

TYPE I—TYPE II COMPETITION IN THE PHOTOLYSIS OF ALIPHATIC KETONES

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Summary

The photochemistry of several aliphatic ketones which decompose simultaneously by α bond cleavage and γ hydrogen transfer has been investigated under different experimental conditions. The results obtained show that the rate of α bond cleavage is almost completely determined by the α substituent, and that the rate of γ hydrogen transfer is determined by the substituent at the γ carbon. Both reaction rates are then determined by a single parameter and can be transferred from one ketone to another, thus allowing a quantitative prediction of the photochemical behaviour of complex ketones from the results obtained for simpler systems. Both k_I and k_{II} are higher in acetonitrile than in n-hexane, showing that there must be some amount of charge separation at both critical configurations. The Arrhenius parameters obtained are compatible with this interpretation.

Introduction

Most kinetic data on the primary photoprocesses of aliphatic ketones have been obtained by employing ketones which decompose mainly by a single process, either type I photocleavage [1, 2, 3] or type II intramolecular hydrogen transfer [4, 5]. Nevertheless, both photoprocesses are competitive in the triplet state in most ketones [6 - 11], and it is interesting to know whether or not the photochemical behaviour of these compounds can be predicted from results obtained in simpler systems. Some of the results obtained seem to contradict this simple picture. For example, Carlsson *et al.* [12] obtained a completely different type I to type II ratio for 4-methyl-2-pentanone and 2,6-dimethyl-4-heptanone in decahydronaphthalene. Similarly, results obtained by Anpo and Kubokawa [11] in the gas phase photolysis of 3-methyl-2-pentanone show a type I to type II relationship that is contrary to that expected from the results obtained in the photolysis of 2-pentanone [5] and isopropyl ketones [2].

Systematic studies of the photochemistry of ketones which decompose simultaneously by type I and type II photoprocesses have been carried out

employing cyclic [13] and alkyl phenyl ketones [14], but have not been made for aliphatic ketones. In this communication we present experimental results which allow the evaluation of the rate constants for type I and type II photoreactions for a series of ketones which decompose simultaneously by both processes, and we discuss the effects of solvent and temperature upon the rates of both processes.

Experimental

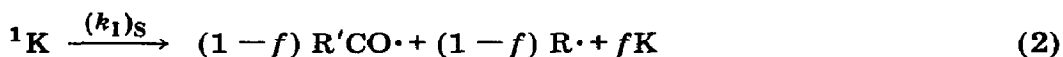
The experimental method employed was similar to that previously described [8]. The quantum yields of the type I photoproducts were measured in the presence of ethanethiol in order quantitatively to convert the free radicals produced into the corresponding hydrocarbons. Secondary reactions of the sulphur-centred free radicals were minimized by the addition of small amounts of cyclohexene. At the concentrations employed, neither the thiol [15] nor the cyclohexene [16] interfere with the primary photoprocesses.

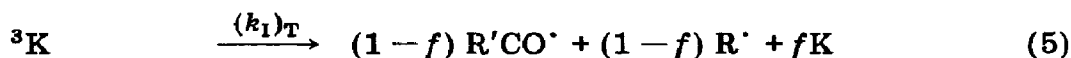
Decahydronaphthalene (Aldrich, high purity) was distilled under reduced pressure. The product obtained was completely transparent to 3130 Å radiation.

For those ketones in which type I photocleavage is the main reaction, *N,N*-diethylhydroxylamine was employed as a quencher to obtain the lifetime of the excited triplets. The value of the quenching rate constant was assumed to be $10^9 \text{ M}^{-1} \text{ s}^{-1}$, the same as that obtained for the quenching of 4-methyl-2-pentanone triplets [17]. *cis*-1,3-Pentadiene was employed as a quencher in those systems where the photoelimination products could be accurately measured. The values of the quenching rate constants, as well as their dependence upon solvent viscosity and temperature, were estimated as before [8, 16].

