PHOTOCHEMICAL PROCESSES INVOLVING THE $^1n,\pi^{\star}$ EXCITED STATE OF ALIPHATIC KETONES BEARING γ HYDROGENS

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Summary

The triplet quantum yield was measured as a function of temperature for several alkyl ketones that photodecompose by intramolecular hydrogen abstraction. From these data Arrhenius parameters for the singlet reactions were derived. These reactions were treated as a transfer of a hydrogen atom across a potential energy barrier involving the formation of a six-membered ring in the transition state with concerted internal conversion and surface crossing located after the point of maximum energy. The A factors obtained per hydrogen atom lay between 1×10^{10} and 2×10^{10} s^{-1} for all the ketones investigated. The activation energies are determined by the substitution at the γ carbon and change from 1.1 (tertiary γ hydrogen) to 4.2 kcal/mol (primary γ hydrogen).

The similarity between the kinetic behaviour of the excited singlet and triplet states of aliphatic ketones is discussed.

Introduction

The intramolecular hydrogen abstraction by $n,\pi^{\star}$ excited carbonyl triplets has been widely investigated [1], and its main kinetic features explained in terms either of an adiabatic reaction [2, 3] or a non-adiabatic process which involves a surface crossing located after the point of maximum energy [4]. The photoprocesses from the excited singlet state have been less studied. The only reported Arrhenius parameters for an excited singlet state reaction are those obtained for the intramolecular hydrogen abstraction of 4-methyl-2-pentanone [5]. The results obtained in this work were interpreted in terms of a mechanism in which all singlet reactions other than intersystem crossing to the first excited triplet state take place after the formation of a singlet 1,4-biradical. In the present work we extend the previous study to a series of aliphatic ketones and discuss the kinetic significance of a concerted internal conversion.

Experimental

The experimental conditions were similar to those employed previously [5]. All the photolyses were carried out in n-hexane solution (Merck, spectroscopic grade). Ketone concentrations were lower than 0.4 M. The conversions (measured by the *trans-* to *cis*-1,3-pentadiene ratio) were lower than 4%. At these conversions the results obtained were independent of reaction time.

Results

The triplet quantum yield at a given temperature T was obtained using the equation:

$$(\Phi_3)_K^T = (\Phi_3)_A^T \times (trans\text{-}1,3\text{-pentadiene})_K / (trans\text{-}1,3\text{-pentadiene})_A \qquad (1)$$

where $(\Phi_3)_K^T$ is the triplet quantum yield of ketone K at temperature T; $(\Phi_3)_A^T$ is the triplet quantum yield of acetone at temperature T; and (*trans*-1,3-pentadiene)$_K$ and (*trans*-1,3-pentadiene)$_A$ are the *trans*-1,3-pentadiene concentrations obtained when the ketone K and acetone A were photolyzed under identical conditions in the presence of *cis*-1,3-pentadiene.

cis-1,3-Pentadiene concentrations in the 0.2 to 0.9 M range were employed. At these concentrations all the triplets are quenched [6, 7], and singlet quenching [8, 9] and chain reactions [10] can be considered as negligible. In agreement with these assumptions, the values of Φ_3 obtained were found to be independent of 1,3-pentadiene concentration.

The data obtained are shown in Table 1. These results were obtained taking $(\Phi_3)_A = 1$ at all the temperatures employed [11].

Discussion

The singlet lifetimes of aliphatic ketones bearing γ hydrogens are related to whether these hydrogens are primary, secondary or tertiary [6, 12]. This fact leads to the conclusion that all singlet reactions other than intersystem crossing to the first excited triplet state involve a strong interaction with the γ hydrogens [6, 13]. This can imply that all the photochemical processes go through a free singlet biradical [14], or that the concerted reactions (mainly internal conversion to the ground state) involve a considerable amount of O–H bonding at the point of the surface crossing. The reactions to be considered are then:

$$^1K \longrightarrow \, ^3K \qquad (2)$$

$$^1K \longrightarrow \, ^1\text{Biradical} \qquad (3)$$

$$^1K \longrightarrow K \qquad (4)$$

where reaction (4) considers the possibility of a "concerted" internal conversion. Since the ^1K state correlates with the biradical in its ground state and this surface intercepts the one leading from the ground state ketone to

