PHOTOCHEMICAL α CLEAVAGE OF KETONES AS RADIATIONLESS TRANSITIONS

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Summary

The tunnel effect theory, which has previously been employed to interpret the reactivity and efficiency of photochemical hydrogen abstractions, is extended to the interpretation of the α cleavage of ketones. The theory has been used to calculate the reactivity of a large number of ketones and good agreement is found between calculated and experimental values. The reactivity towards α cleavage depends essentially on the strength of the $CO-C_\alpha$ bond, and is also affected by the reduction potential of the ketones. The results of the present model are compared with those from thermal activation studies. It is found that, within the approximations of the models, thermal activation rate constants never exceed those for nuclear tunnelling. The conventional view of the $^3(n,\pi^*)$ excited states of ketones as alkoxy radicals is questioned.

1. Introduction

The homolytic α cleavage of the $^3(n,\pi^*)$ states of ketones has been interpreted in terms of a thermal activation mechanism in which alkoxy radicals are taken as models for n,π^* states [1]. It was recently shown [2] that a similar interpretation of hydrogen atom abstraction reactions by n,π^* states of ketones fails to account for the efficiency and the deuterium isotopic effects of these abstraction reactions. In contrast, the tunnel effect mechanism that was proposed [3] to interpret these photochemical reactions was shown [2] to be a mechanism consistent with existing data. The failure of the conventional alkoxy radical model and the success of the tunnelling model lead us to extend the latter to the study of the photochemical homolytic α cleavage of ketones.

According to the tunnel effect mechanism, photochemical reactions may be viewed as non-radiative transitions between reactant and product potential energy surfaces. The study of such reactions requires a knowledge of the vibrational modes that suffer changes in frequency and/or geometry, because only the energy regions corresponding to these changes are important for electronic energy relaxation [4]. Therefore, the choice of the modes

used to build the potential energy surfaces for the α cleavage can be restricted to the vibrations of bonds that undergo appreciable changes. These are the C=O and C—C bonds in the reactants and the products.

2. Model

Acetone is the smallest ketone and therefore it would be natural to take its reactivity towards α cleavage as the prototype for larger ketones. However, there is not sufficient experimental information concerning the geometry and the force constants of the $^3(n,\pi^*)$ state of acetone and the ground state of the acetyl radical to allow reliable calculations to be performed (Tables 1 and 2 and Fig. 1). The data available for formaldehyde are more complete and it is tempting to take its cleavage as a prototype for the α cleavage of ketones. However, it was recently suggested that formaldehyde is a poor model for the photodissociation of larger carbonyls [16]. Anyway, a deeper insight into α cleavage can be obtained by exploring both the differences and the similarities between formaldehyde and larger carbonyls. We can expect the electrons of the larger carbonyls to behave qualitatively in the same way as formaldehyde upon n,π^* excitation and to follow the behaviour observed for the strengths of the adjacent σ bonds of formaldehyde.

The lone-pair orbital results from the out-of-plane mixing of the π_{CH_2} orbital and the in-plane mixing of the $\pi^*_{CH_2}$ orbital of the methylene fragment with a pure p oxygen orbital p_O. The dominant mixing contribution

TABLE 1

Geometric parameters

		d_{CO} (nm)	d_{CC_α} (nm)	d_{CR} (nm)	β (deg)	δ (deg)	η (deg)
Formaldehyde[a]	S_0	0.12033	0.11005		116.30	—	0
	T_1	0.13070	0.108354		121.766	—	41.144
Formyl radical[b]	S_0	0.117115	—	0.11102	—	127.426	—
Acetone[c]	S_0	0.1214[d]	0.1520[d]				0[d]
	S_0	0.1222[e]	0.1507[e]		117.2[e]		0[e]
Acetyl radical[f]	S_0	0.1245	—	0.1532	—	128.7	—
Cyclopentanone	S_0[g]	0.1226	0.1519		112.4		
Cyclohexanone	S_0[h]	0.1229	0.1503		115.3		

[a]See ref. 5.
[b]See ref. 6.
[c]See ref. 7.
[d]From gas electron diffraction studies.
[e]From microwave studies.
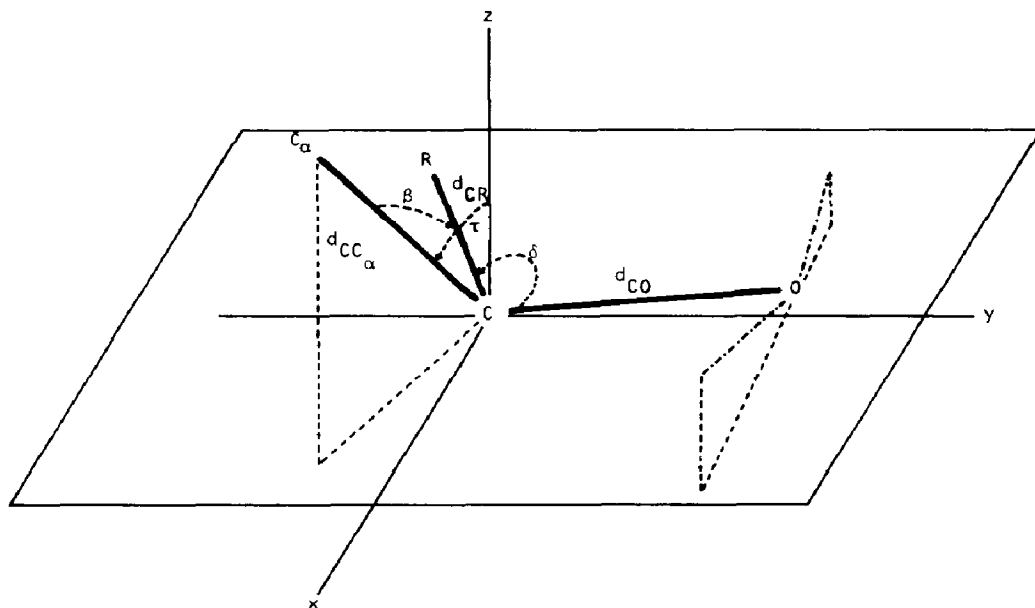[f]Calculated values of ref. 8.
[g]See ref. 9.
[h]See ref. 10.

