

## EXCIMER FORMATION IN THE PHOTOCHEMISTRY OF ALIPHATIC KETONES II: FLUORESCENCE DECAY KINETICS

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### Summary

The fluorescence spectra and the fluorescence decay following excitation by means of a light flash were studied for a few simple aliphatic ketones to obtain evidence for excimer formation.

The fluorescence spectra of 2-pentanone recorded in iso-octane and in *tert*-butanol at a number of ketone concentrations show no sign of excimer luminescence. The monomer fluorescence decay kinetics were studied for 2-pentanone in two solvents over a wide range of ketone concentration and for acetone, methyl isopropyl ketone and diisopropyl ketone at one concentration. For all these ketones under all the conditions investigated only double-exponential functions gave a satisfactory fit to the experimental data. The observations were interpreted as evidence for singlet excimer formation in a reversible process. The lifetimes of the excited singlet monomer and excimer and the rate coefficients of the formation and removal of the excimer were determined for 2-pentanone in iso-octane and *tert*-butanol.

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### 1. Introduction

In a study of the photochemistry of 2-pentanone at 313 nm in iso-octane [1], we have presented convincing evidence for the enhancement of singlet  $\rightarrow$  triplet intersystem crossing by ground state ketone molecules. The observations were interpreted by assuming the formation of a singlet excimer.

Much evidence has been accumulated in the past decade to support the role played by excimers and exciplexes in primary photophysical and photochemical processes. It is well established that exciplexes are intermediates in some fluorescence quenching processes [2 - 4]. Internal conversion is known to occur with a significant efficiency via excited complexes [5]. Dissociative intersystem crossing of the singlet exciplex has been proved to provide an additional route for population of the molecular triplet state [6, 7]. Further-

more, the intermediacy of both singlet and triplet excited complexes was suggested for a wide variety of photochemical reactions. The role of exciplexes in cycloaddition reactions has been demonstrated [5, 8] and it was shown that quenching of photocycloaddition paralleled exciplex fluorescence quenching, thus demonstrating the intermediacy of the exciplex [8].

Direct evidence for the participation of the excited state complex is provided by its luminescence which is structureless and is shifted to wavelengths longer than those of molecular fluorescence. Indirect methods have to be used for the identification of complexes which do not emit luminescence. Investigations of the decay kinetics of molecular fluorescence may be successful under certain circumstances [5, 9].

It should be remarked that the overwhelming majority of photokinetic studies of excimers carried out so far have been confined to aromatic or heteroaromatic molecules. Among the very few exceptions are the investigations of saturated amine excimers carried out by Halpern *et al.* [10].

In the study presented in this paper we made an attempt to find direct evidence for the assumed 2-pentanone excimer by observing its fluorescence. Furthermore, we report on the kinetic study of fluorescence decay carried out for a number of simple aliphatic ketones to show that excimer formation is a common phenomenon among carbonyl compounds.

## 2. Experimental details

### 2.1. Materials

#### 2.1.1. Ketones

Spectroscopic grade acetone (Fluka) was used without further purification. Fluka puriss grade methyl isopropyl ketone and 2-pentanone were purified by preparative gas chromatography on a Carbowax 20M column. Diisopropyl ketone was prepared from isobutyric acid [11] and purified by gas-liquid chromatography on a Carbowax 20M column.

#### 2.1.2. Solvents

Fluka (puriss pro analyse grade) iso-octane was refluxed with concentrated sulphuric acid and with acidic sodium permanganate solution, washed with sodium carbonate solution and dried. In the final stage of purification the iso-octane was distilled from sodium on a high performance column. Reanal (a.t.) reagent grade *tert*-butanol was treated overnight with lithium aluminium hydride and distilled from lithium aluminium hydride. The purified solvents iso-octane and *tert*-butanol emitted luminescence that contributed less than 10% and less than 20% respectively to the fluorescence of a 0.01 mol dm<sup>-3</sup> solution of 2-pentanone.

