

SINGLET QUENCHING OF METHYL PYRUVATE

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Summary

The singlet quenching of methyl pyruvate by several hydrogen donors was measured in various solvents. The excited state is efficiently quenched by amines, aliphatic alcohols, hexanethiol, isovaleraldehyde and phenols. For these compounds it is found that the rate constants for quenching by *p*-substituted phenols can be fitted to a Hammett-type equation with $\rho = -1.8$.

1. Introduction

The photoreduction of pyruvic acid [1 - 4] and alkyl pyruvates [5 - 7] is a well-known photoprocess that readily takes place when these compounds are irradiated in the presence of hydrogen donors. The reactive excited state is usually considered to be the triplet, the excited singlet being regarded as almost unreactive. Recently Shima *et al.* [8] have measured the rates of methyl pyruvate singlet quenching by several olefins; they have found that the reaction is very efficient and that at high olefin concentration elimination of the excited singlets is almost quantitative. These results prompted us to investigate the singlet quenching by hydrogen donors. The results reported in this work show that also with these compounds the singlet quenching of methyl pyruvate is an efficient process.

2. Experimental

Methyl pyruvate (Aldrich) was vacuum distilled and was used immediately. Fluorescence measurements were carried out using a Hitachi-Perkin-Elmer 204-S spectrofluorimeter employing an exciting wavelength of 370 nm. The measurements were carried out in air at room temperature. The positions of both the absorption and the emission spectra were independent of the added quencher in all the solvents considered.

Acetonitrile (Fluka, fluorescence spectroscopy grade), benzene (Fluka, fluorescence spectroscopy grade) and *p*-dioxane (Fluka, UV spectroscopy grade) were employed as solvents. All the quenchers employed were obtained from commercial sources and were distilled or recrystallized before use.

3. Results and discussion

The absorption and emission spectra of a freshly prepared solution of methyl pyruvate in acetonitrile solution are given in Fig. 1. The emission band centred at 415 nm can be assigned to the fluorescence of the first excited state of methyl pyruvate and its intensity change was employed to measure the amount of singlet quenching when various additives were incorporated in the solution [8].

A singlet lifetime of 8.2 ns has been determined by Shima *et al.* [8] for a 0.1 M solution in acetonitrile in air at room temperature. The fluorescence spectrum does not change when the solution is degassed. In the other solvents employed singlet lifetimes were estimated from the integrated absorption band and the fluorescence quantum yields employing

$$\tau (\text{ns}) = 8.2 \frac{\phi_F}{(\phi_F)_A} \frac{\epsilon_A}{\epsilon} \left(\frac{\eta_A}{\eta} \right)^2 \quad (1)$$

where ϵ is the integrated absorption band coefficient, η is the refractive index, ϕ_F is the fluorescence quantum yield and the subscript A denotes acetonitrile. The values obtained were 8.0 ns in benzene, 13 ns in hexane and 4.0 ns in dioxane. The shorter lifetime in dioxane is most probably the result of impurities but this is not relevant to the following discussion.

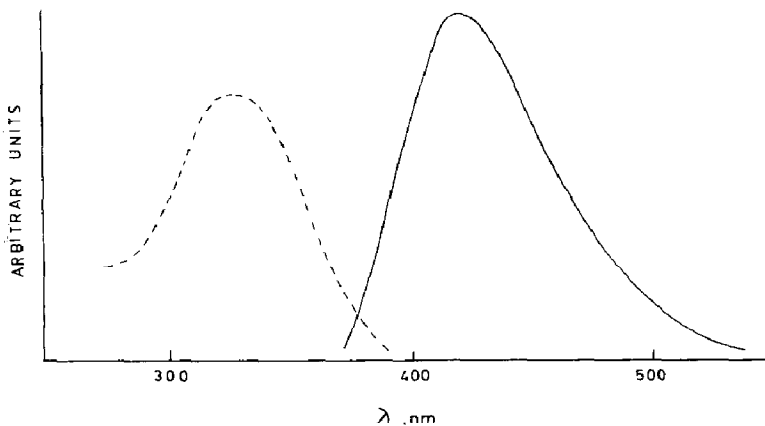


Fig. 1. Absorption (---) and fluorescence (—) spectra ($\lambda_{\text{exc}} = 370 \text{ nm}$) of methyl pyruvate in acetonitrile. The absorbance and fluorescence intensities are given in arbitrary units. (The molar extinction coefficient at λ_{max} is $14.8 \text{ M}^{-1} \text{ cm}^{-1}$.)