Fig. 1. Geometric parameters: for the reactive excited state the angle β between the C—C_α and the C—R bonds, and the angle η between the C=O bond and the C_αCR plane, were used to calculate the angle τ. For the optimized reaction path, the same β was used and η was adjusted to seek agreement between calculated and observed α-cleavage rate constants.

TABLE 2

Force constants

	f_{CC}^{s} (N m^{-1})	f_{CO}^{s} (N m^{-1})	f_{CO}^{bi} (N m^{-1})	f_{CO}^{bo} (N m^{-1})	f_{CO}^{b} (N m^{-1})
Formaldehyde[a]	496.3 symmetric 485.2 antisymmetric	1290.3	33.4	23.6	
Formyl radical[b]	342	1424			56.1
Acetone S_0 [c]	432.13	1270.81	131.17	33.19	
T_1 [d]		725			
Cyclopentanone[e]	425.2	1014.9	53.0	20.0	
Cyclohexanone[f]	456.4	965.2	53.6	31.3	

[a] See ref. 11.
[b] See ref. 12.
[c] See ref. 13.
[d] See ref. 3.
[e] See ref. 14.
[f] See ref. 15.

depends on the relative proximity of p_O to π_{CH_2} and $\pi^*_{CH_2}$. In the case of formaldehyde, the out-of-plane mixing of π_{CH_2} represents the main contribution of the resulting n orbital. Thus, when an electron is removed from

the n molecular orbital, some CH bonding character is lost and a decrease in electronic density along these bonds results. This is the driving force for adjacent σ-bond cleavage in n,π^* states. When the CH bond is stretched along its valence direction, the energy gaps separating the p_O and π_{CH_2} orbitals and the p_O and $\pi^*_{CH_2}$ orbitals decrease, allowing the degree of mixing to increase. Therefore semi-occupation of the n orbital weakens the σ bond more and more as elongation proceeds and thus α cleavage is favoured [17].

This qualitative view, together with existing experimental data concerning the energy distribution in reactants and products [18], indicates that the modes promoting the α cleavage of ketones are the C=O stretching vibration (force constant, $f_{CO}{}^s$) and the out-of-plane C=O wag ($f_{CO}{}^{bo}$), which are strongly excited after the electronic excitation, the in-plane C=O wag ($f_{CO}{}^{bi}$), which increases the proximity between the p_O orbital and the reactive σ bond, and the C—C$_\alpha$ stretching vibration ($f_{CC}{}^s$). By the same reasoning, we can expect that the most important acceptor modes in the radical products are the C=O stretch ($f_{CO_p}{}^s$) and the C=O bend ($f_{CO_p}{}^b$).

The same modes are deduced from the tunnel effect theory [4], because they correspond to the bonds C=O and C—C$_\alpha$ which change more significantly in the course of the reaction, as can be seen from Tables 1 and 2. The C—R bond also changes (in formaldehyde there is a 30% decrease in the force constant and a 2.4% increase in the bond length), but to a much smaller extent than the other bonds, so its contribution can be neglected.

The choice of adequate force constants and geometric parameters for use in the calculations of the α-cleavage rate constants deserves comment. To use the values of formaldehyde for the formyl radical in these calculations would be to take the analogy with formaldehyde too far. As the data on acetone are limited, a compromise between what is known from acetone and what can be taken from formaldehyde has to be reached, so that the following assumptions are made.

(i) The C—R bond is not considered to change in the course of the reaction.

(ii) The excited state geometry is the geometry of the T_1 state of formaldehyde, except for the angle η. This angle is taken as 30° for aliphatic ketones [19] and 0° for phenyl ketones [20].

(iii) The angle β of the ketones is taken as that of the T_1 state of formaldehyde and is kept constant along the reaction coordinate.

(iv) The geometry of the radical products is taken from that of the acetyl radical.

(v) The force constants for the reactant ketone are taken as the force constants for acetone in the ground state, except for $f_{CO}{}^s$ which is taken as 725 N m^{-1}.

(vi) The force constants for the radical products are taken as those of the formyl radical.

(vii) The ground state values of β and force constants are used for the T_1 state of cyclopentanones and cyclohexanones except for $f_{CO}{}^s$.

According to the tunnel effect theory, a photochemical reaction is seen as a non-radiative transition from the potential energy curve of the reactants to that of the radical products. The rate of conversion between these two potential energy curves is [3]

$$k_{nr} = \nu \exp \left\{ - \frac{2\pi}{h} |2\mu(D - E_v)|^{1/2} \Delta x \right\} \tag{1}$$

where μ is the reduced mass of the oscillators, $D - E_v$ is the height of the energy barrier and ν is the average frequency of the vibrational modes of the reactant involved in the transition. The transition from the $^3(n,\pi^*)$ states of the reactants to the radical products is taken as adiabatic and no forbidden factor is included in eqn. (1).

In previous applications of the tunnel effect theory it was assumed that the contributions of all the oscillators involved in the transition were equal along the reaction coordinate. However, in the α cleavage of ketones the contributions of the CO and the CC oscillators are distorted, because they participate to different extents in the cleavage. It is still possible to treat these oscillators as a single diatomic molecule for the reactants and another diatomic molecule for the products, but the reduced mass μ of the system has to be taken as a weighted sum of the reduced masses μ_{CO} and μ_{CC} of the CO and CC oscillators.

