

EXCIMER FORMATION IN THE PHOTOCHEMISTRY OF ALIPHATIC KETONES I: CONCENTRATION DEPENDENCE OF QUANTUM YIELDS

L. BICZÓK, T. BÉRCES, S. FÖRGETEG and F. MÁRTA

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

(Received January 31, 1984)

Summary

The photochemistry of 2-pentanone was studied in iso-octane at 313 nm. The quantum yields of the Norrish type I and II primary processes were found to increase with increasing ketone concentration and to attain limiting values at high concentrations (above about 0.3 mol dm^{-3}). The triplet yield, studied by means of the sensitized biacetyl phosphorescence technique, showed a similar concentration dependence. The enhancement of singlet \rightarrow triplet intersystem crossing by ground state ketone molecules was interpreted by assuming singlet excimer formation. The excimer may redissociate into singlet state and ground state ketone molecules or may enter intersystem crossing followed by dissociation of the excimer triplet state. Evaluation of the experimental results yielded rate coefficients for the first-order intersystem crossing step and for the type II decomposition from the triplet state.

1. Introduction

The photochemistry of carbonyl compounds has been the subject of many investigations, and a fairly well-established mechanism for the primary photochemical-photophysical processes has already been developed [1 - 4]. As a result of light absorption in the near-UV range, aliphatic carbonyl compounds are excited to the n, π^* singlet state. In the absence of reactive additives, decay of the lowest excited singlet state may be expected to occur by fluorescence emission, by internal conversion to the ground state and by intersystem crossing to the triplet state as well as by chemical reactions. Similar processes may originate from the triplet state as well. From this classical scheme of primary processes the fluorescence and triplet yields and the quantum yields for singlet and triplet state reactions as well as the singlet and triplet lifetimes are expected to be independent of the concentration of the carbonyl compound.

When we started the work reported in this paper, there were some, although very sparse, indications suggesting that the classical scheme of primary processes may not be generally valid for aliphatic carbonyl compounds. Thus, triplet yields and type II quantum yields reported for longer-chain aliphatic ketones showed considerable scattering and a slight indication of a potential concentration dependence. For instance, the triplet yields of 2-pentanone in benzene ranged from 0.25 (at $[\text{ketone}] = 0.87 \text{ mol dm}^{-3}$) [5] to 0.81 (at $[\text{ketone}] = 0.15 \text{ mol dm}^{-3}$) [6]. Our own measurements with 2-pentanone in iso-octane definitely showed that both type I and type II quantum yields increase with increasing ketone concentration [7]. Furthermore, self-quenching was observed in the photolysis of aliphatic carbonyl compounds (see refs. 8 and 9).

A systematic study of the concentration dependence of the basic photochemical characteristics of simple aliphatic aldehydes and ketones has not so far been carried out, and a probable explanation for the potential concentration dependence has not been suggested. A possible cause for the change in importance of the photophysical and photochemical primary processes with increasing carbonyl concentration could be the formation of an excimer. In this paper we present the results of an investigation of the concentration dependence of product quantum yields and triplet yields in the photolysis of 2-pentanone in iso-octane. This study was carried out to explore the role played by the singlet excimer in the photochemistry.

2. Experimental details

2.1. Materials

Fluka (puriss pro analyse grade) iso-octane, after distillation from sodium, was washed with concentrated sulphuric acid and with potassium permanganate solution. The solvent was purified further by distillation on a high performance column.

2-Pentanone (Fluka; purum grade) was purified by preparative gas chromatography on a Carbowax 20M column.

Biacetyl was distilled in vacuum and stored in the dark.

2.2. Product quantum yield determination

A carefully degassed solution of 2-pentanone in iso-octane was prepared on a vacuum line (residual air pressure, less than 0.01 Pa) and was poured into the photolysis cell, a cylindrical quartz cell with end windows 22 mm in diameter and an optical depth providing 20% - 80% transmittance at the photolysis wavelength. Irradiation was carried out at $298 \pm 2 \text{ K}$ with a parallel light beam of wavelength $313 \pm 1.5 \text{ nm}$. Details of the light filtering and intensity measurements have been described elsewhere [10]. The photolysis products were measured by gas chromatography [7], and the product quantum yields were calculated as the ratio of the rate of product formation to the rate of light absorption.

