ACTIVATION PARAMETERS FOR THE α CLEAVAGE OF ALKANONES
AND AZOALKANES MEASURED BY TEMPERATURE DEPENDENCE
OF FLUORESCENCE

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Summary

The temperature dependence of fluorescence of several alkanones and
several azoalkanes has been measured and Arrhenius parameters have been
derived from the data. It is shown that the activation energies derived from
an Arrhenius treatment refer directly to the rate of reaction from S_1 only
when reaction is the major pathway for deactivation. When fluorescence
and/or intersystem crossing determine the rate of deactivation of S_1, fluores-
cence is generally found to be temperature independent. The previously
reported activation energies for α cleavage from S_1 are discussed and
compared with the values obtained in this work.

1. Introduction

The photochemical α cleavage of carbonyl compounds (eqn. (1)) is a
reaction of wide synthetic scope [1] and of considerable mechanistic
interest [2]. Recent theoretical analyses [3] of the α cleavage of ketones
have indicated the existence of two distinct reaction pathways (one in-
volving linearization of the acyl fragment during homolysis and the other
maintaining a bent acyl fragment during homolysis). Activation parameters
for the α cleavage process could be of significant value in evaluating this
theoretical model. However, reliable activation parameters for photochemi-
cal reactions are relatively scarce, especially for reactions in solution (*e.g.*
temperature effects on type II reactions and intermolecular hydrogen
abstractions [4]). For example, scrutiny of values for the activation para-
meters for α cleavage reported in the literature (Table 1) shows large discre-
pancies for the same molecule (*e.g.* acetone triplet, E_a = 6.4 kcal mol^{-1} [5]
or E_a = 10 kcal mol^{-1} [6]) and unexpectedly large contrasts between differ-
ent molecules (*e.g.* methyl tert-butyl ketone singlet E_a = 0.2 kcal mol^{-1}
[10], but cyclohexanone singlet E_a > 25 kcal mol^{-1} [11]).

TABLE 1

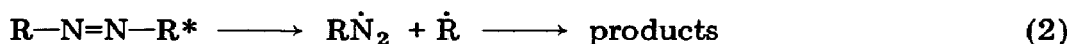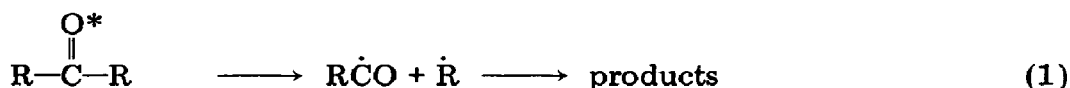Reported activation energies E_a and pre-exponential factors A for the α cleavage of ketones

| No.	Ketone	E_a^S (kcal mol^{-1})	A^S	E_a^T (kcal mol^{-1})	A^T	Ref.	Method
1	CH$_3$COCH$_3$	17	2.5×10^{16}	6.4	2.5×10^{10}	5	a
			-	≈ 10	$\approx 10^{10}$	6	a
			-	≈ 7.5	-	7	b
2	CH$_3$COCH$_2$CH$_3$		-	≈ 12.7	$\approx 4 \times 10^{14}$	8	c
3	CH$_3$COCH$_2$CH(CH$_3$)$_2$		-	≈ 14.4	$\approx 10^{16}$	9	d
4	(CH$_3$)$_2$CHCOCH$_2$CH$_3$			≈ 7.2	$\approx 3.1 \times 10^{13}$	10	e
5	CH$_3$COC(CH$_3$)$_3$	≈ 0.2	$\approx 1.3 \times 10^8$	-	-	10	f
6	(CH$_3$)$_3$CCOC(CH$_3$)$_3$	≈ 0.4	$\approx 10^8$	-	-	10	f
7	Cyclopentanone	≈ 15	-	-	-	11	g
8	Cyclohexanone	> 25	-	-	-	11	g
9	Cyclobutanone	≈ 4	-	-	-	11	g

S, singlet; T, triplet; a, gas phase kinetic; b, temperature dependence of the phosphorescence lifetime in acetonitrile; c, gas phase triplet quenching with biacetyl; d, solution phase triplet quenching with 1,3-pentadiene; e, solution phase triplet quenching with naphthalene; f, temperature dependence of fluorescence in solution; g, wavelength dependence of fluorescence quantum yields in vapor.

