

STRUCTURE-EFFICIENCY RELATIONSHIPS IN HYDROGEN PHOTOABSTRACTION REACTIONS BY KETONES: THERMAL ACTIVATION *VERSUS* NUCLEAR TUNNELLING

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Summary

The tunnel effect theory is applied to a study of the efficiency of hydrogen photoabstractions by excited states of carbonyl compounds. Efficiency depends on the energy of the crossing point ω of the potential energy curves of S_0 and of the radical intermediate state I and consequently depends on the CH bond strengths, the oscillator displacements, the nature of the electronic states, the ionization energy of the substrates, the affinity of the ketones and the solvent polarity. The theory shows that the dependence of the efficiency on the molecular structure provides a good criterium to distinguish between the mechanisms of tunnelling and thermal activation. Experimental data support the view that hydrogen photoabstractions occur via a tunnelling mechanism and not via a thermal activation process. Qualitative rules of structure-efficiency relationships are presented.

1. Introduction

Photochemical hydrogen abstractions by carbonyl compounds have so far been interpreted in terms of either thermal activation [1-3] or tunnelling processes [4-7]. Since thermal activation and tunnelling lead to different mechanisms and can provide different energy contents for excited molecules, attempts have been made to distinguish between these two mechanisms in intramolecular hydrogen photoabstraction reactions. Encina and coworkers [8, 9] have tried to establish such a distinction in terms of the magnitude of the pre-exponential factor A and claim that tunnelling is not a viable mechanism, because the experimental A values are very high (10^{12} - 10^{13} s⁻¹). Nevertheless, this is not a good criterium, because very large frequency factors (10^{14} - 10^{12} s⁻¹) are also found in non-radiative processes in large molecules. Carbonyl triplet states of n, π^* nature are generally considered to react like free radicals and alkoxy radicals have been used as models for hydrogen photoabstraction reactions [1-3]. However, n, π^* triplets also show very low deuterium isotope effects and such observations cannot be understood within the alkoxy-type model [10], although they can be well

explained in terms of a tunnelling mechanism [4, 5]. Here we show that, for photochemical hydrogen abstraction, structure–efficiency relationships [11–16] can provide a clear criterium to distinguish between thermal and tunnelling processes.

2. Theoretical model

2.1. Thermal activation versus nuclear tunnelling

On energy surfaces energy barriers to chemical transformation are overcome through nuclear motion. For a photochemical reaction nuclear motion on potential energy surfaces involves a conversion of electronic energy into vibrational and/or rotational energy. Such an energy conversion requires the population of promoting modes in reactant states to allow coupling of vibronic motion in the reactants and products, but may also require the population of accepting modes to accommodate the excess internal energy developed during the reaction. If a photochemical reaction is controlled by an energy barrier on a reaction coordinate that involves promoting modes, but no accepting modes, reaction can only proceed through thermal activation, because nuclear motions along the reaction coordinate do not provide the necessary ingredients for radiationless transitions to occur. An example of such a kind of reaction may be the *cis*–*trans* photoisomerization, where the energy barrier caused by an internal rotation around a π bond cannot be overcome easily through tunnelling owing to the large masses involved. However, if the reaction coordinate involves promoting and accepting modes, energy barriers can be overcome by thermal activation (over-the-barrier) or tunnelling (through-the-barrier) processes. Photochemical hydrogen abstractions by carbonyl compounds are reactions of this second type, because the vibrational modes, CO, CH and OH, that suffer large displacements between the reactants and products are good accepting modes for radiationless transitions. Consequently, in principle, for hydrogen atom photoabstractions competition between thermal activation and a nuclear tunnelling mechanism can exist.

Salem diagrams [17] for hydrogen abstractions reveal the existence of a crossing point ω between the excited state surfaces and the S_0 surface along the reaction coordinate. Such a crossing has the characteristics of an inter-system crossing (ISC) process when the excited state is a triplet state and is an internal conversion (IC) when the excited state is a singlet state. On the basis of such correlation diagrams Turro and Ramamurthy [18] suggested that inefficiency in photochemical triplet cycloadditions and hydrogen abstractions may result before the formation of intermediates rather than be the result of any secondary reaction of the intermediates. These researchers have also pointed out a correlation between the efficiency and the magnitude of the spin–orbit coupling in the ISC process. Wagner *et al.* [19] have suggested a similar mechanism to interpret the heavy-atom effects for γ hydrogen abstraction in δ haloketones.

Analysis of a nuclear configuration diagram for hydrogen abstraction reactions, involving T_1 (or S_1), S_0 and the intermediate ground state I, reveals that other molecular factors can also play a significant role in the efficiency of these reactions. Since the excited T_1 and S_1 states of the reactant ketone molecules are not strongly displaced or distorted with respect to the S_0 state, no crossing between S_0 and T_1 or S_1 energy curves occurs at low energies. However, because strong distortions and displacements of chemical bonds occur during the reaction, a crossing ω between the S_0 and the intermediate ground state potential energy curves can occur at low energies; ω can be energetically above or below the electronically excited reactant states. As Fig. 1 shows, when reactions proceed through thermal activation, the molecules will always "feel" the presence of the crossing point ω , independently of its energy. Consequently, depending on the extent of the electronic coupling at ω , the photochemical reaction can be more or less efficient for the formation of intermediates. However, a completely different situation can occur if the reaction proceeds via a tunnelling mechanism, because the energy content of the molecules is lower than in the former case. If ω is energetically above the excited states of the reactants, after tunnelling the molecules remain on the potential energy curve of the intermediate well after the crossing point ω and consequently the efficiency of formation of the intermediates should be close to unity, independent of the strength of the coupling between S_0 and I. However, if ω is below the excited states of the reactants, after tunnelling the molecules cross to states of the intermediate before the crossing point ω and consequently the efficiency of intermediate formation can be less than unity. For the latter situation thermal activation and tunnelling are equivalent mechanisms as far as the efficiency of the reaction is concerned, but for the former situation tunnelling and thermal activation are clearly distinct mechanisms.