### 2.2. Recording of fluorescence spectra

The spectra of the iso-octane solutions were recorded in the presence of air, but deaerated *tert*-butanol solutions were used to eliminate the effect of photo-oxidation products.

The fluorescence spectra were recorded at an excitation wavelength of  $297 \pm 6$  nm with a spectrofluorometer as follows. An HBO 200 W mercury arc combined with a Bausch and Lomb high intensity monochromator was used to produce the 297 nm excitation light. The fluorescence was detected by a photon-counting system (Princeton Applied Research model 1140 A/B) at right angles to the excitation beam. A grating monochromator (Applied Photophysics model M300) with a bandpass of 4 nm was placed in the analysing line. The spectra were stored in a multichannel analyser which was also employed to subtract the background radiation in cases where the spectra were very weak.

### 2.3. Fluorescence decay measurements

A time-correlated single-photon counting technique was employed to determine the fluorescence decay curves. A commercial Applied Photophysics SP-3 nanosecond spectrofluorometer was used which was interfaced to a computer, facilitating data handling. The light source was a gated spark discharge lamp filled with an  $H_2-N_2$  gas mixture ( $H_2:N_2$  ratio, 4:1) to a pressure of 40 kPa and operated at a repetition frequency of 30 kHz. A high intensity grating monochromator served to select the 316 nm excitation wavelength. The fluorescence was detected at right angles to the excitation beam with a 4 nm Schott GG 13 glass filter placed in front of the "stop" photomultiplier (Mullard XP 2020Q) to eliminate scattered light. A start-to-stop ratio of 100:1 was used and 8192 counts were accumulated in the channel of the multichannel analyser corresponding to the maximum of the profile.

The profile of the excitation pulse, recorded with an empty quartz cuvette positioned at the sample cell, had a width of 3 ns at half-height. Separate experiments showed that the instrument response was independent of the detection wavelength between 300 and 500 nm.

The observed fluorescence decay curve  $i(t)$  is a convolution of the true decay function  $g(t)$  of the fluorescence and the instrument response function  $h(t)$  (excitation pulse shape distorted by the detection system), *i.e.*

$$i(t) = \int_0^t g(t - t')h(t') dt' \quad (1)$$

The true fluorescence decay function was recovered from the experimentally available fluorescence decay curve and the excitation pulse shape using a weighted least-squares iterative reconvolution technique [12]. The  $\chi^2$  values, plots of residuals and plots of the autocorrelation of the residuals were used to characterize the accuracy of the fit [13].

## 3. Results and discussion

### 3.1. Fluorescence spectra

As mentioned in the preceding sections, direct evidence for the role played by the excimer in the photochemistry of aliphatic ketones could be

