

## THE KINETICS OF PHOTOCHEMICAL REACTIONS PART III. TEMPERATURE DEPENDENCE OF SOME TYPE II PHOTO- FRAGMENTATIONS OF AROMATIC KETONES\*

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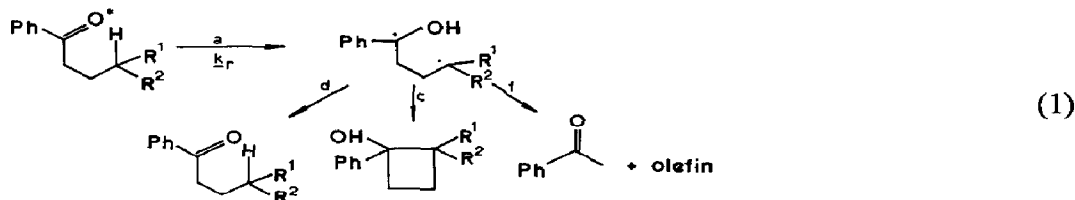
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### SUMMARY

Type II photofragmentations of several aromatic ketones bearing  $\gamma$ -hydrogen atoms have been studied in benzene over a range of temperatures in competition with the triplet quenching by penta-1,3-diene. From this study the Arrhenius parameters for the intramolecular hydrogen abstractions have been derived; the dependence of these parameters on the carbon-hydrogen bond dissociation energy is discussed. The possibility of using semi-empirical methods to predict the kinetics of these processes is also examined.

### INTRODUCTION

Type II photoelimination and photocyclization reactions of aromatic ketones bearing  $\gamma$ -hydrogen atoms is one of the most largely studied photochemical processes<sup>1</sup>. The products are known to arise from the triplet state according to:



Most of the studies reported in the literature have been concerned with the effects of structural changes<sup>1</sup> and solvent effects<sup>1,2</sup> on the quantum yields and reactivities of the substrates. Pitts *et al.*<sup>3</sup> and independently Barltrop and Coyle<sup>4</sup> have examined the temperature dependence of the quantum yields; the changes observed

\* A preliminary report of this work has been published<sup>5</sup>. For Part II, see ref. 6.

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reflect the changes in the relative values of  $k_{1d}$ ,  $k_{1c}$  and  $k_{1f}$ , rather than changes in the primary hydrogen abstraction step,  $k_r$  (ref. 4).

The value of  $k_r$  can be obtained by studying the effect of triplet quenchers on the quantum yield of one of the molecular products; if the activation energy for the quenching process can be independently estimated, the Arrhenius parameters for reaction (1a) can be obtained from a series of Stern–Volmer plots at different temperatures<sup>5</sup>.

In this paper we report a study of the temperature dependence of the photofragmentation of butyrophenone, valerophenone and 2-methyl-5-phenyl-pentan-5-one in competition with the triplet quenching by penta-1,3-diene. A method which allows the study of the temperature dependence of  $k_r$  using conventional experimental techniques is also discussed.

The possibility of using an extended bond energy–bond order (BEBO) method<sup>6–8</sup> to evaluate the activation energies combined with an independent estimation of the entropies of activation is also examined.

#### EXPERIMENTAL

The purity of the ketones employed (Eastman, Aldrich or Fluka) was checked by gas–liquid chromatography (g.l.c.). The samples (under vacuum or oxygen-free nitrogen) were contained in matched Pyrex tubes. The solutions were usually 0.1–0.3 *M* in ketone, containing small amounts (0.0002–0.002 *M*) of *n*-dodecane as an internal standard, and varying amounts of penta-1,3-diene; no difference could be detected between samples containing *cis*-penta-1,3-diene (Fluka) or the commercial mixture of isomers (Aldrich, containing 23% of the *cis* isomer) as the starting material. The solvent was benzene.

Irradiations were carried out in a merry-go-round apparatus immersed in a thermostated water bath, and fitted with a 125 W medium pressure mercury arc as light source. The radiation dose was usually around  $10^{15}$  quanta  $\text{ml}^{-1} \text{s}^{-1}$ . Irradiation times were chosen so as to keep conversion under 2%. The ratio of dead volume-to-volume of liquid was kept under or around two. This ensures that even assuming large positive deviations from the ideal solution behaviour, the concentration of penta-1,3-diene in solution (owing to its high vapour pressure) will not change significantly over the temperature range studied (5 to 75°C).

Photolyzed solutions were examined for product formation (acetophenone) on a Varian 2440 or Perkin-Elmer F11 chromatograph, using Carbowax 20M or Apiezon L on Chromosorb P columns.