The present model predicts that the magnitude of the coupling between S_0 of the ketone and the ground state of the intermediate can affect the

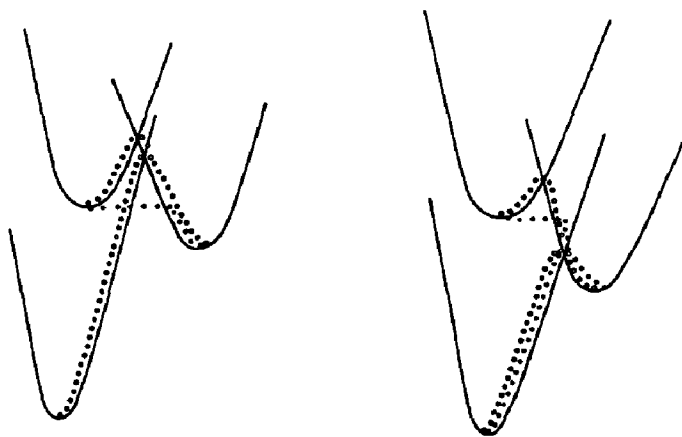


Fig. 1. Nuclear configuration diagrams for hydrogen photoabstraction reactions: $\circ \circ \circ$, thermal activation; $\bullet \bullet \bullet$, nuclear tunnelling.



Fig. 2. Effect of the horizontal displacement R and the vertical displacement ΔE of intermediates on the energy of the crossing point ω .

efficiency of hydrogen photoabstraction reactions, but that for a tunnelling mechanism such an effect depends on the energy of the crossing point ω . Such an energy depends on the vertical and horizontal displacements of the potential energy curves (Fig. 2) of three electronic states, S_0 , T_1 (or S_1) and I, and consequently depends on several structural factors such as the electronic energies, the bond strengths, the bond lengths, the affinity of the ketones and the ionization energy of the substrates [4, 5].

2.2. Probability of a jump at the crossing point

The formation efficiencies of intermediates are controlled by the probability of a jump between the energy curves of I and S_0 at ω . The probability of an electronic jump near a crossing point of the potential energy curve of a discrete state and a quasi-continuum was given by Coulson and Zalewski (ref. 20, eqn. (22) with the conditions of eqns. (38) and (39)) as $1 - \gamma$ with

$$\gamma = \exp \left\{ -2\pi^2 \left(\frac{V_i}{\Delta E_i} \right)^2 \right\} \quad (1)$$

γ represents the probability of non-crossing, V_i is the matrix element for coupling between the two electronic states and ΔE_i is the energy separation between two neighbouring energy levels in the quasi-continuum, near the crossing point. Table 1 presents the non-crossing probability, *i.e.* the efficiency γ of intermediate formation for several values of $V_i/\Delta E_i$.

Nuclear motions along the reaction coordinate in a hydrogen abstraction reaction can be represented [4] by the vibrations of a diatomic oscillator with a vibrational frequency of about 1000 cm^{-1} , and consequently the energy level separation $\Delta E_i \leq 1000 \text{ cm}^{-1}$. The matrix element for an ISC process involving n, π^* states in carbonyl compounds has been estimated to be about 130 cm^{-1} for acetone [21] and 60 cm^{-1} for acetophenone [22]. The matrix element V_i between the I and S_0 states of a supermolecule ketone plus substrate is expected to be of a similar magnitude and, therefore, for

TABLE 1

Non-crossing probabilities at the crossing point ω

$V_i/\Delta E_i$	γ
0.01	1.0
0.03	0.98
0.07	0.91
0.1	0.82
0.2	0.45
0.3	0.17
0.4	0.04

carbonyl compounds $V_i/\Delta E_i$ is about 0.1; according to eqn. (1) the efficiency of intermediate formation is expected to be about 0.9 - 0.8. Higher $V_i/\Delta E_i$ values can be observed for ISC in the presence of heavy atoms in the reactants [18, 19] and for IC processes in hydrogen abstractions from excited singlet states. For these situations the crossing probability increases and the reaction efficiency decreases.

2.3. Energy of the crossing point

In order to distinguish between thermal activation and nuclear tunnelling mechanisms in photochemical hydrogen abstraction reactions, it is necessary to estimate the energy of the crossing point ω . For such a calculation we shall use the nuclear configuration diagrams previously employed [4] for the estimation of the kinetic rate constants of hydrogen abstraction reactions for several ketones with various substrates by a tunnel effect theory. Such two-dimensional diagrams consider the reactant and product states of the supermolecule carbonyl compound plus substrate only for the strongly displaced and distorted bonds which are reduced to harmonic oscillators $C=O^*$ and CH for reactants and $C-O$ and OH for the intermediates. The reaction rates were estimated with an energy difference $\Delta E = E_e + D(OH) - D(CH)$ between the reactants and products, where E_e is the electronic excitation energy and $D(XH)$ is the bond dissociation energy of the XH bond. The model did not consider explicitly, in energy terms, the strength of the π bond of the carbonyl group and changes in the energy of reorganization of the radicals, factors which vary with the nature of the carbonyl compound and of the substrate [23, 24]. These effects were taken into account by the horizontal displacement R of the oscillators, which was treated as an adjustable parameter and was found to vary with the reduction potential of the carbonyl compound and the ionization energy of the substrate [4]. However, in the present calculations, since we aim to estimate the energy of ω with respect to the three electronic states relevant to the reaction, an "absolute" scale of energies must be employed. Therefore the difference in energy between the reactants and the intermediates is given by