2.3. Triplet yield and triplet lifetime measurements

The yield ${}^3\phi(\text{K})$ and the lifetime ${}^3\tau_0(\text{K})$ of the triplet ketone were obtained by using the method of sensitized biacetyl phosphorescence elaborated by Sandros [11]. At a given ketone concentration, ${}^3\phi(\text{K})$ and ${}^3\tau_0(\text{K})$ were derived from the intercept and the slope of the straight line obtained by plotting experimental data according to

$$\frac{{}^3\tau(\text{Bi})}{I(\text{Bi})} = \frac{1}{\kappa {}^3\phi(\text{K})} \left\{ 1 + \frac{1}{k_{\text{tr}} {}^3\tau_0(\text{K})} \frac{1}{[\text{Bi}]} \right\} \quad (1)$$

where $I(\text{Bi})$ is the sensitized biacetyl phosphorescence intensity, κ is a calibration parameter and k_{tr} is the rate coefficient for triplet energy transfer. The biacetyl concentration was varied in these experiments from 8×10^{-5} to 2×10^{-3} mol dm $^{-3}$. The sensitized biacetyl phosphorescence intensity $I(\text{Bi})$ was measured on a Farrand MK-1 spectrofluorometer at a wavelength of 530 nm using 313 ± 5 nm excitation irradiation. The absorbances of the samples were determined with the same spectrofluorometer under identical conditions.

The biacetyl phosphorescence lifetime ${}^3\tau(\text{Bi})$ was measured on an instrument equipped with an Applied Photophysics gated flash-lamp ($\text{H}_2\text{-N}_2$ filling ratio, 5:1). The counting of the phosphorescence photons was performed in a multichannel analyser using the multiscaling mode.

According to eqn. (1), the derivation of the triplet lifetime and the triplet yield from the slope and the intercept required a knowledge of the rate coefficient k_{tr} for triplet energy transfer and the calibration parameter κ respectively. Energy transfer was assumed to occur at a diffusion-controlled rate, while the instrumental parameter κ was obtained from calibration experiments carried out with sensitizers for which values of the triplet yields were well established. Benzophenone, acetophenone and acetone, which have triplet yields very close to unity at 313 nm [12], were used in the calibration experiments. The κ versus absorbance curves obtained with the three sensitizers were in excellent agreement.

3. Results

3.1. Product quantum yields

The product quantum yields were studied for 2-pentanone concentrations of 0.01 - 1.0 mol dm $^{-3}$. The concentration dependences for the Norrish type I and type II primary processes are presented in Fig. 1. The type II quantum yields were calculated as the average of the product quantum yields for ethylene and acetone, which were always found to be in good agreement. Propane was taken, in a first approximation, as a measure of the type I quantum yields.

A characteristic concentration effect on the primary photochemical processes is apparent. The quantum yields increase by a factor of about 2

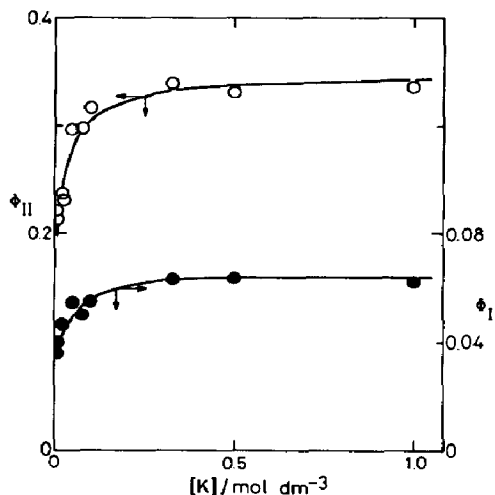


Fig. 1. Concentration dependences of quantum yields for type I (●) and type II (○) primary processes.

over the concentration range studied and attain limiting values at high concentrations. The concentration dependences can be described by empirical functions of the type

$$\phi = \frac{a + b[K]}{c + [K]} \quad (2)$$

The limiting low and high concentration values for the type II yield, obtained by a least-squares procedure, are

$$(\phi_{II})_0 = 0.17 \pm 0.02 \quad (3a)$$

and

$$(\phi_{II})_\infty = 0.37 \pm 0.02 \quad (3b)$$

3.2. Triplet yields and triplet lifetimes

It is well established that triplet reactions predominate in the photolysis of 2-pentanone at 313 nm. Therefore, it may be assumed that the observed concentration dependence of the quantum yields of the primary photochemical processes indicates an increase in the triplet yield with increasing ketone concentration. To investigate this possibility we have studied the triplet yields in the ketone concentration range 0.01 - 0.5 mol dm⁻³ in iso-octane solvent.