The force constant of the CO and CC motions in the reactants, for equal displacements from the equilibrium position, is [3]

$$f_r = |f_r cc^2 + f_r co^2 - 2f_r cc f_r co \cos \theta|^{1/2} \tag{2}$$

where $f_r cc$ is the projection of $f_{CC}{}^s$ along the reaction coordinate and $f_r co$ is the sum of the projections $f_{CO}{}^{bi}$ and $f_{CO}{}^{bo}$ along the reaction coordinate of $f_{CO}{}^s$. The values projected are those of the reactive excited state.

For the products, we have

$$f_p = f_p co \cos \left| \arcsin \left(\frac{f_r cc \sin \theta}{f_r} \right) \right| \tag{3}$$

where $f_p co$ is the sum of the projections $f_{CO}{}^s$ and $f_{CO}{}^b$ of the radical products along the reaction coordinate. The arcsine factor accounts for the change in direction of the reaction coordinate after the cleavage.

The coordinate displacement between the potential energy curves of the activated molecule and the radical products is evaluated as [3]

$$R = |r_{CO}{}^2 + r_{CC}{}^2 - 2r_{CO}r_{CC} \cos \theta|^{1/2} \tag{4}$$

As was mentioned above, r_{CO} is evaluated as the change in the projection of the CO bond length along the reaction coordinate from the triplet state of formaldehyde to the ground state of the acetyl radical. However, r_{CC} is difficult to estimate because it involves a dissociative bond. Therefore R is treated as an adjustable parameter.

Assuming that all the oscillators have harmonic behaviour, it is possible to calculate the energy term $(D - E_v)^{1/2}$ in eqn. (1) by making use of the previously defined force constants, the coordinate displacement and the enthalpy of the reaction. The evaluation of k_{nr} also requires a knowledge of $\mu^{1/2}$ and Δx. This last term is given by the sum of two contributions Δx_{CC} and Δx_{CO} which are expected to be proportional to the contributions r_{CC} and r_{CO} of each oscillator to R.

$$\Delta x_{CO} = \frac{\Delta x}{r_{CO} + r_{CC}} r_{CO} \tag{5a}$$

$$\Delta x_{CC} = \frac{\Delta x}{r_{CO} + r_{CC}} r_{CC} \tag{5b}$$

The rate constant for α cleavage becomes

$$k_{te} = \nu \exp\left\{- \frac{2\pi}{h} |2(D - E_v)|^{1/2} \left(\mu_{CC}^{1/2} \frac{r_{CC}}{r_{CC} + r_{CO}} + \mu_{CO}^{1/2} \frac{r_{CO}}{r_{CC} + r_{CO}}\right)\Delta x\right\} \tag{6}$$

and we can define the reduced mass of the system as

$$\mu = \left(\frac{\mu_{CC}^{1/2}r_{CC} + \mu_{CO}^{1/2}r_{CO}}{r_{CC} + r_{CO}}\right)^2 \tag{7}$$

This expression for the reduced mass accounts for the relative distortion of the CO and CC oscillators in the α cleavage of ketones.

It is possible to compare the predictions of the tunnel effect theory with those of a thermal activation model within the previously defined approximations. The rate constant for a unimolecular reaction such as α cleavage is given by standard thermal activation theory as [21]

$$k_{ta} = \kappa \frac{kT}{h} \frac{q_0^{\ddagger}}{q_0(A^*)} \exp\left(- \frac{\Delta U_0^{\ddagger}}{RT}\right) \tag{8}$$

where κ is the transmission coefficient, $q_0(A^*)$ is the molecular partition function for the activated reactant molecule, $q_0^{\ddagger}$ is the partition function of the activated complex divided by the partition function for the vibration along the reaction coordinate, $\Delta U_0^{\ddagger}$ is the zero-point internal activation energy (which can be considered equal to $D - E_v$) and the other symbols have their usual meaning.

$q_0(A^*)$ can be calculated but the precise evaluation of $q_0^{\ddagger}$ is not possible because it requires the structure of the activated complex to be known. A maximum for the pre-exponential factor of eqn. (8) can be estimated by taking $\kappa = 1$ and assuming that the transition state for α cleavage resembles the excited ketone rather than the radical pair [22 - 24].

Under these circumstances, the pre-exponential factor is

$$A = \frac{kT}{h} \left\{ 1 - \exp\left| - \frac{h}{kT} \frac{1}{2\pi} \left(\frac{f_\tau}{\mu}\right)^{1/2} \right| \right\} \qquad (9)$$

In our calculations we adjust two parameters. One of these is the angle η between the C_α—CO bond and the RCO plane; its adjustment optimizes the force constants. The other parameter is R and its adjustment reproduces the effect of the media and the substituents on the rate constants.

3. Results and discussion

In Tables 3, 4 and 5 the results of our calculations for 22 ketones are presented. Using the force constant defined in eqn. (2) and the reduced mass given by eqn. (7), we obtain $\nu \approx 3 \times 10^{13}$ s^{-1}. The pre-exponential factor of eqn. (8) was found to be close to 6×10^{12} which is commonly used for unimolecular decomposition reactions and which is close to the pre-exponential factors recently used by Encina et al. [1] for α-cleavage reactions.

For endothermic cleavages it was considered that the radiationless transitions occur from the thermally populated level with just the necessary amount of energy for the transition. The population of the levels was considered to follow a simple Boltzmann distribution, which is a reasonable approximation for large polyatomic molecules.