$$\Delta E' = E_e + D(\text{OH}) - D(\text{CH}) - E_\rho$$

where E_ρ takes into consideration both the energy of the π bond of the CO group in the ground state of the carbonyl compound and the reorganizational energies of the radical intermediates. The E_ρ values cannot be accurately estimated for the reactions under study and consequently both E_ρ and R are treated as adjustable parameters (R is the displacement between the excited state and the radical products). The same force constants were employed for the reactants and the products as in previous studies; in intermolecular reactions $f_r = 46.9 \times 10^4 \text{ cm}^{-1} \text{ \AA}^{-2}$ and $f_p = 43.2 \times 10^4 \text{ cm}^{-1} \text{ \AA}^{-2}$ [4], while for intramolecular γ hydrogen abstractions which proceed via a cyclohexane chair configuration $f_r = 11.5 \times 10^4 \text{ cm}^{-1} \text{ \AA}^{-2}$ and $f_p = 9.8 \times 10^4 \text{ cm}^{-1} \text{ \AA}^{-2}$ [5].

The main contribution to E_ρ is the energy of the π bond of the carbonyl group from which the reorganizational energies E_{ro} of the radicals must be subtracted. Estimates of E_π vary between 24 000 and 22 000 cm^{-1} [23] in carbonyl compounds. We have taken the lowest value as $E_\rho = 22\,000 \text{ cm}^{-1}$ to calibrate the reaction between benzophenone and isopropanol, by adjusting the displacement R to fit the experimental rate of hydrogen photoabstractions. R is constant for radical abstractions, but varies with the ionization energy of the substrates for charge transfer reactions. The variation in R with the ionization energy of the substrates was considered to be the same as that found in previous work [4, 6]. With these R values, E_ρ is adjusted to fit the experimental rate of abstraction. E_ρ is found to vary with the nature of the substrate. E_ρ increases with a decrease in the CH bond strength and the variation agrees with the changes in the reorganizational energies, e.g. a change in $D(\text{CH})$ from 98 to 91 kcal mol^{-1} corresponds to typical values of $E_{\text{ro}}(\text{C}_2\text{H}_5) = 1.5 \text{ kcal mol}^{-1}$ and $E_{\text{ro}}(\text{tert-C}_4\text{H}_9) = -1.7 \text{ kcal mol}^{-1}$, giving an increase in E_ρ of 1000 cm^{-1} , in good agreement with our findings.

For the ground state S_0 , the horizontal displacement is $R(S_0) - R(T_1) = 0.12 \text{ \AA}$, estimated by the difference between the CO bond lengths in the non-excited and the excited carbonyl groups in ketones ($d_{\text{C=O}} = 0.121 \text{ \AA}$, $d_{\text{C=O}^*} \approx 0.131 - 0.135 \text{ \AA}$). The S_0 force constant cannot be estimated by fitting the $I \rightarrow S_0$ rate constant since there are no reliable estimates for such reactions for reversible hydrogen abstractions by the ground state. For a linear configuration of reactants, f_{S_0} is higher than f_r because the C=O force constant is higher than that of C=O^* . From the ratio of frequencies $\nu_{\text{C=O}}/\nu_{\text{C=O}^*} = 1.15$ a maximum value of f_{S_0} close to $60 \times 10^4 \text{ cm}^{-1} \text{ \AA}^{-2}$ was found. For a harmonic oscillator a value of $f_{S_0} = 62 \times 10^4 \text{ cm}^{-1} \text{ \AA}^{-2}$ was required to place ω above T_1 in the photoabstraction reaction of benzophenone from benzhydrol. The same value was employed for the calculations of E_ω in other intermolecular reactions. Although the model is established in terms of an empirical fit of rate constants calculated by a tunnel effect theory, this does not introduce any bias for a distinction between thermal activation and tunnelling from the efficiency of the photochemical reactions.

3. Intermolecular hydrogen abstraction

3.1. Abstractions by n, π^* triplets

Benzophenone is the most studied ketone as far as efficiencies of photoabstractions are concerned, not only because it covers a wide spectrum of radical-like and charge transfer reactions, but also because a number of quantum yields of the intermediates have been reported [10, 14, 16]. Table 2 reports the ω crossing point energy, together with other relevant data, for several radical-like and charge transfer reactions. The energy of E_ω was calibrated to be placed above ${}^3(n, \pi^*)$ for the reaction with benzhydrol because the reaction quantum yield is unity, whilst according to our model we would expect a quantum yield of less than unity if E_ω were below E_{T_1} . Another alcohol, isborneol, where $E_\omega < E_{T_1}$, has a quantum yield of less than unity ($\phi \approx 0.9$) [27], suggesting that with alcohols the ISC coupling at ω can be significant for the molecules to cross from the radical intermediates to the ground state. However, since coupling is not high enough to lead to a significant decrease in the reaction yields, further experiments have been carried out to test the present calibration.

The ISC coupling at the crossing point ω is strongly dependent on the presence of heavy atoms on the substrates. For example, for a reaction where E_ω is below E_{T_1} , the quantum yield of radical formation decreases from $\phi = 0.91$ in the hydrogen photoabstractions of benzophenone with *p*-fluorophenol to $\phi = 0.61$ with *p*-iodophenol [10]. Therefore we have determined experimentally the yields of the reaction of benzophenone with benzhydrol and bromobenzhydrols. For a thermal activation process a strong decrease (20% - 30%) in the yields of reactions with heavy-atom substitution is expected, whilst for a tunnelling mechanism we expect the same decrease if $E_\omega \leq E_{T_1}$, but the quantum yield will be unity for all the substrates if $E_\omega > E_{T_1}$. Table 3 presents the experimental results for 0.1 mol of benzophenone and 0.2 mol of benzhydrols per litre. All the quantum yields extrapolated at infinite substrate concentration [26] are unity, within the experimental error (8%). Therefore these experiments reveal that tunnelling is the dominant mechanism (greater than 98%) in these photoabstraction reactions. Thermal activation can be a more significant mechanism when the energy barriers are small such as in charge transfer reactions, but even in the fastest processes with amines tunnelling is calculated [4] to be the dominant mechanism (greater than 80%).

