

## INTERMOLECULAR PRIMARY PROCESSES OF TRIPLET 2-PENTANONE WITH TRIBUTYL STANNANE AND *n*-BUTYRALDEHYDE

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### Summary

Intermolecular reactions of triplet 2-pentanone with tributyl stannane (TBS) and *n*-butyraldehyde (BA) were studied in iso-octane. Three types of interactions between the triplet ketone (K) and additives TBS and BA were investigated, namely intermolecular hydrogen abstraction, triplet energy transfer and bimolecular deactivation. The overall quenching efficiencies were found to be high and similar for TBS and BA. However, intermolecular hydrogen abstraction is predominant in the K-TBS system, whereas triplet energy transfer prevails in the K-BA system. From the experimental data, rate constants were derived for the intermolecular primary processes of triplet 2-pentanone. Finally, competitive intramolecular and intermolecular hydrogen abstraction reactions of triplet 2-pentanone were studied and a rate constant for type II decomposition was derived.

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### 1. Introduction

The photochemistry of alkyl ketones has been the subject of extensive studies and several features of the photoreactivity of these ketones have been elucidated [1 - 4]. Most studies dealt with the unimolecular reactions of the  $n, \pi^*$  excited states. Comparatively little attention has been devoted to the intermolecular reactions of the excited alkyl ketones. Although hydrogen atom abstraction reactions by excited aliphatic ketones are of considerable theoretical interest [5] and play an important role in our understanding of the excited state reactivity in solutions, work performed along this line can be said to be neither extensive nor systematic. This is particularly true for alkyl ketones other than acetone. In this paper we present experimental data for the intermolecular primary processes (hydrogen abstraction, radiationless deactivation and energy transfer) of triplet 2-pentanone with tributyl stannane (TBS) and *n*-butyraldehyde (BA) and report on the com-

petition between intermolecular and intramolecular hydrogen abstractions of triplet-excited 2-pentanone.

## 2. Experimental procedure

### 2.1. Materials

The iso-octane solvent was obtained from Fluka puriss. grade iso-octane via distillation on a high performance column.

2-Pentanone was purified by preparative gas chromatography on a Carbowax 20M column. The impurity in the purified sample was less than the detection limit of the flame ionization detector.

Tributyl stannane was prepared from tributyl tin chloride by lithium aluminium hydride reduction [6]. It was purified by vacuum distillation and stored *in vacuo*. Commercial puriss. grade *n*-butyraldehyde (Fluka) was purified by sodium bisulphate precipitation [7].

### 2.2. Quantum yield determinations

2-Pentanone dissolved in iso-octane was irradiated at 298 K in the presence and absence of additives (TBS or BA) with a parallel light beam of wavelength  $313 \pm 1.5$  nm. Details of light filtering and intensity measurements have been described previously [7, 8]. Quantum yields for product formation were determined in the photolysis of 2-pentanone without additives using a cylindrical quartz cell equipped with plane parallel windows (optical depth, 5 mm).

Relative product quantum yields were measured in the photolysis of 2-pentanone in the presence of additives (TBS or BA) using a merry-go-round apparatus. These relative values together with the quantum yields of 2-pentanone photolysis (without additive) were used to obtain the quantum yields of product formation in the presence of TBS and BA. 2 cm<sup>3</sup> of the deaerated solutions were irradiated in cylindrical quartz tubes of internal diameter 5 mm. In experiments with TBS additive, the additive was added from a microsyringe to the solution containing the ketone and an internal standard (acetonitrile); then the sample tubes were degassed on a vacuum line and sealed off. In experiments with BA additive, the samples were prepared in a vacuum apparatus: a known amount of BA vapour was frozen onto the degassed solution of ketone plus standard and then the sample tube was sealed off.

