PHOTOCHEMISTRY OF ALKYL KETONES BEARING γ-HYDROGENS

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Summary

The Arrhenius parameters for the intramolecular hydrogen abstraction from the excited triplet state have been measured for several alkyl ketones. The pre-exponential factors were similar for all the ketones investigated, and their values are compatible with an adiabatic reaction path taking place through a six-membered ring activated complex. The activation energy is determined by the type of γ hydrogen being abstracted.

The photodecomposition quantum yields from the excited singlet and triplet states were measured at several temperatures. Combining these data with measurements of the triplet quantum yield provides information on the behaviour of the 1,4-biradicals produced. It is concluded that most of the biradical reactions are controlled by rotation around C–C bonds.

Introduction

The photochemistry of alkyl ketones bearing γ-hydrogens has been the subject of extensive studies [1], and several general features of the photo-processes involved have been elucidated. The reactivity of the excited singlet is almost completely determined by the substitution at the γ-carbon [2, 3], and the activation energies of the intramolecular hydrogen abstraction are almost insensitive to structural changes other than γ-substitution [3]. The photoreactions from the excited triplet state follow a similar pattern [3, 4], but no systematic studies under comparable experimental conditions have been carried out for a series of ketones having the same type of γ-hydrogen. This type of data has been obtained only for 2-pentanone and 4-methyl-2-pentanone [5, 6], and the conclusions were similar to those reached for the singlet reaction [2, 3]. The only reported Arrhenius parameters for the triplet reaction have been obtained employing 4-methyl-2-pentanone [6].

The effect of structure on the quantum yield for photoelimination from the singlet and triplet states has been only partly studied, and mostly at a single temperature [7 - 10]. Furthermore, since in most of these studies the

cis-1,3-Pentadiene (Fluka) was the quencher employed to measure τ_T and $(\Phi_{II})^S$ [11].

Results and Discussion

The experimental data obtained in the present work are shown in Table 1. The $(k_q \tau_T)$ values were obtained from standard Stern–Volmer plots. Although some of the values shown in Table 1 have been reported previously [4, 7, 9, 10, 12, 13], for the sake of consistency most of the following discussion will be carried out employing data obtained in this laboratory.

Effect of structure on the intramolecular hydrogen abstraction rate constant

The data of Table 1 allow the estimation of the intramolecular hydrogen abstraction rate constant from the triplet state if k_q is known [6, 14], and the reaction:

$$^3K \longrightarrow {}^3Bir \tag{1}$$

is the only reaction of the excited triplet. This assumption implies that inter-system crossing, photoreactions with the solvent, and type I photocleavage are negligible. These are reasonable assumptions since: (i) all $(k_q \tau_T)$ values are smaller than those obtained employing 2-pentanone [5]; (ii) photoreduction and type I photocleavage are minor processes in the photolysis of 2-pentanone at 20 °C in n-hexane [7]; and (iii) the rate constant for the type I photoreaction can be considered similar in all the ketones studied in the present work since it is almost exclusively determined by the α-substitution [15]. In support of this argument it must be stated that type I photoproducts were only minor products for ketones bearing primary γ-hydrogens, and could not be detected in the photolysis of ketones with secondary or tertiary γ-hydrogens.

The values of k_1 per hydrogen atom, obtained employing:

$$k_1/M^{-1}\ s^{-1} = 1.08 \times 10^{10}/n_H (k_Q \tau_T) \tag{2}$$

are shown in Table 2, together with previously reported values for 2-pentanone and 4-methyl-2-pentanone obtained under identical experimental conditions [5, 6]. The data of Table 2 show that substitution at the α'-, β-, or ϵ-position has an effect upon the rate constant of intramolecular hydrogen abstraction which lies within the experimental error. These results are similar to those obtained for the singlet reaction [2, 3], and show that the reactivity is almost exclusively determined by the degree of substitution at the γ-carbon. The same result has been obtained previously for aryl alkyl [16] and cyclic ketones [17].

