STRUCTURAL AND SOLVENT EFFECTS IN THE PHOTOCHEMISTRY OF ALIPHATIC KETONES

S. FÖRGETEG and T. BÉRCES

Central Research Institute for Chemistry, Hungarian Academy of Sciences, Pusztaszeri u. 59/67, H-1025 Budapest (Hungary)

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Summary

Structural and solvent effects have been investigated by determining triplet yields, triplet lifetimes and fluorescence decay times with the sensitized T–T absorption and time-resolved fluorescence techniques. Methyl ethyl ketone, methyl isopropyl ketone and methyl *tert*-butyl ketone were studied in iso-octane, alcohols and acetonitrile. The triplet lifetimes and quantum yields for triplet state formation were found to decrease significantly with increasing substitution in the α position. The triplet yields as well as the fluorescence decay times also changed with the nature (polarity and hydrogen-donating ability) of the solvent and with ketone concentration. The results were explained by assuming that singlet and triplet excimers contributed to the primary photophysical processes.

1. Introduction

Considerable progress has been made in the last 15 years in elucidating the main factors which influence the photochemistry of aliphatic carbonyl compounds [1 - 3]. Nevertheless, data demonstrating the effect of solvent and of carbonyl concentration on the basic photochemical properties have been presented only sporadically.

The rates of non-radiative transitions of singlet acetone, acetone-d_6 and hexafluoroacetone are greater in solution than in the gas phase, while acetone singlet lifetimes appear to be independent of solvent polarity [4]. Encina *et al.* [5] derived relative singlet lifetimes for various aliphatic ketones and found a pronounced solvent dependence only for ketones with γ-hydrogen atoms. The decrease in fluorescence lifetime with increasing solvent polarity was attributed to the increase in the Norrish type II rate coefficient.

The principal mode of reaction of singlet excited states of aliphatic ketones without a γ-hydrogen atom is believed to be intersystem crossing (ISC). The rate of this process is known to depend on substitution in the

α-position (ISC rates decrease with increasing α-methyl substitution) [6]; however, no systematic study of the solvent effect has been published.

Porter [7] found considerably shorter triplet acetone lifetimes in solution (50 μs in acetonitrile and 22 μs in water and *tert*-butanol) than in the vapour phase (for which 200 μs was reported [8]). In accordance with these findings, Encina *et al.* [5] observed a decrease in the triplet lifetime of aliphatic ketones with increasing solvent polarity. However, Naito and Schnabel [9] found no solvent effect in an investigation of similar aliphatic ketones.

There are few systematic studies of the effect of the variation in ketone concentration in the literature. We reported [10] on the concentration dependence of the yield of triplet formation in the photolysis of 2-pentanone in iso-octane, and this was rationalized [10, 11] by assuming singlet excimer formation. As a continuation of the investigation of basic photochemical–photophysical properties of simple carbonyl compounds, we determined singlet and triplet lifetimes and triplet yields for α-methyl-substituted acetones in various solvents using different ketone concentrations. The results are described in this paper.

2. Experimental details

2.1. Materials

Spectroscopic grade acetone (Carlo Erba) was used without further purification. Fluka puriss grade methyl ethyl ketone and methyl isopropyl ketone were purified by preparative gas chromatography. Methyl *tert*-butyl ketone was synthesized from acetone [12] and purified by distillation.

Anthracene was brominated to yield 9,10-dibromoanthracene. Both 9,10-dibromoanthracene and biphenyl (Reachim, puriss grade) were purified by repeated recrystallization from ethanol until the transmittance at 310 nm became constant.

Spectroscopic grade methanol (Loba Chemie) and HPLC grade acetonitrile (Fluka) were used without further purification. Iso-octane and *tert*-butanol were purified as described previously [11]. Water was distilled twice in all-glass apparatus.

2.2. Lifetime and triplet yield measurements

The time-correlated single-photon counting technique was used to measure singlet lifetimes.