Quantum yields for product formation were calculated as the ratio of the rate of formation of the product to the overall rate of light absorption. The overall rate of light absorption was obtained from

$$I_a = 2I_0 \int_0^r [1 - 10^{-\{\epsilon(K)[K] + \epsilon(QH)[QH]\}l}] dx \quad (1)$$

by numerical integration. In eqn. (1),  $I_0$  is the incident light intensity, [K] and [QH] designate the concentrations of the ketone and the additive

respectively and  $\epsilon(K)$  and  $\epsilon(QH)$  denote the molar absorption coefficients of the ketone and the additive respectively. Furthermore,  $r$  ( $= 2.5$  mm) is the radius of the sample tube,  $x$  designates the radial distance measured from the axis of the tube ( $0 \leq x \leq r$ ) and  $l = 2(r^2 - x^2)^{1/2}$  is the optical depth ( $0 \leq l \leq 2r$ ). At 313 nm, light absorption is only due to the ketone in the K-TBS system (*i.e.*  $\epsilon(QE) = 0$ ), whereas both the ketone and the aldehyde absorb in the K-BA system (*i.e.*  $\epsilon(QH) = \epsilon(BA)$ ).

Interpretation of the results obtained in the K-BA system (where two absorbing species occur) requires knowledge of the fraction of light absorbed by the ketone and the aldehyde which we shall designate by  $I(K)$  and  $I(BA)$  respectively. ( $I(K) + I(BA) = 1$ .) Taking into consideration the inner filter effect, it can be shown [9] that for a cuvette characterized by a given constant optical depth the light fraction absorbed by the ketone is

$$I(K) = \frac{\epsilon(K)[K]}{\epsilon(K)[K] + \epsilon(BA)[BA]} \quad (2)$$

For a cylindrical sample tube, where the optical depth varies with  $x$ , the average fraction of light absorbed by the ketone is given by

$$I(K) = \frac{\int_0^r (\epsilon(K)[K] / \{\epsilon(K)[K] + \epsilon(BA)[BA]\}) dx}{\int_0^r dx} \quad (3)$$

where all designations have the meanings already indicated. The fraction  $I(K)$  was evaluated according to eqn. (3) by numerical integration. At the concentrations applied,  $I(K)$  varied from 0.71 to 0.92 in the K-BA system (naturally,  $I(K) = 1$  for K-TBS).

Absorption coefficients required in the application of eqns. (1) and (3) were measured in a 5 mm quartz cell, using the same light beam and reactant concentrations as in the photolysis experiments. This was desirable in order to minimize errors arising from the finite bandwidth (approximately 3 nm) of the excitation light.

### 2.3. Product analysis

Product analysis was made with gas chromatography. The volatile products ethylene, propane, acetaldehyde and acetone were separated on a 3 m Porapak QS column (440 K) and measured against an acetonitrile internal standard. 2-Pentanol and *n*-butanol were measured (using a Carbowax 20M column 2 m long) relative to a cyclohexanone internal standard. (Cyclohexanone was added to the sample after photolysis because of its photochemical activity.)

### 3. Results

The main products of 2-pentanone photolysis in the absence of additives were ethylene and acetone (in equal amounts) as well as propane. The quantum yields for these products were found to depend on the 2-pentanone concentration (Table 1). This indicates either the concentration dependence of the triplet yield or the influence of the media on the fate of radical and biradical intermediates. A detailed study of the observation is in progress.

TABLE 1

Product quantum yields  $\Phi$  of 2-pentanone photolysis in the absence of quenchers

[2-pentanone] (mol dm <sup>-3</sup> )	$\Phi$	
	$CH_3COCH_3$	$C_3H_8$
0.02	0.23	0.043
0.10	0.28	0.051
0.50	0.33	0.058

The type II yields obtained in the photolysis of 2-pentanone alone are similar to the value 0.23 reported by Encina and Lissi [3]. Unfortunately, the 2-pentanone concentration used by these researchers is not given in their paper.

