PHOTOCHEMISTRY OF ALKYL PYRUVATES

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Summary

The photochemistry of alkyl pyruvates of the type $CH_3COCOOCHR_2$ has been examined in solution using a combination of product studies and laser flash photolysis techniques. The results indicate that the main reaction path for triplet decay is the intramolecular abstraction of hydrogen to yield the biradical $CH_3\dot{C}(OH)COO\dot{C}R_2$ which decays predominantly to regenerate the parent substrate and to a lesser extent to yield fragmentation products. Efficient self-quenching by photoproducts makes the determination of triplet lifetimes difficult; triplet parameters need to be extrapolated to zero concentration and zero conversion. Under these conditions the triplet lifetimes (*n*-heptane; 20 °C) are 280 ns and 130 ns for the methyl esters and isopropyl esters respectively.

1. Introduction

The photochemistry of alkyl pyruvates has been the subject of several studies, starting with the classical work of Hammond and Leermakers (see refs. 1 and 2). More recently, a comprehensive study of the photolysis of several alkyl pyruvates has been reported by Davidson and Goodwin [3], who employed steady state photolysis and transient spectroscopy to determine the triplet lifetimes. From a comparison of the photochemical behaviour of several alkyl pyruvates, in particular from the longer lifetime and the photostability of *tert*-butyl pyruvate, it was concluded that alkyl pyruvates bearing α-hydrogens fragment by a Norrish type II mechanism involving as a first step the intramolecular transfer of a hydrogen atom to the carbonyl

oxygen. Nevertheless, several questions remained, and some crucial points were not completely resolved. Among these points were the following: (i) shorter triplet lifetimes were obtained from quenching experiments than by laser flash photolysis [3], (ii) noticeable upward curvatures were observed in quenching experiments [3], (iii) the rate of 1,4-biradical formation did not seem to be related to the lability of the abstracted hydrogen, (iv) the photoreactive state was not firmly established although, from quenching [3] and photosensitization [2] experiments, it was considered to be the triplet state and (v) the rate of pyruvate consumption was much faster than the rate of carbonyl compound production.

We have recently reported a study of the photochemistry of phenyl-glyoxalic derivatives in which some of the questions were answered by combining steady state photolysis and transient spectroscopy studies [4, 5]. In the present work, we report a similar study for alkyl pyruvates which shows that strong similarities exist between their photobehaviour and that of aromatic α-ketoesters.

2. Experimental details

The method employed is similar to that previously described [5]. Methyl pyruvate and ethyl pyruvate (Fluka products) were distilled under vacuum prior to their use. Other alkyl pyruvates were prepared from the alcohols and pyruvoyl chloride [6]. Spectral and physical data agree with those reported in the literature. Only fresh solutions were employed. Measurements were carried out at room temperature (20 ± 2 °C).

Laser flash photolysis experiments were carried out using a nitrogen laser for excitation (337.1 nm; about 8 ns; up to 10 mJ pulse^{-1}) and a detection system including an R-7912 transient digitizer and a PDP11/23 computer which provided suitable facilities for experiment control, data acquisition and processing and hard copy output. Further details have been reported elsewhere [7]. Unless otherwise indicated the samples (1 ml) were deaerated with oxygen-free nitrogen and were contained in Suprasil cells made of rectangular 3 mm × 7 mm tubing.

After excitation at 337.1 nm, all the alkyl pyruvates investigated generate a transient of similar spectra (Fig. 1). These spectra are similar to those reported by Davidson and Goodwin [3] who found that alkyl pyruvate triplets have maximum absorption at 685 nm, and closely resemble that of the triplet state of pyruvic acid [8].

The shape of the transient spectra is essentially independent of the delay time and their intensity shows a single exponential decay and leads to triplet lifetimes τ_T which depend on the pyruvate concentration. Typical plots of $1/\tau_T$ against the pyruvate concentration are shown in Fig. 2. These data can be readily interpreted in terms of a self-quenching process