Triplet lifetimes for methyl ethyl ketone were obtained by the triplet-sensitized dibromoanthracene fluorescence technique [13]. Shorter triplet lifetimes were derived from transient absorption measurements of biphenyl triplets sensitized by the carbonyl triplet molecules. Degassed samples containing a fixed amount of ketone and different biphenyl concentrations were excited by 25 mJ XeCl excimer laser pulses and the maximum values of the transient absorption observed at 370 nm were read from the screen of a 100

MHz oscilloscope. Similar transient absorption measurements were made with acetone solutions of matched absorbance containing 0.003 mol dm^{-3} biphenyl. Absolute values for the sensitized biphenyl triplet yields were derived by assuming $^3\phi = 1$ for acetone. Finally, results were plotted according to the equation

$$\frac{1}{^3\phi_{sens}} = \frac{1}{^3\phi}\left(1 + \frac{1}{k_q^3\tau}\frac{1}{[BPh]}\right) \tag{1}$$

where $^3\phi_{sens}$ and [BPh] are the sensitized biphenyl triplet yield and the biphenyl concentration respectively, $^3\phi$ and $^3\tau$ are the yield of triplet formation and the triplet lifetime of the studied ketone molecule and k_q is the rate coefficient for triplet quenching by biphenyl. Quenching constants were obtained from the intercepts and slopes, and triplet lifetimes were derived from $k_q^3\tau$ values by assuming that all the ketones have the same k_q as methyl ethyl ketone. (For the latter, $k_q = 4.8 \times 10^8$ and 6.8×10^8 dm^3 mol^{-1} s^{-1} were determined in iso-octane and acetonitrile solvents respectively, resolving $k_q^3\tau$ with an independently determined $^3\tau$ value; see footnotes to Table 1.)

The yields of triplet formation were obtained for all ketones by the triplet-sensitized biphenyl technique simply as the reciprocal of the intercepts of the straight lines plotted according to eqn. (1).

TABLE 1

Triplet yields and triplet lifetimes of α-methyl-substituted acetones

Solvent	π^*	α	[Ketone] (mol dm^{-3})	$^3\phi$ [a]	$^3\tau$ (ns)
Methyl ethyl ketone					
Iso-octane	−0.08	0.00	0.090	1.07 ± 0.11	1890[b]
Acetonitrile	0.75	0.19	0.086	0.96 ± 0.07	667[b]
Methyl isopropyl ketone					
Iso-octane	−0.08	0.00	0.057	1.00 ± 0.10	27 ± 4[a,c]
tert-Butanol	0.41	0.68	0.019	0.85 ± 0.33	11 ± 6[a,d]
			0.038	0.86 ± 0.06	15 ± 2[a,d]
			0.114	0.72 ± 0.04	13 ± 2[a,d]
Methanol	0.60	0.93	0.114	0.56 ± 0.12	11 ± 3[a,d]
Acetonitrile	0.75	0.19	0.019	0.40 ± 0.12	16 ± 7[a,d]
			0.038	0.33 ± 0.05	18 ± 5[a,d]
			0.114	0.31 ± 0.08	14 ± 3[a,d]
Methyl tert-butyl ketone					
Iso-octane	−0.08	0.00	0.049	0.58 ± 0.34	2 ± 2[a,c]
Acetonitrile	0.75	0.19	0.032	0.59 ± 0.30	2 ± 1[a,d]

[a]Triplet-sensitized biphenyl technique.
[b]Sensitized dibromoanthracene technique.
[c]$k_q = 4.8 \times 10^8$ dm^3 mol^{-1} s^{-1} assumed.
[d]$k_q = 6.8 \times 10^8$ dm^3 mol^{-1} s^{-1} assumed.

2.3. Results and discussion

Yields of triplet state formation and triplet lifetimes determined for methyl ethyl ketone, methyl isopropyl ketone and methyl *tert*-butyl ketone at room temperature in various solvents are given in Table 1. Included in Table 1 are certain solvatochromic parameters [14 - 16] which serve to characterize the solvents; the parameter π^* is an index of solvent dipolarity which measures the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect, while parameter α describes the ability of the solvent to donate a proton in a solvent-to-solute hydrogen bond.

The triplet lifetimes presented in Table 1 span a range of three orders of magnitude. The data obtained under comparable experimental conditions show the well-known shortening of lifetime with increasing α substitution and support the statement that the rate of α cleavage (which is the predominant primary process of ketones with no γ-hydrogens) is almost completely determined by the α substituent [3].

Adopting the treatment of Encina *et al.* [5], which involves the assumption that decay of the triplet state of simple aliphatic ketones via routes other than type I cleavage occurs at the same rate as in the case of acetone, allows ^3k_I to be estimated from the equation

$$^3k_I = \frac{1}{^3\tau} - \left(\frac{1}{^3\tau}\right)_A \tag{2}$$

These results together with literature values are given in Table 2. The data show a considerable increase in the rate of α cleavage with methyl substitution in the α position which results in a substantial shortening of the triplet lifetimes.