Quenching of acetone formation by TBS and BA additives is shown in Fig. 1. It can be seen that type II product formation from 2-pentanone is

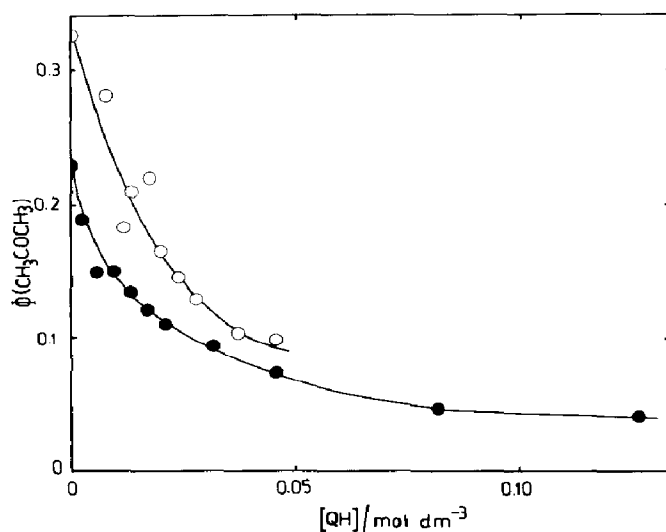


Fig. 1. Quenching of Norrish type II decomposition in the photolysis of 2-pentanone: ●, TBS quencher,  $[K]_0 = 0.02$  mol dm<sup>-3</sup>; ○, BA quencher,  $[K]_0 = 0.5$  mol dm<sup>-3</sup>.

quenched efficiently by TBS to a limiting value of about 0.04 (at TBS concentrations above  $0.10 \text{ mol dm}^{-3}$ ). The unquenchable type II reaction occurs from the short-lived excited singlet state of 2-pentanone. BA is nearly as effective as TBS in quenching the acetone formation. (The BA concentration could not be increased enough to attain total 2-pentanone triplet quenching without causing excessive direct photolysis of BA at the same time.) It is to be noted, however, that at the highest BA concentration applied 30% of the total light absorption is due to BA in spite of more than a tenfold excess of 2-pentanone. Therefore one part of the quenching by BA seen in Fig. 1 is apparent, caused by the screening effect of BA, since the quantum yields presented in the figure were calculated with the overall rate of light absorption.

Both TBS and BA are efficient hydrogen donors. Therefore a significant part of the quenching caused by these compounds may be expected to be of a chemical nature (*i.e.* photoreduction of the ketone to the ketyl radical). Indeed, analysis of the photochemical products formed in the K-TBS system showed significant 2-pentanol formation. No other ketyl radical product (photoreduction product) could be detected in this system. 2-Pentanol quantum yields increased with increasing TBS concentrations to a limiting value of 0.53 which was attained at TBS concentrations of about  $0.1 \text{ mol dm}^{-3}$  (Fig. 2). This limiting quantum yield for 2-pentanol is close to the triplet yield reported for 2-pentanone in solution [10]. This indicates that most (if not all) ketone triplets are photoreduced to 2-pentanol at high TBS concentrations.

Very low 2-pentanol quantum yields were found in the K-BA system. The 2-pentanol yield slightly increased with increasing BA concentrations, but it did not exceed 0.02 at any aldehyde concentration. Thus, chemical quenching (photoreduction) of the excited ketone is not very efficient in