TABLE 1

Triplet quantum yield data

Ketone	Temperature (°C)	Φ_3 [a]
2-heptanone	20	0.31 ± 0.03
	45	0.26 ± 0.03
	70	0.21 ± 0.03
3-heptanone	20	0.40 ± 0.02
	44	0.35 ± 0.03
	70	0.29 ± 0.03
2-hexanone	20	0.39 ± 0.02 (0.37)[b], (0.27)[c]
	44	0.36 ± 0.03
	70	0.30 ± 0.02
5-methyl-3-heptanone	20	0.26 ± 0.03
	45	0.22 ± 0.03
	70	0.18 ± 0.02
5-methyl-2-hexanone	20	0.145 ± 0.015 (0.18)[b], (0.11)[c]
	44	0.135 ± 0.015
	71	0.120 ± 0.015

[a] Errors quoted include only the dispersion of the data. Systematic errors are not included and can amount to ± 10%. These last errors would not influence appreciably the relative change in Φ_3 with temperature.
[b] Ref. 1.
[c] Ref. 6.

the excited biradical [3, 15], the possible situations to be considered are depicted in Figs. 1 and 2. There are several arguments against an early crossing as the one shown in Fig. 2.

(1) Salem has carried out calculations for the relative position of both surfaces as a function of the O–H distance for a typical hydrogen abstraction, and the results obtained indicate that the crossing point lies near the products [3].

(2) The singlet biradical reverts to the ground state ketone with low activation energies [16]. This result is not compatible with the rather high barriers implicit in Fig. 2 for the reaction:

$$^1\text{Biradical} \longrightarrow \text{K} \tag{5}$$

since simple thermochemical calculations indicate that in this case $E_5 \approx$ 18 kcal/mol + E_3 for a secondary γ hydrogen [17].

(3) The values of $\Phi_{II}^s/(1 - \Phi_3)$ obtained for 4-methyl-2-pentanone [5] were found to be nearly independent of temperature in the 20 to 70 °C range (Φ_{II}^S is the acetone quantum yield from the singlet state). This result is not compatible with the presence of an energy barrier after the point where the paths leading to reactions (3) and (4) separate.
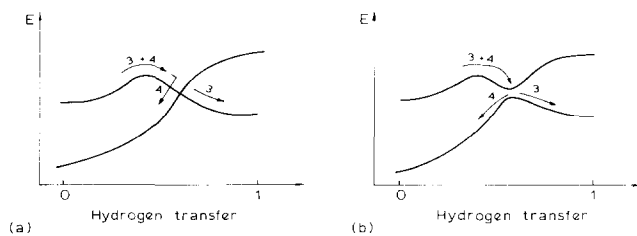
Fig. 1. Schematic representation of the surfaces involved in an intramolecular hydrogen abstraction. (a) With allowed crossing; (b) with slightly avoided surface crossing. The arrows indicate the reaction paths leading to reactions (3) and (4).
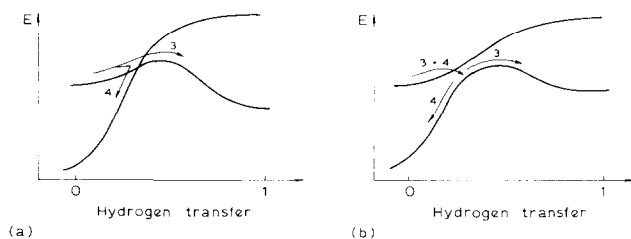

Fig. 2. Schematic representation of the surfaces involved in an intramolecular hydrogen abstraction with early crossing. (a) Allowed crossing; (b) slightly avoided surface crossing. The arrows indicate the reaction paths leading to reactions (3) and (4).

(4) The values of $\Phi_{II}^S/(1 - \Phi_3)$ were found to be similar for 4-methyl-2-pentanone, 2-heptanone and 5-methyl-2-hexanone [18] in spite of the fact that the energy barriers are different (see following discussion). A similar argument to that applied in point (3) shows that this result is also incompatible with a situation such as that shown in Fig. 2.