As Table 2 shows E_ω is only predicted to be above E_{T_1} for radical-like reactions with substrates of high CH bond strengths. For charge transfer reactions the decrease in R leads to a decrease in E_ω for all these reactions and ω is below T_1 . Consequently, low reaction yields are expected for the charge transfer abstractions with benzophenone and in particular the yields are very low when the spin-orbit coupling is high, as with sulphur substrates [18] ($\phi_1 \approx 0.1$ [16, 27]).

Isotope substitution by deuterium atoms does not alter the potential energy curves and, although it decreases the reactivity, it does not change

TABLE 2

Efficiencies of radical and product formation for the intermolecular hydrogen abstractions of $^3(n,\pi^*)$ benzophenone ($E_T = 24\,100\text{ cm}^{-1}$)

Substrate	Bond	$D(XH)$ (kcal mol $^{-1}$)	E_p (cm $^{-1}$)	$R(I-T_1)$ (Å)	$E_\omega - E_{T_1}$	ϕ_{int}	ϕ_{red}	log k_T
Cyclohexane	CH	94	20800	0.38	300	1.0 ^a		5.65
Isopropanol	CH	88	22000	0.38	490	1.0 ^b	1.0 ^b	6.04
Benzhydrol	CH	82	22900	0.38	300	1.0 ^c	1.0 ^c	6.70
Isoborneol	CH	82	22900	0.371	-250		0.90 ^d	7.03
Bu ₃ SnH	SnH	70	24800	0.38	40		0.90 ^e	7.68
Di- <i>n</i> -butylsulphide	CH	94	20500	0.302	-4400		0.05 ^f	8.93
<i>tert</i> -C ₄ H ₉ NH ₂	NH	103	19300	0.308	-3600	0.9 ^a	0.06 ^a	7.84
Triethylamine	CH	94	20500	0.288	-5100	1.0 ^a	0.30 ^a	9.36
DABCO	CH	94	20500	0.277	-5600	0.73 ^a	0.06 ^a	9.65
Aniline	CH	80	22600	0.303	-5600		0.55 ^g	9.8
Phenol	OH	85	22000	0.315	-3900	0.84 ^h		9.11
<i>p</i> -Fluorophenol	OH	85	22000	0.307	-4300	0.91 ^h		
<i>p</i> -Bromophenol	OH	85	22000	0.307	-4300	0.71 ^h		
<i>p</i> -Iodophenol	OH	85	22000	0.307	-4300	0.61 ^h		9.35
Di- <i>n</i> -propylether	CH	91	21400	0.355	-1000			7.00

DABCO, diazabicyclo [2.2.2]octane.

^a Ref. 14.^b Ref. 25.^c Ref. 26.^d Ref. 27.^e Ref. 28.^f Ref. 29.^g Ref. 30.^h Ref. 10.

TABLE 3

Quantum yields of photoreduction and efficiencies of benzophenone triplet with benzhydrols

Substrate	ϕ_r^a	ϕ_I^b
Benzhydrol	0.81 ± 0.05	1
4,4'-Dichlorobenzhydrol	0.84 ± 0.05	1.04
4-Bromobenzhydrol	0.78 ± 0.05	0.96
4,4'-Dibromobenzhydrol	0.83 ± 0.05	1.02

^a Experimental values in benzene solution.

^b Relative quantum yields based on unity efficiency of the first reaction at infinite substrate concentration [26].

E_ω or the spin-orbit coupling and, consequently, does not alter ϕ_I . For example, this has been observed experimentally by Cohen and coworkers [14] in the hydrogen abstraction reactions of benzophenone and *tert*-butylamine- $N-d_2$. For charge transfer hydrogen abstractions an increase in the solvent polarity reduces R but, since ω is already below T_1 in a non-polar solvent, the efficiencies for intermediate formation should not be affected, as long as the solvent does not increase the spin-orbit coupling or favour other competing reactions. For the reactions of benzophenone with benzhydrol and amines, ϕ_I does not vary significantly from benzene to acetonitrile [14]. With diazabicyclo[2.2.2]octane the quantum yield decreases to 0.2 in the presence of acetonitrile, but other competing and rapid ion formation processes can occur.

The overall yield of photoreduction depends on the secondary reactions of the intermediate radicals, namely on the reversible hydrogen abstraction reaction to the ground state carbonyl compound. Since the energy and width barriers between I and S_0 follow the same trends as the energy and width barriers for the process $T_1 \rightarrow I$, the $I \rightarrow S_0$ rates are higher when the hydrogen abstraction rates from T_1 are higher. In fact, for several hydrogen abstractions the photoreduction yields appear to decrease with an increase in reactivity rate constant k_r [27].

Very few experimental kinetics studies on radical back reactions have been undertaken. Cohen and coworkers [14] have analysed the ketyl radical decay for the reaction of benzophenone with *tert*-butylamine and, by curve fitting, have estimated a rate of reversible hydrogen abstraction of $3 \times 10^9 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$. Within the tunnel effect theory the present model leads to a rate of $2 \times 10^2 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ ($\nu = 10^{11} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$) for equal displacements of the CO and CH bonds. However, since the energy for the reaction is not concentrated in the CO mode, as it is for the excited states, reversible hydrogen abstraction can be viewed, in the extreme situation, as tunnelling of the OH mode alone. For such situations the estimated rate from the recombination of radicals in bulk solution is $5 \times 10^8 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$ and a large isotope effect (about 8) is predicted in this case. The rates can be even

higher if the recombination of radicals in the solvent cage is taken into consideration.