#### RESULTS

Photolysis of the ketones resulted in linear Stern–Volmer plots of the type:

$$\frac{\Phi^0}{\Phi} = 1 + \tau k_q [\text{penta-1,3-diene}] \quad (2)$$

where  $\Phi^0$  and  $\Phi$  are the quantum yields of acetophenone production in the absence and presence of quencher, respectively;  $\tau$  is the lifetime of the carbonyl triplet and  $k_q$  the rate constant for the bimolecular quenching:



If the lifetime of the carbonyl triplet is determined solely by reaction (1a), eqn. (4) will hold:

$$\frac{\Phi^0}{\Phi} = 1 + (k_q/k_r) [\text{penta-1,3-diene}] \quad (4)$$

The values obtained from a series of Stern–Volmer plots were plotted in an Arrhenius form and fitted by the least squares treatment (Fig. 1 and Table 1).

The values given in the last column of Table 1 agree well with those found in previous studies<sup>1,9,10</sup>.

In order to obtain the absolute activation energies for reaction (1a), it is necessary to know the temperature dependence of  $k_q$ . To the best of our knowledge

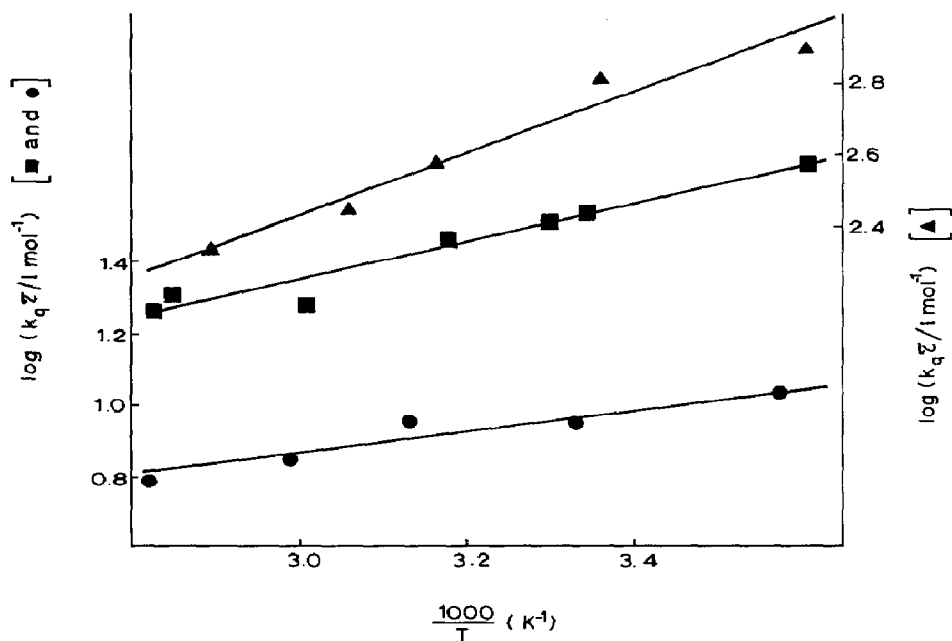


Fig. 1. Arrhenius plot for the competition between the type II photofragmentation and the quenching by penta-1,3-diene: ▲, butyrophenone (right scale); ■, valerophenone (left scale); ●, 2-methyl-5-phenyl-pentan-5-one (left scale).

TABLE 1  
EXPERIMENTAL RESULTS

R <sup>1</sup>	R <sup>2</sup>	log (A <sub>q</sub> /A <sub>r</sub> ) (M)	(E <sub>r</sub> - E <sub>q</sub> ) (kcal mol <sup>-1</sup> )	log A <sub>r</sub> (M <sup>-1</sup> s <sup>-1</sup> )	E <sub>r</sub> (kcal mol <sup>-1</sup> )	k <sub>r</sub> at 20°C (M <sup>-1</sup> s <sup>-1</sup> )
H	H	-0.13 ± 0.20	3.9 ± 0.5	12.08	6.95	6.93
Me	H	-0.35 ± 0.30	2.6 ± 0.5	12.30	5.65	8.12
Me	Me	-0.20 ± 0.20	1.6 ± 0.4	12.15	4.65	8.72

this information is not available in the literature. We have assumed that  $k_q$  follows an Arrhenius type temperature dependence, with a 'formal' activation energy obtained by graphical derivation of the modified Debye equation<sup>11</sup>:

$$E_q = \frac{-R\partial[\ln(8RT/3000\eta)]}{\partial(T^{-1})} = \frac{-R\partial[\ln(T/\eta)]}{\partial(T^{-1})} \quad (5)$$