Our rate coefficients for type I decomposition of methyl ethyl ketone are in reasonable agreement with literature values, while our results for methyl isopropyl ketone in iso-octane differ considerably from the data given by Encina and Lissi for $R'CO$—CHR_2 bond scission in hydrocarbon

TABLE 2

Triplet state Norrish type I decomposition rate coefficients ^3k_I (s^{-1})

Ketone	Iso-octane		Acetonitrile	
	This work[a]	Literature	This work[a]	Literature
$CH_3COC_2H_5$	$< 5 \times 10^5$	1.5×10^5 [b]	1.5×10^6	3.6×10^6 [c]
$CH_3COCH(CH_3)_2$	3.6×10^7	1.4×10^8 [b]	6.2×10^7	
$CH_3COC(CH_3)_3$	4.9×10^8	3×10^8 [d]	4.5×10^8	

[a] Determined in this work using $(^3\tau)_A = 0.94$ μs and $(^3\tau)_A = 45$ μs in iso-octane and acetonitrile respectively.
[b] From ref. 3.
[c] From ref. 5.
[d] Calculated from $^3\phi_I = 0.33$ [17] with $^3\phi$ and $^3\tau$ taken from Table 1.

solvents [3]. The ^3k_I values determined in the present work form a self-consistent pattern.

Analysis of the kinetic data given in Table 2 and consideration of the triplet lifetimes shown in Table 1 suggest a slight enhancement of type I decomposition in polar solvents. A similar observation has been made by Encina and Lissi [3] for 4-methyl-2-pentanone decomposition, and the greater reaction rate in polar solvents was explained by a moderate amount of charge separation in the transition state.

We have also studied the effect of varying the ketone concentration on the triplet lifetimes and on the rate coefficients of type I decomposition from the triplet state. No definite effect could be established, as indicated by the constancy of the triplet lifetimes in the concentration range investigated.

Consideration of the triplet yields given in Table 1 reveals that the quantum yield of triplet state formation in the series of α-substituted aliphatic ketones depends on three major factors: (i) the extent of α substitution (i.e. the structure of the ketone), (ii) the concentration of the ketone and (iii) the nature of the solvent.

Regarding the effect of a change in structure, there is definitely an observable decrease in the triplet yields with increasing methyl substitution in the α position. This is in accordance with the results of Yang et al. [6] who observed that the rates of singlet–triplet intersystem crossing of poly α-substituted ketones are appreciably lower than those of straight-chain ketones. In addition to the change in $^1k_{ISC}$ with structure, one also expects the rate coefficient of the competitive type I decomposition from the singlet state to vary with α substitution. Namely, on thermochemical grounds an increase in the number of substituents should increase the value of ^1k_I as the strength of the α C—C bond weakens. Thus, the larger k_I and smaller $^1k_{ISC}$ values of the poly α-substituted compounds result in the quantum yields of triplet state formation being appreciably lower than unity for these ketones.

The influence of the nature of the solvent and of the ketone concentration on $^3\phi$, although not as significant as the structural effect, can be easily recognized from an examination of the data in Table 1. It is apparent that the triplet yields for methyl isopropyl ketone tend to decrease with increasing solvent polarity and ketone concentration. In the case of methyl ethyl ketone the solvent and concentration effects were not sufficiently large to result in a significant deviation from $^3\phi = 1$, while the methyl tert-butyl ketone data were too imprecise to merit detailed study.