There are large uncertainties associated with the enthalpies of the cleavages. Most of these come from the enthalpies of formation of the radical products. For example, although the heat of formation of the tert-butyl radical was until recently accepted as 32 ± 5.0 kJ mol^{-1} [28], this has been questioned in the last few years and a value of 43.9 kJ mol^{-1} is now accepted [37]. For some ketones of interest we were not able to find experimental data concerning the heats of formation of the reactant molecule and/or the radical products. In such cases, the heats of formation were estimated using group additivity [27, 39].

An effort has been made to include an updated and coherent set of heats of formation in Tables 3 and 4; nevertheless a few discrepancies can be noticed. The largest of these is between 2-pentanone and 2-butanone. They have similar structures and we can also expect their reactivity to be similar. However the enthalpies for their cleavages differ by 6.7 kJ mol^{-1}. This difference is, again, a reflection of the uncertainty of the heats of formation of the radical products.

The inherent limitations of the calculations do not blur the striking result that the calculated rate constants for thermal activation never exceed those for nuclear tunnelling, although for a few cases competition between the two mechanisms may exist.

It is also remarkable that for a reaction path with a CO out-of-plane angle 10° larger than the CO out-of-plane angle of the excited reactive ketone, the force constants thus obtained reproduce reasonably well the

TABLE 3

Rates of photochemical α cleavage of alkanones and cycloalkanones ($\eta = 40°$)

Ketones	Experimental conditions	E_T (kJ mol⁻¹)	$\Delta H_f°$ (RCO—R'(g)) (kJ mol⁻¹)	$\Delta H_f°$ (RCO(g)) (kJ mol⁻¹)	$\Delta H_f°$ (R·(g)) (kJ mol⁻¹)	$\Delta H_r°$ (kJ mol⁻¹)	$E_{1/2}$ (V)	R (nm)	$\log k_{ta}$[a]	$\log k_{te}$[a]	$\log k_r$[a]
Acetone 1	Gas phase 298 K [25]	326.4 [26]	−217.15 ± 0.50 [27]	−24.3 ± 1.7 [28, 29]	146.9 [30]	−13.35	−2.53 [31] −2.57 [32] −2.59 [32]	0.063	2.4	2.6	2.8 [32]
Butanone 2	Gas phase 303 K [33]		−238.57 ± 0.84 [27]	−24.3 ± 1.7 [28, 29]	108.4 [28, 29, 34]	3.73		0.063	4.6	4.9	4.8 [33]
3-Methyl-butanone 3	Gas phase 303 K [33]		−262.59 ± 0.88 [27]	−24.3 ± 1.7 [28, 29]	76.1 ± 6.3 [28, 29]	12.01		0.063	5.5	6.9	6.8 [35]
Butanone 2	Water [36]		−238.57 ± 0.84 [27]	−24.3 ± 1.7 [28, 29]	108.4 [28, 29, 34]	3.73		0.057	6.1	6.7	6.7 [36]
2-Pentanone 4	n-Hexane 293 K [35]		−259.07 ± 1.09 [27]	−24.3 ± 1.7 [28, 29]	94.6 [28, 29, 34]	−2.97		0.0555	5.5	5.5	5.2 [35]
4-Methyl-3-pentanone 5	n-Hexane 293 K [35]		−286.10 ± 1.13 [27]	−42.7 ± 4.2 [28, 29]	76.1 ± 6.3 [28, 29]	6.90		0.0555	6.7	7.8	8.1 [35]
3,3-Dimethyl-2-butanone 6	n-Hexane 293 K [35]		−289.87 ± 1.05 [27]	−24.3 ± 1.7 [28, 29]	43.9 [37]	16.93		0.0555	7.8	9.5	9.9 [35]
Dibenzyl ketone 7	Benzene [38]	330.5 [38]	5.0 ± 6.3 [27]	92.0 [39]	188.7 [28, 29]	54.8	−2.10 [31]	0.071	7.5	10.0	>10 [38]
Cyclohexanone 8	Benzene [40]	326.4 [26]	−226.10 ± 2.18 [27]	95.4[b]		4.90	−2.40 [32]	0.061	5.8	6.4	6.7 [40]
2-Methyl-cyclohexanone 9	Benzene [40]		−250.12[b]	58.95[b]		17.33		0.061	7.3	8.8	8.4 [40]
2,2-Dimethyl-cyclohexanone 10	Benzene [41]		−277.40[b]	25.1[b]		23.90		0.061	8.0	9.7	9.3 [41]
2-Phenyl-cyclohexanone 11	Benzene [42]		−153.3[b]	133.3[b]		39.8	−2.21	0.067	8.0	10.0	10.0 [42]
Cyclopentanone 12	Methanol 298 K [40]	326.4 [26]	−192.59 ± 1.67 [27]	109.2[b]		24.61	−2.46 [32]	0.060	6.0	8.3	8.1 [40]
2-Methyl-cyclopentanone 13	Methanol [40]		−216.61[b]	77.0[b]		32.79		0.060	6.8	9.2	9.5 [40]

For ketones 1 - 7 $\tau = 53.92°$, $f_r = 387.6$ N m⁻¹ and $f_r = 92.7$ N m⁻¹. For ketones 8 - 11 $\tau = 50.42°$, $f_r = 390.5$ N m⁻¹ and $f_r = 8.15$ N m⁻¹. For ketones 12 and 13 $\tau = 48.93°$, $f_r = 370.7$ N m⁻¹ and $f_r = 123.1$ N m⁻¹.

[a] k_{ta} and k_{te} are rate constants (per RCO—R' bond) calculated from the theories of thermal activation and tunnelling; k_r is experimentally observed rate constant per RCO—R' bond.
[b] Estimated using group additivity (see ref. 27, p. 590 and ref. 39, p. 338).