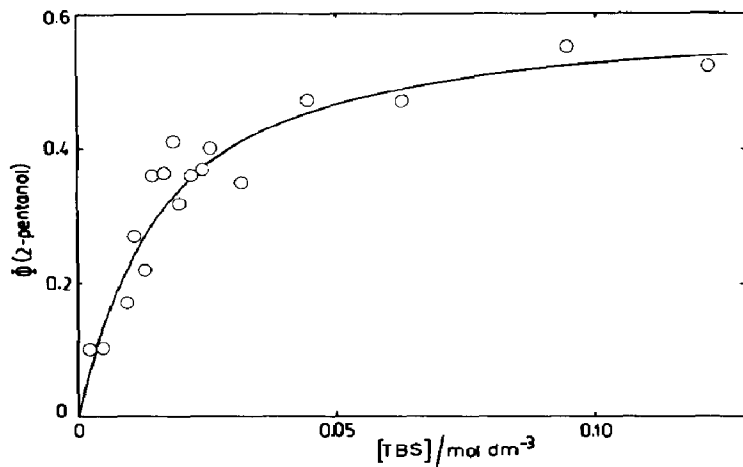


Fig. 2. The dependence of the quantum yield of 2-pentanol formation on TBS concentration ( $[K]_0 = 0.02 \text{ mol dm}^{-3}$ ).

the K-BA system. However, relatively high quantum yields for *n*-butanol and acetaldehyde were obtained. As shown in Fig. 3, the *n*-butanol quantum yields were two to four times higher than the 2-pentanol yields at  $[BA] = 0.01 - 0.05 \text{ mol dm}^{-3}$  in spite of fiftyfold to tenfold excesses of 2-pentanone in the reaction mixture. These results strongly suggest that most of the *n*-butanol and acetaldehyde is formed via BA decomposition sensitized by energy transfer from the excited 2-pentanone (physical quenching of the ketone).

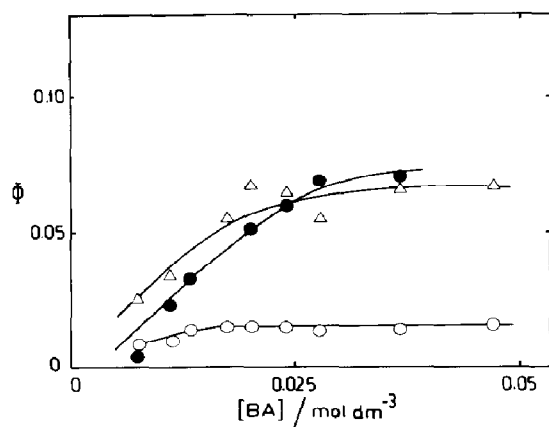
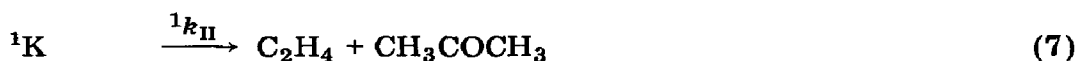


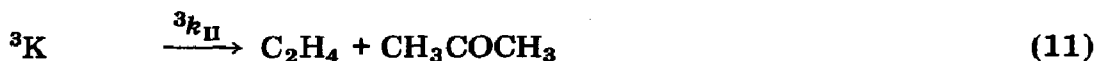
Fig. 3. The dependences of the quantum yields of 2-pentanol (○), *n*-butanol (●) and acetaldehyde (△) formation on BA concentration ( $[K]_0 = 0.5 \text{ mol dm}^{-3}$ ).

## 4. Discussion

### 4.1. Reaction scheme

Rate constants for the intermolecular reactions of excited 2-pentanone with TBS and BA can be obtained from the quantum yields presented earlier by considering the kinetics of the excited state processes involved. The important excited state processes taking place in the systems investigated can be summarized as given in the following scheme:





In the scheme K,  ${}^1\text{K}$  and  ${}^3\text{K}$  are the ground state, the first excited singlet state and the triplet state respectively of 2-pentanone and QH designates the quencher (either TBS or BA). Reactions (4) - (11) are well-documented primary processes of aliphatic ketones bearing  $\gamma$  hydrogen atoms [3], and reactions (12) - (14) are bimolecular interactions between the triplet ketone and the quencher QH. In this scheme reactions (7) and (11) represent processes leading to Norrish type II products (and not the steps for type II biradical formation). Chemical deactivation via type II biradical processes and physical deactivation are lumped into processes (5) and (9) respectively. Furthermore, reaction (14) denotes the formation of photoreduction products, and chemical quenching via disproportionation of the radical pair  $\dot{\text{Q}}$  and  $\text{C}_3\text{H}_7\dot{\text{C}}(\text{CH}_3)\text{OH}$  is lumped into bimolecular deactivation process (12).

