

## Temperature Effects in the Photochemistry of Cycloalkanones in Solution

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The effect of temperature changes on product ratios in the photochemical reactions of cycloalkanones is discussed. Data obtained for  $\alpha$ -cleavage products and photoelimination products from monocyclic cyclopentanones and cyclohexanones at different temperatures are consistent with previously suggested reaction mechanisms. The need for closer temperature control in quantitative photochemical investigations is emphasised.

THE effect of changes in temperature on photochemical reactions in the gas phase has been studied in detail for a number of systems, but little is known of the detailed effects of temperature on photochemical reactions in solution. There are several reports in the literature of differences in quantum yield or product ratios caused by changing temperature, and of apparent activation energies in the formation of particular products, but little is known of the origin of such changes for multi-step reactions. Differences in activation energies for competing single-step reactions are of interest in comparing processes which are 'allowed' on orbital symmetry grounds with those which are 'forbidden'. Absolute values of activation energies are not obtainable for single-step photochemical reactions from product measurement. Apparent activation energies for product formation in multi-step reactions have been reported

and discussed for aromatic ketones in intermolecular hydrogen abstraction,<sup>1</sup> and for aromatic ketones in intramolecular photoelimination.<sup>2</sup> In multi-step reactions the rate constants whose variation with temperature is reflected in product ratios or yields are either for primary physical or chemical steps from the excited states of the reactant molecule, or for secondary processes undergone by a first-formed intermediate. Temperature effects on primary rate constants are not directly apparent from product yields if secondary steps are involved. Results obtained with added excited-state quencher must be interpreted with caution because the variation with temperature of the quenching rate constant may not follow simply the change in viscosity of the solution, although in low-viscosity solvents the activation energy for triplet quenching of anthracene does correspond to the activation energy of diffusion.<sup>3</sup> A recent suggestion<sup>4</sup> that triplet quenching in

<sup>1</sup> P. Suppan in 'The Chemistry of Ionization and Excitation,' eds. G. R. A. Johnson and G. Scholes, Taylor and Francis, London, 1967, p. 103.

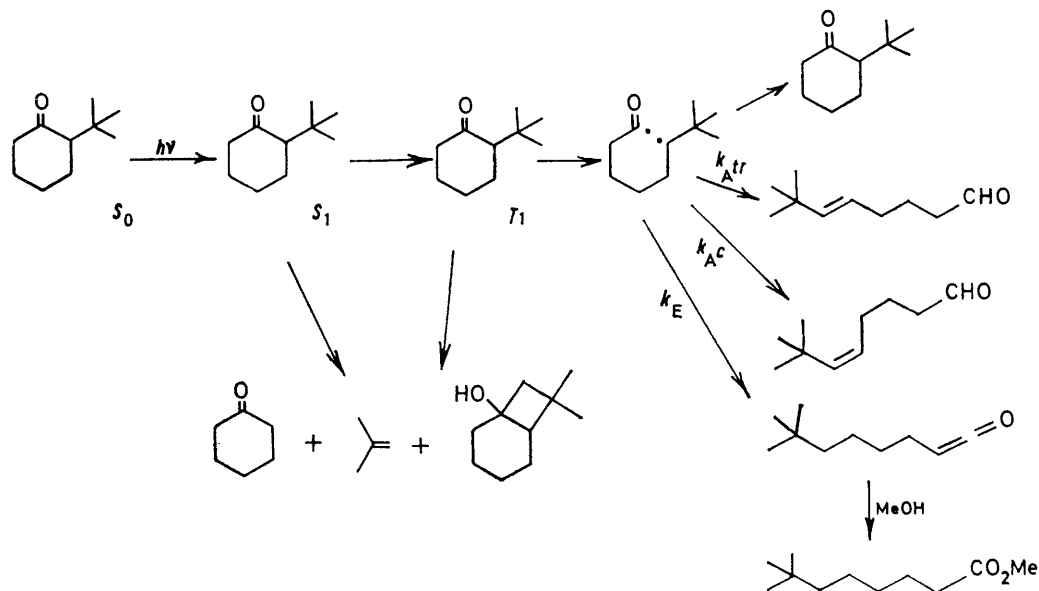
<sup>2</sup> J. A. Barltrop and J. D. Coyle, *J. Amer. Chem. Soc.*, 1968, **90**, 6584.