Table 4 presents the calculated E_{ω} values for a few hydrogen abstraction reactions with ketones of higher and lower triplet energies than benzophenone. The relevant predictions are the possible occurrence of efficiencies of less than unity for reactions with alcohols of low CH bond strengths, such as benzhydrol, with an increase in triplet energy or with a reduction in R . In contrast, a decrease in excited state energy (biacetyl) leads to an increase in E_{ω} and, consequently, even reactions with sulphides are predicted to have $\phi_1 \approx 1.0$. There are no experimental data for comparison with the theoretical predictions, but recently Wagner and Puchalski [33] have found that the quantum yield of photoreduction of acetophenone by 1-phenylethanol is lower than unity ($\phi_r = 0.6$) and increases slightly by deuteration of the OH bond ($\phi_r = 0.7$). Since this photoreduction has a quantum yield of less than unity Wagner and Puchalski have proposed that this ketone would abstract from an OH bond. In spite of the change in ϕ on deuteration, the slope of the double reciprocal plot ϕ^{-1} versus [substrate] $^{-1}$ is the same for both alcohols, revealing that the rate of hydrogen abstraction is also the same. The difference in yields seems to be caused by a higher quenching rate of the acetophenone triplet by the protonated alcohol, possibly due to a stronger hydrogen bond interaction with the OH group. As Table 4 shows ω is calculated to be below T_1 for an abstraction from a CH bond. Consequently the small yields reported by Wagner and Puchalski can be attributed to a decrease in the efficiency of the hydrogen abstraction by the acetophenone triplet.

3.2. Abstractions by π, π^* triplets

Triplet states of a π, π^* nature are less reactive than ${}^3(n, \pi^*)$ states in photoabstracting hydrogen atoms and this fact has been interpreted in terms of a decrease in the Franck-Condon factors caused by a larger displacement of the CO bonds between the reactant and the intermediates [4]. In the ketones studied the n, π^* states must be well above the ${}^3(\pi, \pi^*)$ states to make any significant contribution to the overall reactivity. In spite of the fact that $R({}^3(\pi, \pi^*)-I) > R({}^3(n, \pi^*)-I)$ in the ketones, the displacement between the ground state S_0 and the intermediate state I should be independent of the electronic nature of the excited states and, therefore, the efficiencies with π, π^* states should be similar to those for n, π^* states, as long as the electronic energies are the same. In fact although it is about three orders of magnitude less reactive towards isopropanol than benzophenone, phenylbenzophenone is photoreduced with a quantum efficiency of unity [35], because ω is above the lowest excited triplet state (Table 5).

Yields of the phenoxy radical have been determined for the hydrogen abstraction reactions of the ${}^3(\pi, \pi^*)$ state of *p*-methoxypropiophenone with several substituted phenols [10]. As Table 5 shows for these reactions ω is quite well below the triplet state and, for significant spin-orbit coupling, the quantum yields of intermediate formation are much smaller than unity.

TABLE 4

Efficiencies of product formation for the intermolecular hydrogen abstraction of $^3(n,\pi^*)$ states

Ketone	Substrate	Bond	$D(XH)$ (kcal mol $^{-1}$)	E_ρ (cm $^{-1}$)	$R(I-T_1)$ (Å)	$E_\omega - E_{T_1}$	ϕ_p	$\log k_r$
Acetophenone ($E_T = 25750$ cm $^{-1}$)	Isopropanol	CH	88	23000	0.384	-800	0.75 ^{a,b}	6.26
	1-Phenylethanol	CH	88	23000	0.38	-900	0.6 ^c	6.45 ^a
Acetone ($E_T = 27300$ cm $^{-1}$)	Isopropanol	CH	88	24000	0.405	-600		5.73
Biacetyl ($E_T = 19215$ cm $^{-1}$)	Isopropanol	CH	88	20000	0.384	6200	1.0 ^d	4.11
	Phenol	OH	85	18300	0.32	-400 ^e	0.1 ^f	8.53

^a Ref. 31.^b Ref. 32.^c Ref. 33.^d Ref. 3.^e $^1(n,\pi^*)$.^f Ref. 34.

TABLE 5

Efficiencies of product formation for the intermolecular hydrogen abstraction from π,π^* triplets

Substrate	Bond	$D(XH)$ (kcal mol $^{-1}$)	E_ρ (cm $^{-1}$)	$R(I-T_1)$ (Å)	$E_\omega - E_{T_1}$	ϕ_p	$\log k_r$	
Phenylbenzophenone ($E_T = 23200$ cm $^{-1}$)	Isopropanol	CH	88	22000	0.413	4000	1.0 ^a	3.90
<i>p</i> -Methoxypropiofenone ($E_T = 25200$ cm $^{-1}$)	Phenol	OH	85	22500	0.368	-2500		9.69
	Bromophenol	OH	85	22500	0.358	-2600	0.55 ^b	9.80
	Iodophenol	OH	85	22500			0.21 ^b	
Fluorenone ($E_T = 18650$ cm $^{-1}$)	Triethylamine	CH	94	18300	0.298	1500	1.0 ^c	7.51
	FC ₆ H ₄ N(CH ₃) ₂	CH	98	17000	0.298	-700	0.76 ^d	8.43
	ClC ₆ H ₄ N(CH ₃) ₂	CH	98				0.37 ^d	
	BrC ₆ H ₄ N(CH ₃) ₂	CH	98				0.31 ^d	

^a Ref. 14.^b Ref. 10 (these values refer to ϕ_{int} and not to ϕ_p).^c Ref. 36.^d Ref. 37.

