and at a methyl pyruvate concentration of 5×10^{-2}M in acetonitrile solution was found to be 140 ns.[6] These results are in accord with those obtained by Scaiano and his co-workers.[7] Laser flash photolysis studies have also shown that ethyl and isopropyl pyruvates have similar self-quenching rate constants to methyl pyruvate.[7]

We found that the addition of MV^{2+} (10^{-2}M) to an aqueous acetonitrile solution (1 : 9 v/v) of methyl pyruvate (10^{-1}M) led, upon flash photolysis, to the production of $MV^{+\cdot}$. A similar observation has been noted in the analogous reaction of pyruvic acid.[4] Furthermore, the addition of MV^{2+} had little effect upon the fluorescence and triplet lifetimes of methyl pyruvate. Thus, under these conditions $MV^{+\cdot}$ is *not* predominantly produced by the reaction of MV^{2+} with the excited states of methyl pyruvate.

Several alkyl pyruvates have been found to undergo direct photoinduced decarboxylation in degassed solution (Table 1). From the yields of carbon dioxide obtained (Table 1 and ref. 3) it appears that decarboxylation is a minor pathway for the degradation of these esters. The observation of $MV^{+\cdot}$ formation demonstrates that alkyl pyruvates are capable of undergoing electron transfer reactions. Therefore it is possible that the carbon dioxide produced under direct conditions could arise from a bimolecular electron transfer reaction from the excited triplet state of the alkyl pyruvate to a molecule of alkyl pyruvate in its ground state (Scheme 1). This mechanism, analogous to that proposed to account for the direct photoinduced decarboxylation of pyruvic acid,[4] could account for



where R = CH_3, C_2H_5, or $(CH_3)_2CH$

Scheme 1.

the concentration dependence of the lifetime of triplet methyl pyruvate.

Bimolecular reactions are far more likely to occur from the triplet state than from the excited singlet state which has a short fluorescence lifetime and low quantum yield of fluorescence.[8] Hence, we suggest that the decarboxylation reaction occurs from the triplet state, although reaction *via* the excited singlet state cannot be rigorously excluded. The finding by Hammond and his co-workers,[3] that benzophenone sensitised carbon dioxide formation from ethyl pyruvate, strongly suggests that the triplet state of the ester is responsible for the decarboxylation.

The formation of MV$^{+\cdot}$ can be attributed to electron transfer from a reduced species of the alkyl pyruvate to MV^{2+} (Scheme 2), and also to quenching of the triplet pyruvate by MV^{2+}, as in the case of t-butyl pyruvate [reaction (2)]. When MV^{2+} and the pyruvate ester are present at similar concentrations, quenching of the triplet ester by the ground state ester will be in competition with quenching of MV^{2+} and may well predominate.

The laser flash photolysis results substantiate the formation of MV$^{+\cdot}$ and show that the fluorescence and triplet lifetimes of methyl pyruvate are little affected by the presence of MV^{2+}. This suggests that MV$^{+\cdot}$ does not arise from reaction of MV^{2+} with either singlet or triplet methyl pyruvate directly but *via* a mechanism as shown in Scheme 2.

The bimolecular electron transfer process leading to decarboxylation, as proposed in Scheme 1, will be in direct competition with the Type II fragmentation reaction for the photodegradation of the alkyl pyruvates. This could account for the finding that the fragmentation of methyl pyruvate to give formaldehyde is a minor pathway for the destruction of this ester.[1] n-Hexyl pyruvate, upon irradiation in degassed acetonitrile solution, was found to be capable of undergoing both decarboxylation (*via* the proposed bimolecular electron transfer process) and the Type II fragmentation reaction leading to hexanal production. This result confirms that both pathways can occur simultaneously and are in competition for the degradation of the alkyl pyruvate. However, the yield of hexanal reported in Table 2 may be artificially low due to the possibility of its consumption in a reduction reaction with triplet n-hexyl pyruvate.[1]

