KINETICS OF THE TYPE I PHOTOCLEAVAGE OF ALIPHATIC KETONES*

E. ABUIN and E. A. LISSI

Departamento de Quimica, Universidad Técnica del Estado, Santiago (Chile)

(Received December 12, 1975)

Summary

The triplet lifetime of 2-methylpentan-3-one was determined at several temperatures employing naphthalene as triplet quencher. The rate constant for the type I photocleavage of the triplet state is given by:

$$\log k \ (\text{s}^{-1}) = 13.5 - 7200/4.6 \ T$$

The kinetic behaviour of the singlet excited state of t-butyl ketones was investigated by measuring the fluorescence quantum yield between 15 and 80 °C. From the data obtained it is concluded that the photocleavage from the excited singlet occurs with low activation energies and with pre-exponential factors lower than $10^9 \ \text{s}^{-1}$.

The differences between both sets of data, as well as previous data obtained in the thermal and hot photocleavage of excited ketones, are discussed in terms of state correlation diagrams.

Introduction

The type I photocleavage of aliphatic ketones is one of the most studied photoprocesses, and the available experimental data for the thermalized reactions show that: (i) the rate constant from the triplet state increases with α-methyl substitution[1]; and (ii) the rate constant is higher from the triplet state [2].

The first point has been usually related to the larger exothermicity of the reactions of the α-substituted ketones [1, 3], but no definitive proof of the relationship between thermochemistry and activation energies has been provided.

The second point is most surprising since it is contrary to that expected from thermochemical considerations, and to the behaviour of the ketones decomposing by a type II mechanism [4, 5]. The higher reactivity of the

---

* Part of this work was presented at the VIII International Conference on Photochemistry, Edmonton, 1975.

triplet state has been interpreted in several ways [6], but the most likely explanation relies on the fact that there is no repulsive singlet surface leading to the ground state photoproducts [7]. If this argument is correct, the main difference between the singlet and triplet photoreactions must be in the pre-exponential factors. The available experimental data are not enough to support this assumption, since there are no reported Arrhenius parameters for the singlet reaction.

In the present communication we report experimental data bearing on these points and propose a general reaction pattern for the type I photocleavage.

Experimental

Fluorescence measurements

Fluorescence intensities were measured with a MPF-2A Hitachi–Perkin-Elmer spectrofluorometer, in the 15 to 83 °C temperature range. The ketones were excited with wavelengths between 3080 and 3180 Å and the full fluorescence spectrum was recorded. Iso-octane (Merck, Uvasol for fluorescence measurements) was the solvent employed. The ketone concentrations (between 2 and 5%) were adjusted at each temperature until the maximum emission was obtained. This procedure assures that, at any temperature and for all the ketones employed, the light absorbed is the same. Furthermore, since the shape of the emission spectra changes very little with temperature, the total area under the emission band can be related directly to the total intensity emitted [8]. In the temperature range investigated, the refractive index of the solvent changes by less than 7%. No correction was introduced to take this effect into consideration.

The shape of the emission spectra, as well as the relative emission intensities, were in agreement with previously reported data for all the ketones investigated [9, 10]. The relative changes of the fluorescence intensities with temperature were practically independent of the excitation wavelength.

Quenching experiments

The experimental method employed in the photolysis of ketones in the presence of naphthalene (Riedel-De Haän, sublimated) or 1,3-pentadiene (Fluka) were similar to those previously reported [4]. The solvent employed was a 9:1 mixture of n-hexane (Merck, Uvasol) and iso-octane (Merck, Uvasol). The C_3 hydrocarbons produced were analyzed together by g.l.c.

Carbon monoxide was measured volumetrically after trapping all condensables at −196 °C.

Azoisopropane (Merck Sharp & Dohme of Canada) was selectively photolyzed in the presence of ketones and naphthalene employing a Corning 0-52 filter.

Results

Singlet reactions

If we assume that the fluorescence rate constant is nearly independent of temperature [11], the change in the intersystem crossing rate constant (k_{isc}) with temperature can be obtained employing eqn. (1):

$$(k_{isc})_{T_2}/(k_{isc})_{T_1} = (\Phi_F)_{T_1} \ (\Phi_{isc})_{T_2} / [(\Phi_F)_{T_2} \ (\Phi_{isc})_{T_1}] \tag{1}$$

The change in k_{isc} with temperature was evaluated for acetone, 4-methylpentan-2-one, and heptan-2-one, by measuring Φ_F between 14 and 80 °C, and employing the Φ_{isc} values previously reported [5]. For the three ketones investigated we obtain that: $E_{isc} = 0.0 \pm 0.5$ kcal/mol, in agreement with previous results obtained in similar systems [11 - 15].