The so-called "activation energies" E_a reported in the literature may not, in fact, refer to the primary photochemical process given in eqn. (1). Care must be taken in the selection of the temperature dependent property in measuring E_a and in the interpretation and derivation of E_a from experimental data. We report here an analysis of the temperature dependence of the fluorescence of some cyclic ketones (for a review of the fluorescence of cyclic alkanones see ref. 12) and derive apparent activation energies and discuss the data with regard to the above considerations. We also report some results concerning the temperature dependence of the fluorescence of cyclic azoalkanes (for a review of the fluorescence of cyclic alkanones see ref. 13), a family of compounds known [14] to undergo homolytic α cleavage from S_1 (eqn. (2)):

$$R-\overset{\overset{\displaystyle O^*}{\|}}{C}-R \longrightarrow R\dot{C}O + \dot{R} \longrightarrow \text{products} \qquad (1)$$

$$R-N=N-R^* \longrightarrow R\dot{N}_2 + \dot{R} \longrightarrow \text{products} \qquad (2)$$

2. Results and treatment of data

The fluorescence intensity of acetonitrile solutions of the cyclic alkanones (compounds 10 - 14) and the azoalkanes (compounds 15 - 20) (Scheme I) was measured as a function of temperature. Analyses were
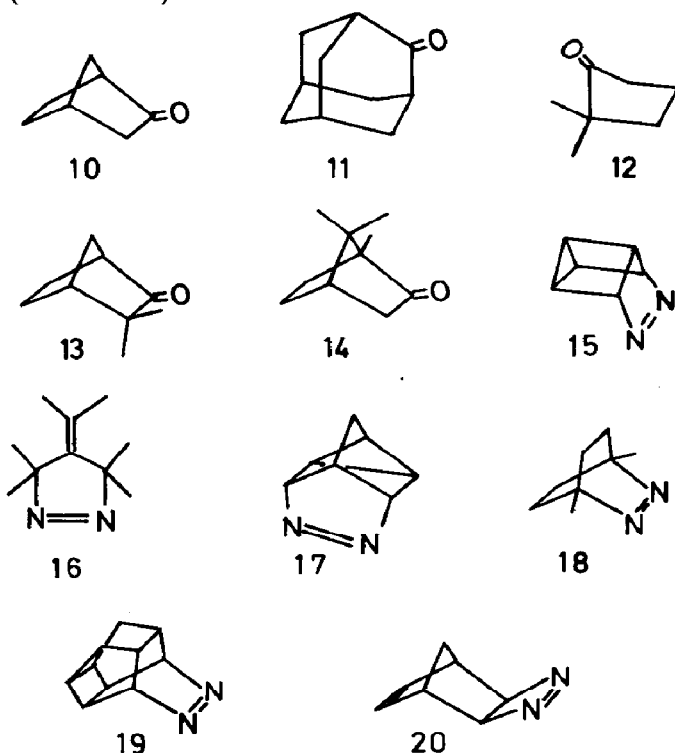
Scheme I.

TABLE 2

Apparent activation energies E_a for α cleavage of alkyl ketones and azocompounds determined by temperature dependent fluorescence intensity

Compound	E_a (kcal mol^{-1})	k_r (s^{-1})[a]
10	b	$< 10^8$
11	b	$< 10^8$
12	b	$\approx 10^8$
5	b	$\approx 5 \times 10^7$
13	5.0	$\approx 3 \times 10^8$
14	5.5	$\approx 2 \times 10^8$
15	6.0	–
16	6.5	–
17	5.5	–
18	b	–
19	b	–
20	b	–

[a] The values for k_r are approximate and are taken from ref. 12.
[b] The activation energy for these compounds could not be determined by this method (see text for an explanation).
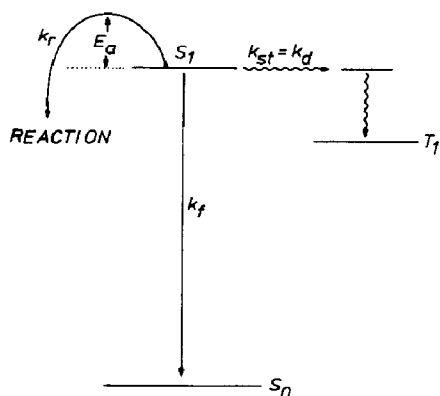

Fig. 1. Energy diagram depicting the important rate constants for deactivation of S_1. In general the lifetime of S_1 is determined by the sum of all rates of deactivation. In the case of the ketones and azoalkanes investigated in this work, the singlet lifetime is given by $\tau_s = k_f + k_{st} + k_r$ or to a good approximation $\tau_s \approx k_{st} + k_r$.

performed on a Hitachi–Perkin–Elmer MPF-2 spectrophotometer. Data were taken over the temperature range −5 - +80 °C.