However, the reactivity of this propiophenone presents some anomalous features because the hydrogen abstraction rates from phenol are about 2 - 4 times higher than with benzophenone. Nevertheless, the isotope effect in rates is only 1.2 with benzophenone and 3.9 for *p*-methoxypropiophenone. Such findings can be interpreted in terms of an association of the *p*-methoxybenzophenone and the phenol in the ground state, probably through hydrogen bonding [10]. Such an association would increase the frequency factor ν for the hydrogen abstraction reaction from a collisional process frequency ($\nu = 10^{11} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$) to a rotational factor ($\nu = 10^{13} \text{ s}^{-1}$) and this would compensate for the decrease in the Franck-Condon factors of the π, π^* state. The tunnel effect model can reproduce the experimental rates with the usual R displacement for π, π^* states, but with $\nu = 10^{13} \text{ s}^{-1}$. This agrees with the increase in the experimental pre-exponential factors for these reactions [10], which are about 25 times higher for methoxypropiophenone than for benzophenone.

Owing to the higher R values, the isotope effects are higher for reactions of the π, π^* states. Table 6 presents the deuterium isotope effect for several hydrogen abstraction reactions calculated by the tunnel effect theory under the assumption that the reaction coordinate involves equal displacements of the CO and the XH bonds. Good agreement with experiment is found with the exception of the reactions of *p*-methoxypropiophenone and biacetyl (T_1) with phenol. The deuterium isotope effect is very sensitive to the mass of the oscillators that are involved in the tunnelling process. Consequently, changes in the relative contribution of the CO and XH modes to the radiationless transitions can significantly alter the magnitude of such effects. For example, for the reaction of *p*-methoxypropiophenone with phenol, a reaction coordinate for which the XH modes contribute 2.3 times more than the CO

TABLE 6

Calculated deuterium isotope effects for equal displacements of CO and XH bonds

Ketone	Substrate	k_H/k_D	
		Calculated	Observed
Benzophenone $^3(n, \pi^*)$	<i>tert</i> -C ₄ H ₉ NH ₂ (D ₂)	2.0	1.9 ^a
	<i>sec</i> -C ₄ H ₉ NH ₂ (D ₂)	1.8	1.4 ^a
	Benzhydrol (CD)	2.7	2.8 ^b
	Phenol (OD)	1.5	1.2 ^c
<i>p</i> -Methoxypropiophenone $^3(\pi, \pi^*)$	Phenol (OD)	2.1	3.9 ^c
Acetone $^3(n, \pi^*)$	Methanol (CD)	3.5	3.7 ^d
Biacetyl $^3(n, \pi^*)$	Phenol (OD)	1.8	3.4 ^e
	$^1(n, \pi^*)$	Phenol (OD)	1.5

^a Ref. 14.^b Ref. 26.^c Ref. 10.^d Ref. 38.^e Ref. 34.

modes do gives $k_H/k_D = 2.8$ whereas, when the relative contribution is as high as 5.5, then $k_H/k_D = 3.5$, a value close to the experimental value. Such distortions in the relative contribution of the CO and XH modes for the reaction coordinate can be understood if the displacement of the bond to be broken, XH, is much larger than that of the CO bond, and such an effect could be caused, for example, by strong hydrogen bonds between the ketone and the OH bond of the substrate.

4. Intramolecular hydrogen abstractions

4.1. γ hydrogen abstractions

Intramolecular photoabstractions of γ hydrogen atoms in ketones do not present the variety of reactivities of the intermolecular processes, but we can expect for these reactions a higher spin-orbit coupling I-S₀ and consequently lower efficiencies. The vibronic matrix element V_i between the 1,4 biradical intermediate and the ketone ground state is higher, because it is the result of internal spin-orbit coupling whereas for the intermolecular process ISC is caused by a kind of external spin-orbit coupling. However, the force constants of the diatomic oscillators that represent the nuclear configurations along the reaction coordinate for the intramolecular reactions are lower than in the intermolecular reactions, and consequently ΔE_i is smaller for the former reactions. Consequently $V_i/\Delta E_i$ is expected to be smaller than 0.1 and $\phi_I < 0.8$. According to this reasoning it is not surprising that in non-polar solvents intramolecular hydrogen abstractions by $^3(n,\pi^*)$ states of alkyl and phenyl ketones have photoreduction quantum yields as low as 0.3 in contrast with ϕ_r values of 1.0 - 0.9 found for the equivalent intermolecular hydrogen abstractions from alcohols. The efficiencies for $^1(n,\pi^*)$ state intramolecular abstractions are even smaller than for $^3(n,\pi^*)$ states, because the I \rightarrow S₀ transition is then an IC process.

Polar solvents increase appreciably the quantum efficiencies for triplet reactions in spite of the fact that reactivity is not significantly affected by solvent polarity [12, 13]. In pure solvents the change in ϕ_r is sudden between non-polar and polar solvents, *e.g.* for valerophenone $\phi_r = 0.45$ in benzene and *n*-hexane and 1.0 in *tert*-butanol, isopropanol, ethanol and acetonitrile [12]. The efficiency of the singlet reactions, however, is independent of the solvent polarity [13]. The increase in the efficiency in the triplet case has been attributed to solvation of the hydroxy biradical intermediates, whereas for singlet reactions suggestions have been made that the corresponding biradical intermediates do not exist [13] or are so short lived that they do not undergo any appreciable solvation [39]. However, these interpretations are questionable, because the singlet reactivity of the n,π^* states can be interpreted within the same framework as the n,π^* triplet reactivity [4] and because it is difficult to find a possible reason why the thermally equilibrated biradical intermediate formed via the S₁ state is much shorter lived than the intermediate formed via the T₁ states.