TABLE 4

Rates of photochemical α cleavage of aryl ketones ($\eta = 10°$, $\tau = 80.05°$, $f_r = 433.7$ N m^{-1} and $f_p = 307.0$ N m^{-1})

Ketones	Solvent and temperature	E_T (kJ mol^{-1})	$\Delta H_f°$ (RCO—R') (kJ mol^{-1})	$\Delta H_f°$ (RCO(g)) (kJ mol^{-1})	$\Delta H_f°$ (R'·(g)) (kJ mol^{-1})	$\Delta H_r°$ (kJ mol^{-1})	$E_{1/2}$ (V)	R (nm)	$\log k_{ta}$	$\log k_{te}$	$\log k_r^a$
Ph—C(=O)—CH(CH₃)₂ 14	Dodecane 298 K [1]		-140.1^b	109.2 ± 8 [28, 29]	76.1 ± 6.3 [28, 29]	-26.2	-1.495 [43]	0.0454	0.3	3.9	3.9 [1]
Ph—C(=O)—C(CH₃)₃ 15	n-Hexane 298 K [1]	299.2 [22]	-167.4^b	109.2 ± 8 [28, 29]	43.9 [37]	-21.3	-1.550 [43]	0.036	4.4	6.9	6.9 [1]
Ph—C(=O)—CH₂—Ph 16	Benzene 295 K [22]	301.2 [22]	22.2 ± 5.4 [27]	109.2 ± 8 [28, 29]	188.7 [28, 29]	25.5	-1.370 [44]	0.054	1.2	6.2	6.2 [22]
Ph—C(=O)—CH(CH₃)Ph 17	Benzene 295 K [22]	305.4 [22]	-1.84^b	109.2 ± 8 [28, 29]	165.7 [45]	28.7		0.0515	2.7	7.3	7.3 [22]
Ph—C(=O)—C(CH₃)₂Ph 18	Benzene 295 K [22]	305.4 [22]	-29.12^b	109.2 ± 8 [28, 29]	135.6 [45]	31.5		0.0498	3.8	8.1	8.1 [22]

a k_{ta} and k_{te} are rate constants calculated by the theories of thermal activation and tunnel effects; k_r is the experimentally observed rate constant.

b Estimated using group additivity (see ref. 27, p. 590).

TABLE 5

Substituent effects[a]

	$E_{1/2}$[b] (V)	R (nm)	$\log k_r$[c]
$4\text{-CH}_3\text{—C}_6\text{H}_4\text{—CH}_2\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—Ph}$ 19	−1.531	0.054	6.18
$4\text{-F—C}_6\text{H}_4\text{—CH}_2\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—Ph}$ 20	−1.502	0.05495	5.83
$\text{C}_6\text{H}_5\text{—CH}_2\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—Ph}$ 16	−1.497	0.0551	5.75
$4\text{-Cl—C}_6\text{H}_4\text{—CH}_2\text{—}\overset{\displaystyle O}{\overset{\|}{C}}\text{—Ph}$ 21	−1.440	0.0558	5.59
$3\text{-F—C}_6\text{H}_4\text{—CH}_2\text{C}\overset{\displaystyle O}{\overset{\|}{}}\text{—Ph}$ 22	−1.430	0.05605	5.45

[a]The enthalpy, geometries and force constants of 16 were used. Carbon tetrachloride was used as the solvent.
[b]$E_{1/2}$ for substituted benzophenones, assumed to be proportional to the value of $E_{1/2}$ of substituted deoxybenzoins [46].
[c]See ref. 23.

reactivity of all the ketones studied. This includes both a wide range of reactivities (from 1.4×10^3 to above 10^{10} s^{-1}) and a large diversity of structures (alkanones, cycloalkanones and aryl ketones).

Our results are not significantly dependent upon the assumptions made concerning the reactant or product geometry and the force constants involved in the cleavages. For example, a 20% decrease in the angle η of the $^3(n,\pi^*)$ state of the aliphatic alicyclic ketone increases the calculated value of $\log k$ by only 7% so that the tunnel effect mechanism is still dominant. If R is adjusted for the decrease in this angle, or for a 20% decrease in the force constants, the dominance of the tunnel effect becomes even clearer and the good fit between the experimental and the calculated rate constants is maintained. Although decreasing the force constants by 20% appears to make the thermal activation mechanism dominant for a few aliphatic alicyclic ketones, it is not possible to adjust R to reproduce the variations between the experimental values. Under these circumstances, a poor repro-

duction of these variations can be obtained by optimizing the angle η for the reaction path, but this optimization also re-establishes the dominance of the tunnel effect mechanism. In summary, within this model we have not found a case where the thermal activation mechanism is dominant.

The values of R are also reasonable. For example, with $R = 0.063$ nm the contribution of r_{CC} is 0.0727 nm. Adding this to $d_{CO-C_\alpha} = 0.152$ nm, the radius of each newly formed radical centre becomes 0.112 nm which compares fairly well with half the C—C bond distance between two layers of graphite (0.167 Å) [47].

In previous applications of the tunnel effect mechanism, a correlation was found between R and the reduction potential of the reactive ketone [3]. Such a correlation should also exist for α cleavage reactions.

One problem is that no single set of reduction potentials has been obtained for these ketones. As the values of $E_{1/2}$ obtained for the same ketones vary between different groups of workers, some discussion is necessary concerning the most suitable values for one-electron reduction in the present case.