The value of the triplet yield depends on the amount of competition from singlet state reactions. Thus, to explain the observed effect of solvent and concentration on the triplet yield, knowledge is required of the kinetics of the processes occurring from the excited singlet state, and in particular of the singlet lifetimes under various experimental conditions. The lifetimes of methyl isopropyl ketone were determined in five different solvents and over a wide range of ketone concentrations. In all experiments, double-exponential fluorescence decay was observed by using the time-resolved
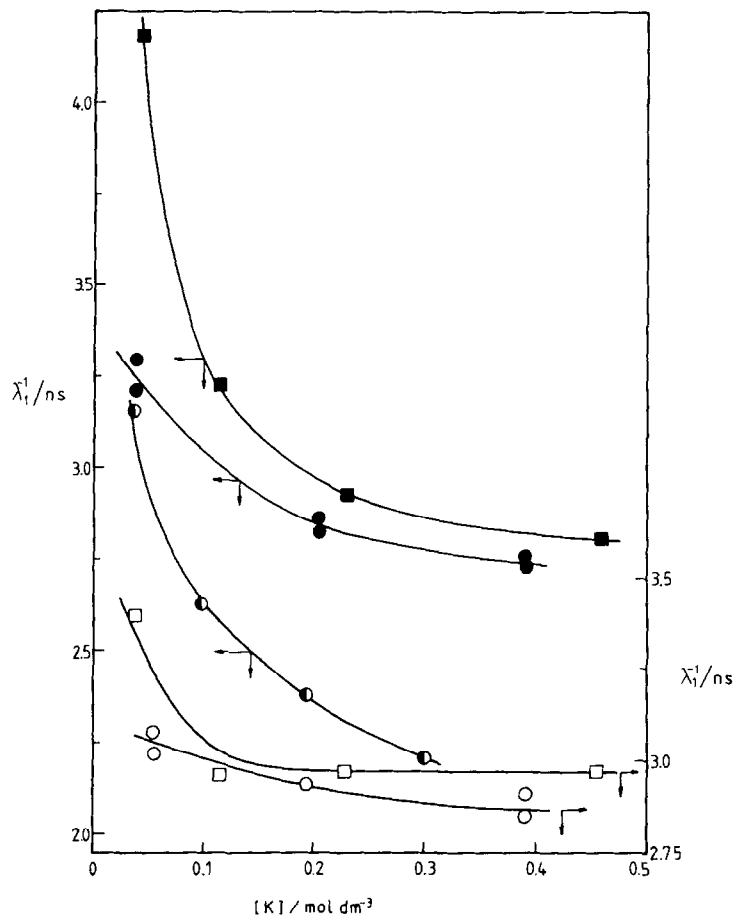
Fig. 1. Reciprocal fluorescence decay parameters λ_1^{-1} of methyl isopropyl ketone in different solvents: $\bigcirc$, iso-octane; $\bullet$, acetonitrile; $\square$, tert-butanol; $\blacksquare$, methanol; $\mathbb{O}$, water. (λ_{exc} = 316 nm; T = 298 K.)

single-photon counting technique. Of the two decay parameters λ_1 and λ_2, one was large ($1/\lambda_2 \approx 0.1 - 0.2$ ns), and its concentration dependence could not be measured with the required accuracy. However, the value of decay parameter λ_1 has been determined under various experimental conditions. The experimental data are presented in Fig. 1 in the form of plots of $1/\lambda_1$ vs. ketone concentration. These results clearly show that the values of $1/\lambda_1$ depend on the solvent as well as on the ketone concentration. The greatest concentration dependence of $1/\lambda_1$ was found in the polar solvents water, acetonitrile and methanol, especially in water, which in addition to its significant dipolarity is also a very good proton donor. In contrast, $1/\lambda_1$ was observed to be only moderately concentration dependent in the non-polar aprotic solvent iso-octane and in the slightly polar solvent tert-butanol.

The double-exponential fluorescence decay and the concentration-dependent decay parameter, as well as the dependence of the triplet yields on the solvent and on the ketone concentration, suggest the reversible formation and reactions of singlet excimers. Similar observations were made [10, 11] in a detailed investigation of the photochemistry of 2-pentanone. Our results require the intermediate excimer to be formed more easily from ketones highly substituted in the α position, and the rate of formation of singlet excited dimer (excimer) appears to be enhanced in polar solvents. Since the yields of triplet state formation appear to decrease with increasing α substitution, increasing ketone concentration and solvent polarity (*i.e.* with the factors which promote excimer formation), we assume that there are two major competitive reaction paths for the disappearance of the singlet excimer: energy dissipative decomposition supplying two ground state ketone molecules, and ISC forming a triplet excimer. The latter can subsequently decompose, giving a triplet and a ground state ketone molecule. Thus, the primary processes in the photochemistry of α-substituted aliphatic ketones are given by Scheme I, where K, ^{1}K and ^{3}K denote the ground state, the singlet excited state and the triplet state respectively of the ketone, while ^{1}E is the singlet and ^{3}E is the triplet excimer.
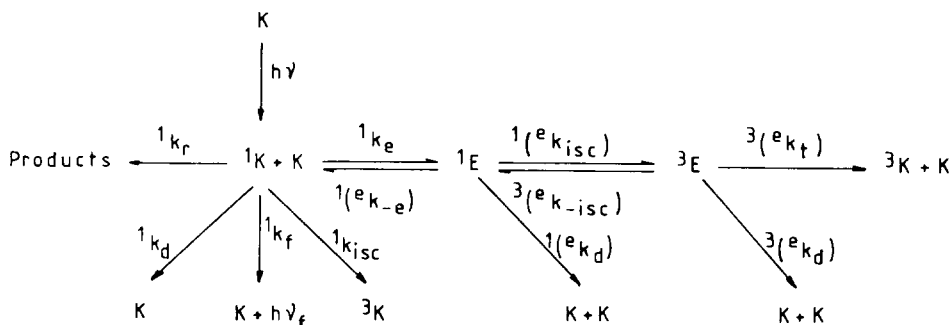
Scheme I.