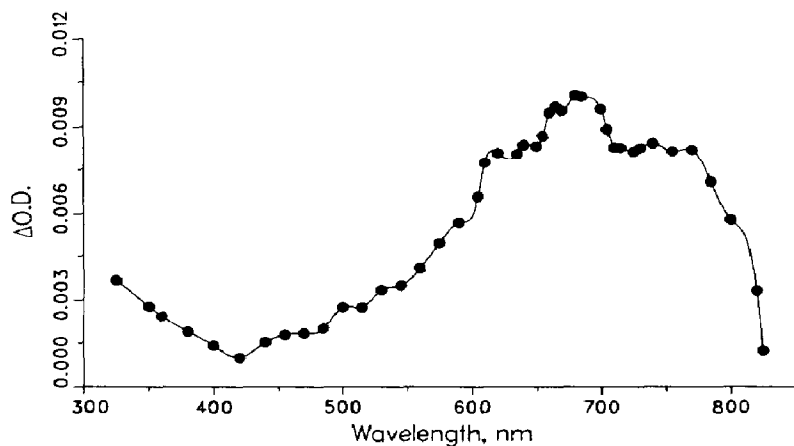$$^3\text{Pyr} + \text{Pyr} \xrightarrow{k_{sq}} \text{deactivation} \tag{1}$$

Fig. 1. Absorption spectra of the transient produced in the photolysis of methyl pyruvate in heptane at 293 K.
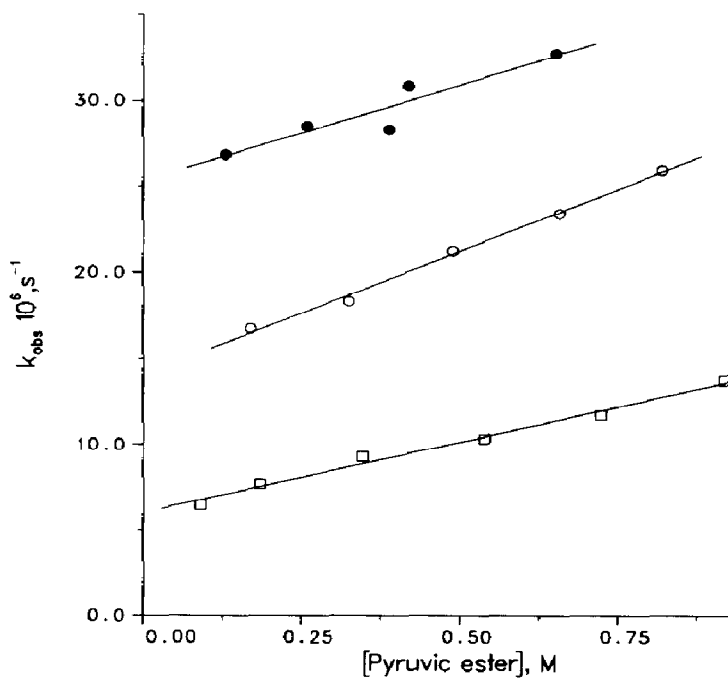

Fig. 2. Effect of pyruvate concentration on the triplet decay in acetonitrile: ●, isopropyl pyruvate; ○, ethyl pyruvate; □, methyl pyruvate.

where Pyr represents the pyruvate. This would probably involve a charge transfer mechanism [9]. The observed lifetime is related to the lifetime τ_0 at zero pyruvate concentration by

$$\frac{1}{\tau} = \frac{1}{\tau_0} + k_{sq}[\text{Pyr}] \tag{2}$$

The values of τ_0 and k_{sq} obtained by this procedure are given in Table 1.

TABLE 1

Kinetics data for the triplet state

Pyruvate	Solvent	$\tau_T{}^a$ (ns)	$k_{sq}{}^b$	$(k_Q)_{MN}{}^b$ $(M^{-1} s^{-1})$	$(k_Q)_{HD}{}^b$ $(M^{-1} s^{-1})$
Methyl	Acetonitrile	175 (70)	8.4×10^6	8.0×10^9	7.4×10^9
	n-Heptane	280	3.7×10^6		
Ethyl	Acetonitrile	75 (60)	1.4×10^7	8.0×10^9	7.4×10^9
	n-Heptane	145	9.3×10^6	6.6×10^9	6.4×10^9
Isopropyl	Acetonitrile	40 (66)	9.6×10^6	6.0×10^9	
	n-Heptane	130	1.5×10^7		

[a] From triplet decays extrapolated at zero concentration. The values in parentheses are from ref. 3 and were obtained at 0.1 M concentrations.
[b] Typically ±10%.

The dependence of the triplet lifetime on the concentration of added triplet quenchers allows the evaluation of the triplet quenching rate constants; the values obtained employing 1-methylnaphthalene (MN) and 2,5-dimethyl-2,4-hexadiene (HD) as triplet quenchers, $(k_Q)_{MN}$ and $(k_Q)_{HD}$ respectively, are also given in Table 1.

Product yields Φ were determined by steady state irradiation and gas–liquid chromatography in heptane and acetonitrile solutions. The values obtained decrease with irradiation time, pointing to secondary reactions of the aldehydes produced [3]. The values obtained by extrapolation to zero photolysis time are given in Table 2.