For ketones which photodecompose from the singlet state, the change in the photoreaction rate constant k_r can be obtained from the change in Φ_F with T if Φ_{isc} and the singlet lifetime are known at a single temperature, and it is assumed that $E_{isc} = 0$. This method has been applied to the t-butyl ketones.

For 2,2,4,4-tetramethylpentan-3-one we have taken that, at 25 °C $\Phi_{isc} = 0.56$ and $\tau_S = 5 \times 10^{-9}$ s [16]. The measured Φ_F decreases by 10% when the temperature changes from 25 to 80 °C. From these data we obtain that:

$$(k_r)_{80 °C}/(k_r)_{25 °C} = 1.13 \pm 0.25$$

and the Arrhenius parameters shown in Table 1.

TABLE 1

Arrhenius parameters for the type I photocleavage

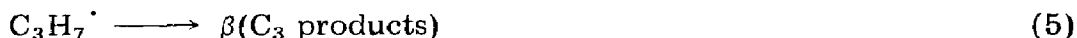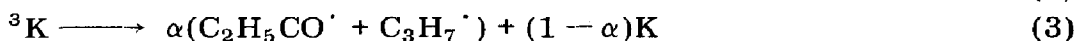| Ketone	Singlet reaction		Triplet reaction		Ref.
	E/kcal	A/s^{-1}	E/kcal	A/s^{-1}	
Butan-2-one (gas phase)			12.7	4×10^{14}	24
4-Methylpentan-2-one (n-hexane)			14.4	10^{16}	4
2-Methylpentan-3-one			7.2	3.1×10^{13}	
3,3-Dimethylbutan-2-one	0.2 ± 1	1.3×10^8			
2,2,4,4-Tetramethylpentan-3-one	0.4 ± 1	$10^{8\ a}$			

^{a} Per t-butyl group.

For 3,3-dimethylbutan-2-one we have taken that, at 25 °C, $\tau_S = 3.7 \times 10^{-9}$ sec and $\Phi_{isc} = 0.7$ [16]. This last value was obtained by assuming that cage recombination amounts to nearly 30% [17]. From these values and the change in Φ_F with temperature, we obtain the Arrhenius parameters given in Table 1.

2-Methylpentan-3-one triplet lifetime

The decrease in the quantum yield of photoproducts as a function of naphthalene concentration gives the triplet lifetime if the quenching rate constant is known. In order to estimate this rate constant we have studied the effect of naphthalene concentration upon 4-methylpentan-2-one photoproducts at several temperatures. The $(k_Q \tau_T)$ values obtained were similar to those previously determined employing 1,3-pentadiene as quencher [4]. These results indicate that both quenchers have similar k_Q values over all the temperature range investigated.

The results obtained in the photolysis of 2-methylpentan-3-one in the presence of naphthalene were analyzed in terms of the following reaction scheme:

$$K + h\nu \longrightarrow {}^3K \tag{2}$$

$${}^3K \longrightarrow \alpha(C_2H_5CO^{\cdot} + C_3H_7^{\cdot}) + (1 - \alpha)K \tag{3}$$

$${}^3K + Q \longrightarrow \text{quenching} \tag{4}$$

$$C_3H_7^{\cdot} \longrightarrow \beta(C_3 \text{ products}) \tag{5}$$

This reaction scheme leads to:

$$\Phi_{C_3}^0 / \Phi_{C_3} = 1 + (k_4/k_3)[C_{10}H_8] \tag{6}$$

To obtain eqn. (6) we have assumed that: (i) there is no photodecomposition from the excited singlet; (ii) the naphthalene neither decreases the light absorbed by the ketone (due to an internal screen effect), nor does it increase the number of excited ketone molecules by sensitization; (iii) the naphthalene does not quench the excited singlet; (iv) the value of β is independent of the experimental conditions.

The first point is supported by results obtained employing 2,4-dimethylpentan-3-one [18]. For this ketone it was observed that, even at 80 °C, the singlet photodecomposition quantum yield was lower than 0.1. Furthermore, the data obtained in the present work when plotted according to eqn. (6), gave a linear relationship at all naphthalene concentrations investigated.

Points (ii) and (iii) are supported by the results obtained in the photolysis of 4-methylpentan-2-one in the presence of naphthalene. At high naphthalene concentration (0.1 *M*) the propylene quantum yield was similar to that obtained employing 1,3-pentadiene under conditions of total triplet quenching [4].