Reaction (14) is a chemical quenching process required to explain the formation of 2-pentanol observed in the presence of both quenchers. As shown by the results presented in Section 3, chemical quenching (reaction (14)) is the predominant interaction between  ${}^3\text{K}$  and QH if QH is TBS, whereas reaction (14) is of little importance if QH is BA.

Energy transfer from triplet acetone to ground state BA was found to occur at a fairly high rate [11], and the same may be expected for energy transfer from triplet 2-pentanone to BA (reaction (13)). Deactivation of triplet 2-pentanone by BA (reaction (12)) has also to be considered. This may occur via physical and chemical routes; the chemical route is the disproportionation of the radical pair formed in the photoreduction of the triplet state by QH. Energy transfer (reaction (13)) and deactivation (reaction (12)), which are predominant in the K-BA system, are of little importance in the interaction between  ${}^3\text{K}$  and TBS.

In accordance with the experimental results presented in Fig. 1, quenching of singlet 2-pentanone by QH has not been taken into account in this scheme. Kinetic data on analogous reactions support the conclusion that quenching of the singlet ketone by BA or TBS is unimportant at the quencher concentrations used in this study: quenching of the excited singlet aliphatic aldehydes by ground state aldehydes was found to occur with rate constants of about  $10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  [12, 13]. If we accept this value for the quenching rate constant of singlet 2-pentanone by BA and if we use  ${}^1\tau(\text{K}) = 2 \times 10^{-9} \text{ s}$  for the lifetime of singlet 2-pentanone [10, 14], we estimate that less than

10% of the singlet ketone molecules are quenched by the aldehyde at  $[BA] = 0.05 \text{ mol dm}^{-3}$ . However, if we use the highest rate constant (*i.e.*  $5 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) reported for the quenching of singlet alkanones by TBS [15], it can be shown that at the highest TBS concentrations used in this study the singlet lifetime of the ketone could be shortened by 12% at the most.

#### 4.2. Rate constants

The sum of the rate constants for the intermolecular primary processes of the triplet ketone can be obtained from the Stern–Volmer-type plot of acetone formation.

The relationship

$$\frac{\phi_{II}^0 - {}^1\phi_{II}^0}{\phi_{II}/I(K) - {}^1\phi_{II}^0} = 1 + ({}^3k_q + {}^3k_{tr} + {}^3k_r)^3 \tau_0(K)[QH] \quad (15)$$

is obtained from the suggested reaction scheme by the usual steady state treatment. In this equation  ${}^1\phi_{II}^0$  and  $\phi_{II}^0$  are the quantum yields for acetone formation in the absence of quencher from the singlet and from both (singlet plus triplet) excited states respectively and  $\phi_{II}$  designates the overall quantum yield at quencher concentration  $[QH]$ . Acetone quantum yields measured at various quencher concentrations are plotted according to eqn. (15) in Fig. 4. The slopes of the straight lines give values for  $({}^3k_q + {}^3k_{tr} + {}^3k_r)^3 \tau_0(K)$  of  $63 \pm 7 \text{ dm}^3 \text{ mol}^{-1}$  and  $35 \pm 9 \text{ dm}^3 \text{ mol}^{-1}$  for TBS and BA quenchers respectively. Using  ${}^3\tau_0(K) = 2.5 \times 10^{-7} \text{ s}$  [16] for the lifetime of the triplet ketone, we obtain  ${}^3k_q + {}^3k_{tr} + {}^3k_r = (2.8 \pm 0.2) \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $(1.4 \pm 0.4) \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for systems K–TBS and K–BA respectively.