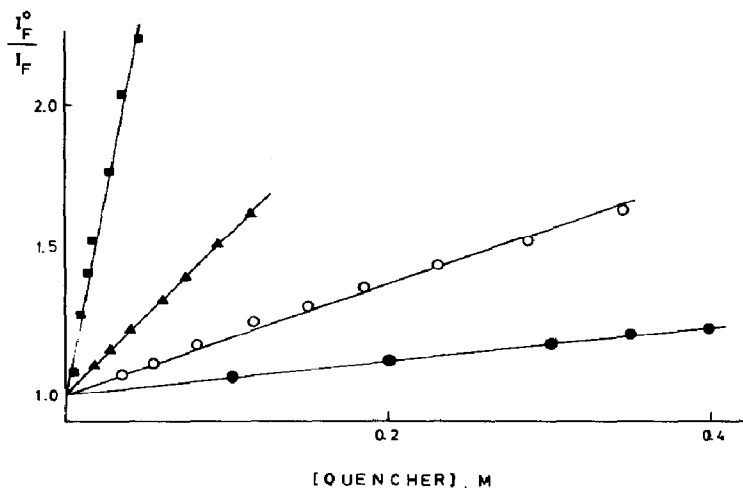


Fig. 2. Stern-Volmer plots for the fluorescence quenching of methyl pyruvate in acetonitrile: ■, hexanethiol; ▲, phenol; ○, isovaleraldehyde; ●, phenylmethanol.

The fluorescence intensity decreased in the presence of olefins [8] and hydrogen donors. Stern-Volmer plots were obtained by measuring the intensity at 415 nm as a function of the added quencher concentration. Typical results are shown in Fig. 2. The plots obtained were linear over the whole concentration range considered for all the compounds employed with the exception of the amines. When these compounds were used there was evidence of association in the ground state (shown by a broadening of the absorption band). Furthermore, when amines bearing N—H bonds were considered, a photoproduct showing a broad emission centred at 460 nm was generated during the irradiation time. The results were then obtained at low quencher concentrations (to minimize association) and employing short irradiation times to minimize product formation; however, they will have rather large uncertainties.

The values of k_q obtained in acetonitrile from the slopes of the Stern-Volmer plots and the singlet lifetimes are given in Table 1. Values of $k_q\tau_s$ employing 2,5-dimethyl-2,4-hexadiene as quencher were evaluated at two different methyl pyruvate concentrations (6.6×10^{-2} and 0.28 M). The fact that the same value of $k_q\tau_s$ was obtained at both concentrations shows that autoquenching is negligible up to a methyl pyruvate concentration of 0.28 M.

Quenching by the amines is similar to that reported previously for several singlet state [9 - 11] and triplet state [11, 12] excited carbonyls. The results obtained show very little dependence on the ionization potential of the amine. A similar lack of dependence was obtained when alkanone singlets were employed [9 - 11].

The lack of correlation can be partly a result of the fact that the reaction is nearly diffusion controlled and partly a result of the multiplicity of reaction paths (*i.e.* N—H and α -C—H hydrogen abstraction and exciplex

TABLE 1
Quenching of methyl pyruvate fluorescence

Quencher	k_q ($\times 10^7 \text{ M}^{-1} \text{ s}^{-1}$)	Quencher	k_q ($\times 10^7 \text{ M}^{-1} \text{ s}^{-1}$)
Triethylamine	490	Methanol	0.8
Diethylamine	530	Diphenylmethanol	<1.2
Isopropylamine	400	<i>tert</i> -Butanol	<0.1
Diethylhydroxylamine	230	2,3,5-Trimethylphenol	460
Hexanethiol	350	2,6-Di- <i>tert</i> -butyl-4- methylphenol	340
Isovaleraldehyde	24	4-Hydroxyphenol	330
Isopropylbenzene	<0.1	4- <i>tert</i> -Butylphenol	220
Phenylmethanol	6.6	2,3-Dihydroxyphenol	200
2-Methyl-1-propanol	2.9	Phenol	57
Ethanol	2.4	4-Chlorophenol	36
2-Propanol	2.2	2-Chlorophenol	24

The methyl pyruvate concentration in acetonitrile was 0.1 M.

intersystem crossing) by which the charge transfer complex can be deactivated.

The results given in Table 1 show that methyl pyruvate is efficiently quenched by phenols. The rate of quenching is enhanced by electron donor groups and the effect is more important for *para* substitution than for *ortho* or *meta* substitution. The results obtained for the *p*-substituted phenols are plotted according to a Hammett equation in Fig. 3 and a correlation is obtained with a slope of approximately -1.8 . Similar plots obtained for the quenching of biacetyl singlets [13] and *tert*-butoxy radicals [14] also gave linear relationships with slopes of -1.8 and -1.3 respectively. These results