This plot, using viscosities from the literature<sup>12</sup>, is surprisingly linear, with a "formal" activation energy of 3050 cal mol<sup>-1</sup>. Combining this value with a rate constant equal to  $5 \times 10^9$  l mol<sup>-1</sup> s<sup>-1</sup> in benzene at 20°C (in order to be consistent with previous studies), the following expression can be obtained:

$$\log k_q (1 \text{ mol}^{-1} \text{ s}^{-1}) = 11.95 - (3050/2.3 RT) \quad (6)$$

The activation energies and  $A$ -factors obtained using this expression are also shown in Table 1.

## DISCUSSION

It has been previously suggested that an activation energy might be involved in the hydrogen transfer reaction of carbonyl compounds in excited states<sup>13</sup>. Surprisingly enough, even though the type II reaction is one of the best studied photochemical processes, the temperature dependence of the primary photochemical abstraction has not been systematically examined. Nicol and Calvert<sup>14</sup> examined a series of alkanones with structures of the type n-C<sub>3</sub>H<sub>7</sub>COR in the gas phase; however, it must be pointed out that in these systems part of the type II products might arise from a singlet state reaction. Some of the ketones, *e.g.* 4-octanone, have two possible modes of type II decomposition, involving primary and secondary H-atom abstraction. From an Arrhenius plot of  $\Phi_{IIa}/\Phi_{IIb}$  they obtained a difference in activation energy of 1.3 kcal mol<sup>-1</sup>, a result which would be consistent with our values for butyrophenone and valerophenone. Similarly, in the photochemistry of 4-methyl-2-hexanone Ausloos<sup>15</sup> obtained a difference of 0.9 kcal mol<sup>-1</sup>. When the two modes of type II decomposition involve abstraction of primary H-atoms, the ratio  $\Phi_{IIa}/\Phi_{IIb}$  is independent of the temperature<sup>14</sup>. In the case of 2-pentanone, using biacetyl quenching data from Michael and Noyes<sup>16</sup>,

Nicol and Calvert<sup>14</sup> were able to obtain an activation energy of 5.5 kcal mol<sup>-1</sup>, assuming an *A*-factor of  $2.7 \times 10^{12}$  s<sup>-1</sup>. The activation energy compares well with our value for butyrophenone, particularly if one takes into account the higher triplet energy of the alkanones; the choice of *A*-factor has certainly proved to be a wise one.

In the case of aromatic ketones the studies of temperature dependence have been focused on the quantum yield<sup>3,4</sup>, leading to information about the behaviour of the intermediate biradical, rather than to the hydrogen abstraction step.

The choice of the substrate and method reported in this paper allows, for the first time, the determination of absolute activation energies in a system where the multiplicity of the state involved is clearly established. Obviously, the derivation of an activation energy for the quenching process using eqn. (5) can be questioned; however, we believe that most chemists would accept that the activation energy for diffusion in benzene must be around  $3 \pm 1$  kcal mol<sup>-1</sup>. Even assuming an error of 1 kcal mol<sup>-1</sup> for the value used in eqn. (6), the general conclusions reached in this paper will still be valid and the differences in activation energies and ratios of *A*-factors will not be affected.

#### *Activation energies*

In previous papers in this series<sup>6,7</sup>, we reported an extension of the BEBO method which allows the estimation of activation energies and *A*-factors for the intermolecular hydrogen abstraction reaction of the *n*,  $\pi^*$  triplet state of carbonyl compounds:



Although the applicability of the method was in principle restricted to the gas phase, the extension to non-polar solutions was fairly successful<sup>6,8</sup>.

In fact, reaction (1a) is very similar to reaction (7). If one can assume that: (a) the bond orders of the bonds being broken and formed (to the H-atom being transferred) add to one, even when the transition state is not linear and that repulsive contributions are not largely affected by this factor, and (b) that contributions from ring strain can be neglected, then the activation energy of reaction (1a) can be estimated using the extended BEBO method<sup>6,7</sup>. The triplet energies for the ketones studied here are around 74 kcal mol<sup>-1</sup><sup>17</sup>; therefore, from plots previously reported<sup>6</sup>, we estimate the activation energies as 7.4, 5.6 and 4.6 kcal mol<sup>-1</sup> for butyrophenone, valerophenone and 2-methyl-5-phenyl-pentan-2-one, respectively. The values are in good agreement with experiment, suggesting very low contributions from ring strain. This conclusion is also supported by the small changes in rates observed by introduction of  $\alpha$ -substituents in the alkyl group<sup>18</sup>.