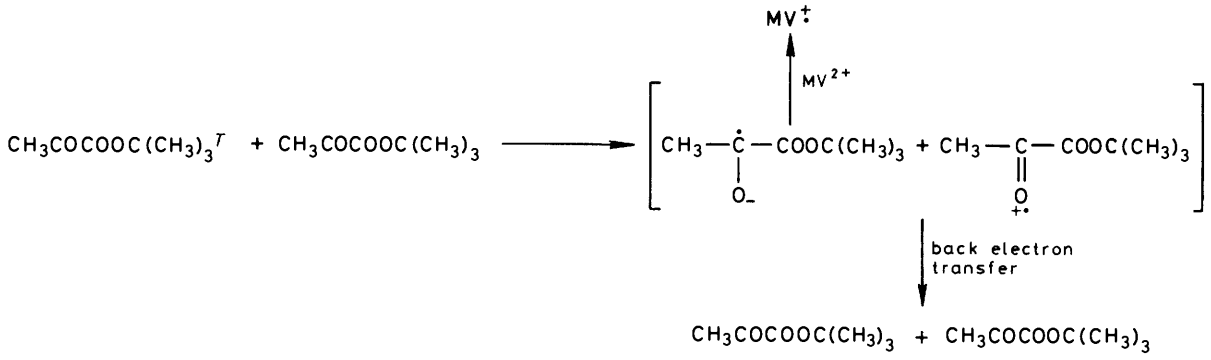
$$CH_3\!-\!\underset{\displaystyle O^-}{\overset{\bullet}{C}}\!-\!COOR + MV^{2+} \longrightarrow CH_3COCOOR + MV^{+\cdot}$$

where R = CH_3, C_2H_5, $(CH_3)_2CH$, or $(CH_3)_3C$

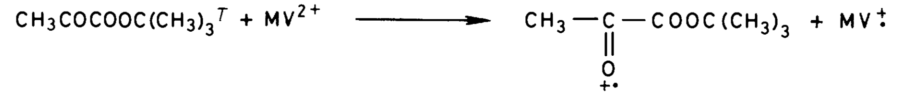
Scheme 2.

t-Butyl pyruvate has been shown to be photostable[1] and did not lead to carbon dioxide production upon direct irradiation (Table 1). t-Butyl pyruvate does not fragment *via* a Type II process.[1] However, t-butyl pyruvate was found to produce MV$^{+\cdot}$ when irradiated in the presence of MV^{2+}, and the elucidation of the mechanism of this reaction is particularly complicated. As the t-butyl pyruvate is photostable upon direct irradiation, it could be considered that any bimolecular electron transfer which takes place may be accompanied by an efficient back electron transfer reaction, leading to the formation of ground state t-butyl pyruvate, as opposed to decarboxylation, hence conferring photostability upon this ester (Scheme 3). In the presence of MV^{2+} the production of MV$^{+\cdot}$ (by electron transfer from the radical anion of t-butyl pyruvate to MV^{2+}) will be in direct competition with the back electron transfer reaction if a mechanism as shown in Scheme 3 is operative.

Alternatively, the bimolecular electron transfer reaction of t-butyl pyruvate could be very inefficient and may not occur to any appreciable extent. The bulky t-butyl groups of this ester could lead to steric hindrance, making electron transfer from the triplet to a ground-state molecule of this ester an unfavourable process. Das[9] has recently demonstrated that aromatic carbonyl compounds undergo electron transfer reactions from the carbonyl triplet state to MV^{2+} with the concomitant formation of MV$^{+\cdot}$. Thus, the possibility exists, for the long lived triplet t-butyl pyruvate, that a similar reaction could ensue in the presence of MV^{2+}. The MV$^{+\cdot}$ in this case could arise from electron transfer from the triplet



Scheme 3.



$$\mathrm{CH_3COCOOC(CH_3)_3{}^{T} + MV^{2+} \longrightarrow CH_3-\underset{\underset{+\bullet}{\overset{\|}{O}}}{C}-COOC(CH_3)_3 + MV^{+\bullet}} \qquad (2)$$

Table 2. Yields of carbon dioxide from irradiation[a] of alkyl pyruvates (10^{-2}M) in degassed solutions containing electron acceptors (10^{-2}M)

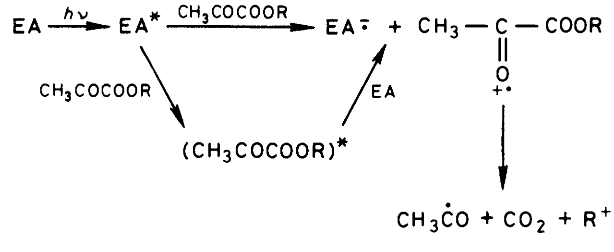
Alkyl pyruvate	Electron acceptor	Solvent	Yield (%) of carbon dioxide
Methyl pyruvate	Dichlorodicyanobenzoquinone	Acetonitrile	11.8
Methyl pyruvate	Tetracyanoethylene	Acetonitrile	12.8
Methyl pyruvate	1-Cyanonaphthalene	Acetonitrile	15.2
Methyl pyruvate	1-Cyanonaphthalene	Benzene	21.5
Methyl pyruvate	9,10-Dicyanoanthracene[b]	Acetonitrile	11.6
Isopropyl pyruvate	1-Cyanonaphthalene	Acetonitrile	23.6
t-Butyl pyruvate	1-Cyanonaphthalene	Acetonitrile	14.6
t-Butyl pyruvate	9,10-Dicyanoanthracene[b]	Acetonitrile	7.7