On the other hand, all these points are compatible with a "late" crossing as shown in Fig. 1. The analysis of this figure leads to three important considerations: (1) the "concerted" internal conversion appears naturally as a consequence of the surface crossing; (2) even if reaction (4) is important, the total singlet reaction (given by $v_3 + v_4$) can be treated as a single reaction with Arrhenius parameters determined by the height and configuration of the maximum shown in Fig. 1; (3) whether the surfaces cross or avoid each other is irrelevant to the kinetic treatment. A similar conclusion has been reached for the triplet reactions of aromatic ketones by Lewis et al. [4].

If $v_{\neq}$ is the rate of passage over the maximum shown in Fig. 1, we have that:

$$k_{\neq}/k_2 = (1 - \Phi_3)/\Phi_3 \tag{6}$$

and a plot of $\log 1 - \Phi_3)/\Phi_3$ against the reciprocal temperature should give values of $(E_{\neq} - E_2)$ and $(A_{\neq}/A_2)$. These plots are shown in Fig. 3.

Equation (6) allows the estimation of $k_{\neq}$ if k_2 is known. If we consider that k_2 is not modified by β or γ substitution [6, 12, 19], we can employ the values of k_2 reported for 2-butanone (4.0×10^8 s^{-1}) and 3-pentanone
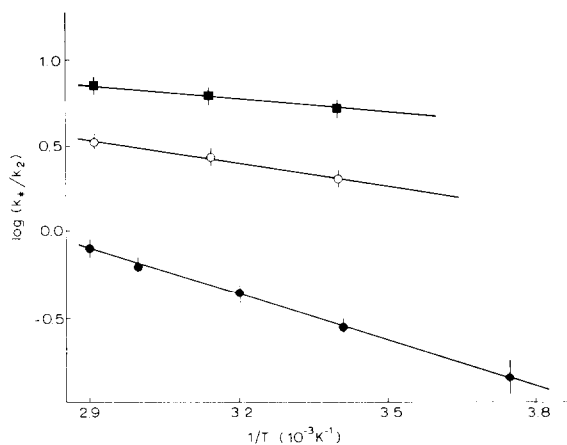
Fig. 3. Arrhenius plot of $k_{\neq}/k_2$. Data of Table 1 represented according to eqn. (6).
●, 4-Methyl-2-pentanone [5]; ○, 2-heptanone; ■, 5-methyl-2-hexanone.

TABLE 2

Experimental data for the excited singlet reactions

Ketone	$k{\neq}/10^8$ (s^{-1})	$E_{\neq}$[a] (kcal/mol)	$\log A_{\neq}$[a]	A[b]
4-methyl-2-pentanone[c]	1.1 ± 0.3	4.2 ± 0.5	11.1 ± 0.4	1.9
2-hexanone	6.0 ± 0.8 (9.9)[d] (8.4)[e]	2.0 ± 0.4	10.3 ± 0.3	1.0
2-heptanone	8.5 ± 1.2	2.1 ± 0.6	10.5 ± 0.5	1.5
3-heptanone	5.3 ± 0.8	2.1 ± 0.6	10.3 ± 0.5	1.0
5-methyl-3-heptanone	10.0 ± 2.0	2.0 ± 0.6	10.5 ± 0.5	1.2[f]
5-methyl-2-hexanone	24 ± 3 (21)[d] (25)[e]	1.1 ± 0.3	10.3 ± 0.3	1.9

[a] Obtained by assuming $E_2 = 0$. [b] Per hydrogen atom in 10^{10} s^{-1}. [c] Ref. 5.
[d] Ref. 6. [e] Ref. 12. [f] Corrected for primary hydrogen abstraction (assumed to be similar to that of 2-pentanone).

$(3.5 \times 10^8$ s$^{-1})$ in the evaluation of $k_{\neq}$ [12, 19]. The values thus obtained are given in Table 2 together with related values obtained by different methods. From these data we can conclude that all methods give similar results. If we divide $k_{\neq}$ by the number of γ hydrogens we find that the value obtained is rather insensitive to differences in the structure of the ketone. For the four ketones bearing secondary γ hydrogens $k_{\neq}$ lies between 2.7×10^8 (3-heptanone) and 5.0×10^8 (5-methyl-2-heptanone). Considering the simplifications involved in the k_2 values employed, we consider this difference to be of low significance.