Results and discussion

In the present work the triplet quantum yield ϕ_T , the photoelimination quantum yield ϕ_{II} , the photoelimination quantum yield $(\phi_{II})_s$ from the singlet state, the quantum yield ϕ_{RH} of saturated hydrocarbons produced by type I cleavage and the slope $k_q \tau_T$ of the Stern-Volmer plot for the triplet quenching were measured for several ketones under a variety of experimental conditions. The results obtained are shown in Table 1 and will be interpreted in terms of the following reaction scheme:





where SH is a hydrogen donor (either the thiol, the solvent or the diethylhydroxylamine), sol is the solvent, Q is the added quencher and ($\text{R}'\text{CO}\cdot + \text{R}\cdot$) is the radical pair produced by cleavage of the weakest bond in the parent ketone. The factor f takes into account the geminate recombination of the radicals produced by type I photocleavage. The values of f were estimated as before [8] assuming that they are determined only by the temperature and the solvent viscosity [18]. This assumption implies that specific solvent effects upon the amount of cage recombination (*i.e.* owing to solvation of the free radicals in polar solvents [19]) can be disregarded. The validity of this assumption was confirmed by photolysing 3,3-dimethyl-2-butanone in *n*-hexane and acetonitrile at 20 °C. The isobutane quantum yield was the same in both solvents, showing that cage recombination in solvents of similar viscosity is independent of the dielectric constant (which changes from 1.89 to 37.7).

The photocleavage quantum yield will be given by

$$\phi_{\text{I}} = \frac{\phi_{\text{RH}}}{1-f} \quad (10)$$

For symmetrical ketones the value of ϕ_{I} was taken as one-half the value obtained by applying eqn. (10), which assumes that the $\text{RCO}\cdot$ radicals obtained decompose quantitatively. This assumption is supported by the high values of ϕ_{CO} observed, the independence of ϕ_{RH} upon light intensity

TABLE 1

Experimental results

Ketone	ϕ_{T}	ϕ_{II}	$(\phi_{\text{II}})_s$	ϕ_{RH}^a	$k_{\text{q}}\tau_{\text{T}}$
4,4-Dimethyl-2-pentanone	0.71	0.16	0.06	0.007	780
4-Heptanone	0.68	0.11	0.02	0.046	1020
2,6-Dimethyl-4-heptanone	0.64	0.11	0.03	0.028	720
3-Methyl-2-heptanone	0.21	0.11	0.07	0.044	28.4
3-Methyl-2-hexanone	0.21	0.1	0.06	0.039	23.6
2-Methyl-3-octanone	0.3	0.09	0.05	0.098	30.4
3-Methyl-2-pentanone	0.72	0.03	0.03	0.504	12.7 ^b

^a These values were obtained under conditions that assure almost complete hydrogen abstraction by the alkyl radicals.

^b Obtained using diethyl hydroxylamine as quencher.

and the ready decomposition of the RCO· radicals reported at the temperatures employed [20].

If reaction (2) is neglected [2], the proposed reaction scheme leads to the following relationships:

$$1/\tau_T = (k_I)_T + (k_{II})_T + k_S(\text{sol}) \quad (11)$$

$$\frac{(k_I)_T}{(k_{II})_T} = \frac{\phi_I}{\phi_T - \phi_I - \phi_S} \quad (12)$$

$$\beta_S = \frac{(\phi_{II})_S}{1 - \phi_T} \quad (13)$$

$$\beta_T = \frac{(\phi_{II})_T}{\phi_T - \phi_I - \phi_S} \quad (14)$$

$$(k_{II})_S = k_{ISC} \frac{1 - \phi_T}{\phi_T} \quad (15)$$

Results in n-hexane

When n-hexane is employed as solvent, reaction (8) can be considered as a minor process. Neglect of ϕ_S in eqns. (11), (12) and (14) will not introduce significant errors. Yang *et al.* [21] did observe significant photoreduction of 2-heptanone when the photolysis was carried out in hydrocarbons at room temperature, but the shorter lifetimes of the ketones employed in the present work should reduce the importance of photoreduction. Furthermore, when higher temperatures are employed the fact that the photoreduction has a smaller activation energy than k_{II} [22] should further reduce its importance.

The results obtained allow the evaluation of k_I , $(k_{II})_S$, $(k_{II})_T$, β_S and β_T in n-hexane. The data obtained are shown in Tables 2 and 3, together with related values determined previously.