Point (iv) is supported by the fact that the results obtained were independent of the ketone concentration and light intensity. Furthermore, when azoisopropane was photolyzed in the presence of 2-methylpentan-3-one, the Φ_{C_3} obtained were independent of the naphthalene concentration at all the light intensities and temperatures employed, showing that addition of the isopropyl radicals to naphthalene is not a significant reaction.

Some of the data obtained are shown in Fig. 1, plotted according to eqn. (6). The results obtained were independent of conversion (always kept below 4%).
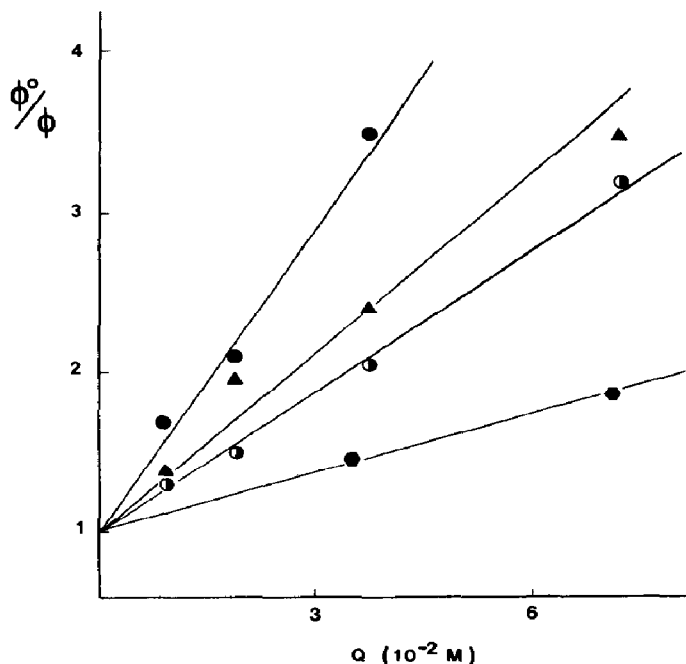
Fig. 1. Data obtained in the photolysis of 2-methylpentan-3-one in the presence of naphthalene plotted according to eqn. (6). ●, 22 °C; ▲, 37 °C; ◐, 41 °C; ◆, 83 °C.
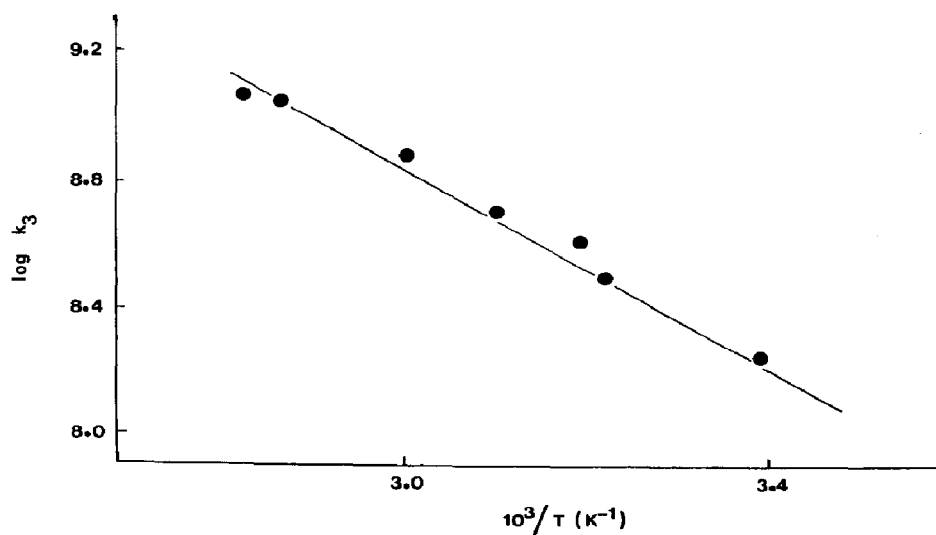

Fig. 2. Arrhenius plot of k_3.

An Arrhenius plot of k_3 is shown in Fig. 2, and the values obtained for the Arrhenius parameters are shown in Table 1. To obtain the values of k_3 shown in the Figure the values of k_4 were taken as equal to those obtained employing 1,3-pentadiene as quencher [4].