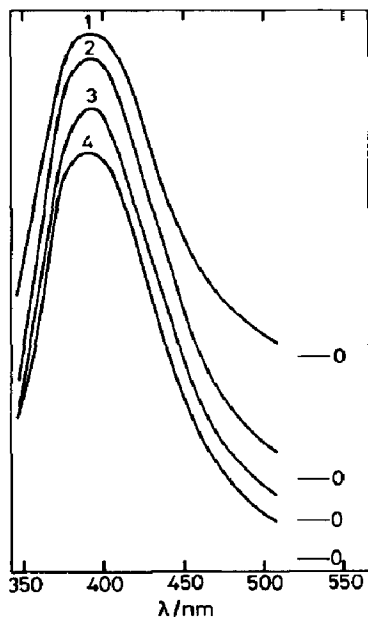


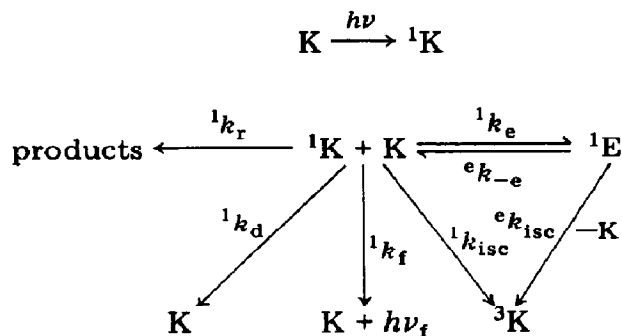
Fig. 1. Fluorescence spectra obtained for various concentrations of 2-pentanone in iso-octane at 298 K: curve 1,  $2 \times 10^{-1}$  M; curve 2,  $1 \times 10^{-1}$  M; curve 3,  $5 \times 10^{-3}$  M; curve 4,  $1 \times 10^{-3}$  M.

expected from the detection and measurement of the excimer fluorescence. Therefore, we have recorded the fluorescence spectra of 2-pentanone in iso-octane and *tert*-butanol solvents. A broad concentration range extending from  $1 \times 10^{-3}$  to  $0.2 \text{ mol dm}^{-3}$  was used. The results obtained in iso-octane are presented in Fig. 1. The spectra recorded in iso-octane and *tert*-butanol show no sign of excimer fluorescence. There is no evidence either for the appearance of a new peak or for any concentration dependence of the spectra. The observed emission with a maximum around 400 nm is the singlet monomer fluorescence well known for aliphatic ketones [14]. These results indicate that the excimer, if formed at all, is of a non-fluorescent nature.

### 3.2. Transient kinetics

By studying the monomer fluorescence kinetics in a flash excitation system, a singlet excimer can be identified and the rate parameters for its formation and removal can be determined even for a non-fluorescent excimer, provided that the formation of the excited dimer is reversible [9, 15].

On the basis of our steady state investigations of the concentration dependence of decomposition and the triplet formation quantum yields [1], let us assume a kinetic scheme:



In this scheme K,  ${}^1\text{K}$  and  ${}^3\text{K}$  denote the ground state, the singlet excited state and the triplet state of the ketone molecule respectively, and  ${}^1\text{E}$  is the singlet excimer. The lifetimes  ${}^1\tau_0$  and  ${}^e\tau$  for the singlet excited molecule (the monomer) and for the singlet excimer respectively are defined by

$${}^1\tau_0 = \frac{1}{{}^1k_f + {}^1k_d + {}^1k_r + {}^1k_{isc}} \quad (2)$$

$${}^e\tau = \frac{1}{{}^e k_{-e} + {}^e k_{isc}} \quad (3)$$

When the coupled kinetic differential equations of the excited monomer and the excimer are solved for excitation represented by a  $\delta$  function the following well-known relation [9, 15] for monomer fluorescence decay is obtained:

$$i(t) = c_1 \exp(-\lambda_1 t) + c_2 \exp(-\lambda_2 t) \quad (4)$$

In this relationship both the decay parameters  $\lambda_1$  and  $\lambda_2$  and the weight factors  $c_1$  and  $c_2$  are concentration dependent as seen from the expressions

$$\lambda_{1,2} = \frac{1}{2} [(X + Y) \mp \{(Y - X)^2 + 4{}^e k_{-e} {}^1k_e [\text{K}]\}^{1/2}] \quad (5)$$

$$c_1 = {}^1k_f \frac{\lambda_2 - X}{\lambda_2 - \lambda_1} \quad (6a)$$

and

$$c_2 = {}^1k_f \frac{X - \lambda_1}{\lambda_2 - \lambda_1} \quad (6b)$$

The designations X and Y are specific decay rates for the excited monomer and the excimer respectively, and are defined as follows:

$$\begin{aligned}
 X &= {}^1k_f + {}^1k_d + {}^1k_r + {}^1k_{isc} + {}^1k_e [\text{K}] \\
 &= \frac{1}{{}^1\tau_0} + {}^1k_e [\text{K}]
 \end{aligned} \quad (7)$$

$$\begin{aligned}
 Y &= {}^e k_{-e} + {}^e k_{isc} \\
 &= \frac{1}{e\tau}
 \end{aligned}
 \tag{8}$$