Dependence of β_S and β_T on the structure of the ketone

The data given in Table 2, together with those reported previously [5], allow a general description of the influence of the biradical structure upon its elimination efficiency. The influence of the length of the alkyl chain R (the alkyl group from which the hydrogen abstraction takes place), the size of R' (the alkyl group that does not participate in the hydrogen abstraction) and the effects of β and γ substitution have been discussed previously [5], and it was concluded that β_T is almost independent of the size of R' and of β substitution and that it increases with the chain length of the R group and its γ substituent. Nevertheless, the more extensive set of data obtained in the present work shows that β_T decreases with the size of the R' group and with β substitution in R. The decrease in β_T with β substitution is similar to that reported for the alkyl phenyl ketones [14]. The dependence of β_T on the size of the R' group has not been observed previously owing to the small

TABLE 2

Values of β_S and β_T in n-hexane at 20 °C

Ketone	β_S	β_T	β_T^a	Ref.
2-Pentanone	0.14	0.26	0.36	23
4-Methyl-2-pentanone	0.14	0.23	0.26	8
4,4-Dimethyl-2-pentanone	0.21	0.14	0.17	This work
4-Heptanone	0.06	0.14	—	This work
2,6-Dimethyl-4-heptanone	0.08	0.13	—	This work
2-Heptanone	0.13	0.36	—	5
2-Hexanone	0.15	0.28	0.33	5
3-Methyl-2-heptanone	0.09	0.27	—	This work
3-Methyl-2-hexanone	0.08	0.26	0.17	This work
2-Methyl-3-octanone	0.07	0.25	—	This work
3-Methyl-2-pentanone	0.11	—	0.28	This work

^a Butyrophenone derivatives with the same substitution (data from ref. 14).

TABLE 3

Values of $(k_I)_T$, $(k_{II})_T$ and $(k_{II})_S$ in n-hexane at 20 °C

Ketone	$(k_I)_T^a$	$(k_{II})_T^b$	$(k_{II})_S^{b,c}$
2-Pentanone	0.17	1.3	18
4-Heptanone	0.23	1.4	31
4-Methyl-2-pentanone ^d	0.10	1.3	18
2,6-Dimethyl-4-heptanone	0.11	1.1	20
4,4-Dimethyl-2-pentanone	0.18	1.3	18
2-Heptanone ^e	—	110	420
2-Methyl-3-pentanone ^f	144	—	—
3-Methyl-2-heptanone	115	135	660
2-Methyl-3-octanone	170	100	410
3-Methyl-2-pentanone	158	—	32
3-Methyl-2-hexanone	113	130	660

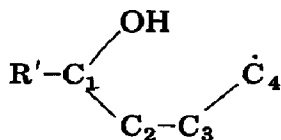
^a Per R'CO-R bond in units of 10^6 s^{-1} .^b Per γ hydrogen in units of 10^6 s^{-1} .^c Obtained assuming that k_{ISC} is determined only by the α substituent [24].^d Ref. 8.^e Ref. 5.^f Ref. 2.

range of R' considered [5]. Nevertheless, this dependence can explain the low ϕ_{II} values observed by Guillet and Somersall [25] in the symmetrical ketones. The reason for this dependence will be discussed after an analysis of the factors controlling β_S .

The data of Table 2 show a decrease in β_T with α substitution. A similar dependence has been reported for alkyl aryl ketones [14] and has been explained in terms of the difficulty in reaching the conformation of maximum overlap for the photoelimination.

In all the ketones investigated (except 4,4-dimethyl-2-pentanone) β_S is considerably smaller than β_T . This effect can be explained either by a concerted internal conversion from the singlet, or by a fast back reaction from the singlet biradical prior to its geometrical randomization [4]. The result obtained employing 4,4-dimethyl-2-pentanone seems anomalous and cannot easily be rationalized in terms of these arguments.

β_S decreases with the size of R' and the substitution at the α carbon atom. This last dependence can be explained by a decreased rate of rotation around the C_1-C_2 bond with substitution at C_2 [26]



since this rotation is needed to obtain a conformation allowing maximum overlap in the elimination. Furthermore, steric hindrance can also disfavour the elimination process [14]. The decrease in β_S with the size of the R' group can also be associated with the larger reduced mass of the rotor around the C_2-C_2 bond. This decreased rate would increase the back reaction from the initial conformation. In contrast, the reactions from the triplet 1,4-biradical are not considered to be rotationally controlled*, and the decrease in β_T with the size of the R' group would indicate that there are other factors acting against elimination from the biradical. One likely explanation could be that the presence of a bulky R' reduces the space in which C_4 can move, "pushing" this carbon towards the $O-H$. Similarly, a bulky R' could orientate the $O-H$ bond in the opposite direction, placing the H atom nearer the C_4 carbon atom.