Kinetic data for similar quenching reactions are very scarce in the literature. The rate constant for quenching of triplet acetone by TBS is  $2 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  (data from Wagner [17] recalculated by Previtali and Scaiano [18]). A value of  $1.4 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  can be calculated for

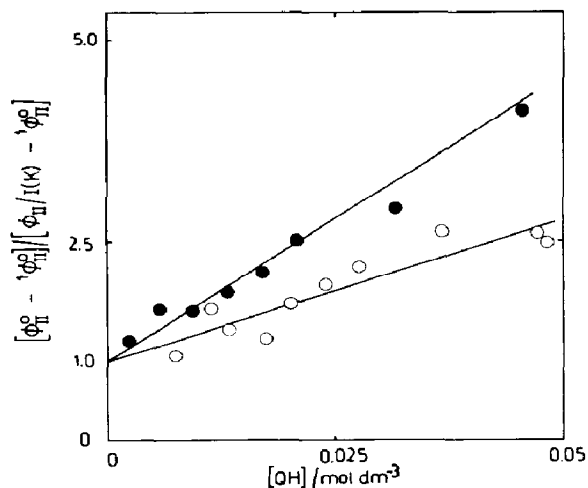


Fig. 4. Stern–Volmer plots for quenching of acetone formation by TBS (●) and BA (○).



the rate constant of triplet acetone quenching by BA from the data of Rebbert and Ausloos [11] if  ${}^3\tau_0 = 2 \times 10^{-4}$  s is used for the triplet lifetime of acetone. The same rate constant (*i.e.*  $1.4 \times 10^8$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup>) was obtained for the self-quenching of BA [19]. Our quenching rate constants are in good agreement with all these reported values.

It would be desirable to decompose the sum of the rate constants of intermolecular primary processes of triplet 2-pentanone into contributions from reactions (12) - (14). This can be done by studying the formation of the photoreduction products 2-pentanol and *n*-butanol. According to the reaction scheme, the dependence of the quantum yield of 2-pentanol formation on the additive concentration may be given by

$$\frac{I(K)}{\Phi(2\text{-pentanol})} = \frac{{}^3k_q + {}^3k_{tr} + {}^3k_r}{{}^3k_r {}^3\phi(K)} + \frac{1}{{}^3k_r {}^3\phi(K) {}^3\tau_0(K)} \frac{1}{[QH]} \quad (16)$$

where  ${}^3\phi(K)$  and  ${}^3\tau_0(K)$  are the triplet yield and the triplet lifetime respectively of the ketone in the absence of quenchers. Data are plotted according to eqn. (16) in Fig. 5. The rate constant  ${}^3k_r$  for chemical quenching of the triplet ketone can be derived both from the slope and from the intercept of the straight line by means of the relations  ${}^3\phi(K) = 0.63$  [10] and  ${}^3\tau_0(K) = 2.5 \times 10^{-7}$  s [16]. Thus we obtain  ${}^3k_r = (2.4 \pm 0.4) \times 10^8$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> and  $(7.0 \pm 2.5) \times 10^6$  dm<sup>3</sup> mol<sup>-1</sup> s<sup>-1</sup> for the systems K-TBS and K-BA respectively.

Triplet energy transfer from 2-pentanone to BA (reaction (13) in the system K-BA) yields triplet excited BA molecules which disappear from the system by reactions analogous to reactions (9) - (14). The fraction of triplet BA molecules that react with ground state BA to give *n*-butanol may be expressed by  $\Phi^0(\text{butanol})/{}^3\phi(\text{BA})$ , where  ${}^3\phi(\text{BA})$  and  $\Phi^0(\text{butanol})$  are the triplet yield and the quantum yield of butanol formation respectively in the