[a] 6 h irradiation. [b] O.D. 1.0 at 370 nm in order that all of the incident light is absorbed by the 9,10-dicyanoanthracene.

t-butyl pyruvate to MV^{2+}, to give the radical cation of the ester [reaction (2)].

Decarboxylation in the Presence of Electron Acceptors.—If the bimolecular electron transfer reaction is to be considered feasible for the direct photoinduced decarboxylation of alkyl pyruvates (Scheme 1) it should be possible to enhance the carbon dioxide production by irradiation of alkyl pyruvates in the presence of electron acceptors. Accordingly, irradiations of degassed solutions of alkyl pyruvates in the presence of various electron acceptors were performed and the yields of carbon dioxide thus obtained are given in Table 2. The addition of electron acceptors was found to sensitise the decarboxylation reaction (Table 2). A mechanism involving electron transfer from the alkyl pyruvate to the electron acceptor is envisaged as being accountable for the sensitisation process (Scheme 4). Since methyl pyruvate quenches the fluorescence of 1-cyanonaphthalene (k_q 14.4 × 10^9 l mol^{-1} s^{-1} in acetonitrile, k_q 7.9 × 10^9 l mol^{-1} s^{-1} in benzene) we cannot be certain as to whether the electron transfer occurs directly from the excited electron acceptor or indirectly *via* the excited ester (Scheme 4).

Higher yields of carbon dioxide were anticipated for sensitised decarboxylation of t-butyl pyruvate, when compared to the other alkyl pyruvates, due to the greater stability of the t-butyl cation over the cations produced from the other esters. However, as can be seen from Table 2, the yields of carbon dioxide from t-butyl pyruvate were in some cases lower than those obtained from the methyl and isopropyl pyruvates which were similarly investigated.



where EA = electron acceptor
and R = alkyl group

Scheme 4.

It is of interest to note that the addition of MV^{2+} to degassed solutions of methyl and t-butyl pyruvates led, upon irradiation, to enhanced carbon dioxide yields (Table 3) together with the formation of $MV^{+\bullet}$. Since irradiation of t-butyl pyruvate alone does not produce carbon dioxide (Table 1), the MV^{2+} is clearly responsible for the observed production of carbon dioxide (Table 3). In the case of t-butyl pyruvate there is no possibility of $MV^{+\bullet}$ formation *via* reaction of a photogenerated biradical with MV^{2+} whereas this possibility cannot be ruled out for methyl pyruvate. The formation of $MV^{+\bullet}$ with t-butyl pyruvate lends credence to the involvement of an electron transfer reaction in the decarboxylation of alkyl pyruvates. The enhanced carbon dioxide yields in the presence of MV^{2+} result from the subsequent fragmentation of the ester radical cation produced in each case, and for the t-butyl pyruvate can be explained by the mechanism shown in Scheme 3 and/or reaction (2). As MV^{2+} does not undergo any appreciable reaction with the excited states of methyl pyruvate, the mechanisms shown in Schemes 1 and 2 can be used to explain the enhanced carbon dioxide yields from this system. This further substantiates the proposed bimolecular electron transfer process.

Further evidence to support an electron transfer reaction in the photoinduced decarboxylation of alkyl pyruvates comes from the finding that irradiation of methyl pyruvate, in degassed acetonitrile and benzene solutions, in the presence of aromatic hydrocarbons leads to enhanced yields of carbon dioxide (Table 4). We [4,6] and others [7] have previously shown, by laser flash photolysis, that naphthalene can quench the triplet states of both methyl pyruvate and pyruvic acid, with the resultant formation of triplet naphthalene [reaction (3)]. The triplet naphthalene can then undergo electron transfer to pyruvic acid to yield the radical cation of naphthalene and pyruvic acid radical anion [reaction (4)].[4]

More recent work [5] has shown that the naphthalene radical cation can react with pyruvic acid to produce carbon dioxide (Scheme 5). An analogous mechanism would account for the enhanced yields of carbon dioxide from methyl pyruvate on irradiation in the presence of naphthalene.