An alternative explanation for the observed agreement would be that the energy requirements for cycle formation are balanced, or even over-ridden by

a greater solvation in the transition state. However, we do not feel that this is the case, since there is a good agreement in the case of linear transition states <sup>6,7</sup>, and there seems to be no reason to expect larger solvation here.

In any case, it is clear that the differences in activation energies do reflect the changes in bond dissociation energies.

#### *Pre-exponential factors*

The calculations of *A*-factors are based on the method reported by O'Neal and Benson<sup>19,20</sup>. The entropy of activation was estimated by evaluating the following contributions: (a) a ring entropy, due to changes in stretching and bending vibrations, (b) a rotational-torsional entropy, due to the replacement of initial-state internal rotations by out-of-plane torsions and (c) a term due to reaction path degeneracy.

The first term was evaluated from the bond orders in the transition state estimated using Figure 2 in ref. 6. Frequency assignments for the partial stretches and bends were estimated from single bond frequencies using an extension of Badger's rule<sup>21</sup>. C-H bond stretching (the reaction coordinate) makes a negligible contribution to  $\Delta S^\ddagger$  at working temperatures (around 300 K)<sup>20</sup>. The C=O bond stretching frequency in the excited triplet can be taken as  $\sim 1300 \text{ cm}^{-1}$ <sup>22</sup>. Its value in the transition state was taken as  $1100 \text{ cm}^{-1}$ . The bending frequencies were reduced by a factor  $n^{1/2}$  (ref. 21) where *n* stands for bond order. The rotational-torsional entropy was taken as  $-4 \text{ gibbs mol}^{-1}$  for each hindered rotation which is tied up when reaching the transition state; this is an over-simplification, which is based on the entropy differences between cyclic and open chain paraffins<sup>23</sup>. In fact, the internal rotations transform into out-of-plane ring vibrations, for which it is almost impossible to assign any reliable frequencies. The value of  $-4 \text{ gibbs mol}^{-1}$  mentioned above is only an upper limit to the entropy loss; it is therefore likely to lead to underestimations of the *A*-factors. The reaction path degeneracy was taken as the number of equivalent abstractable  $\gamma$ -hydrogen atoms. The results of the calculations are given in Table 2.

All the calculated parameters in Table 2 correspond to the gas phase, and the comparison of these values with experimental parameters obtained in solution is a further approximation.

Table 3 shows a comparison of experimental and calculated parameters.

The calculated activation energies are in good agreement with experiment, while the *A*-factors are about one order of magnitude below the experimental value. As pointed out above, this probably reflects an overestimation of the entropy losses arising from hindered internal rotations. The rate constants clearly reflect the underestimation of the *A*-factor, while in the case of relative rate constants this effect is cancelled. We also note that experimental *A*-factors do not seem to reflect the changes in path degeneracy; however, these differences are well within experimental error and any conclusions would be highly speculative.

TABLE 2

SEMIEMPIRICAL ESTIMATION OF THE  $A$ -FACTORS

(a) Butyrophenone (300 K)

$(n^\ddagger)^{1/2} = 0.77$

Triplet state			Transition state		
Vibrations	Frequency ( $\text{cm}^{-1}$ )	Entropy (gibbs/mol)	Vibrations	Frequency ( $\text{cm}^{-1}$ )	Entropy (gibbs/mol)
> C=O (stret)	1300	0.029	> C=O (stret)	1100	0.063
2 CH <sub>2</sub> (bending)	1400	0.038	2 CH <sub>2</sub> (bending)	1080	0.136
CH <sub>3</sub> (deform)	1140	0.052	CH <sub>3</sub> (deform)	875	0.159
		0.119			0.348

$\Delta S^\ddagger_{\text{vib}} = 0.230 \text{ gibbs/mol}$

$\Delta S^\ddagger_{\text{rot-tors}} = -12.0 \text{ gibbs/mol}$

$\Delta S^\ddagger_{\text{reaction path}} = 2.18 \text{ gibbs/mol}; \Delta S^\ddagger = -9.59 \text{ gibbs/mol}; A = 10^{11.27} \text{ sec}^{-1}$

(b) Valerophenone (300 K)