From Table 2 it can be seen that:

$$k_{tert} \approx 12 k_{sec} \approx 180\, k_{prim}$$

for the different γ-hydrogens. The selectivity of the triplet reaction is thus

TABLE 1

Experimental data

Ketone	Temperature (°C)	$(\Phi_{II})_{total}$	$(\Phi_{II})^S$	$(\Phi_{II})^T$	$k_q \tau_T$
2,6-dimethyl-4-heptanone	20	0.11	0.028	0.08	720
4-heptanone	20	0.11	0.022	0.09	1020
2-hexanone	16				110
	20	0.19	0.086	0.114	81
	43	0.20	0.112	0.088	70
	60				39
	70	0.19	0.124	0.066	42
2-heptanone	—3	—	0.056	0.14	125
	16.5	—	—	—	56
	20	—	0.082	0.12	50
	45	—	0.10	0.10	—
	53	—	—	—	38
	70	—	0.117	0.08	23
2-octanone	20	0.20	0.07	0.13	50
3-heptanone	20	0.15	0.066	0.084	82
	46	0.15	0.076	0.074	—
	70	0.17	0.1	0.070	—
5-methyl-3-heptanone	20	0.11	0.057	0.053	52
	45	0.135	0.077	0.058	—
	70	0.151	0.1	0.051	—
5-methyl-2-hexanone	—5	—	—	—	14.3
	20	0.16	0.11	0.05	10.3
	44	0.168	0.121	0.047	—
	65	—	—	—	4.3
	70	0.174	0.138	0.036	—

triplet quantum yields were not measured, it was impossible to obtain information about the behaviour of the 1,4-biradical intermediates [8 - 10].

In the present work we report experimental data for a series of alkyl ketones which allow the evaluation of the rate constant for the intramolecular hydrogen abstraction from the excited triplet, the quantum yield for photoelimination from the excited singlet and triplet states, and the biradical behaviour at several temperatures.

Experimental

The experimental conditions were similar to those previously described [3, 6]. n-Hexane (Merck, spectroscopic grade) was the solvent employed. Ketone concentrations were always less than 0.4 M, and the conversion was kept below 2%. Under these conditions the results were independent of conversion.

The type II photoreaction of 2-heptanone in n-hexane (Φ_{II} = 0.2 at all the temperatures investigated) was used as an actinometer [10].

TABLE 2

Values of k_1 at 20 °C

Ketone	$k_1/10^8$ s^{-1}
	Primary γ-hydrogen
2-pentanone	0.013
4-heptanone	0.016
4-methyl-2-pentanone	0.014
2,6-dimethyl-4-heptanone	0.012
	Secondary γ-hydrogen
2-hexanone	0.8
2-heptanone	1.10
2-octanone	1.08
3-heptanone	0.6
5-methyl-3-heptanone	0.8[a]
	Tertiary γ-hydrogen
4-methyl-2-hexanone	11

[a]Only secondary γ-hydrogens considered.

higher than that of the singlet reaction [2, 3]. This result, as well as the higher reactivity of the singlet, can be related to the larger exothermicity of the singlet reaction [3].

Arrhenius parameters for the intramolecular hydrogen abstraction

The data shown in Table 1 allow the evaluation of the Arrhenius parameters for reaction (1) if the dependence of k_Q with temperature is known. An analysis similar to that employed previously gives the values shown in Table 3 [6]. These results indicate that all the ketones bearing the same type of γ-hydrogens have similar activation energies. The results of Table 3 also show that the reactivity order: $k_{tert} > k_{sec} > k_{prim}$, is due exclusively to differences in activation energies. Similar results have been obtained for alkyl aryl ketones [18]. The pre-exponential factors obtained for the different ketones are similar and compatible with a transition state involving a six-membered ring [19].

Comparison of the data of Table 3 with those reported previously for the singlet reaction show that the higher reactivity of the excited singlet is a consequence of a lower activation energy [3]. Considered together, all the kinetic data available for the singlet and triplet reactions lend support to a common reaction path taking place adiabatically [3, 20]. Nevertheless, the reported A factors for the singlet and triplet reactions differ by approximately one order of magnitude. This difference, with seems to exceed our experimental error, would indicate that the singlet "transition state" is considerably tighter. This result, which cannot be easily explained at the present time, deserves further consideration.

It is interesting to note that, since the intersystem crossing is determined by the α-substitution [21], the Arrhenius parameters of the intramolecular

TABLE 3

Arrhenius parameters for the intramolecular hydrogen
abstraction from the excited triplet

Ketone	A (per hydrogen)/s^{-1}	E/kcal
4-methyl-2-pentanone[a]	10×10^{11}	7.9
2-heptanone	2.5×10^{11}	4.6
2-hexanone	2.5×10^{11}	4.9
3-heptanone	2.5×10^{11}	4.9
5-methyl-2-hexanone	4.0×10^{11}	3.4

[a]Ref. [6].

hydrogen abstraction are determined by the γ-substitution, and the Arrhenius
parameters of the type I photocleavage are almost exclusively determined by
the α-substitution [15], it is possible to completely predict the photochem-
ical behaviour of any alkyl ketone in an inert solvent at any temperature.