The experimental results are presented in Fig. 2. The concentration dependence of the triplet yield appears to be very similar to that of the primary quantum yields. The empirical equation (2) also describes the concentration dependence of the triplet yields, and extrapolation provides the low and high concentration values given as

$$({}^3\phi)_0 = 0.59 \pm 0.06 \quad (4a)$$

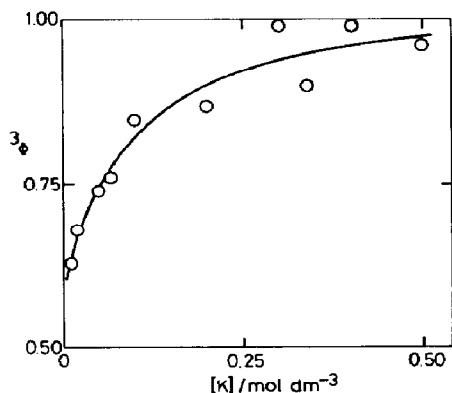


Fig. 2. Concentration dependence of the triplet yield.

and

$$({}^3\phi)_{\infty} = 1.05 \pm 0.10 \quad (4b)$$

Use of the method of sensitized biacetyl phosphorescence also supplies the triplet lifetimes. The results given in Table 1 show no definite trend with increasing ketone concentration. The average value of ${}^3\tau_0 = 0.21 \pm 0.04 \mu\text{s}$ is in good agreement with the lifetime of $0.25 \mu\text{s}$ reported by Abuin *et al.* [13].

TABLE 1

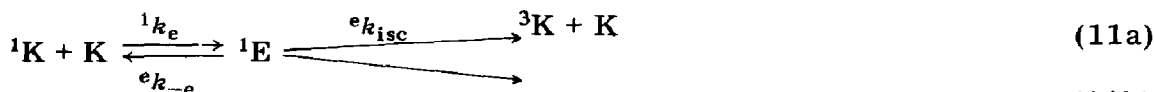
Triplet 2-pentanone lifetimes in iso-octane

[2-pentanone] (mol dm ⁻³)	0.01	0.02	0.05	0.07	0.10	0.20	0.30	0.34	0.40	0.50
³ τ (μs)	0.23	0.24	0.27	0.21	0.22	0.20	0.17	0.15	0.17	0.25

4. Discussion

The outstanding feature of the experimental results presented in the preceding sections is the considerable enhancement in the singlet → triplet intersystem crossing by ground state ketone molecules. The observations can be explained by assuming that first- and second-order intersystem crossing processes exist. The second-order path probably occurs via a singlet excimer as indicated in the reaction mechanism





where K, ${}^1\text{K}$ and ${}^3\text{K}$ designate the ground state, the lowest excited singlet state and the triplet state ketone molecules respectively and ${}^1\text{E}$ is the singlet excimer. From a consideration of the possible fate of the excimer, three types of decay routes must be taken into account.

(i) The excimer may dissociate, re-forming the singlet excited and the ground state ketone molecules. This process is shown below to be of importance.

(ii) The major decay path of the singlet excimer molecule is inter-system crossing followed by dissociation of the excimer triplet state. For simplicity, in the reaction scheme, singlet \rightarrow triplet crossing and subsequent dissociation are presented together as process (11a).

(iii) Process (11b) is meant to include fluorescence, radiationless deactivation and various chemical rearrangements of the singlet excimer. However, since the triplet yield was found to be 1.0 within the limits of experimental error at high concentrations, all types of processes included in (11b) are of minor importance and can be neglected in the following discussion.

A steady state treatment applied to the suggested reaction scheme gives the following expressions for the triplet yield and for the quantum yield of type II decomposition:

$${}^3\phi = \frac{{}^1k_{isc}{}^1\tau_0/\rho + [\text{K}]}{1/\rho + [\text{K}]} \quad (15)$$

$$\phi_{II} = \frac{({}^1k_{II}{}^1\tau_0 + {}^1k_{isc}{}^1\tau_0{}^3k_{II}{}^3\tau_0)/\rho + {}^3k_{II}{}^3\tau_0[\text{K}]}{1/\rho + [\text{K}]} \quad (16)$$

where the parameter ρ is given by

$$\rho = {}^1k_e{}^1\tau_0 \frac{{}^e k_{isc}}{{}^e k_{isc} + {}^e k_{-e}} \quad (17)$$

These are of the same form as the empirical function (2) which was found to describe the experimental concentration dependences very well.