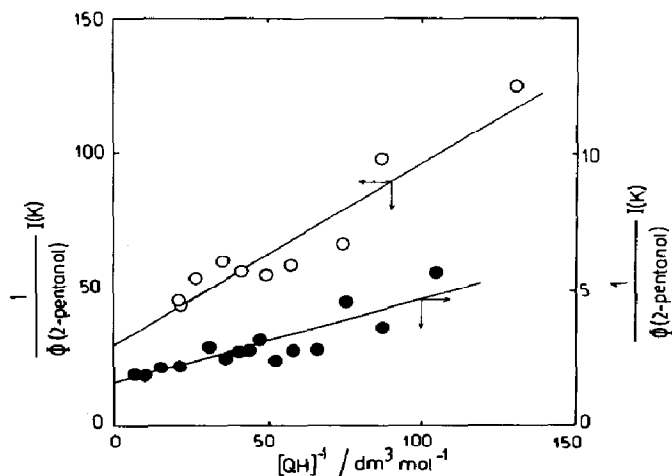


Fig. 5. The dependence of 2-pentanol yields on the TBS (●) and BA (○) concentrations, plotted according to eqn. (16).

direct photolysis of BA. The ratio  $\Phi^0(\text{butanol})/{}^3\phi(\text{BA})$  is known as a function of [BA] from the detailed study of Förstner and Bérces (see ref. 19, Figs. 1 and 3). With this ratio the rate of sensitized butanol formation in the K-BA system may be expressed by

$${}^3k_{\text{tr}}[{}^3\text{K}][\text{BA}] \frac{\Phi^0(\text{butanol})}{{}^3\phi(\text{BA})} \quad (17)$$

In contrast, the rate of 2-pentanol formation in the system K-BA is given by

$${}^3k_{\text{r}}[{}^3\text{K}][\text{BA}] \quad (18)$$

Hence the ratio of the quantum yields for sensitized butanol formation and 2-pentanol formation is

$$\frac{\Phi(\text{butanol}) - I(\text{BA})\Phi^0(\text{butanol})}{\Phi(2\text{-pentanol})} = \frac{{}^3k_{\text{tr}}}{{}^3k_{\text{r}}} \frac{\Phi^0(\text{butanol})}{{}^3\phi(\text{BA})} \quad (19)$$

where the second term in the numerator of the left-hand side of the equation corrects for butanol formation due to light absorption by BA (direct photolysis). Using  ${}^3\phi(\text{BA}) = 0.72$  for the triplet yield in the direct photolysis of BA [20], we obtain  ${}^3k_{\text{tr}}/{}^3k_{\text{r}} = 23 \pm 4$  from eqn. (19). Hence, with the value derived earlier for  ${}^3k_{\text{r}}$ , the rate constant for triplet energy transfer from 2-pentanone to BA is  ${}^3k_{\text{tr}} = (1.6 \pm 0.6) \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ .

Rate constants obtained for intermolecular primary processes of triplet 2-pentanone with TBS and BA are summarized in Table 2. As seen from the data, quenching of triplet 2-pentanone by TBS is very fast and quenching is of a chemical nature (intermolecular hydrogen abstraction). The rate of chemical quenching is similar to the overall quenching rate; thus triplet energy transfer and bimolecular deactivation are unimportant in the K-TBS system ( ${}^3k_{\text{tr}} + {}^3k_{\text{q}} \leq 4 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ).

BA also quenches 2-pentanone triplets with high efficiency. However, triplet energy transfer prevails over chemical quenching in the K-BA system. Intermolecular hydrogen transfer accounts for about 5% of the quenching

TABLE 2

Rate constants for intermolecular primary processes of triplet 2-pentanone with TBS and BA

Quencher	Rate constant	Value ( $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ )
TBS	${}^3k_{\text{r}} + {}^3k_{\text{tr}} + {}^3k_{\text{q}}$	$(2.8 \pm 0.2) \times 10^8$
	${}^3k_{\text{r}}$	$(2.4 \pm 0.4) \times 10^8$
	${}^3k_{\text{tr}} + {}^3k_{\text{q}}$	Small
BA	${}^3k_{\text{r}} + {}^3k_{\text{tr}} + {}^3k_{\text{q}}$	$(1.4 \pm 0.4) \times 10^8$
	${}^3k_{\text{r}}$	$(7.0 \pm 2.5) \times 10^6$
	${}^3k_{\text{tr}}$	$(1.6 \pm 0.6) \times 10^8$
	${}^3k_{\text{q}}$	Small

observed. Bimolecular deactivation is negligible ( ${}^3k_r + {}^3k_{tr}$  is in agreement with  ${}^3k_r + {}^3k_{tr} + {}^3k_q$  within the limits of experimental error).