With the above expressions the limiting values of the decay parameters as the ketone concentration approaches zero or (formally) infinity can easily be calculated:

$$\lim_{[K] \rightarrow \infty} \frac{1}{\lambda_1} = \frac{1}{{}^e k_{isc}}
 \tag{9}$$

$$\lim_{[K] \rightarrow \infty} \frac{1}{\lambda_2} = 0$$

$$\lim_{[K] \rightarrow 0} \frac{1}{\lambda_1} = {}^1\tau_0
 \tag{10}$$

$$\lim_{[K] \rightarrow 0} \frac{1}{\lambda_2} = e\tau$$

Furthermore, the following two equations can be derived from eqn. (5) for the sum and product of the decay parameters:

$$\lambda_1 + \lambda_2 = \frac{1}{{}^1\tau_0} + \frac{1}{e\tau} + {}^1k_e[K]
 \tag{11}$$

$$\lambda_1\lambda_2 = \frac{1}{{}^1\tau_0} \frac{1}{e\tau} + {}^e k_{isc} {}^1k_e[K]
 \tag{12}$$

### 3.3. Photokinetics of 2-pentanone in iso-octane and in tert-butanol

It follows from the discussion presented in Section 3.2 that, in a system where excitation is brought about by a light flash, the monomer fluorescence intensity could exhibit double-exponential decay kinetics. This is expected when an excimer is formed which can dissociate re-forming the excited singlet monomer with a rate coefficient comparable with that of other excimer-consuming reactions.

To examine the role of the singlet excimer in the photophysics of simple ketones, we have made a detailed study of the fluorescence decay of 2-pentanone in iso-octane and *tert*-butanol. A wide range of ketone concentration from  $2 \times 10^{-3}$  to  $3 \times 10^{-1}$  mol dm<sup>-3</sup> was used. No measurement could be analysed in terms of a single-exponential function, but satisfactory fits were obtained using a double-exponential decay function [4]. This is demonstrated in Fig. 2 where a fluorescence decay curve and the residual plots for the single-exponential and the double-exponential decay functions are presented. The  $\chi^2$  values obtained for the single-exponential and double-exponential fits were 12.6 and 1.04 respectively. The random distribution of

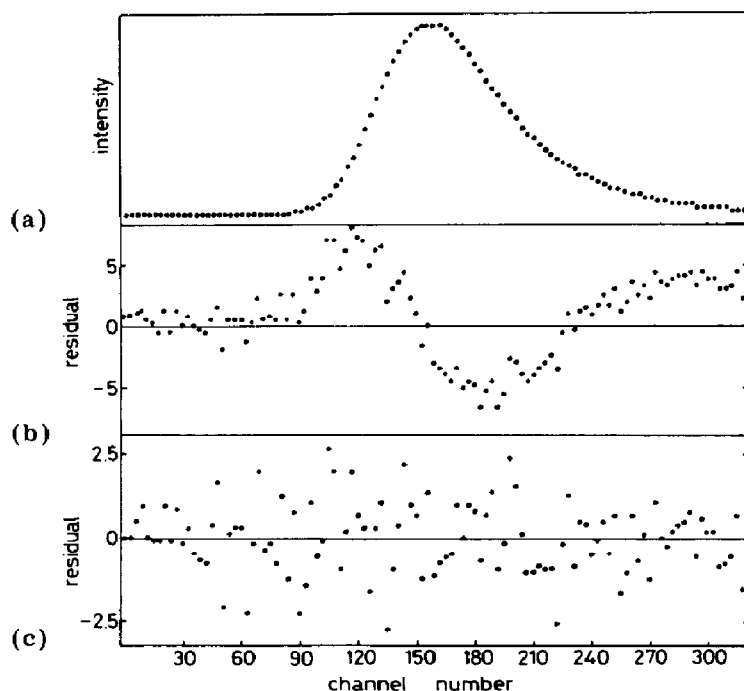


Fig. 2. (a) 2-Pentanone fluorescence decay in iso-octane, (b) residual plot for the single-exponential decay function and (c) residual plot for the double-exponential decay function (ketone concentration,  $0.012 \text{ mol dm}^{-3}$ ; 298 K).