Powers and Day [31] studied the halfwave potentials $E_{1/2}$ of ketones 1, 7 and 8, while Kabasakalian and McGlotten [32] made a similar study of several n-alkyl and cycloalkyl ketones. The value of $E_{1/2}$ for 8 proposed by Powers and Day disagree with the $E_{1/2}$ values of cycloalkyl ketones proposed by Kabasakalian and McGlotten. As these latter authors presented a more complete and coherent set of results, their values for ketones 1 and 8 were employed here. The value of $E_{1/2}$ for 7 given by Powers and Day was corrected for the difference found for that of 1 between the two sets of results. The halfwave potential of 11 was estimated by adding the change in $E_{1/2}$ from acetone to benzyl methyl ketone [31] to that of 8. Figure 2(a) shows the correlation between the halfwave potentials thus obtained and the corresponding values of R optimized to reproduce the α cleavage rate constants in non-polar environments.

In a study of a series of alkylphenones Elving and Leone [43] showed that the variation in the reduction potentials depends mainly on inductive effects. The halfwave potentials reported by Elving and Leone [43] for acetophenone, propiophenone, n-butyrophenone, 14 and 15, and by Calzolari and Furlani [44] for acetophenone and 16, can be employed on correcting the value of $E_{1/2}$ of 16 for the difference in the value of $E_{1/2}$ of acetophenone between the two sets of results. The value of $E_{1/2}$ for 17 and for 18 can be estimated from that of 16, assuming that it changes as does the value of $E_{1/2}$ for acetophenone on going from propiophenone to 14. In Fig. 2(b) the correlation between the optimized values of R for the aryl ketones and their estimated halfwave potentials are presented.

The effect of substituents on photochemical α cleavages can also be interpreted according to the present model. Table 5 shows the results for a series of substituted deoxybenzoins, assuming the enthalpies for their cleavages to be same as that for 16. Figure 2(c) shows the correlation of the optimized values of R for the deoxybenzoins with their halfwave potentials.
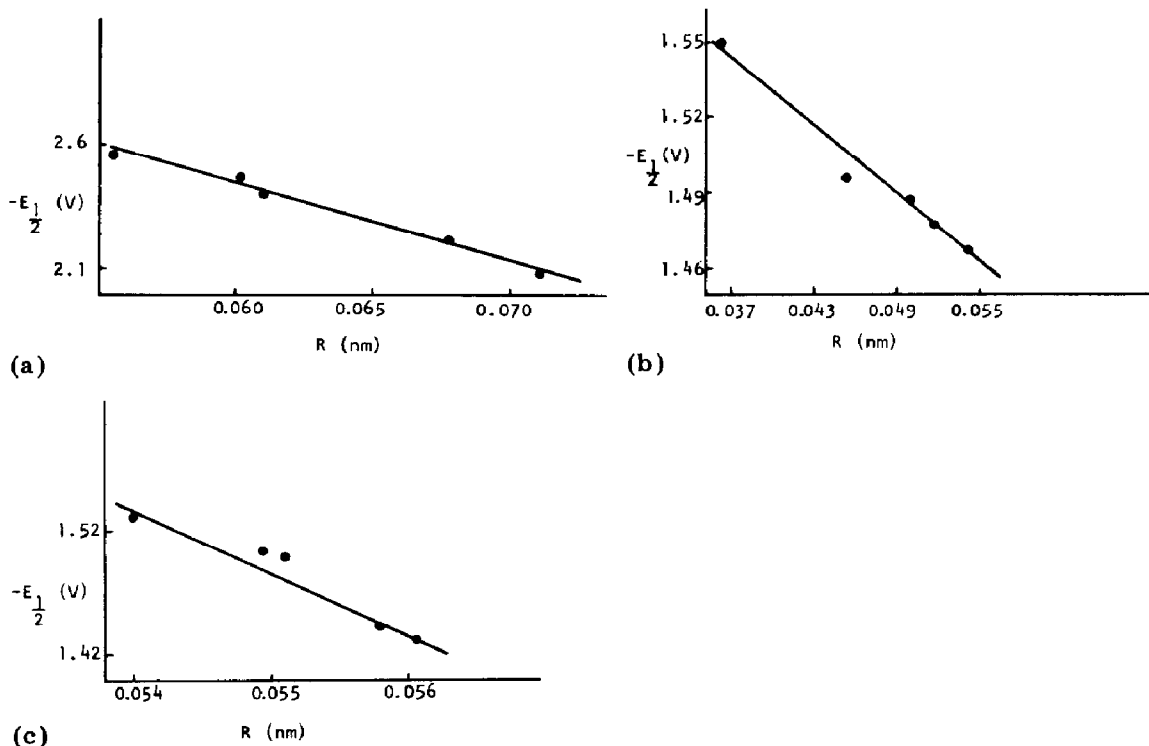
Fig. 2. Correlation between R and $E_{1/2}$: (a) aliphatic ketones of Table 3 in non-polar solvents; (b) aryl ketones of Table 4; (c) ketones of Table 5.

The values of $E_{1/2}$ were taken from Zuman et al. [46] for substituted benzophenones and it is assumed that their relative changes are similar to those of the substituted deoxybenzoins.

The correlation between R and the reduction potentials of the ketones provides an explanation for the reactivity of excited ketones in α cleavage, which is an alternative to the model proposed by Lewis and coworkers [22 - 24].

Not much significance should be attached to the change of R from water to n-hexane, because it is affected by the uncertainties in the heats of formation. However, the dramatic effect of the medium on R from the gas phase to water deserves some comment. This cannot be due to a change in r_{CO} because r_{CO} is kept constant in the course of the calculations, but it may be due to the fact that the radical products in water are trapped in the solvent cage, or may be due to a smaller halfwave potential of the ketone in water.

Encina and Lissi [35] attempted to correlate the solvent dependence of the rate constants k_{II} and k_{I} for hydrogen atom abstraction and α cleavage of ketones respectively with the corresponding rate constants of alkoxy radicals. For the photochemical reactions they found a 3.6-fold increase in k_{II}/k_{I} from the gas phase to the solvent acetonitrile, while for the alkoxy radicals there is a 65-fold decrease for k_{II}/k_{I}. This may be taken as evidence

that alkoxy radicals are not good models of the reactivity of the n,π^* states of ketones.