Unimolecular reactions of the triplet ketone compete with the intermolecular reactions as indicated by the formation of type I and type II decomposition products. Considering the kinetics of this competition we can derive the following relationship from the reaction scheme:

$$\frac{\phi_{II} - I(K)^1 \phi_{II}^0}{\Phi(2\text{-pentanol})} = \frac{{}^3k_{II}}{{}^3k_r} \frac{1}{[QH]} \quad (20)$$

Here the meaning of the symbols is the same as given earlier. Experimental data are plotted according to eqn. (20) in Fig. 6. From the slopes we obtain  ${}^3k_{II}/{}^3k_r = 0.0065 \pm 0.0007 \text{ mol dm}^{-3}$  and  ${}^3k_{II}/{}^3k_r = 0.22 \pm 0.03 \text{ mol dm}^{-3}$  for the systems K-TBS and K-BA respectively. Using these ratios and the rate constants  ${}^3k_r$  for intermolecular hydrogen abstraction given in Table 2,  ${}^3k_{II} = (1.56 \pm 0.26) \times 10^6 \text{ s}^{-1}$  and  ${}^3k_{II} = (1.54 \pm 0.55) \times 10^6 \text{ s}^{-1}$  are finally obtained from the data of experiments carried out in the presence of additives TBS and BA respectively.

Our studies yield  ${}^3k_{II} = (1.6 \pm 0.3) \times 10^6 \text{ s}^{-1}$  for the rate constant of the Norrish type II decomposition product formation from triplet 2-pentanone in iso-octane. Encina and Lissi [2, 3] reported the value  $3.9 \times 10^6 \text{ s}^{-1}$  for the rate constant of the Norrish type II biradical formation in *n*-hexane. Taking into account these results, we can consider the fate of the 1,4-biradical intermediate formed from the triplet ketone molecule by intramolecular hydrogen atom transfer. Comparison of the two rate constants suggests that about 40% of the biradicals decompose giving the type II products and about 60% revert to the ground state (or cyclize to methyl cyclobutanol). Similar results were obtained by Abuin *et al.* [16], whereas somewhat less efficient decomposition was reported by Encina and Lissi [2, 3].

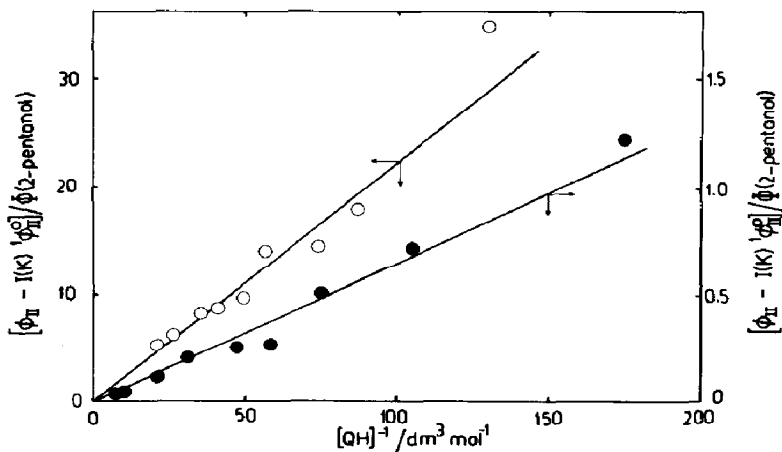


Fig. 6. The ratio of type II yields and 2-pentanol yields as functions of  $[TBS]^{-1}$  (●) and  $[BA]^{-1}$  (○).

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