$(n^\ddagger)^{1/2} = 0.81$

> C=O (stret)	1300	0.029	> C=O (stret)	1100	0.063
1 H-C-H (bending)	1450	0.015	1 H-C-H (bending)	1170	0.024
1 CH <sub>2</sub> (wagging)	1300	0.029	1 CH <sub>2</sub> (wagging)	1050	0.079
1 H-C-C (bending)	1150	0.052	1 H-C-C (bending)	933	0.124
		0.125			0.290

$\Delta S^\ddagger_{\text{vib}} = 0.165 \text{ gibbs/mol}$

$\Delta S^\ddagger_{\text{rot-tors}} = -12.0 \text{ gibbs/mol}$

$\Delta S^\ddagger_{\text{reaction path}} = 1.37 \text{ gibbs/mol}; \Delta S^\ddagger = -10.47 \text{ gibbs/mol}; A = 10^{11.13} \text{ sec}^{-1}$

(c) 2-Methyl-5-phenyl-pentan-5-one (300 K)

$(n^\ddagger)^{1/2} = 0.85$

> C=O (stret)	1300	0.029	> C=O (stret)	1100	0.063
3 H-C-C (bending)	1150	0.156	3 H-C-C (bending)	1020	0.267
		0.185			0.330

$\Delta S^\ddagger_{\text{vib}} = 0.145 \text{ gibbs/mol}$

$\Delta S^\ddagger_{\text{rot-tors}} = -12.0 \text{ gibbs/mol}$

$\Delta S^\ddagger_{\text{reaction path}} = 0.0; \Delta S^\ddagger = -11.85 \text{ gibbs/mol}; A = 10^{10.82} \text{ sec}^{-1}$

N.B. Entropies estimated from the tables in K. S. Pitzer and L. Brewer (revision of Lewis and Randall's) *Thermodynamics*, McGraw Hill, New York, 1961, pp. 431-432.

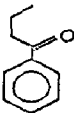
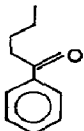
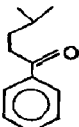
Frequencies taken from R.T. Conley, *Infrared Spectroscopy*, Allyn and Bacon, Boston, 1966.

The term  $\Delta S^\ddagger_{\text{reaction path}}$  was calculated as  $R \ln(g)$ , where  $g$  is the number of equivalent abstractable hydrogen atoms.

The  $A$ -factor is given by:  $A = e^{\frac{kT}{h}} e^{\Delta S^\ddagger/R}$

TABLE 3

COMPARISON OF EXPERIMENTAL AND CALCULATED PARAMETERS

Parameter			
Path degeneracy	3	2	1
$E_a$ (exp)/kcal mol <sup>-1</sup>	6.95	5.65	4.65
$E_a$ (calc)/kcal mol <sup>-1</sup>	7.4	5.6	4.6
log $A$ (exp)	12.08	12.30	12.15
log $A$ (calc)	11.27	11.13	10.82
log $k$ (exp) 20°C	6.93	8.12	8.72
log $k$ (calc) 20°C	5.77	7.00	7.42
Relative $k$ (exp)	1.0	15.5	61
Relative $k$ (calc)	1.0	18	49

## CONCLUSION

From the results and discussion presented above, we conclude that: (i) the intramolecular  $\gamma$ -hydrogen abstraction in aromatic ketones having low-lying  $n, \pi^*$  triplets has the same general characteristics and activation energies as intermolecular photoreductions; (ii) the six-centre abstraction ring is probably quite unstrained; (iii) the activation energies can be estimated using the BEBO method<sup>6,7</sup>; (iv) the calculation of  $A$ -factors by estimation of entropy contributions frequently leads to underestimates, which reflect the difficulties in estimating out-of-plane torsional frequencies in the transition state.

Regarding the experimental technique, we think that the study of the temperature dependence of the competition with diffusion-controlled quenchers provides an insight into the mechanism of these reactions which is not available from isothermal rate constant measurements. If the temperature dependence of reaction (3) could be experimentally measured (*e.g.* by a nanosecond technique)<sup>25</sup>, it would certainly provide a valuable tool for the organic photochemist, since the assumptions involved in eqn. (5) could then be avoided.

Finally, we note that if the technique employed to estimate  $A$ -factors is correct, one would expect the pre-exponential factors for five-centre abstractions, photoenolizations and six-centre abstractions in  $\alpha$ -substituted cyclohexanones to be higher than for 'normal' type II reactions. In the case of seven-centre abstractions the  $A$ -factor is expected to be lower owing to loss of four internal rotations instead of three.



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