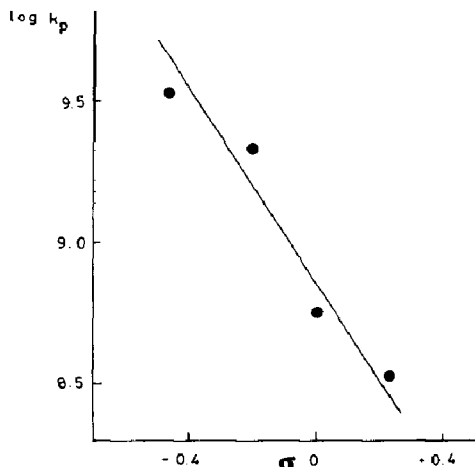


Fig. 3. A Hammett plot for singlet quenching of methyl pyruvate by *p*-substituted phenols. The solvent used was acetonitrile.

show that polar effects are relevant in determining the reactivity of the phenols and that the influence of charge localization at the reactive centre is more important in the excited carbonyls considered than in the *tert*-butoxy radicals. The quenching process could involve a charge transfer mechanism, a radical-like hydrogen abstraction, or a combination of both leading to hydrogen abstraction throughout the formation of the charge transfer complex. In order to decide among these possibilities it is important to note that phenol, in spite of its higher ionization potential, quenches methyl pyruvate faster than does anisole ($k_q = 27 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ [15]). This result indicates that hydrogen transfer plays an important role in the rate-determining step.

Photoreduction of pyruvic acid [1, 2, 4] and pyruvic esters [5, 6] by alcohols has been reported previously and the reaction has been assumed to take place from the triplet state. The results given in Table 1 show that alcohols readily quench the excited singlet of methyl pyruvate. The values of k_q obtained in the present work are nearly an order of magnitude higher than those reported for the excited triplet of pyruvic acid [4], a result which is compatible with the greater exothermicity of the singlet reaction. The low reactivity of *tert*-butanol would indicate that the quenching involves, as in other carbonyl compounds [1], the α -hydrogen atoms. The reactivity of the alcohols could be masked by a solvent effect of the alcohol because of the large concentration required to quench the excited singlets significantly. In order to test this possibility we measured k_q for isopropanol in the presence of a large excess of *tert*-butanol. The value of k_q was similar to that obtained in pure acetonitrile and shows that the "solvent effect" of the alcohols can be disregarded. The relative rates of reaction per α -hydrogen atom are given in Table 2. The values obtained for pyruvic acid are also included in this table. Both sets of data are compatible with a photoreduction mechanism involving the α -hydrogen atoms. The smaller selectivity shown by methyl pyruvate singlets is compatible with its higher reactivity.

The low reactivity of diphenylmethanol is contrary to the low dissociation energy of the C—H bond in this compound and could be attributed to steric hindrance.

TABLE 2

Relative rates of deactivation by alcohols (per hydrogen atom)

Donor	Relative rate	
	Methyl pyruvate	Pyruvic acid ^a
Methanol	0.22	0.15
2-Methyl-1-propanol	1.2	0.82
Ethanol	1.0	1.0
2-Propanol	1.8	3.7
Phenylmethanol	2.8	6.4

^aPhotoreduction attributed to the excited triplet [4].

TABLE 3

Comparison of quenching rate constants^a

Quencher	$k_q (\times 10^7 \text{ M}^{-1} \text{ s}^{-1})$		
	<i>Biacetyl</i>	<i>Methyl pyruvate</i>	<i>Isovaleraldehyde</i> ^b
Diethylhydroxylamine	153	230	122
Triethylamine	300 ^c	490	500
Phenol	10 ^c	57	—
Hexanethiol	1 ^d	350	100
Isovaleraldehyde ^e	1.2 ^d	170	250
Isopropanol	<0.5 ^c	2.2	1 ^f

^a Unless otherwise indicated the values apply to acetonitrile.^b Data taken from ref. 16.^c Data taken from ref. 17.^d Ref. 15.^e *n*-Hexane was used as solvent.^f A considerably larger value has been reported [18]. In the discussion the value obtained in the present work will be considered since the experimental conditions were identical with those employed with methyl pyruvate.

A comparison among the results obtained in the present work and those obtained for other $^1(n\pi^*)$ excited carbonyl compounds is given in Table 3. For diethylhydroxylamine the three excited carbonyls show similar reactivities, a result that can be interpreted in terms of the weakness of the O—H bond in diethylhydroxylamine [19]. In this case the rate can be equated to the pre-exponential factor *A* and would be nearly independent of the excited molecule. For all the other quenchers, Table 3 shows that methyl pyruvate singlets react faster than biacetyl singlets. This result can be related to the higher energy of the excited keto ester. Nevertheless, it is interesting to note that with hexanethiol and isopropanol methyl pyruvate reacts considerably faster than isovaleraldehyde, in spite of the higher energy of the alkanal singlet. With respect to these compounds the excited keto ester then shows a singularly large reactivity. Unfortunately, there are not sufficient thermochemical data to ascertain the origin of these increased reactivities [20].