Dependence of k_I and k_{II} on the structure of the ketone

The data of Table 3 show that the values of $(k_I)_T$ and k_{II} are almost completely determined by α and γ substitution respectively. The anomalous behaviour observed in the gas phase photolysis of 3-methyl-2-pentanone by Anpo and Kubokawa [11] (where the ratio of type II to type I processes was considerably higher than unity) is probably due to decomposition from the hot singlet [23].

The data of Table 3 also indicate that the competition between α cleavage and γ hydrogen transfer does not appreciably modify the rate of either primary process. This result, which is similar to that obtained employing phenyl ketones [14], indicates that both reaction paths are independent and there is no depletion of the reactive species. We can conclude that, at least in the systems investigated, type I cleavage is a primary process competitive with the type II process and not a secondary reaction of the 1,4-biradical as suggested for 2-pentanone in the gas phase [27].

*The lifetime of the triplet biradical is determined by the internal rotation S of the singlet biradical produced after the spin flip.

The results obtained for k_{II} in the present and previous work can be summarized as

$$(k_{II})_S \text{ (primary } \gamma \text{ hydrogen)} = (23 \pm 3) \times 10^6 \text{ s}^{-1}$$

$$(k_{II})_T \text{ (primary } \gamma \text{ hydrogen)} = (1.3 \pm 0.1) \times 10^6 \text{ s}^{-1}$$

$$(k_{II})_S \text{ (secondary } \gamma \text{ hydrogen)} = (4.6 \pm 0.6) \times 10^8 \text{ s}^{-1}$$

$$(k_{II})_T \text{ (secondary } \gamma \text{ hydrogen)} = (1.0 \pm 0.1) \times 10^8 \text{ s}^{-1}$$

for six compounds bearing primary γ hydrogens, and eight compounds bearing secondary γ hydrogens (the values are given per γ hydrogen and the limits are the standard deviations). This insensitivity of k_{II} to ketone structural features other than the number and type of γ hydrogens allows an accurate prediction of the rate constant of the intramolecular hydrogen transfer in any alkyl ketone.

The results obtained for k_I show that, for a given substituent at the α carbon atom, the values of k_I differ by less than a factor of 2 in all the cases considered. The data obtained can be summarized as

$$(k_I)_T (R'-CO-C(H)_2R) = (0.16 \pm 0.02) \times 10^6 \text{ s}^{-1}$$

and

$$(k_I)_T (R'-CO-CHR_2) = (1.4 \pm 0.2) \times 10^8 \text{ s}^{-1}$$

A similar independence of secondary structural features has been reported previously for k_I for ketones decomposing only by bond cleavage in the gas phase [3].

Table 4 shows a comparison between the type I and type II rate constants from the triplet states for several ketones in hydrocarbon solvents at room temperature.

TABLE 4

Values of $(k_I)_T$ and $(k_{II})_T$ for different ketones

	Type of ketone		
	Aliphatic	Aromatic ^a	Cyclohexanone derivative ^b
Bond cleaved			
-CO-CH ₂ R	1.5×10^5	—	$5 \times 10^5 - 5 \times 10^6$
-CO-CHR ₂	1.4×10^8	—	2.5×10^8
-CO-CR ₃	8×10^9 ^c	1×10^8	—
γ Hydrogen abstracted			
Primary	1.3×10^6	2.5×10^6	2.3×10^7
Secondary	1×10^8	0.7×10^8	2.5×10^8
Tertiary	1×10^9	4.5×10^8	8×10^8

^aRef. 14.

^bRef. 13.

^cRef. 29.

Since there are no published values of the Arrhenius parameters for type I photocleavage of aromatic and cyclic ketones, it cannot be determined whether the fact that, for a given amount of α substitution,

$$k_{\text{cyclic}} > k_{\text{aliphatic}} > k_{\text{aromatic}}$$

is due to a difference in the activation energy or in the pre-exponential factor. The fact that aromatic ketones react more slowly than aliphatic ketones has been attributed by Lewis and Hillard [14] to the lower exothermicity of their reactions. This explanation implies that the differences are mainly due to differences in activation energies. Since in the cyclohexanones there are approximately 3.4 kcal of ring strain [29] which are released when the α bond is broken, an energy effect can also be invoked to explain the higher reactivity of these ketones*. Nevertheless, it has to be considered that in the cyclohexanones the activation entropy can also be markedly larger than for the acyclic ketones.