The structure and bonding in the ^{1}E exciplex is of course unknown; however, comparing the present results on triplet state formation with the efficiency of excited triplet carbonyl production in the thermal decomposition of substituted 1,2-dioxetanes may supply valuable information. Richardson *et al.* [18] observed that the efficiency of excited state carbonyl production in the decomposition of variously substituted 1,2-dioxetanes decreased significantly when phenyl groups were substituted on the dioxetane ring. They also reported a decrease in triplet formation efficiency when the solvent was changed from benzene (aprotic) to methanol (protic). Richardson *et al.* [18] assumed a biradical mechanism involving competition between decomposition and ISC of the singlet biradical. They suggested that the triplet excited carbonyl formation was observed to decrease on aryl substitution and on change of solvent because these changes facilitated

decomposition relative to intersystem crossing. The similar effect on the yield of triplet formation observed in the present study as a result of the change in ketone structure and on changing the solvent may indicate that a dioxetane or a dioxetane-biradical-type intermediate participates in the photochemistry of α-substituted aliphatic ketones. This may explain the enhancement of the decomposition of singlet excimer to ground state ketone molecules by α-methyl substitution and by a change to a more polar and protic solvent.

On the basis of Scheme I, the high concentration limiting value of the quantum yield of triplet state formation can be given as the product of two probabilities (assuming $^3(^ek_{-ISC})$ to be small):

$$\lim_{[K] \to \infty} {}^3\phi = \frac{{}^1(^ek_{ISC})}{{}^1(^ek_{ISC}) + {}^1(^ek_d)} \frac{{}^3(^ek_t)}{{}^3(^ek_t) + {}^3(^ek_d)} \tag{3}$$

Both probabilities may be written as a product of the lifetime of an exciplex species and a rate coefficient of a reaction on the path leading to the triplet ketone molecule:

$$\lim_{[K] \to \infty} {}^3\phi = {}^1(^ek_{ISC}) \; {}^1(^e\tau) \; {}^3(^ek_t) \; {}^3(^e\tau) \tag{4}$$

where

$$^1(^e\tau) = \frac{1}{{}^1(^ek_{ISC}) + {}^1(^ek_d)} \tag{5}$$

and

$$^3(^e\tau) = \frac{1}{{}^3(^ek_t) + {}^3(^ek_d)} \tag{6}$$

The triplet yield has been shown to depend considerably on the structure of the ketone and on the solvent (see Table 1). This dependence may arise partly or mainly from the changes in the lifetimes $^1(^e\tau)$ and $^3(^e\tau)$. The former can be determined from the high concentration limiting values obtained from extrapolation of the curves presented in Fig. 1:

$$\lim_{[K] \to \infty} (1/\lambda_1) = \frac{1}{{}^1(^ek_{ISC}) + {}^1(^ek_d)} = {}^1(^e\tau) \tag{7}$$

The lifetimes obtained for the singlet excimer of methyl isopropyl ketone are 2.86 ns, 2.94 ns, 2.76 ns and 2.68 ns in iso-octane, *tert*-butanol, methanol and acetonitrile respectively. There is a shortening of the singlet excimer lifetime with increasing solvent polarity. However, the change is much less than that observed for $^3\phi$ (see Table 1). Thus, we suggest that $^3(^e\tau)$ also changes in a similar manner. In the interpretation of our results we have arbitrarily assumed that the decrease in the triplet quantum yields with increasing α-alkyl substitution and increasing solvent polarity is a result of shortening of singlet and triplet excimer lifetimes which is mainly caused by

the enhancement of the decomposition of the excimers into ground state ketone molecules. Further investigations are required to confirm these assumptions.

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