<sup>3</sup> R. Livingstone and D. R. Ware, *J. Chem. Phys.*, 1963, **39**, 2593.

<sup>4</sup> A. W. Jackson and A. J. Yarwood, *J. Amer. Chem. Soc.*, 1971, **93**, 2801.

the gas phase involves a substantial activation energy cannot be generalised because the energy transfer studied was of the endothermic type. It is therefore possible that changes in rate constants for primary photochemical processes may be masked or magnified by changes in the rate constant for quenching as well as by changes in the rate constants for secondary processes. Effects of changing temperature on the relative rate constants for secondary processes are directly

Cycloalkanones with an alkyl substituent on C(2) may undergo intramolecular photoelimination and photocyclisation in reactions which parallel those of acyclic ketones. The products are a cycloalkanone unsubstituted at C(2) and an alkene, or a cyclobutanol. These reactions occur from both singlet and triplet excited states of the ketone, and do not proceed through the ring-opened biradical intermediate. The chemical processes of importance for cyclopentanones and



SCHEME 1

obtainable from product yield measurements, and it is largely with these effects in the photolysis of cycloalkanones that the present work is concerned.

The photolysis of simple cyclopentanones and cyclohexanones in solution at room temperature leads mainly to isomeric enals and ketens (the latter are trapped as adducts with added nucleophile) through a ring-opened biradical intermediate.<sup>5</sup> For other cycloalkanones decarbonylation products,<sup>6</sup> a cyclic oxacarbene,<sup>7</sup> or epimerised starting material<sup>8</sup> are formed in appreciable yields, and these also are formed through the biradical intermediate. The evidence that a ring-opened biradical is a true intermediate in the reaction sequence is based on studies of isomer ratios of the enal products,<sup>9</sup> of the kinetics of ketone consumption and product formation,<sup>10</sup> of the effects of substitution on quantum yields of enal formation,<sup>11</sup> and on product ratios,<sup>12</sup> and of the labelling pattern in products formed from deuteriated cyclohexanones.<sup>13</sup> The excited state precursor to the biradical is a triplet state, completely quenchable in many cases.

cyclohexanones are illustrated for 2-*t*-butylcyclohexanone in Scheme 1.

#### RESULTS AND DISCUSSION

A series of cyclopentanones and cyclohexanones were irradiated at different temperatures in solution in 3% (v/v) methanol in benzene with light of wavelength around 313 nm. The reaction solution was pre-heated to the required temperature, and this temperature was maintained by immersing the reaction vessel in a thermostatted bath. The lamp was cooled with tap water and was insulated from the reaction solution by a layer of air. The lamp operating temperature is thus not appreciably affected by the temperature of the bath, and the light output is constant. In preliminary work a Rayonet photochemical reaction vessel chamber was used, with the chamber temperature controlled by use of the cooling fan. However, it was found that the lamp output decreased considerably with increasing temperature of the chamber. This does not affect

<sup>5</sup> J. C. Dalton and N. J. Turro, *Ann. Rev. Phys. Chem.*, 1970, **21**, 499.

<sup>6</sup> J. E. Starr and R. H. Eastman, *J. Org. Chem.*, 1966, **31**, 1393.

<sup>7</sup> N. J. Turro and D. M. McDaniel, *J. Amer. Chem. Soc.*, 1970, **92**, 5727.

<sup>8</sup> G. Quinkert, *Pure Appl. Chem.*, 1964, **9**, 607.

<sup>9</sup> C. C. Badcock, M. J. Perona, G. O. Pritchard, and B. Rickborn, *J. Amer. Chem. Soc.*, 1969, **91**, 543.

<sup>10</sup> J. A. Barltrop and J. D. Coyle, *Chem. Comm.*, 1969, 1081.