TABLE 7
Efficiencies of intramolecular γ hydrogen abstractions in phenyl ketones and alkyl ketones

Ketone	R_1	R_2	$D(\text{CH})$ (kcal mol^{-1})	E_p (cm^{-1})	$R(T_1-I)$ (\AA)	$E_{\omega} - E_{\text{exc}}$ (cm^{-1}) for the following f_{S_0} values		ϕ_r		$\log\{k_r$ (s^{-1})}
						48×10^4 $\text{cm}^{-1} \text{\AA}^{-2}$	38×10^4 $\text{cm}^{-1} \text{\AA}^{-2}$	Polar	Non-polar	
$\text{C}_6\text{H}_5\text{COCH}_2\text{CH}_2\text{CHR}_1\text{R}_2$	H	H	98	23000	0.595	1100	-20	1.0	0.36	6.90 ^a
($E_{T_1} = 25000 \text{ cm}^{-1}$)	CH_3	CH_3	91	24000	0.586	500	-600	1.0	0.25	8.73 ^a
$\text{CH}_3\text{COCH}_2\text{CH}_2\text{CHR}_1\text{R}_2$	H	H (T_1)	98	23600	0.60	500	-500	0.85	0.43	7.11 ^b
($E_{T_1} = 26000 \text{ cm}^{-1}$);	(S_1)	(S_1)	98	23600	0.61	-2300	-3600	0.06	0.06	8.26 ^b
($E_{S_1} = 28000 \text{ cm}^{-1}$)	CH_3	CH_3 (T_1)	91	24500	0.605	100	-1100	1.0	0.49	8.50 ^b
		(S_1)	91	24500	0.63	-3300	-4000	0.27	0.24	9.32 ^b

^a Ref. 40.

^b Ref. 13.

The solvent effects on the intramolecular hydrogen abstraction efficiencies can be rationalized in terms of a tunnel effect mechanism if, for n,π^* triplet reactions, ω is below T_1 in non-polar solvents and above T_1 in polar solvents. Polar solvents interact much more strongly with the $C=O$ group in the S_0 state than in the excited state, since the $n \rightarrow \pi^*$ transition almost completely removes an electron from the oxygen atom and sharply decreases the dipole moment of the carbonyl group. Such interactions can lead to steric interference between hydrogen-bonded solvent molecules and other groups of the ketones [12], increasing the angle between the $C=O$ and the γ CH bonds, and consequently this leads to a change in the potential energy curves of the ground state. The reactivity of intramolecular hydrogen abstractions of ketones is currently interpreted in terms of a cyclohexane chair configuration for γ hydrogen abstractions by n,π^* excited states [13], but the average configuration for the ground state is certainly different. The S_0 oscillator force constant should be intermediate between the cyclohexane chair configuration ($f_{S_0} = 14 \times 10^4 \text{ cm}^{-1} \text{ \AA}^{-2}$) and the linear configuration ($f_{S_0} = 60 \times 10^4 \text{ cm}^{-1} \text{ \AA}^{-2}$). For example, for hydrogen abstractions from alkyl and phenyl ketones ω is above T_1 with $f_{S_0} = 48 \times 10^4 \text{ cm}^{-1} \text{ \AA}^{-2}$, which corresponds to a common angle of 136° between the CH-OH and the CO-OH bonds. However, a decrease in this angle by 15° decreases the force constant along the reaction coordinate to $f_{S_0} = 38 \times 10^4 \text{ cm}^{-1} \text{ \AA}^{-2}$ and for this situation E_ω is well below E_{T_1} (Table 7). With the same force constants ω is always below S_1 (Table 7) and consequently the efficiency of the singlet reactions is unaffected; even for a linear configuration, $f_{S_0} = 62 \times 10^4 \text{ cm}^{-1} \text{ \AA}^{-2}$, ω is below S_1 .

The role of the tunnelling mechanism in these intramolecular γ photoabstraction reactions can also be tested experimentally. A convenient molecule to study is valerophenone [12, 40], because it has a large change in quantum yield in going from ethanol to benzene. The test of heavy atom substitution does not allow a distinction between the two mechanisms, because we have found that there is elimination of the bromine atom on irradiation of 4-bromovalerophenone, similar to the findings with 4-bromobutyrophenone [41]. Consequently we have decided to increase the external spin-orbit coupling through bubbling xenon in the solutions. The results are presented in Table 8 and in the absence of xenon they agree with published data [40]. In benzene, xenon produces a strong decrease (about 2.5 times) in

TABLE 8

Quantum yields for the photoreduction of valerophenone triplet

Solvent		ϕ_V	$\phi_V(\text{xenon})/\phi_V(\text{no gas})$
Benzene	No gas	0.44 ± 0.03	0.41
	Xe	0.18 ± 0.03	
Ethanol	No gas	1.00 ± 0.04	0.98
	Xe	0.98 ± 0.04	

the quantum yield of valerophenone disappearance, supporting the view that $E_{\omega} < E_{T_1}$ in this solvent. However, in ethanol, xenon has no effect on the quantum yields of photoreduction within the experimental error (less than 6%). This supports the view that in this solvent $E_{\omega} > E_{T_1}$ and that tunnelling is again the dominant mechanism for this intramolecular reaction.