Equations (15) and (16) yield for the low and high concentration limiting conditions

$$({}^3\phi)_0 = {}^1k_{isc} {}^1\tau_0 \quad (18a)$$

and

$$({}^3\phi)_\infty = 1 \quad (18b)$$

$$\frac{(\phi_{II})_0 - {}^1k_{II} {}^1\tau_0}{(\phi_{II})_\infty} = {}^1k_{isc} {}^1\tau_0 \quad (19a)$$

and

$$(\phi_{II})_\infty = {}^3k_{II} {}^3\tau_0 \quad (19b)$$

Using ${}^1\tau_0 = 2.3$ ns (derived from time-resolved fluorescence measurements [14]) for the singlet lifetime of 2-pentanone and ${}^3\tau_0 = 0.21$ μ s (determined by sensitized biacetyl phosphorescence measurements in this work) for the triplet lifetime and ${}^1k_{II} {}^1\tau_0 = 0.04$ (obtained from type II quantum yield measurements in the presence of a sufficient quantity of the triplet quencher tributylstannane [7]), the rate coefficients

$${}^1k_{isc} = (2.0 \pm 0.5) \times 10^8 \text{ s}^{-1} \quad (20)$$

for the first-order intersystem crossing to the triplet state and

$${}^3k_{II} = (1.7 \pm 0.4) \times 10^6 \text{ s}^{-1} \quad (21)$$

for the type II reaction from the triplet state are obtained from the limiting low and high concentration values of the triplet yield and the type II quantum yield respectively.

Expressions (15) and (16) can be reformulated by substitution from eqns. (18) and (19):

$${}^3\phi = \frac{({}^3\phi)_0/\rho + [K]}{1/\rho + [K]} \quad (22a)$$

$$\phi_{II} = \frac{(\phi_{II})_0/\rho + (\phi_{II})_\infty [K]}{1/\rho + [K]} \quad (22b)$$

Fitting these functions to our experimental data for the triplet yield and for the type II quantum yields we obtain $1/\rho = 0.09$ mol dm⁻³ and $1/\rho = 0.03$ mol dm⁻³ respectively. (These were the parameters used in the calculation of the theoretical curves indicated in Figs. 1 and 2.) Taking $\rho \approx 16$ dm³ mol⁻¹ from the average and assuming a diffusion-controlled rate for the excimer formation (*i.e.* ${}^1k_e = 2.1 \times 10^{10}$ dm³ mol⁻¹ s⁻¹), we can estimate, on the basis of eqn. (17), the fraction of singlet excimers that cross over to the triplet state. Hence

$$\frac{{}^e k_{isc}}{{}^e k_{isc} + {}^e k_{-e}} \approx 0.3$$

which implies that the rates of intersystem crossing and redissociation of the singlet excimer are comparable. A detailed and more accurate account of the kinetics of excimer formation and removal can be given on the basis of time-correlated fluorescence decay measurements [14].

References

- 1 T. Bérces, The decomposition of aldehydes and ketones, *Compr. Chem. Kinet.*, **5** (1972) 234.
- 2 M. V. Encina and E. A. Lissi, *J. Photochem.*, **6** (1977) 173.
- 3 M. V. Encina and E. A. Lissi, *J. Photochem.*, **8** (1978) 131.
- 4 M. V. Encina and E. A. Lissi, *J. Phys. Chem.*, **84** (1980) 948.
- 5 P. Borrell and J. Sedlar, *J. Chem. Soc. B*, (1970) 1536.
- 6 P. J. Wagner, *Acc. Chem. Res.*, **4** (1971) 168.
- 7 L. Biczók, S. Förgeteg and T. Bérces, *J. Photochem.*, **16** (1981) 267.
- 8 S. Förgeteg and T. Bérces, *Int. J. Chem. Kinet.*, **11** (1979) 239.
- 9 J. Kossanyi, S. Sabbah and P. Chaquin, *Tetrahedron*, **37** (1981) 3307.
- 10 S. Förgeteg, T. Bérces and S. Dóbbé, *Acta Chim. Acad. Sci. Hung.*, **96** (1978) 321.
- 11 K. Sandros, *Acta Chem. Scand.*, **23** (1969) 2815.
- 12 S. L. Murow, *Handbook of Photochemistry*, Dekker, New York, 1973.
- 13 E. B. Abuin, M. V. Encina and E. A. Lissi, *J. Photochem.*, **3** (1974) 143.
- 14 B. László, S. Förgeteg, T. Bérces and F. Márta, *J. Photochem.*, **27** (1984) 49.