Dependence of $(\Phi_{II})^{S}$ and $(\Phi_{II})^{T}$ with temperature

A general feature of the data given in Table 1, as well as of those ob-
tained employing 4-methyl-2-pentanone, is that $(\Phi_{II})^{S}$ increases and $(\Phi_{II})^{T}$
decreases with T. Since [1, 5]:

$$(\Phi_{II})^{S} = \beta_{S}(1 - \Phi_{T}) \tag{3}$$

and

$$(\Phi_{II})^{T} = \beta_{T} \Phi_{T} \tag{4}$$

these results mainly reflect the change of Φ_{T} with temperature [3].

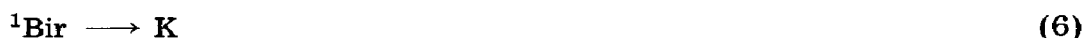*Dependence of β_{T} with temperature and structure*

Very little is known about the reactions of the 1,4-biradical intermediate
and the factors which govern the relative rate constants of cyclization, elim-
ination and reversion to the ground state. The values of β_{S} and β_{T} obtained
in the present work are shown in Table 4. The differences between these
values and others reported previously (i.e. those of ref. [7]) are mainly due
to differences in the measured quantum yield of triplet formation. The
most characteristic feature of the data shown in Table 4 is that, for all the
ketones investigated, $\beta_{S} < \beta_{T}$.

These results have been attributed to a concerted internal conversion
or to reactions of an extremely short-lived singlet biradical [1, 5, 17]. The
behaviour of the triplet biradical is less complex since, owing to the relative-
ly long times required for spin inversion [22], the biradical reacts from a
geometrical configuration which has very little memory of its original shape
[23 - 25]. The behaviour of the triplet biradical can then be represented by
the following reaction scheme:

TABLE 4

Values of β_s and β_T obtained at 20 °C and apparent activation energies

Ketone	β_S	E_{β_s} (kcal)	β_T	E_{β_T} (kcal)
2-pentanone	0.14	—	0.24	—
4-methyl-2-pentanone	0.14	0	0.23	0.6
3-heptanone	0.11	1.0	0.21	0.6
2-hexanone	0.15	0.8	0.28	−0.15
2-heptanone	0.13	0.7	0.36	0.4
2-octanone	0.11	—	0.39	—
5-methyl-3-heptanone	0.08	1.7	0.20	1.5
5-methyl-2-hexanone	0.13	1.5	0.38	−0.6

$$^3\text{Bir} \longrightarrow \, ^1\text{Bir} \tag{5}$$

$$^1\text{Bir} \longrightarrow \text{K} \tag{6}$$

$$^1\text{Bir} \longrightarrow \text{elimination} \tag{7}$$

$$^1\text{Bir} \longrightarrow \text{cyclization} \tag{8}$$

Since it can be expected that, for ketones with secondary α-carbon atoms

$$k_8 \ll k_6 + k_7$$

we shall disregard reaction (8) in the following discussion [8, 16]. The change in β_T with temperature and structure then reflects the competition between reactions (6) and (7), and has been discussed generally in terms of the relative exothermicity of these reactions [26]. This is a dangerous oversimplification since, for highly exothermic reactions which take place with very low activation energies [22, 27], there can be very little relationship between the reaction rates and the relative stabilities of the products. Furthermore, reactions (6) and (7) could be controlled not by the rate of crossing the critical configuration ("chemical control") but by the rate of rotation around primary C–C bonds [25]. This concept of "rotational control" is strongly supported by the data showing that singlet 1,4-biradicals can react prior to their rotation [24, 28, 29]. Unfortunately, the range of β_T values is rather small (all the data of Table 4 can be represented by 0.3 ± 0.1) and the errors involved in their determination are rather high, thus preventing a meaningful analysis of the factors which control the relative biradical behaviour. Nevertheless, the data obtained suggest that: (i) there is little effect of α' or β substitution; (ii) there is a small increase in β_T with γ substitution; and (iii) there is a small increase in β_T with chain length.