4.2. δ hydrogen abstractions

Efficient photochemical abstractions of hydrogen atoms in δ positions were shown to be significant in ketones of restricted conformational mobility [42]. Meador and Wagner [43] have recently studied the photocyclizations to indanols of several α -arylacetophenones and have estimated the rates of δ hydrogen abstraction and the quantum yields of reaction. The quantum yields of reaction are high, but show a variation from unity with the yield for one of the ketones decreasing to 0.6 - 0.4. This has been attributed to biradical disproportionation, but we have decided to study these systems theoretically to investigate the possibility that such findings are also amenable to an explanation in terms of the position of the crossing point ω with respect to E_{T_1} .

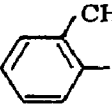
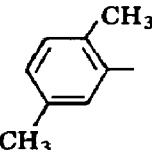
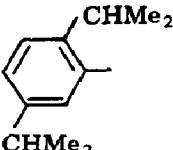
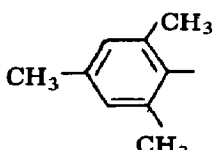
Since the arylacetophenones have greater rigidity than, for example, the butyrophenones and the valerophenones the force constants are expected to be higher for δ abstractions than for γ abstractions. When the tunnel effect model is used and E_p is neglected [4, 5], the force constants can be fitted to reproduce the effect of the CH bond strengths on the abstraction rates. The values estimated are $f_x = 20 \times 10^4 \text{ cm}^{-1} \text{ \AA}^{-2}$ and $f_x = 17 \times 10^4 \text{ cm}^{-1} \text{ \AA}^{-2}$. With these constants and an E_p value equal to that of acetophenone, the energies of the crossing point can be estimated for several force constants of the ground state. The results are presented in Table 9 and show that it is feasible to interpret the experimental results in terms of the value of $E_{\omega} - E_{T_1}$, when $f_{S_0} = 54 \times 10^4 \text{ cm}^{-1} \text{ \AA}^{-2}$.

5. Experimental details

The absolute quantum yields were determined employing a ferrioxalate actinometer. Irradiations were carried with a 150 W xenon arc lamp through a monochromator in 1 cm cells; $\lambda_{\text{exc}} = 345 \text{ nm}$ for benzophenone and $\lambda_{\text{exc}} = 320 \text{ nm}$ for valerophenone (band path, 10 nm). The analyses of the ketone samples were carried out by gas chromatography (Perkin-Elmer 900) with a diethylene glycol succinate column of 34 cm at 105 °C for benzophenone and a column of 215 cm at 153 °C for valerophenone. For the benzophenone reactions the solutions in benzene were bubbled with N_2 and sealed; for valerophenone (0.1 mol dm^{-3}) the solutions were degassed and then bubbled with xenon (L'Air Liquide) for 10 min. The reagents benzophenone (BDH), benzhydrol (Aldrich), 4,4'-dichlorobenzhydrol (Aldrich) and 4-bromobenzhydrol (K&K) were purified by crystallization from benzene. 4,4'-Dibromobenzhydrol (K&K) was crystallized from ether, valerophenone (EGA) was doubly dis-

TABLE 9

Intramolecular δ hydrogen abstractions in α -arylacetophenones ($E_T = 25\,000\text{ cm}^{-1}$)^a

Aryl group	$D(\text{CH})$ (kcal mol ⁻¹)	E_ρ (cm ⁻¹)	R (Å)	$E_\omega - E_{T_1}$ (cm ⁻¹)	ϕ_r	$\log\{k_r\text{ (s}^{-1})\}$
	98	22800	0.463	80	1.0	8.2
	98	22800	0.455	-200	0.62	8.4
	91	23900	0.463	-100	0.44	9.2
	98	22800	0.446	-500	0.42	9.0 ^b

^a Ref. 43.^b The frequency is twice that used for the other ketones.

tilled at 135 °C under low pressure and 4-bromovalerophenone (EGA) was crystallized from *n*-hexane. Benzene (Merck) spectrograde and ethanol (Merck) pro analyse were employed without further purification.

6. Conclusions

We have shown both theoretically and through some selected experiments that a tunnelling process is the dominant mechanism in photochemical hydrogen abstractions, supporting the theoretical interpretation of these reactions with this kind of model [4 - 7]. Previous work has established quantitative and qualitative predictions on relationships between molecular structure and reactivity [4]. This work allows us to summarize some qualitative rules on molecular structure and efficiency relationships for photochemical hydrogen abstraction reactions. The following rules can be proposed for hydrogen abstraction by a carbonyl triplet of energy E_T , given an energy

E_{ω} for crossing of the potential energy curves between the reactant state and the intermediate states.

(1) An increase in coupling decreases the efficiency of the triplet reactions when $E_{\omega} \leq E_{T_1}$, but has no effect when $E_{\omega} > E_{T_1}$.

(2) For reactions of a ketone triplet with a series of substrates or for intramolecular processes with substituted ketones a decrease in the bond strength of the labile CH bonds can change the efficiency from unity to less than unity, because ΔE increases with a decrease in $D(\text{CH})$ and consequently E_{ω} decreases.

(3) An increase in the reduction potential of a ketone and in the ionization energy of the substrate or substituted fragments can decrease the efficiency of reactions. All these factors decrease R and consequently decrease E_{ω} .

(4) Efficiency is expected to be independent of deuteration of CH in substrates or in the ketone for intramolecular reactions.

(5) An increase in the solvent polarity can decrease an efficiency of unity for intermolecular hydrogen abstractions; for intramolecular hydrogen abstractions the solvent polarity can increase the efficiency up to unity.

(6) For reactions of excited singlet states the efficiencies are expected to be smaller than those for triplet reactions, because the probability of a jump at the crossing point is higher and it is more difficult to have $E_{\omega} > E_{S_1}$.

(7) Excited states of π, π^* nature are expected to have efficiencies comparable with those of n, π^* states of identical energy, because the displacement between the ground state and the intermediates is almost the same for both states.

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