<sup>11</sup> P. J. Wagner and R. W. Spierke, *J. Amer. Chem. Soc.*, 1969, **91**, 4437.

<sup>12</sup> J. D. Coyle, *J. Chem. Soc. (B)*, 1971, 1736.

<sup>13</sup> W. C. Agosta and W. L. Schreiber, *J. Amer. Chem. Soc.*, 1971, **93**, 3947.

relative product yields, but does affect relative quantum yields from one temperature to another. Additional checks were made to ensure that the absorbance of the

TABLE 1

Ratios of enal (A) to ester (E) in the photolysis of cycloalkanones in 3% (v/v) methanol in benzene <sup>a,b</sup>					
Cyclopentanone	T/K	283	307	321	334
	A/E	24.3	19.5	17.0	15.5
2-Methylcyclopentanone	T/K	283	307	323	336
	A <sup>tr</sup> /E <sup>c</sup>	34.7	27.3	22.4	19.5
Cyclohexanone	T/K	282	307	321	336
	A/E	1.64	1.60	1.57	1.54
2-Methylcyclohexanone	T/K	283	308	321	336
	A <sup>tr</sup> /E <sup>c</sup>	2.54	2.25	2.13	2.00
2-t-Butylcyclohexanone	T/K	283	307	321	336
	A <sup>tr</sup> /E <sup>c</sup>	1.61	1.48	1.42	1.37
2-n-Propylcyclohexanone	T/K	281	307	321	337
	A <sup>tr</sup> /E <sup>c</sup>	2.18	1.96	1.86	1.77
2-Isobutylcyclohexanone	T/K	283	307	321	337
	A <sup>tr</sup> /E <sup>c</sup>	1.72	1.57	1.50	1.43
4-Methylcyclohexanone	T/K		307		338
	A/E		1.01		1.02
4-t-Butylcyclohexanone	T/K	283	307	322	338
	A/E	0.143	0.165	0.180	0.204
2,4-Dimethylcyclohexanone	T/K		308		338
	A <sup>tr</sup> /E <sup>c</sup>		1.34		1.26

<sup>a</sup> Each ratio is the average of 4–10 measurements.

<sup>b</sup> Small variations from previously published values<sup>12</sup> result from a smaller % conversion and more accurate control of temperature. <sup>c</sup> For 2-substituted cycloalkanones the ratios of *trans*-enal to ester are used to avoid the error which would otherwise occur because of the different activation energies for formation of *cis*- and *trans*-enal.

TABLE 2

Ratios of <i>trans</i> -enal (A <sup>tr</sup> ) to <i>cis</i> -enal (A <sup>c</sup> ) formed in the photolysis of cycloalkanones in 3% (v/v) methanol in benzene					
2-Isobutylcyclopentanone	T/K	283	307	321	336
	A <sup>tr</sup> /A <sup>c</sup>	3.94	3.57	3.37	3.22
2-Methylcyclohexanone	T/K	283	308	321	336
	A <sup>tr</sup> /A <sup>c</sup>	3.12	2.84	2.72	2.62

irradiated solution did not change with temperature, and that the photoproducts were not consumed in a thermal reaction.

The products were estimated by g.l.c.,<sup>12</sup> and the results are shown in Tables 1–3. The extent of reaction was less than 5% in most cases, and in others an extrapolation was made to obtain the product ratios at 0% conversion.