Conclusion (ii) is similar to that reached by Yang *et al.* from an analysis of the photochemical behaviour of 2-pentanone, 4-methyl-2-pentanone and 5-methyl-2-hexanone [7]. On the other hand, these data show striking differences with the results reported for aryl alkyl ketones. For these ketones

it has been reported that β_T is almost independent of chain length [30], and that it decreases slightly with β- and γ-substitution [16]. The influence of γ-substitution is most interesting since it is opposite to that found in the present work. We have to conclude then that the behaviour of alkyl and aryl alkyl biradicals is determined by different factors, since any analysis in terms of a single factor (*i.e.* relative exothermicity) would predict a similar behaviour.

The data given in Table 1, together with previously reported data on the change in triplet quantum yield with temperature [3], allow an estimate of the apparent activation energy of β_T. If this apparent activation energy is defined by:

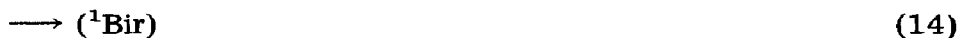$$E_{\beta_T} = -R \, \mathrm{d}(\ln \beta_T)/\mathrm{d}(1/T) \qquad (9)$$

we obtain the results shown in Table 4. If we disregard the value obtained for 5-methyl-3-heptanone (since for this ketone the total photoelimination is being measured and the importance of the primary hydrogen abstraction increases at high temperatures) our results resemble those reported for the aryl alkyl ketones [26], although the magnitudes of the measured activation energies are smaller in the present case. These differences can be partly due to differences in the polarity of the solvents employed, since the reactions of the biradicals [31], and the apparent activation energies of the photoelimination quantum yields [26, 32], are sensitive to the solvent polarity.

The very small (or even negative) activation energies obtained for several alkyl and aryl alkyl ketones would strongly argue against complete "chemical control" of these reactions. These values, together with the fact that $\beta_T < 0.5$, indicate that: $A_6 > A_7$.

This result seems incompatible with the structures of the transition states associated with these reactions since in reaction (6) four internal rotational degrees of freedon are lost, while in reaction (7), even if we accept that the elimination requires continuous overlap of both radical p orbitals with the bond undergoing cleavage [25], only two rotations are lost. Furthermore, a certain amount of "rotational control" in reactions (6) and (7) is also required to explain the behaviour of the singlet biradical [24, 28, 29].

Dependence of β_S with temperature and structure

If an analysis of the factors affecting the β_T values is difficult, the situation with regard to β_S is even more complicated. A reaction scheme for the singlet must include the following reactions:

$$^1K \longrightarrow K \qquad (10)$$

$$^1K \longrightarrow (^1Bir)^* \qquad (11)$$

$$(^1Bir)^* \longrightarrow K \qquad (12)$$

$$\longrightarrow \text{elimination} \qquad (13)$$

$$\longrightarrow (^1Bir) \qquad (14)$$

followed by reactions (6) to (8). In the present reaction scheme $(^1Bir)^*$ stands

for the biradical produced in reaction (11) before there is any rotation around a C–C bond (in Stephenson's reaction scheme (^{1}Bir)* could stand for the "hot" species [29]). In this reaction scheme we have not included a "concerted" elimination since there is no correlation between ^{1}K and the elimination ground state products [33].

The fact that β_S is always smaller than β_T can be due to a significant contribution of reaction (10), or to an unfavoured elimination from (^{1}Bir)* relative to the reversion to the ground state. There are no experimental data in favour of or against an internal conversion. On the other hand, the effect of phase changes on β_S [5], and the results of Casey and Boggs [28] and Stephenson [29] on the stereospecificity of olefin elimination, would indicate that reactions from (^{1}Bir)* compete with C–C rotation. Furthermore, since the geometry of (^{1}Bir)* is the optimum for reaction (12) but not for reaction (13), the predominance of reaction (12) can be easily understood.

The proposed reaction scheme leads to: $\beta_S/\beta_T \geqslant f$ where f measures the fraction of systems that, after crossing the critical configuration [3], reaches the state of thermally equilibrated and geometrically randomized singlet biradical. The values of β_S/β_T derived from the data given in Table 4 show that most of the systems reacting from the singlet state do not reach the state of ^{1}Bir. The same conclusion can be reached from the photolysis of stereospecific ketones [28, 29].

The preceding discussion shows that the factors which determine the value of β_S are so numerous that any attempt to rationalize the data shown in Table 4 is meaningless. The most remarkable characteristic of these data is the small range of β_S values covered by all the ketones considered in the present work, and the small values of the apparent activation energies. We can only conclude that the factors which determine the singlet behaviour are extremely insensitive to both temperature and ketone structure.

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