residuals and the small  $\chi^2$  value show that the double-exponential function is suitable for describing the fluorescence decay kinetics.

The concentration dependence of the decay parameters in iso-octane is given in Table 1 and the results obtained in both solvents are plotted in Fig. 3. The observed concentration dependence of the decay parameters is

TABLE 1

Fluorescence decay characteristics of 2-pentanone in iso-octane at 298 K

[2-pentanone] ( $\text{mol dm}^{-3}$ )	$\lambda_1$ ( $\text{ns}^{-1}$ )	$\lambda_2$ ( $\text{ns}^{-1}$ )	$\chi^2$
0.203	0.52	7.69	1.03
0.166	0.56	19.93	1.27
0.165	0.56	5.88	1.27
0.096	0.56	4.35	1.24
0.049	0.50	2.42	0.93
0.030	0.55	3.57	1.13
0.027	0.57	6.67	1.26
0.012	0.47	2.36	1.04
0.0088	0.40	1.54	1.37
0.0033	0.41	1.59	1.24
0.0023	0.39	2.50	1.29

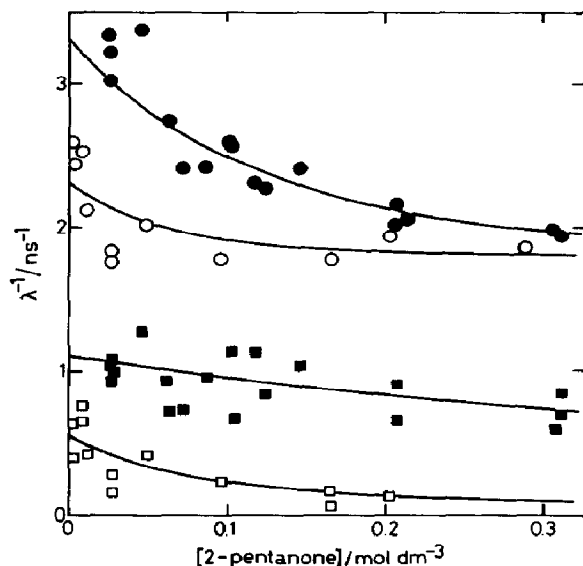


Fig. 3. The concentration dependence of the reciprocal fluorescence decay parameters for 2-pentanone: ●,  $1/\lambda_1$  in *tert*-butanol; ○,  $1/\lambda_1$  in iso-octane; ■,  $1/\lambda_2$  in *tert*-butanol; □,  $1/\lambda_2$  in iso-octane.

in accordance with eqn. (5) and the kinetic results of the fluorescence decay are in agreement with those expected for reversible excimer formation (see eqn. (4)).

It can be established from Fig. 3 (by considering eqns. (9) and (10)) that the lifetimes of the excited monomer singlet state and of the singlet excimer are a few nanoseconds and around 1 ns or less respectively. More detailed kinetic information can be obtained by studying the concentration dependence of  $\lambda_1\lambda_2$  and  $\lambda_1 + \lambda_2$ . Plots of the sum  $\lambda_1 + \lambda_2$  of the decay parameters *versus* the ketone concentration are shown in Fig. 4, while the products  $\lambda_1\lambda_2$  are plotted against the ketone concentration in Fig. 5. The intercepts of the straight lines in Fig. 4 and Fig. 5 supply the sum and the product respectively of the reciprocal lifetimes of the singlet monomer and excimer molecules. From these, the lifetimes indicated in Table 2 are calculated. The slopes of the straight lines give the rate coefficients of excimer formation and of singlet  $\rightarrow$  triplet intersystem crossing from the excimer state. Finally, the specific rate coefficient of excimer redissociation can be calculated as the difference  $(\epsilon\tau)^{-1} - \epsilon k_{isc}$  (see eqn. (3)). The kinetic data pertaining to the 2-pentanone system are summarized in Table 2.