The α cleavage of 2-phenylcyclohexanone provides an interesting test of the reaction coordinate used in this work. This cleavage was suggested [42] to proceed through two kinetically distinct triplets. During cleavage, the α-carbon can move below or above the plane of the cyclohexanone ring, with the axial α-hydrogen concurrently turning in towards or out away from the ring. It was suggested that the former motion produces a trans-enal with $k_r \approx 1.0 \times 10^{10}$ s^{-1} and the latter produces a biradical which would perform more rotations before forming a cis-enal and also some trans-enal with $k_r \approx 2 \times 10^9$ s^{-1} [42]. In our model, the angle of the cyclohexanones should decrease on excitation to their $^3(n,\pi^*)$ states, in which the sp^2-hybridized carbon atom acquires some sp^3 character, approaching the angle β of cyclohexane (111.4° $\pm$ 0.2°) [48]; concurrently, if the axial atom turns in towards the ring, steric interactions should lead to an increase in β and compensate the decrease on excitation. This situation corresponds to the higher reactivity possible for cyclohexanones and is represented in Table 3. In the case where the axial α atom turns out away from the ring we can expect a smaller β and a lower reactivity. In fact, with $\beta = 113.8^\circ$ (1.5° smaller than the value of β used to calculate the values in Table 2 for cyclohexanones) the reactivity of 2-phenylcyclohexanone drops to 2×10^9 s^{-1}. This result supports the reaction pathway used in this work.

Recently we have shown that, for photochemical hydrogen abstraction reactions by carbonyl compounds, structure–efficiency relationships provide an experimental criterion to distinguish between thermal activation and nuclear tunnelling [2]. The same is also true for the photochemical α cleavage of ketones. In this reaction the ground state of the ketone is correlated with the energy curve of the radical products [49]. Along the reaction coordinate in the radical products there is some probability P_{S_0} of a jump from the radical energy curve to the ground state. Such a probability, according to the Landau–Zener expression [50], is high when the molecular fragments move with a low velocity v along the product energy curve and decreases markedly as v increases. For any reaction where the yield Φ_C of conversion for triplet radicals is unity, the yield Φ_D of decomposition can be temperature dependent for a tunnelling mechanism because v can increase with an increase in temperature (Fig. 3). However, it is expected that Φ_D is independent of temperature for a thermal activation mechanism, because v is independent of temperature for all the molecules which go over the energy barrier. Therefore

$$\Phi_D = \Phi_T \Phi_C (1 - P_{S_0}) \qquad (10)$$

where Φ_T is the yield of triplet formation. For a tunnelling mechanism Φ_D must also increase with the exothermicity of the cleavages, while a thermal activation mechanism does not distinguish between endothermic and exothermic cleavages through the yields of decomposition (Fig. 3).
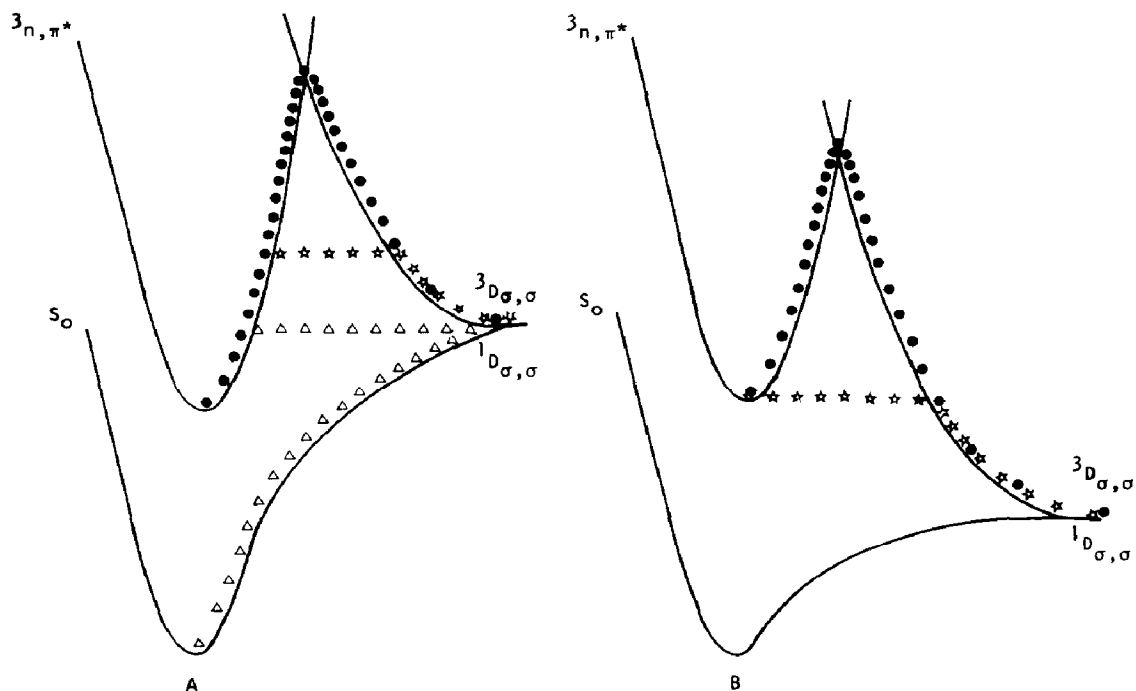
Fig. 3. Correlation of the potential energy curves of the excited state, ground state and radical products: ●, thermal activation; △, tunnelling with low velocity near the touching region; ☆, nuclear tunnelling with high velocity near the touching region. Curve A shows an endothermic cleavage and the effect of temperature in the tunnelling mechanism. Curve B shows an exothermic cleavage.