Scheme 5 can also be used to account for the carbon dioxide production from methyl pyruvate which is observed in the presence of other aromatic hydrocarbons.

Scheme 6 summarises the possible routes leading to carbon dioxide production from methyl pyruvate under both direct irradiation and irradiation in the presence of aromatic hydrocarbons, *e.g.* naphthalene. Our results showing that the addition of what should be a quencher for a reaction can lead to enhanced carbon dioxide formation, *via* electron transfer reactions, are not unique [5] and provide a further example of this phenomenon.

A similar mechanism to that outlined in Scheme 6 was proposed to account for the acceleration of reduction of dyes by allylthiourea in the presence of azulene.[10] Allylthiourea is capable of reducing thionine, on irradiation, to leucothionine.[10] The addition of azulene to the thionine and alyllthiourea solution resulted in an increase in the rate of formation of leucothionine. It was found that an electron transfer process between the azulene and thionine produced radicals which subsequently underwent reaction with the allylthiourea to yield leucothionine.[10]

Table 3. Yields of carbon dioxide from the direct irradiation [a] of alkyl pyruvates (10^{-2}M) in degassed solutions containing MV^{2+} (10^{-2}M)

Alkyl pyruvate (10^{-2}M)	Solvent	Yield (%) of carbon dioxide
Methyl pyruvate	Acetonitrile–water [b]	19
t-Butyl pyruvate	Acetonitrile–pyridine–water [c]	11.4

[a] 6 h irradiation. [b] 9 : 1 v/v. [c] 8 : 1 : 1 v/v.

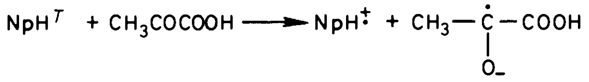
Conclusions.—That alkyl pyruvates are capable of undergoing decarboxylation *via* a bimolecular electron transfer process is consistent with the finding that pyruvic acid produces carbon dioxide *via* an analogous mechanism. The decarboxylation reactions of alkyl pyruvates appears to be a minor route for photoreaction, indeed the decarboxylation reaction is in competition with the Type II reaction for fragmentation of these esters. The sensitisation of carbon dioxide production by electron acceptors further validates the involvement of a bimolecular electron transfer process in the direct decarboxylation of alkyl pyruvates. The irradiation of methyl pyruvate in the presence of aromatic hydrocarbons also gives rise to enhanced carbon dioxide yields, *via* a mechanism suggested to involve electron transfer.

Experimental

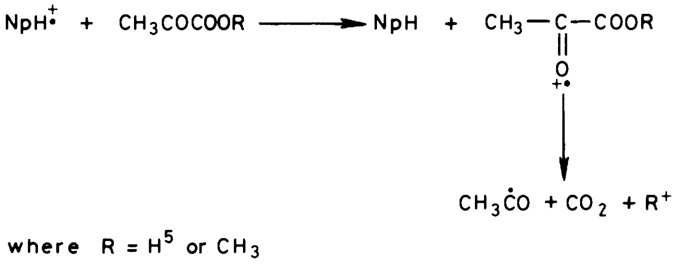
Materials.—The following chemicals were used as supplied: methyl pyruvate, ethyl pyruvate, methylviologen hydrate, dichlorodicyanobenzoquinone, hexanal, biphenyl, 2,6-dimethylnaphthalene, 9,10-dimethylanthracene, pyrene (all Aldrich), 9,10-dicyanoanthracene (Eastman-Kodak), tetracyanoethylene, 1-cyanonaphthalene, pyridine (AnalaR),

$$\mathrm{NpH} + \mathrm{CH_3COCOOR}^{T} \longrightarrow \mathrm{CH_3COCOOR} + \mathrm{NpH}^{T} \qquad (3)$$

where $R = H^{4,7}, CH_3^{6,7}$



$$\mathrm{NpH}^{T} + \mathrm{CH_3COCOOH} \longrightarrow \mathrm{NpH}^{\overset{+}{\bullet}} + \mathrm{CH_3}-\underset{\mathrm{O}^{-}}{\underset{|}{\dot{\mathrm{C}}}}-\mathrm{COOH} \qquad (4)$$