One of the first observations that can immediately be made when the results given in Table 2 are considered is that the excimer is formed in a very fast process. Using the modified Debye equation [16]

$$k_{diff} = \frac{8RT}{2000\eta} \quad (13)$$



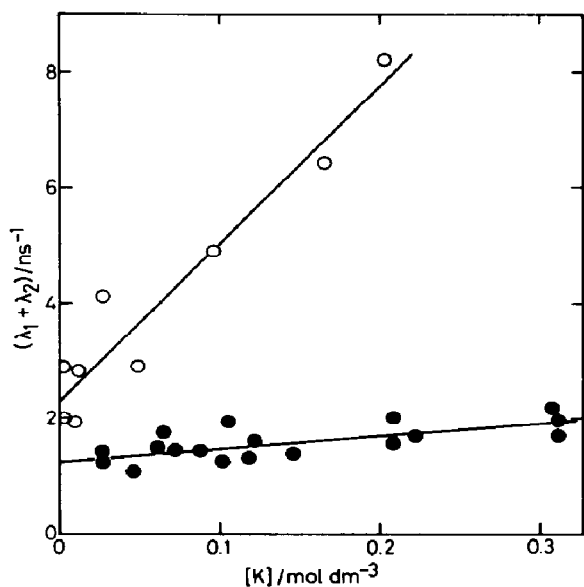


Fig. 4. Plots in accordance with eqn. (11) of the experimental data in iso-octane (○) and in *tert*-butanol (●).

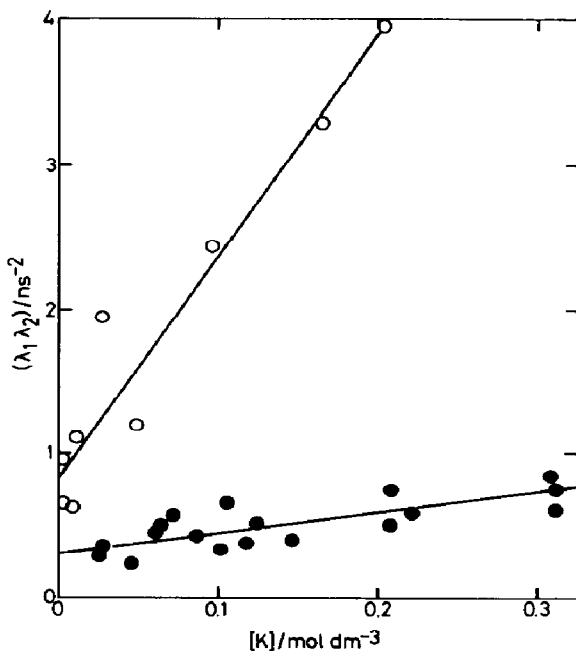


Fig. 5. Plots in accordance with eqn. (12) of the experimental data in iso-octane (○) and in *tert*-butanol (●).