Discussion

Triplet lifetimes of isopropyl ketones

There are no previous estimates of the triplet reactivity of 2-methyl-pentan-3-one. The data obtained in the present work give:

$$(k_3)_{25\,°C} = 1.8 \times 10^8 \text{ s}^{-1}$$

This value is more than one order of magnitude higher than that expected from data obtained in the gas phase photolysis of 3-methylbutan-2-one [1]. Similarly, the data obtained in the neat photolysis of 2,4-dimethylpentan-3-one and in the photolysis of 3-methylbutan-2-one in n-hexane solution, gave shorter lifetimes than those obtained in the gas phase [18]. Some of the differences can be due to the fact that the gas phase lifetime reported for 3-methylbutan-2-one could be in the pressure dependent region, but a phase effect cannot be disregarded. The importance of the phase in the rate of the type I photocleavage has not yet been evaluated and deserves further investigation.

Comparison between singlet and triplet Arrhenius parameters

The data shown in Table 1 can be rationalized in terms of the energy diagram shown in Fig. 3. This diagram shows the electronic state correlation as proposed by Salem [19].

The data of Table 1 show that the low reactivity of the singlet is due to extremely low pre-exponential factors. This fact can be related to the restriction imposed by the singlet to triplet surface crossing that must take place before reaching the ground state photoproducts. The triplet reaction does not involve any spin-forbidden surface crossing and shows A factors almost 10^6 times higher.

The diagram shown in Fig. 3 shows that there are two alternative reaction paths for the decomposition of the excited singlet: one crossing to the $^3(\pi, \pi^*)$ repulsive surface leading to the ground state photoproducts, and another adiabatically leading to the excited $^1(\sigma, \pi)$ radical pair. The first reaction path would require a low activation energy but would have a very low A factor. The Arrhenius parameters reported in Table 1 can be assigned to this process. The second reaction path would require higher energies but would have A factors probably higher than 10^{14} s^{-1}. This process would have an estimated energy requirement of nearly 20 kcal [19], and would become important at high temperatures or short exciting wavelengths. Cundall and Davies have measured an activation energy of nearly 17 kcal for the decomposition of excited acetone singlets [20], and Lee et al. have observed that in pentan-3-one and 2,4-dimethylpentan-3-one a new non-radiative process appears when the energy of the exciting radiation is higher than 106 kcal/mol [14]. In both cases the results can be explained by assuming a decomposition leading to the excited products. This interpretation is supported by the high A factor reported by Cundall and Davies [20].
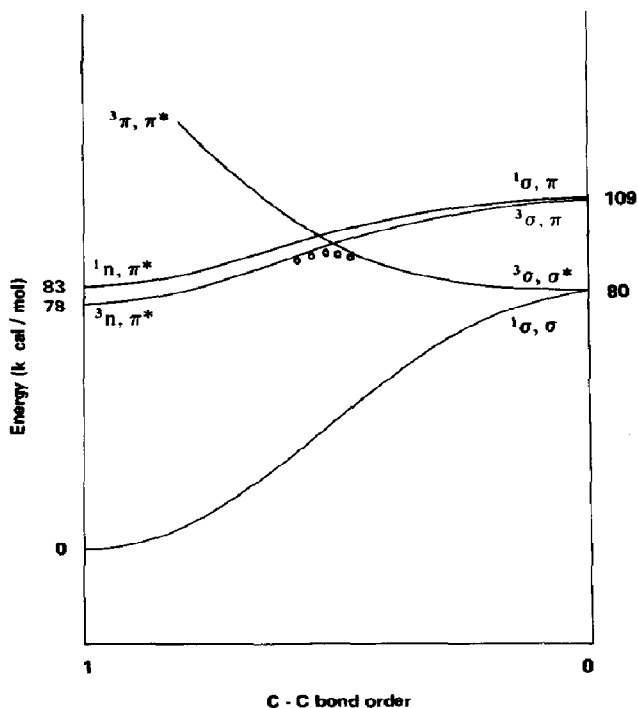
Fig. 3. Schematic representation of the potential energy surfaces (obtained after Salem [19]).

The A factors for the triplet photocleavage are larger than 10^{13} s^{-1}. These values are of the order expected for a unimolecular reaction which has a critical configuration located near the reactant. This result implies that, in spite of the lack of electronic state correlation between the $^3(n, \pi^*)$ state and the ground state photoproducts these can be reached without significant restriction [19].

The high A factor for the triplet reaction implies that hot triplet decomposition must be an efficient process every time that the triplet is produced with internal energy above the barrier that leads to the ground state photoproducts. This conclusion is supported by the available experimental data [1, 3, 19, 21]. On the other hand, efficient hot singlet photodecomposition will take place only when the energy is high enough to reach the excited photoproducts.