The data of Table 2 show that, for each hydrogen atom,

$$k_{\text{tertiary}} \approx 7k_{\text{secondary}} \approx 130k_{\text{primary}}$$

Regarding the intramolecular hydrogen abstraction the singlet state is then less selective than the excited triplet state [7]. This result is in agreement with the higher exothermicity of the singlet reactions.

The results obtained employing 5-methyl-3-heptanone are compatible with the different reactivity of primary and secondary γ hydrogens. Although the butenes were not completely resolved under our experimental conditions it was observed that, even at the higher temperatures employed, 1-butene amounted to less than 20% of the olefins produced.

The plots shown in Fig. 3 can afford the values of $E_{\neq}$ and $A_{\neq}$ if we assume an activation energy for E_2 since:

$$E_{\neq} = E_2 + \Delta E \tag{7}$$

and

$$\log A_{\neq} = \log(A_{\neq}/A_2) + \log k_2 + 0.75\,E_2 \tag{8}$$

If we consider that E_2 is nearly zero [20], we obtain the values of $E_{\neq}$ and $\log A_{\neq}$ given in Table 2.

Pre-exponential factors

The values of A per hydrogen atom are similar for all the compounds studied and they are compatible with the formation of a strain-free six centre transition state [2, 4, 21]. This result is then consistent with a reaction path similar to that depicted in Fig. 1 and indicates that, regarding the entropies of activation, singlet and triplet reactions show a similar behaviour [4].

The similarity between the pre-exponential factors indicates that nearly all the differences in the behaviour of the singlet states of aliphatic ketones bearing primary, secondary or tertiary γ hydrogens must be attributed to differences in activation energies.

Activation energies

The data of Table 2 show that the activation energies depend upon the type of γ hydrogen abstracted. Furthermore, they show that the four ketones studied in which the more reactive γ hydrogen is secondary have similar activation energies. We can conclude that the activation energy is nearly insensitive to α, β or δ substitution.

The relationship between activation energy and type of γ hydrogen can be seen in a Polanyi type plot. This is shown in Fig. 4. The values of $\Delta(\Delta H)$ were obtained assuming that the $D_{(C-H)}$ is only determined by the substitution at the γ position [22]. The slope of this plot indicates a considerable amount of C–H bond breaking in the transition state. A similar conclusion has been reached through an analysis of the data obtained in the gas phase photolysis of alkyl ketones [22], although in this case the singlet and triplet reactions were not isolated [23].

In Fig. 4, the data obtained for the triplet state reaction of 4-methyl-2-pentanone [5] have been included. In order to put all the data in a common scale, 5 kcal was taken as the difference between the excited singlet and triplet state energies [24]. Furthermore, if we assume that for other triplet reactions the A factors per hydrogen atom are similar to that
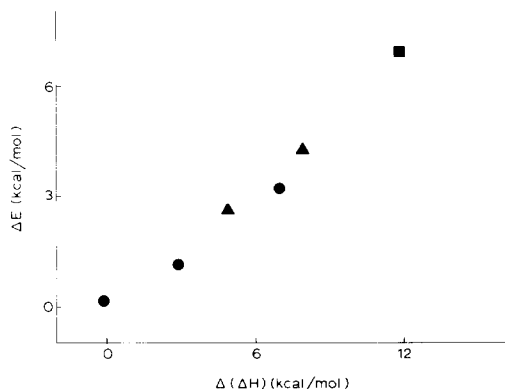
Fig. 4. Polanyi type plot for the singlet and triplet reactions. ●, Singlet reactions; ▲, triplet 4-methyl-2-pentanone [5]; ■, triplet reactions estimated from the triplet lifetime (see text).

obtained using 4-methyl-2-pentanone, we can estimate the activation energies for 2-hexanone and 5-methyl-2-hexanone triplet reactions from their triplet lifetimes [8]. The values so obtained have been included in Fig. 4. From this Figure we can conclude that the lower activation energies of the singlet reactions can be accounted for almost quantitatively by the higher exothermicity involved in their reactions. We can conclude then that there are not significant differences in the kinetic behaviour of both excited states.