The rate constants for the type II reactions are similar for the three kinds of ketones considered in the present discussion. The only anomalous value is that derived from the data of Dalton *et al.* [13] for ethylcyclohexanone, but it has to be considered that in this ketone the type II reaction is a very minor process and the assumptions involved in the estimation of k_{II} are rather gross. Furthermore, both from considerations of the activation entropies and the release of ring strain, a higher type II reaction rate can be expected in the cyclic ketones than in the aliphatic ketones.

The similarity between the values of k_{II} in aromatic and aliphatic ketones is contrary to semi-empirical estimates carried out by the BEBO method [30], but is analogous to that observed for the intermolecular photoreduction of ketones [31]. The arguments given in the analysis of these data by Steel *et al.* [31] can also be applied to the intramolecular transfer.

Solvent dependence of β_{S} and β_{T}

Decahydronaphthalene was employed as a solvent by Carlsson *et al.* [12] in a study of the photochemical behaviour of 2,4-dimethyl-4-heptanone and 4-methyl-2-pentanone. The results obtained were interpreted disregarding quenching of the excited triplets by the solvent. The results obtained in the present work employing n-hexane and decahydronaphthalene (DHN) are given in Table 5. These data show that for all the ketones bearing primary γ hydrogens whose triplet lifetimes are longer than 5×10^{-8} s, ϕ_{I} and ϕ_{II} are smaller in DHN than in n-hexane. However, ϕ_{II} is identical in both solvents for 2-heptanone, a ketone with a considerably shorter triplet lifetime. These results indicate that in the ketones bearing primary γ hydrogens there is considerable triplet quenching by DHN. This conclusion is quite reasonable when the behaviour of DHN is compared with that observed

*This argument assumes that there is strain in the excited state. Since n states are bent, this strain could be considerably smaller than that of the ground state molecule.

TABLE 5

Experimental results obtained in DHN at 70 °C

Ketone	Solvent	ϕ_I	ϕ_{II}
2-Pentanone	n-Hexane	0.11	0.23
	DHN	0.04	0.1
4-Methyl-2-pentanone	n-Hexane	0.04	0.21
	DHN	0.02	0.10
	DHN ^a	0.01	0.10
2,6-Dimethyl-4-heptanone	n-Hexane	0.04	0.12
	DHN	0.023	0.06
	DHN ^a	0.5	0.2
4-Heptanone	n-Hexane	0.13	
	DHN	0.08	
2-Heptanone	n-Hexane		0.2
	DHN		0.2

^aData of ref. 12 at 30 °C uncorrected for cage recombination.

employing cyclohexane as the solvent [22]. When the contribution of reaction (8) is taken into account, DHN behaves as a normal solvent (*i.e.* the relationship ϕ_I/ϕ_{II} is similar to that observed employing n-hexane as solvent, and is determined only by the number of γ hydrogens and CO-R bonds). The only anomalous result is that obtained in the photolysis of 2,6-dimethyl-4-heptanone at 30 °C [12]. The reason for the high ϕ_I/ϕ_{II} value obtained is not clear at the present time.

Reaction (8) can be disregarded in eqns. (11) - (15) when tert-butanol, acetonitrile or ethyl acetate are employed as solvents [32], allowing the estimation of β_S , β_T , k_I and k_{II} . The data obtained are shown in Tables 6 and 7.

It is generally recognized that the behaviour of the singlet biradical is solvent independent [33]. This conclusion is based on the fact that $(\phi_{II})_S$ does not change with the solvent and assumes that the triplet quantum yield is solvent independent. We have measured ϕ_T for 4-methyl-2-pentanone in n-hexane and acetonitrile, and the results obtained confirm the near indepen-

TABLE 6

Dependence of β_S and β_T on the solvent in the photolysis of 4-methyl-2-pentanone

Solvent	Temperature (°C)	β_S	β_T
n-Hexane	20	0.14	0.23
Acetonitrile	20	0.17	0.39
n-Hexane	70	0.14	0.26
Ethyl acetate	70	0.14	0.27
tert-Butanol	70	0.12	0.34
Acetonitrile	70	0.15	0.31

TABLE 7

Kinetic data for 4-methyl-2-pentanone in different solvents

Solvent	Dielectric constant	k_{II}/k_I^a	k_{16}/k_{17}^b	k_I^c
n-Hexane	1.89	13		5.2
Benzene	2.28	13	7.6	
Ethyl acetate	6.02	11.3		
Tert-Butanol	10.9	9		3.3
Acetonitrile	37.7	9	2.3	14
Gas phase		2.5 ^d	150	5 ^e