The results can be interpreted on the basis of a reaction scheme, such as the one given earlier for 2-t-butylcyclohexanone, and provide further support for the scheme. The enal to ester product ratios (A/E) reflect the relative rate constants for hydrogen transfer,  $k_A$  for transfer from C(3) to C(1), and  $k_E$  for transfer from C(6) to C(2). There are two methods of estimating the difference in activation energy between the two pathways from the tabulated data. (i) It can be assumed that  $k_A$  and  $k_E$ , expressed as  $k_A = A_A \exp(-E_A/RT)$  and  $k_E = A_E \exp(-E_E/RT)$ , have similar pre-

exponential factors (*i.e.*, that  $A_A = A_E$ ), and then ( $E_A - E_E$ ) can be expressed as in equation (1). The

$$\Delta E_{A/E} = E_A - E_E = -RT \ln(k_A/k_E) \quad (1)$$

assumption is reasonable since each reaction involves hydrogen transfer through a transition state resembling a half-chair cyclohexane conformation.<sup>12</sup> A check on the validity of the assumption is possible by comparing the estimates for  $\Delta E_{A/E}$  at different temperatures. If  $A_A/A_E$  is significantly different from unity, estimates of  $\Delta E_{A/E}$  will vary uniformly with temperature change, but it was found that the estimates obtained for a given ketone at the temperatures of the experiments showed

TABLE 3

Relative yields of unsubstituted cycloalkanone (C) and total enal (A) in the photolysis of cycloalkanones in 3% (v/v) methanol in benzene <sup>a</sup>

2-Isobutylcyclopentanone	T/K	307	336
	A	1.00	0.763
	C	0.218	0.309
	A/C	4.59	2.47
2-t-Butylcyclohexanone	T/K	307	336
	A	1.00	0.723
	C	1.03	1.22
	A/C	0.971	0.593
2-n-Propylcyclohexanone	T/K	307	338
	A	1.00	0.810
	C	1.13	1.71
	A/C	0.885	0.474
2-Isobutylcyclohexanone	T/K	307	336
	A	1.00	0.748
	C	1.83	2.36
	A/C	0.546	0.317

<sup>a</sup> The values are given for each ketone relative to the yield of enal at 307 K.

no regular variation and were equal within the experimental error.

(ii) An independent estimate of  $\Delta E_{A/E}$  which does not rest on the assumption that  $A_A = A_E$  can be obtained from a plot of  $\ln(k_A/k_E)$  against  $T^{-1}$ . For the systems studied the estimates of  $\Delta E_{A/E}$  by methods (i) and (ii) are given in Table 4. The error in the numerical values is in the region of 3–8%, although those for 4-methylcyclohexanone and 2,4-dimethylcyclohexanone are subject to greater possible error. Similarly derived values are included in Table 4 for the differences in activation energy between the pathways leading to *cis*- and *trans*-enal (A<sup>c</sup> and A<sup>tr</sup>) for two of the cycloalkanones.

There is good agreement between the estimates of activation energy differences obtained by the two methods, and this indicates that the enals and ketens are formed in competing reaction steps directly from a common precursor. The rate constants for the processes have similar Arrhenius pre-exponential factors, and activation energy differences are as given in Table 4. It is not proved from these results alone that the common precursor is the ring-opened biradical, as it may simply be the triplet excited state of the ketone. These alternatives can be distinguished in principle by con-

sidering the triplet state photoelimination process, which takes place from the triplet excited state but not through the ring-opened biradical. In practice there

TABLE 4

Activation energy differences in the photoreactions of cycloalkanones

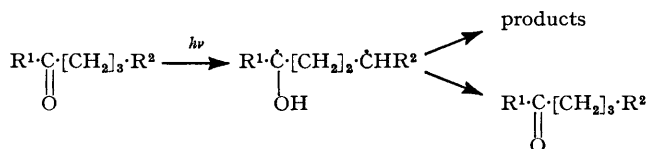
	$\Delta E_{A/E}/\text{kJ mol}^{-1}$	
	Method (i) <sup>a</sup>	Method (ii)
Cyclopentanone	-7.6	-7.1
2-Methylcyclopentanone	-9.0	-8.4
Cyclohexanone	-1.2	-1.1
2-Methylcyclohexanone	-2.8	-2.8
2-t-Butylcyclohexanone	-1.8	-1.7
2-n-Propylcyclohexanone	-2.5	-2.2
2-Isobutylcyclohexanone	-1.9	-2.0
4-Methylcyclohexanone	-0.04	0.28
4-t-Butylcyclohexanone	4.6	4.9
2,4-Dimethylcyclohexanone	-1.5	-1.1