The values of E_a, derived from measurements of fluorescence intensity as a function of temperature, were obtained after corrections for solvent expansion, viscosity change and photomultiplier response at different temperatures as described by Kirby and Steiner [15] (Table 2). Without these corrections "apparent" activation energies of about 0.2 - 2.0 kcal mol^{-1} are derived from the measurements.

In order to derive activation parameters from the experimental data we used a modified Arrhenius expression (eqn. (3))[†]

$$\ln\left(\frac{1}{\phi_f} - 1 - \frac{k_d}{k_f}\right) = -\frac{E_a}{RT} + \ln\left(\frac{A}{k_f}\right) \qquad (3)$$

where A is the pre-exponential factor, E_a is the activation energy for α cleavage and k_f and k_d are the rate constants for fluorescence and for all unimolecular (or pseudo unimolecular) pathways of S_1 other than fluorescence and α cleavage (Fig. 1). From eqn. (3) we note that ϕ_f is not always directly related to $1/T$.

Three limiting cases can be delineated.

2.1. Case (a)

$$k_r \gg k_d + k_f \qquad (4)$$

In this case k_f and k_d are negligible and we have

$$\ln\left(\frac{1}{\phi_f}\right) = -\frac{E_a}{RT} + \ln\left(\frac{A}{k_f}\right) \qquad (5)$$

Thus, for the case in which α cleavage determines the lifetime of S_1, a plot of $\ln(1/\phi_f)$ *versus* $1/T$ should be linear, with slope equal to $-E_a/R$.

2.2. Case (b)

$$k_r \ll k_d + k_f \qquad (6)$$

Here, the variation of ϕ_f with temperature is completely unrelated to the α cleavage process and reflects only the effect of temperature on $k_d + k_f$. For alkanones and azoalkanes, k_d may be identified with k_{st}, the rate constant for intersystem crossing (ISC) from S_1 to T_1. Since both k_{st} and k_f are found to be temperature independent[††], a plot of $\ln(1/\phi_f - 1)$ *versus* $1/T$ will yield a straight line with zero slope. *i.e.* will yield a value of $E_a = 0$.

2.3. Case (c)

$$k_r \approx k_d + k_f \qquad (7)$$

[†]This model follows naturally from those discussed previously in the literature [15 - 17].

[††]For compounds which have ISC as the main deactivation pathway for the S_1 state, *e.g.* compounds 5, 10 - 12 and 20, no temperature dependence of ϕ_f is observed. It can therefore be assumed that k_{ISC} is temperature independent for the temperature range applied in these experiments. This is in agreement with previous reports. (Compare ref. 10, p. 3 and references cited therein).
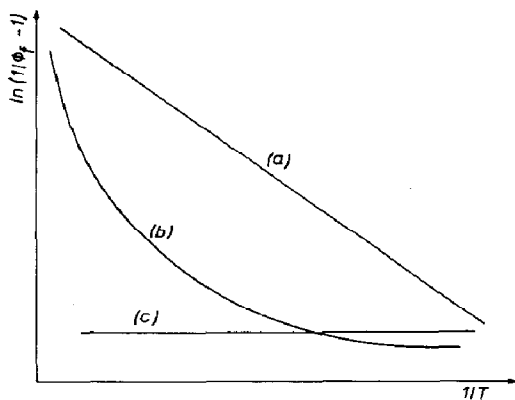
Fig. 2. Qualitative Arrhenius plots of ln $(1/\phi_f - 1)$ or ln $(1/\phi_f)$ *versus* $1/T$ from eqns. (3) or (5) respectively (see footnote): (a) $k_f + k_d \ll k_r$; (b) $k_f + k_d \approx k_r$ with $k_d \gg k_f$; (c) $k_f + k_d \gg k_r$.
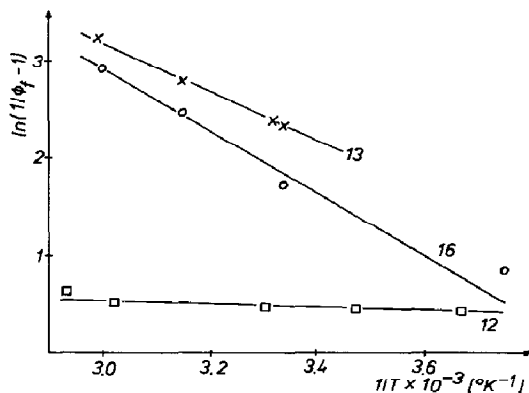
Fig. 3. Arrhenius plots for compounds 12, 13 and 16 obtained by measurement of the temperature dependence of the fluorescence intensity. Arbitrary units for ln $(1/\phi_f - 1)$. (See footnote.)