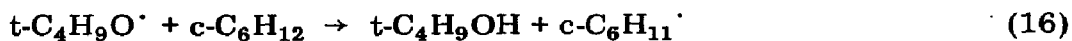
^aData at 70 °C.^bData at 70 °C from ref. 7.^cData at 70 °C.^dFrom data obtained in the photolysis of 2-pentanone at high pressure at 58 °C [6].^e2-Butanone value from ref. 3.

dence of the triplet quantum yield on the solvent dielectric constant. The values given in Table 6 corroborate the insensitivity of the singlet biradical to the characteristics of the solvent. The slightly lower value found for β_S in tert-butanol is due either to the experimental error or to the high viscosity of this solvent [34]. In contrast, the values of β_T consistently show a moderate increase when the polarity of the solvent increases. This dependence is smaller than that observed for alkyl aryl ketones [35], and decreases when the temperature increases. This temperature dependence is in agreement with the explanation put forward by Wagner *et al.* [36] to account for the decrease in β_T with solvent polarity since the formation of complexes between the biradical and the solvent should become less important at higher temperatures.

Solvent dependence of k_I and k_{II}

The results of Table 7 show that there is a small decrease in $(k_{II}/k_I)_T$ with the dielectric constant of the solvent. A similar dependence was reported by Anpo and Kubokawa [10] for the ratio of type I to type II, but in this study only the total change in product distribution was measured.

The dependence of k_{II}/k_I on the solvent can be compared with that observed in the competition between



and



since these reactions have frequently been considered as models for the photoreactions of $n\pi^*$ excited states [33]. The data of Table 7 show that k_{II}/k_I is smaller in polar solvents. A similar dependence on the solvent polarity has been reported for k_{16}/k_{17} . This dependence has been explained in terms of a difference in the degree of solvation at both transition states

[37]. A similar argument can explain the small differences observed in the present work. Furthermore, the fact that both k_I and k_{II} are larger in acetonitrile than in n-hexane would indicate that there must be a moderate amount of charge separation at both transition states. The Arrhenius parameters obtained for the reaction in n-hexane and acetonitrile (which are shown in Table 8) also support this interpretation since they show that in the polar solvent there is a decrease in both E and A . It is interesting to note that the moderate effect of the solvent found in the present work seems to be contrary to the conclusion reached by Lewis *et al.* [38] that charge separation at the critical configuration is one of the more important factors in determining the rate of the type I photocleavage.

TABLE 8

Arrhenius parameters for 4-methyl-2-pentanone reactions

Solvent	$\log A_I$	E_I (kcal mol ⁻¹)	$\log A_{II}$	E_{II} (kcal mol ⁻¹)
n-Hexane	16.0	14.4	12.8	7.9
Acetonitrile	15.5	13.1	12.2	6.5

The results obtained in *tert*-butanol show that in this solvent both k_I and k_{II} are smaller than in aprotic solvents. Although the measurements in *tert*-butanol involve a considerable uncertainty, they are supported by similar results obtained in the photolysis of valerophenone [35] and can be explained by a stabilization of the $n\pi^*$ triplet similar to that proposed for the *tert*-butoxy radicals in the presence of acetic acid [37].

In the preceding discussion it was assumed that both type I and type II reactions could be treated by transition state theory implying that they occur, at least as far as the critical configuration, on a single potential surface [2, 4, 39]. Our analysis of the type II reaction is therefore different to that proposed by Formosinho [40], who described the reaction using the tunnel effect theory of radiationless transitions. We consider that the use of transition state theory is supported by the high A factors obtained in this and previous work for these reactions [8].

Summarizing remarks

The results obtained in the present work, as well as the previously published data, indicate that each significant process is almost exclusively determined by a single structural factor: k_I and k_{ISC} by the α substituent [2, 24], k_{II} by the γ substituent [4, 5, 41] and k_Q by the solvent employed [16]. It is therefore possible to predict the photochemical behaviour of any aliphatic ketone in different solvents at room temperature. Furthermore, since the Arrhenius parameters and the influence of several solvents upon k_I

and k_{II} have been evaluated, we are now able to predict, at least approximately, the photochemical behaviour of aliphatic ketones over a wide range of experimental conditions. Since the values of β are fairly insensitive to temperature [5], solvent and structural changes in the ketone and most of these effects can be evaluated from the available data, the quantum yields of the type II photoproducts can also be predicted with a fair degree of accuracy over a wide range of conditions.

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