	$\Delta E_{A^0/E^0}/\text{kJ mol}^{-1}$	
	Method (i) <sup>a</sup>	Method (ii)
2-Isobutylcyclopentanone	3.2	3.0
2-Methylcyclohexanone	2.7	2.6

<sup>a</sup> Average value over the temperature range studied.

are too many variables for any quantitative conclusion to be drawn. The ratio of singlet to triplet participation in the elimination reaction varies with temperature, and is not easy to estimate since for some of the ketones the triplet reaction cannot be completely quenched with accessible concentrations of quencher. In addition the triplet photoelimination reaction is thought to go through a hydroxy-biradical which can give rise to products or undergo reverse hydrogen transfer to give the ground state of the reactant ketone.<sup>14</sup>



SCHEME 2

The partitioning of this biradical will be affected by temperature changes, and it is therefore not possible from product yield data to present quantitative evidence in favour of or against a common immediate precursor of the photoelimination product and the ring-opened products. However, a qualitative argument based on the differences between 2-t-butyl-, 2-n-propyl- and 2-isobutyl-cyclohexanone can be presented.

The hydrogen-abstraction step in the photoelimination reaction is affected by the strength of the C-H bond broken, and the apparent activation energy for formation

of products has been estimated<sup>2</sup> for aromatic ketone triplet state reaction, and is found to decrease considerably as the  $\gamma$ -hydrogen atom changes from primary to secondary to tertiary (it is actually negative for 4-methyl-1-phenylpentan-1-one). A similar order is expected for the singlet-state reaction since the rate constants for this are similarly affected by the C-H bond strength,<sup>15</sup> and it is a reasonable assumption that similar effects will operate in the cycloalkanone systems. The ring-opening reactions of the triplet excited state of the cycloalkanones are not greatly affected by the nature of the alkyl substituent at C(2), and the variations in enal: ester ratios found for 2-t-butyl-, 2-n-propyl-, and 2-isobutyl-cyclohexanones are relatively small. It would therefore be expected, if ring-opening and hydrogen abstraction products are formed in directly competing steps from the triplet excited state, that the decrease in the enal: unsubstituted cycloalkanone ratio over a given temperature range should be considerably smaller for 2-isobutylcyclohexanone (with a tertiary hydrogen atom that is abstracted) than for 2-t-butylcyclohexanone (with a primary hydrogen atom that is abstracted). No such effect is observed, the decrease in this ratio over the temperature range used in the experiments being approximately equal for the two ketones, and this provides a qualitative argument in favour of an intermediate subsequent to the triplet state in the formation of enal and keten. It is noteworthy that for cycloalkanones the ratio of  $\alpha$ -cleavage to photoelimination products decreases with increasing temperature, whereas the opposite is true for acyclic ketones.<sup>16</sup> This may arise because the excited singlet state plays a greater part in the photoelimination reaction for cycloalkanones, or because recombination after initial  $\alpha$ -cleavage is more important for the cyclic systems.

These results of variations in product ratios with changing temperature are thus consistent with Scheme 1 for the photochemical reactions of cycloalkanones: the hydrogen-abstraction step occurs directly from the excited states of the ketone, whereas ring-opened hydrogen-transfer products are formed through a common intermediate in turn formed from the triplet state of the ketone.

In the systems studied it is apparent that product ratios and quantum yields of product formation vary considerably with the temperature of the reaction, and the observations emphasise that there must be strict control of temperature in photochemical investigations when quantitative comparisons are required.

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<sup>14</sup> P. J. Wagner, *Accounts Chem. Res.*, 1971, **4**, 168.

<sup>15</sup> N. C. Yang, S. P. Elliott, and B. Kim, *J. Amer. Chem. Soc.*, 1969, **91**, 7551; J. C. Dalton and N. J. Turro, *ibid.*, 1971, **93**, 3569.

<sup>16</sup> C. H. Bamford and R. G. W. Norrish, *J. Chem. Soc.*, 1938 1544.