In this case a change in k_r with temperature is reflected only to a small extent in ϕ_f, and for $k_d \geqslant k_f$ curvature will appear in a plot of ln $(1/\phi_f - 1)$ *versus* $1/T$ (eqn. (3)).

The three limiting cases are summarized in Fig. 2. The activation energies listed in Table 2 were obtained by plotting[†] ln $(1/\phi_f^{rel} - 1)$ *versus* $1/T$. The experimental data of three representative compounds are plotted in Fig. 3.

Such plots were linear in all cases but were found to fall into one of two categories: a class for which the experimental slopes are about zero and a class for which the experimental slopes correspond to E_a values of 5 - 6.5 kcal mol^{-1}.

3. Discussion

From our model we note that observation of an apparent activation energy of about zero may be interpreted in two ways relevant to the activation energy for α cleavage.

(1) α cleavage is "unactivated", *i.e.* there is no energy barrier for eqns. (1) or (2).

(2) α cleavage is highly activated, such that $k_r \ll k_d + k_f$ and k_d and k_f are temperature independent.

[†]For small fluorescence quantum yields ($\phi_f \ll 0.1$), $1/\phi_f$ is large and the term -1 becomes negligible. In this case it is sufficient to determine relative fluorescence quantum yields ϕ_f^{rel}.

It seems to us that the second interpretation is more reasonable because (a) a barrier for α cleavage in S_1 of alkanones is predicted by theory [3]; (b) the major deactivating process of S_1 of simple alkanones is ISC, a process expected to be temperature independent (see footnote to p. 5); (c) as strain and radical stability are introduced, significant activation energies are measurable. For example, methyl tert-butyl ketone (compound 5) is reported (Table 1) to have $E_a \approx 0$ kcal mol^{-1}, yet camphor (compound 14) possesses an E_a of 5.5 kcal mol^{-1}. Based on structure—reactivity relationships the activation energy for α cleavage of compound 14 is expected to be less than that of compound 5 because of the presence of ring strain in the camphor structure. This expectation can be made consistent with that data, however, if we consider the E_a of about 0 kcal mol^{-1} for compound 5 as irrelevant to E_a for α cleavage, i.e. compound 5 falls into case (b) for which $k_r \ll k_d + k_f$. The same conclusion is derived from inspection of other pairs of compounds (e.g. compounds 10 and 14, compounds 12 and 13) and also seems to apply to cyclic azoalkanes (e.g. compounds 18 and 17).

We thus conclude that the actual activation energies for α cleavage of S_1 for compounds 5, 10 - 12 and 18 - 20 have not yet been measured, because their values are considerably greater than 5 - 6 kcal mol^{-1}. If the values for the activation energies for α cleavage of acetone and cyclohexanone are roughly correct, in order for k_r to become larger than $k_f + k_d$ a temperature range much higher than that applied so far must be employed.

The validity of the above arguments is further supported by a more quantitative argument. The radiative rate constant for fluorescence of alkanones varies little with structure (typical value about 10^5 s^{-1} [18]). Moreover, the rate constant for ISC is usually much larger than that for fluorescence (typical values about 5×10^8 s^{-1} - 1×10^8 s^{-1} [19]). It follows that only when k_r approaches values of about 10^9 s^{-1} will the values of ϕ_f be related to k_r via eqn. (8). It is therefore quite natural to find that eqn. (8) is obeyed only for strained cyclic alkanones that can undergo α cleavage to produce a tertiary alkyl radical, since it is for exactly these compounds that k_r is expected to be fastest. In fact, for methyl tert-butyl ketone the value of k_r, as deduced from measurements [19] of its ISC yield ($\phi_{ISC} \approx$ 0.7 - 0.8) and rate constant ($k_{ISC} \approx 2 \times 10^8$ s^{-1}), is about 5×10^7 s^{-1}. From fluorescence lifetime measurements [12] it can be deduced that compounds 13 and 14 possess values of $k_r \approx 2 \times 10^8$ s^{-1} and $k_r \approx 3 \times 10^8$ s^{-1}, respectively, at room temperature.

4. Conclusion

The present status of activation parameters for α cleavage reactions is confusing because of wide discrepancies in experimental values of E_a. In evaluating activation energies one must be careful to determine whether the quantity that is being measured as a function of temperature is a true measure of the reaction of interest. A direct method would be most suitable,

but when indirect methods are employed it is advisable to use as many independent checks (*e.g.* structure–reactivity, quantum yields etc.) as possible to confirm the assumptions. It is important to recognize that indirect methods (*e.g.* fluorescence intensity) can only yield true values of E_a when the reaction of interest possesses a rate constant that dominates the rates of all other competing processes from the reactive state.

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