The effect of the solvent on the rate of quenching is shown in Table 4. The solvent effect depends on the relative stabilization of the transition state and the reactants. The largest effect is observed when the phenols are considered. The effect observed is contrary to that expected if the stabilization of the transition state were the determining factor. A similar result has been observed in the quenching of biacetyl fluorescence by phenols [11] and it is probably the result of a hydrogen bonding between the phenol and the solvent. This explanation is also in agreement with the lower rate observed in dioxane than in acetonitrile. It is interesting to note that for isovaleraldehyde, where bonding to the solvent by the reactive hydrogen atoms can be much less significant, the reactivities are similar in all solvents considered. In this case the differences can be explained in terms of a small amount of pro-

TABLE 4

Effect of the solvent on k_q

Quencher	k_q ($\times 10^9$ M ⁻¹ s ⁻¹)			
	<i>n</i> -Hexane	Benzene	Acetonitrile	Dioxane
2,3-Dimethyl-2-butene	—	2.6	2.9	1.2
Diethylhydroxylamine	2.1	2.3	2.3	3.1
Isovaleraldehyde	1.1	0.4	0.24	0.22
Phenol	—	3.5	0.6	0.35

tection of the reactive centre of the excited carbonyl by the polar solvents. The small solvent effect observed for diethylhydroxylamine is also expected because of the high reactivity of this compound. It is interesting to note that the reaction of this compound with di-*tert*-butyl nitroxide radicals shows a considerably larger rate in benzene than in acetonitrile [21]. The large difference observed in these systems is compatible with the smaller rate of the process.

The results obtained for olefins do not show a clear dependence on the solvent dielectric constant. This lack of dependence, which appears to be contrary to that expected for a process controlled by charge transfer interactions, is similar to that observed in closely related systems [12].

References

- 1 P. A. Leermakers and G. F. Vesley, *J. Am. Chem. Soc.*, **85** (1963) 3776.
- 2 D. S. Kendall and P. A. Leermakers, *J. Am. Chem. Soc.*, **88** (1966) 2766.
- 3 P. B. Ayscough and M. C. Brice, *J. Chem. Soc. B*, (1971) 491.
- 4 P. B. Ayscough and R. C. Sealy, *J. Photochem.*, **1** (1972/73) 83.
- 5 P. A. Leermakers, P. C. Warren and G. F. Vesley, *J. Am. Chem. Soc.*, **86** (1964) 1768.
- 6 R. W. Binkley, *J. Org. Chem.*, **41** (1976) 3030.
- 7 B. C. Monroe, *Adv. Photochem.*, **8** (1971) 77.
- 8 K. Shima, T. Sawada and H. Yoshinaga, *Bull. Chem. Soc. Jpn.*, **51** (1978) 608.
- 9 J. C. Dalton, M. W. Geiger and J. J. Snyder, *J. Am. Chem. Soc.*, **98** (1976) 398.
- 10 M. V. Encina, H. Soto and E. A. Lissi, *J. Photochem.*, **3** (1975) 467.
- 11 N. J. Turro and R. Engel, *J. Am. Chem. Soc.*, **91** (1969) 7113.
- 12 R. W. Yip, R. O. Loufty, Y. L. Chow and L. K. Magdzinski, *Can. J. Chem.*, **50** (1972) 3426.
- 13 P. J. Wagner and A. E. Kemppainen, *J. Am. Chem. Soc.*, **91** (1969) 3085.
- 14 R. O. Loufty and R. O. Loufty, *Can. J. Chem.*, **50** (1972) 4052.
- 15 N. J. Turro and T. J. Lee, *Mol. Photochem.*, **2** (1970) 185.
- 16 K. U. Ingold, *Can. J. Chem.*, **41** (1963) 2816.
- 17 M. V. Encina and E. A. Lissi, unpublished results, 1980.
- 18 M. V. Encina, E. A. Lissi and A. Olea, *J. Photochem.*, **14** (1980) 233.
- 19 N. J. Turro and R. Engel, *Mol. Photochem.*, **1** (1969) 235.
- 20 P. Lebourgeois, R. Arnaud and J. Lemaire, *J. Chim. Phys. Phys.-Chim. Biol.*, **73** (1976) 135.
- 21 T. Cáceres and E. A. Lissi, *Int. J. Chem. Kinet.*, **10** (1978) 1167.
- 22 C. M. Previtali and J. C. Scaiano, *J. Chem. Soc., Perkin Trans. II*, (1972) 1672.
- 23 E. A. Lissi, M. A. Rubio, G. Zanoce and D. Araya, *Int. J. Chem. Kinet.*, in the press.