Acknowledgements

References

1 P. J. Wagner, Acc. Chem. Res., 4 (1971) 168.
2 J. Grotewold, D. Soria, C. M. Previtali and J. C. Scaiano, J. Photochem., 1 (1972/73) 471.
3 L. Salem, J. Am. Chem. Soc., 96 (1974) 3486.
4 F. D. Lewis, R. W. Johnson and D. R. Kory, J. Am. Chem. Soc., 96 (1974) 6100.
5 M. V. Encina, A. Nogales and E. A. Lissi, J. Photochem., 4 (1975) 75.
6 N. C. Yang, S. P. Elliot and B. Kim, J. Am. Chem. Soc., 91 (1969) 7551.
7 C. H. Bibart, M. G. Rockley and F. S. Wettack, J. Am. Chem. Soc., 91 (1969) 2802.
8 F. S. Wettack, G. D. Renkes, M. G. Rockley, N. J. Turro and J. C. Dalton, J. Am. Chem. Soc., 92 (1970) 1793.
9 R. Hautala and N. J. Turro, J. Am. Chem. Soc., 93 (1971) 5595.
10 R. Hurley and A. C. Testa, J. Am. Chem. Soc., 92 (1970) 211.
11 R. F. Borkman and D. R. Kerns, J. Chem. Phys., 44 (1966) 945; R. B. Cundall and A. S. Davies, Proc. Roy. Soc. (A), 290 (1966) 563.
12 J. C. Dalton and N. J. Turro, J. Am. Chem. Soc., 93 (1971) 3569.
13 L. M. Stephenson, P. R. Vavigli and J. L. Parlett, J. Am. Chem. Soc., 93 (1971) 1984.
14 N. J. Turro, J. C. Dalton, K. Dawes, G. Farrington, R. Hautala, D. Morton, N. Niemczyk and C. Shore, Acc. Chem. Res., 5 (1972) 92.

15 J. Michl, Mol. Photochem., 4 (1972) 243; *ibid.*, 4 (1972) 257; L. Salem, W. G. Dauben and N. J. Turro, J. Chim. Phys., 70 (1973) 694.
16 N. C. Yang and S. P. Elliot, J. Am. Chem. Soc., 91 (1969) 7550; C. P. Casey and R. A. Boggs, J. Am. Chem. Soc., 94 (1972) 6457; L. M. Stephenson and T. A. Gibson, J. Am. Chem. Soc., 94 (1972) 4599; H. E. O'Neal, R. G. Miller and E. Gunderson, J. Am. Chem. Soc., 96 (1974) 3351.
17 F. D. Lewis and T. A. Hilliard, J. Am. Chem. Soc., 94 (1972) 3852.
18 M. V. Encina and E. A. Lissi, to be published.
19 J. C. Dalton and N. J. Turro, A. Rev. Phys. Chem., 21 (1970) 499; A. C. Somersall and J. E. Guillet, Macromolecules, 5 (1972) 410; M. O. Sullivan and A. C. Testa, J. Am. Chem. Soc., 92 (1970) 5842; D. A. Hansen and E. K. C. Lee, J. Chem. Phys., 62 (1975) 183.
20 H. E. O'Neal and C. W. Larson, J. Phys. Chem., 73 (1969) 1011; H. Steinmetzer, A. Yekta and N. J. Turro, J. Am. Chem. Soc., 96 (1972) 282; G. M. Breuer and K. C. Lee, J. Phys. Chem., 75 (1971) 989.
21 H. E. O'Neal and S. W. Benson, J. Phys. Chem., 71 (1967) 2903.
22 A. A. Scala, J. P. Colangelo, G. E. Hussey and W. T. Stolle, J. Am. Chem. Soc., 96 (1974) 4069.
23 C. H. Nicol and J. G. Calvert, J. Am. Chem. Soc., 89 (1967) 1790.
24 N. J. Turro, Molecular Photochemistry, Benjamin, New York, 1965.