The triplet yield and the triplet lifetime, as well as the state from which the photoproducts arise, can be obtained from selective quenching experiments and by measuring the cis-to-trans isomerization of 1,3-pentadiene. In the present system these experiments must take into account that most

TABLE 2

Triplet yields and product quantum yields at low conversion

Pyruvate	Solvent	$\Phi_{acetaldehyde}$	$\Phi_{carbonyl}$	Φ_T
Methyl	n-Heptane	0.004	—	1.02
	Acetonitrile	<0.001	—	
Ethyl	n-Heptane	0.05	0.29	0.98
	Acetonitrile	<0.001	0.38	
n-Propyl	n-Heptane	0.03	0.27	1.04
	Acetonitrile	<0.001	0.38	
n-Butyl	n-Heptane	0.03	0.28	
	Acetonitrile	<0.001	0.41	
Isopropyl	n-Heptane	0.05	0.38	
	Acetonitrile	<0.001	0.51	
tert-Butyl	n-Hexane	—[a]	—[a]	1.03

[a] No products were observed.

"selective" triplet quenchers (such as MN and HD) can also interact with the excited singlet [10]. The quantum yields Φ_T for intersystem crossing obtained by measuring the cis-to-trans 1,3-pentadiene isomerization are also given in Table 2. These values have been corrected to take singlet quenching into account.

The formation of the acetaldehyde and of the carbonyl compound derived from the alkyl substituent is quenched by MN or HD. At high MN concentrations, the product yields decrease by more than 95% in spite of the fact that singlet quenching (as monitored by the fluorescence intensity) is a minor process. When HD is employed as the quencher, particularly in polar solvents, singlet quenching is more relevant and the Stern–Volmer plots for the product formation show noticeable upward curvatures. These plots were then corrected to take into account the quencher–singlet interaction. The "corrected" triplet Stern–Volmer plots were fairly linear (Fig. 3). The Stern–Volmer coefficients K_{SV} obtained from these plots are given in Table 3.
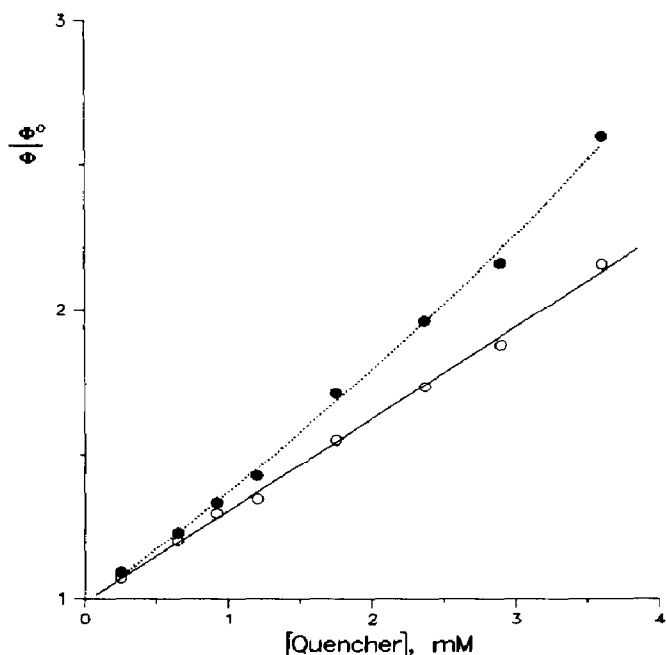

Fig. 3. Effect of HD on the acetone yield in the photolysis of isopropyl pyruvate in acetonitrile: ●, uncorrected; ○, corrected for fluorescence quenching.
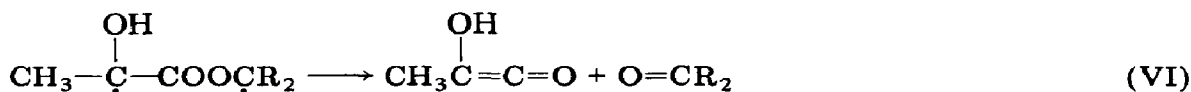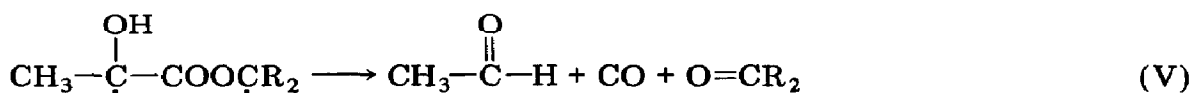
3. Discussion