Table 6 shows some experimental quantum yields of aryl ketones which are uncorrected for cage recombination, as well as values of Φ_C calculated taking the rate of non-radiative decay for aromatic ketones in benzene solution as 3×10^5 s^{-1} [51]. The tunnelling model predicts that Φ_D for **16, 17** and **18** will be close to unity because strongly exothermic cleavages lead to a large v. However, it is expected that the endothermic cleavages of **14** and **15** have lower values of Φ_D which increase with increase in temperature. After correcting for all cage effects in the cleavage of **17**, Lewis and Maggar [52] indeed proposed $\Phi_D = 1.0$ for this ketone. Furthermore, considering the similarities in structure and quantum yields of **16, 17** and **18**, it is reasonable to suppose that for all these ketones $\Phi_D \approx 1.0$. Making use of Table 6 and eqn. (10), and knowing that for these ketones $\Phi_T = 1.0$, we obtain $P_{S_0} \approx 0$. The quantum yields for **14** and **15** are smaller than the quantum yields for the other ketones under similar conditions. Assuming the cage effects in the photochemistry of **15** to be proportional to those of **16**, we estimate $\Phi_D = 0.68$ for this ketone, which leads to $P_{S_0} \approx 0.29$. The cleavages of **14** and **15** are also strongly temperature dependent.

The interpretation of the data on aryl ketones is limited by the difficulty in quantifying the effect of the temperature on the probability of

TABLE 6

Quantum yields of aryl ketones

Ketone	ΔH_r (kJ mol^{-1})	log k_r	T (K)	Φ_{obs}[a]	Φ_c
O‖ Ph—C—CH(CH$_3$)$_2$ 14	−26.2	$12.7 - \dfrac{7.3}{2.3RT}$[b]	369 453	0.09[c] 0.32[c]	0.55 0.96
O‖ Ph—C—C(CH$_3$)$_3$ 15	−21.3	$12.3 - \dfrac{12}{2.3RT}$[b]	298 363	0.3[d] 0.78[e]	0.96 1.0
O‖ Ph—C—CH$_2$Ph 16	25.5	6.2[f]	298	0.44[g]	0.84
O‖ Ph—C—CH(CH$_3$)Ph 17	28.7	7.3[f]	298	0.44[g]	0.99
O‖ Ph—C—C(CH$_3$)$_2$Ph 18	31.5	8.1[f]	298	0.45[g]	1.0

[a] Quantum yield for formation of benzaldehyde uncorrected for cage recombination.
[b] See ref. 1.
[c] Dodecane was used as the solvent (in the presence of hexanethiol to trap alkyl radicals produced) [1].
[d] Benzene was used as the solvent (containing 1-dodecanethiol; conversion below 2%) [51].
[e] n-Hexane used as solvent [1].
[f] See ref. 22.
[g] See ref. 52. Using conditions of ref. 51 but extrapolating to zero conversion.

cage recombination, but the change in P_{S_0} with the enthalpy of the reactions provides support for a tunnelling model.

Tunnelling is also supported by experimental data in the vapour phase. Φ_D for acetone in the gas phase decreases from 1.00 at 423 K to 0.28 at 317 K [25]. Throughout this temperature range Φ_T is unity. Φ_C can be estimated from the value of k_r and the triplet decay rate k_{nd} in the absence of reaction. Using the values of O'Neal and Learson [25] with $\Phi_C = 1.0$ at 413 K we can estimate $\Phi_C = 0.37$ at 317 K, which leads to $P_{S_0} = 0$ at 413 K but $P_{S_0} = 0.25$ at 317 K. It is interesting to note that the values of P_{S_0} for the endothermic cleavages of acetone at 317 K and 2-phenylpropiophenone are rather similar.

The cleavage of butanone follows the same trend as that of acetone. Φ_D is reported to be 1.0 at 373 K, 0.95 at 330 K and 0.35 at 321 K, while

Φ_T is always unity [33]. Considering k_{nd} for butanone to be identical with that of acetone $(4.3 \times 10^{-3} \text{ s}^{-1}$ at 303 K), we estimate $\Phi_C \approx 0.94$ at 303 K. This leads to $P_{S_0} \approx 0$ at 373 K and $P_{S_0} = 0.63$ at 303 K. This last value must be regarded as an upper limit because the low Φ_D at 321 K has been questioned in terms of incomplete acetyl radical dissociation and biacetyl quenching of the reactive excited state [33].

For α cleavages of ketones which have been suggested to proceed from singlet states or lowest excited states of π,π^* character, the present kinetic or thermochemical data are too imprecise to allow a quantitative application of the tunnelling model.

4. Conclusions

The extension of the tunnel effect theory to the photochemical α cleavage of ketones provides a unifying explanation for the observed reactivities.

The extended tunnelling model is able to explain the effects of the medium, substituents, CO—C_α bond strength and structure of the ketone on its reactivity. According to this model, the reactivity of α cleavage depends essentially on the stability of the radicals formed immediately after the cleavage as well as on the inductive effects of substituents. The dependence on the inductive effects can be analysed in terms of the change of the displacement R with the reduction potential of the ketones, which is considered to depend essentially on inductive effects [43]. The proposed model is a valuable alternative to the conventional model in which the n,π^* excited states of ketones are considered to behave just like alkoxy radicals, although the conventional alkoxy radical model may remain helpful for purely qualitative interpretations.

The tunnelling model is experimentally supported by the relationship between the thermochemistry of the cleavages and their observed quantum yields.

Acknowledgments

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