TABLE 2

Kinetic data for the excited monomer singlet state and for the singlet excimer of 2-pentanone

Solvent	${}^1\tau_0$ (ns)	$e\tau$ (ns)	${}^1k_e$ ( $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ )	${}^0k_{-e}$ ( $\text{s}^{-1}$ )	${}^0k_{isc}$ ( $\text{s}^{-1}$ )
Iso-octane	$2.3 \pm 0.4$	$0.55 \pm 0.25$	$(2.7 \pm 0.3) \times 10^{10}$	$(1.3 \pm 0.6) \times 10^9$	$(5.6 \pm 0.7) \times 10^8$
<i>Tert</i> -butanol	$3.3 \pm 0.7$	$1.1 \pm 0.3$	$(2.2 \pm 0.5) \times 10^9$	$(2.8 \pm 2.0) \times 10^8$	$(6.3 \pm 1.1) \times 10^8$

with the solvent viscosity coefficients  $\eta(\text{iso-octane}) = 0.47$  cP [17] and  $\eta(\text{tert-butanol}) = 4.74$  cP [18], the diffusion-controlled specific rate coefficients in iso-octane and *tert*-butanol are calculated to be  $2.1 \times 10^{10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $2.1 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  respectively. These are close to the  ${}^1k_e$  rate coefficients derived for the specific rates of excimer formation.

Singlet  $\rightarrow$  triplet intersystem crossing is known to be a predominant factor in determining the lifetime of the  ${}^1(n, \pi^*)$  excited states of aliphatic ketones [19, 20]. This is also the case for 2-pentanone in iso-octane where we obtained [1] from the limiting low concentration triplet yield  ${}^1k_{isc} {}^1\tau_0 = 0.59 \pm 0.1$  for the participation of intersystem crossing in the reactions of the singlet excited monomer molecules. It is of interest to consider the importance of intersystem crossing for the singlet excimer. Our kinetic

results indicate that  ${}^e k_{isc} \tau = 0.31 \pm 0.1$  and  ${}^e k_{isc} \tau = 0.69 \pm 0.2$  in iso-octane and *tert*-butanol respectively. (The former value is in excellent agreement with the  ${}^e k_{isc}/({}^e k_{isc} + {}^e k_{-e})$  estimation given on the basis of steady state measurements [1].) The results given in Table 2 show that the specific rate of intersystem crossing from the excimer state is not significantly different in the two solvents, and the greater participation of intersystem crossing in *tert*-butanol is a consequence of the increased stability in this solvent.

Finally, the different specific rates for excimer redissociation deserve attention. The greater stability (with respect to dissociation) of the singlet excimer in the more polar *tert*-butanol solvent is probably due to the charge transfer character of the complex.

### 3.4. Fluorescence decay kinetics of other aliphatic ketones

Fluorescence decay measurements were also carried out with simple aliphatic ketones other than 2-pentanone. The ketones studied were acetone, methyl isopropyl ketone and diisopropyl ketone. For all these ketones only double-exponential functions gave satisfactory fits to the experimental data. Some of the results obtained at ketone concentrations of around 0.1 mol dm<sup>-3</sup> are given in Table 3.

The decay parameters summarized in Table 3 appear to show some trend with the change in structure of the ketone. The  $\lambda_1$  values determined at low concentrations seem to decrease with  $\alpha$  substitution, which we explain in terms of the decrease in the intersystem crossing rate of the excited singlet monomer. A similar decrease in  ${}^1 k_{isc}$  with increasing  $\alpha$  substitution was previously observed [19 - 21]. (The greater  $\lambda_1$  value for 2-pentanone reflects the contribution of type II decomposition.) The possible trend in the  $\lambda_2$  values is less reliable and its explanation has to be postponed until more results are available.

The results presented in this paper seem to establish the role played by singlet excimers in the photophysics of aliphatic ketones.

TABLE 3

Fluorescence decay characteristics of methylated acetones in iso-octane at 298 K

<i>Ketone</i>	[K] (mol dm <sup>-3</sup> )	$\lambda_1$ (ns <sup>-1</sup> )	$\lambda_2$ (ns <sup>-1</sup> )	$\chi^2$
Acetone	0.060	0.48	1.64	1.18
2-Pentanone	0.096	0.56	4.35	1.24
Methyl isopropyl ketone	0.100	0.40	6.17	1.34
Diisopropyl ketone	0.072	0.32	9.09	1.22

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