The present results can be interpreted in terms of the following reaction scheme:

$$CH_3COCOOCHR_2 \xrightarrow{h\nu} {}^1CH_3COCOOCHR_2 \qquad (I)$$

$$ {}^1CH_3COCOOCHR_2 \longrightarrow {}^3CH_3COCOOCHR_2 \qquad (II)$$

TABLE 3

Stern–Volmer data from quenching experiments

Pyruvate	Solvent	K_{SV} (M^{-1})		τ_T (ns)	
		MN	HD	MN	HD
Methyl	n-Heptane	1300	812	200	127
Ethyl	Acetonitrile	360	408	45	55
	n-Heptane	640	560	98	88
n-Propyl	Acetonitrile	350	392	44	53
	n-Heptane	645	560	99	88
n-Butyl	Acetonitrile	365	390	46	53
	n-Heptane	625	555	96	86
Isopropyl	Acetonitrile	330	315	42	43
	n-Heptane	375	420	60	66

$$^3CH_3COCOOCHR_2 \longrightarrow CH_3 - \overset{\overset{\displaystyle OH}{|}}{C} - COOCR_2 \qquad (III)$$

$$CH_3 - \overset{\overset{\displaystyle OH}{|}}{C} - COOCR_2 \longrightarrow CH_3COCOOCHR_2 \qquad (IV)$$

$$CH_3 - \overset{\overset{\displaystyle OH}{|}}{C} - COOCR_2 \longrightarrow CH_3 - \overset{\overset{\displaystyle O}{||}}{C} - H + CO + O{=}CR_2 \qquad (V)$$

$$CH_3 - \overset{\overset{\displaystyle OH}{|}}{C} - COOCR_2 \longrightarrow CH_3 \overset{\overset{\displaystyle OH}{|}}{C}{=}C{=}O + O{=}CR_2 \qquad (VI)$$

This scheme is similar to that proposed for the photolysis of phenylglyoxylic acid derivatives [5]. The facts that $\Phi_T \approx 1$ and that (after correction for singlet quenching) the Stern–Volmer plots are linear show that the only photoactive state is the triplet state. Further, in n-heptane it is possible to quench over 95% of the products with MN when the singlet quenching is below 5%, showing that the singlet contribution to product formation is negligible. Similar ideas have been advanced previously [1, 3, 11], although the data were not as conclusive. This result is particularly relevant since for other aliphatic ketoesters it has been proposed that the excited singlet is the photoactive state [12].

The facts that, even when the results are extrapolated to zero conversion, $\Phi_{acetaldehyde}$ is small and $\Phi_{R_2C=O}/\Phi_{acetaldehyde}$ is larger than unity would indicate that reaction (V) is only a minor reaction path of the 1,4-biradical. The most likely source of the excess ketone is reaction (VI). The formation of a hydroxyketene has been postulated to explain the formation of lactic acid esters when the photolysis is carried out in alcohols as solvents [13]; our results also point to a significant ketene production. The IR spectrum of an ethyl pyruvate sample photolysed in carbon tetrachloride shows bands at

3350 and 2120 cm^{-1} that increase with the photolysis time. The band at 2120 cm^{-1} disappears when the photolysed sample is exposed to air or when a small portion of water is added. The bands at 2120 cm^{-1} and 3350 cm^{-1} could be attributed to the $>$C=C=O and —OH groups respectively [14] and are consistent with the formation of the hydroxyketene in non-polar solvents. Further, the absorbance from the sample below 350 nm markedly increases with the photolysis time. This additional absorbance is bleached when air or water is admitted to the photolysis cell. This absorption can also be rationalized in terms of the ketene produced in reaction (VI).

The fact that the total quantum yield for product formation from the alkyl pyruvates is less than unity could be due to inefficient biradical formation, the occurrence of another reaction from the biradical and/or the occurrence of reaction (IV). From the large difference in triplet lifetimes between *tert*-butyl pyruvate and the other compounds, it can be estimated that reaction (III) is the only important route for triplet decay. Further, from the known behaviour of other 1,4-biradicals [15], reaction (IV) is likely to be one of the main reactions of the biradical and the reaction scheme proposed probably comprises all significant reactions.

The product yields measured decrease when the conversion increases. This dependence is the expected consequence of triplet quenching by the aldehydes and of the inner filter effect by the other reaction products. The quantum yields and the triplet lifetimes need to be extrapolated to zero photolysis time. The data of Table 2, obtained by this procedure, show that carbonyl yields are larger in acetonitrile. This result is similar to those reported for other carbonyl compounds and can be explained in terms of a decrease in the relative rate of reaction (IV) in polar solvents [15].