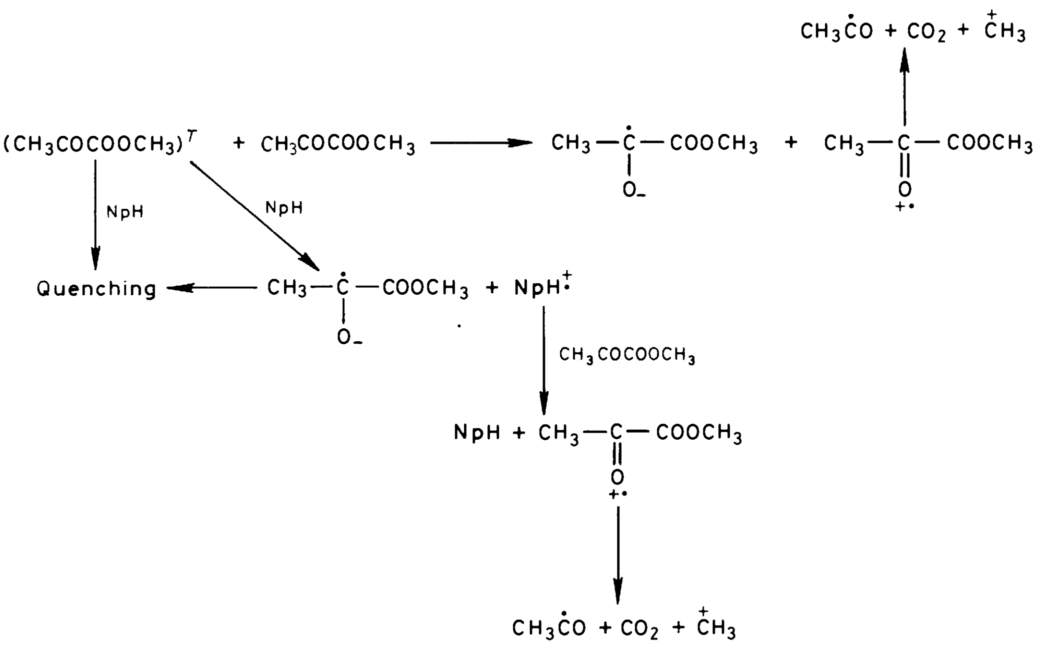
Scheme 5.

Table 4. Yields of carbon dioxide from irradiation [a] of methyl pyruvate (10^{-2}M) in benzene (A) and in acetonitrile (B) solutions containing various aromatic hydrocarbons (10^{-2}M) under degassed conditions

Aromatic hydrocarbon	% Light absorption *	Yield (%) of carbon dioxide (A)	(B)
None		5.3	7
Naphthalene	7	10.4	12
2,6-Dimethylnaphthalene	25	7.1	17.5
9,10-Dimethylanthracene	100	13.4	22.3
Biphenyl	0	11.4	20.9
Phenanthrene	70	11.6	11.8
Pyrene	93	— [b]	10.2

[a] 6 h irradiation. [b] Not measured.

* Refers to the percentage of incident light absorbed by the additive in each case, prior to irradiation.



Scheme 6.

phenanthrene (all B.D.H.), benzene (AnalaR) (Fisons), and acetonitrile (AnalaR) (Cambrian).

Isopropyl, t-butyl, and n-hexyl pyruvate esters were prepared by the reaction of the appropriate alcohol with pyruvoyl chloride[11] under the experimental conditions previously described.[12] Spectral and physical data confirmed the structures of the prepared esters.

Irradiation Procedure and Determination of Carbon Dioxide.—The prepared solutions (25 ml) were flushed with a stream of dry, carbon dioxide and oxygen free, 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 argon 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 alkyl pyruvate initially present.

Determination of Hexanal from the Direct Irradiation of n-Hexyl Pyruvate.—An acetonitrile solution of n-hexyl pyruvate (25 ml, 5×10^{-2}M) was degassed and irradiated as described in the above procedure. G.l.c. analyses of the solution were recorded, prior to and upon cessation of illumination, on a Perkin-Elmer Sigma 3 gas chromatograph, equipped with a Perkin-Elmer 10% SE 30, Chromosorb W 60—80 mesh, column which had been pre-calibrated with hexanal. In this way the yield of hexanal was determined and the presence of hexanal in the irradiated solution was confirmed by peak enhancement.

Irradiation of Alkyl Pyruvates in the Presence of Methylviologen.—Quartz cuvettes containing the prepared solutions (3 ml) were degassed (4 min), stoppered, and irradiated as described above. Absorption spectra were recorded, using a Perkin-Elmer 402 u.v.–visible spectrophotometer, before and after illumination.

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