The experimental results of Table 1 show that methyl substitution decreases the activation energies and the pre-exponential A factors. Both results can be related to the increase in exothermicity associated to the α-substitution [1], and can be explained by the diagram shown in Fig. 3. A decrease in the energy of the C–C bond would decrease the energy of both the ground state and excited radical pairs, leading to lower activation energies. The data of Table 1, as well as the estimates given in ref. [1], indicate that the activation energies change almost as much as the bond dissociation energies. These data would then fit a Polanyi type relationship with an unusually high value for the coefficient [22].

The higher exothermicity associated to the α-substitution would displace the critical configuration towards the reactants. This effect, as well as the restricted rotation associated to the substitution [23], would reduce the A factor. The results of Table 1, even if we consider the relatively high errors involved and the phase differences, would qualitatively support this conclusion.

We consider then that a simplified surface diagram such as that shown in Fig. 3 is able to explain, at least semi-quantitatively, all the experimental data reported for the hot and thermal photocleavage of excited aliphatic ketones.

Acknowledgements

References

1 E. A. Lissi, E. Abuin and M. V. Encina, J. Photochem., 2 (1973/74) 377.
2 J. C. Dalton, D. M. Pond, D. S. Weiss, F. D. Lewis and N. J. Turro, J. Am. Chem. Soc., 92 (1970) 2564; N. J. Turro, J. C. Dalton, K. Daves, G. Farrington, R. Huatala, D. Morton, M. Niemczyk and N. Schore, Acc. Chem. Res., 5 (1972) 92.
3 H. E. O'Neal and C. W. Larson, J. Phys. Chem., 73 (1969) 1011.
4 M. V. Encina, A. Nogales and E. A. Lissi, J. Photochem., 4 (1975) 75.
5 M. V. Encina and E. A. Lissi, J. Photochem., 5 (1976) 287.
6 J. C. Dalton and N. J. Turro, Am. Rev. Phys. Chem., 21 (1970) 499.
7 W. G. Dauben, L. Salem and N. J. Turro, Acc. Chem. Res., 8 (1975) 41.
8 J. N. Demas and G. A. Crosby, J. Phys. Chem., 75 (1971) 991.
9 M. O'Sullivan and A. C. Testa, J. Am. Chem. Soc., 92 (1970) 5842.
10 A. C. Somersall and J. E. Guillet, Macromolecules, 5 (1972) 410.
11 J. C. Hemminger and E. K. C. Lee, J. Chem. Phys., 56 (1972) 5284; J. Caldwell and D. E. Hoare, J. Am. Chem. Soc., 84 (1962) 3987; A. M. Halpern and W. R. Ware, J. Chem. Phys., 54 (1971) 1271.
12 H. Steinmetzer, A. Yekta and N. J. Turro, J. Am. Chem. Soc., 96 (1974) 282.
13 T. Thomas, B. Matuszewki and R. S. Givens, J. Am. Chem. Soc., 78 (1974) 2637; G. M. Breuer and E. K. C. Lee, J. Phys. Chem., 75 (1971) 989.
14 D. A. Hansen and E. K. C. Lee, J. Chem. Phys., 62 (1975) 183.
15 A. M. Halpern and W. R. Ware, J. Chem. Phys., 53 (1970) 1969.
16 N. C. Yang, E. D. Feit, Man Him Hui, N. J. Turro and J. C. Dalton, J. Am. Chem. Soc., 92 (1970) 6974.
17 F. D. Lewis and J. G. Magyar, J. Am. Chem. Soc., 95 (1973) 5973; P. J. Wagner, J. M. McGrath and R. G. Zepp, J. Am. Chem. Soc., 94 (1972) 6883.
18 E. B. Abuin and E. A. Lissi, unpublished results.
19 L. Salem, J. Am. Chem. Soc., 96 (1974) 3486.
20 R. B. Cundall and A. S. Davies, Proc. R. Soc., A290 (1966) 563.
21 E. Abuin, M. V. Encina and E. A. Lissi, J. Photochem., 1 (1972/73) 387.
22 A. A. Scala, J. P. Colangelo, G. E. Hussey and W. T. Stolle, J. Am. Chem. Soc., 96 (1974) 406.
23 S. W. Benson and R. Hiatt, Int. J. Chem. Kinet. IV (1972) 151.
24 E. B. Abuin and E. A. Lissi, J. Photochem., 5 (1976) 65.