The data of Table 1 conclusively show that the triplet lifetime, in a given solvent, is determined by the nature of the α-hydrogens. This dependence, as in the case of the alkyl esters of phenylglyoxylic acid, is smaller than that observed for other carbonyl excited triplets [5]. This can also be explained in terms of the electronic structure of the excited triplet and/or in terms of the effect of the α-oxygen atom. In acetonitrile the triplet lifetimes are shorter than in *n*-heptane, a result that implies a faster rate of intramolecular hydrogen abstraction in the more polar solvent. This has also been observed for other carbonyl triplets [16]. Similar conclusions regarding the dependence of the triplet lifetime on the type of α-hydrogen and the solvent can be derived from the K_{SV} values obtained from product analysis. It is noteworthy that both the triplet lifetimes and the K_{SV} slopes obtained in this work show noticeable differences from those previously reported [3]. The differences in K_{SV} can be, at least partially, due to the large differences in the degree of conversion and in the alkyl pyruvate concentrations employed in both studies. Given the product yield dependence on the photolysis time (and hence product accumulation) both the concentration of substrate and the photolysis time must be kept at a minimum to obtain reliable values. It is interesting to note that the τ_T values obtained by product analysis show a similar pattern to those directly measured from time-resolved studies. The

differences between both sets of values, as well as the differences in τ_T obtained when different quenchers are employed (see Table 3), can be attributed to the difficulty in obtaining accurate K_{SV} values as a consequence of the singlet quenching and the effect of the products on the triplet lifetimes.

In conclusion, we consider that the data obtained in the present work indicate that alkyl pyruvates follow photochemical paths similar to those of other carbonyl compounds. The photoactive state is the triplet state, and the triplet lifetime is determined by the type of α-hydrogen present.

Interestingly, no time-resolved evidence for the 1,4-biradicals was obtained. This is probably due to their short lifetime, which may be comparable with those of Paterno–Buchi biradicals [17, 18].

Acknowledgments

References

1 G. S. Hammond, P. A. Leermakers and N. J. Turro, *J. Am. Chem. Soc.*, *83* (1961) 2395.
2 P. A. Leermakers, P. C. Warren and G. F. Vesley, *J. Am. Chem. Soc.*, *86* (1964) 1768.
3 R. S. Davidson and D. Goodwin, *J. Chem. Soc., Perkin Trans. II*, (1982) 993.
4 A. Zanocco, F. Castañeda, J. C. Scaiano, M. V. Encinas and E. A. Lissi, *Acta Sudam. Quim.*, *2* (1982) 5.
5 M. V. Encinas, E. A. Lissi, A. Zanocco, L. C. Stewart and J. C. Scaiano, *Can. J. Chem.*, *62* (1984) 386.
6 H. C. J. Ottenheijm and J. H. M. de Mans, *Synthesis*, (1975) 163.
7 J. C. Scaiano, *J. Am. Chem. Soc.*, *102* (1980) 7747.
8 R. S. Davidson, D. Goodwin and Ph. Fornier de Violet, *Chem. Phys. Lett.*, *78* (1981) 471.
9 R. S. Davidson, D. Goodwin and J. E. Pratt, *J. Chem. Soc., Perkin Trans. II*, (1983) 1729.
10 M. V. Encinas and E. A. Lissi, unpublished results, 1985.
11 R. S. Davidson, D. Goodwin and Ph. Fornier de Violet, *Tetrahedron Lett.*, *22* (1981) 2485.
12 M. De Bergalis, *Diss. Abstr. Int. B, 40* (1979) 244.
13 B. W. Binkley, *J. Org. Chem.*, *41* (1976) 3030.
   B. M. Monroe, *Adv. Photochem.*, *8* (1971) 77.
14 J. R. Dyer, *Applications of Absorption Spectroscopy of Organic Compounds*, Prentice-Hall, New York, 1965, pp. 34 - 36.
15 J. C. Scaiano, E. A. Lissi and M. V. Encinas, *Rev. Chem. Intermed.*, *2* (1978) 139.
16 M. V. Encinas and E. A. Lissi, *J. Photochem.*, *8* (1978) 131.
   M. V. Encinas, E. A. Lissi, E. Lemp, A. Zanocco and J. C. Scaiano, *J. Am. Chem. Soc.*, *105* (1983) 1856.
17 S. C. Freilich and K. S. Peters, *J. Am. Chem. Soc.*, *103* (1981) 6255.
18 R. A. Caldwell, T. Majima and C. Pac, *J. Am. Chem. Soc.*, *104* (1982) 629.