

PHOTOCYCLOADDITION OF KETONES TO OLEFINS AS RADIATIONLESS TRANSITIONS

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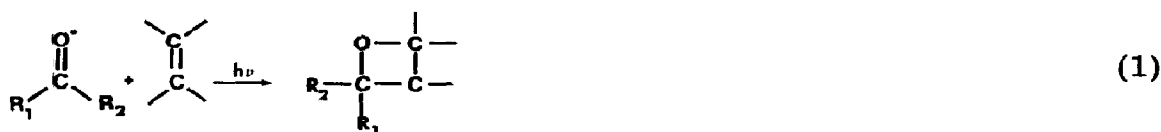
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Summary

The tunnel effect theory is applied to study the photocycloaddition of ketones to olefins. This theory can quantitatively explain the reactivity, regioselectivity, stereospecificity and efficiency of the photocycloadditions studied. The study covers a large diversity of olefins (electron rich and electron poor) and ketones (alkyl, alkylphenyl and phenyl), in both their $^1(n,\pi^*)$ and $^3(n,\pi^*)$ states. The theory does not need to postulate the questionable intermediacy of an exciplex to explain the characteristics of these reactions. Evidence for the dominance of tunnelling over thermal activation is presented. The results of this study are in line with previous applications of tunnel effect theory and complete the explanation of ketone photoreactivity in solution under the framework of the general intersecting-state model.

1. Introduction

The photocycloaddition of carbonyl compounds to olefins to yield oxetanes (the Paterno-Büchi reaction)



is a well-known reaction, of both mechanistic and synthetic interest [1].

Oxetane formation has been suggested to proceed via an exciplex, formed between the excited n,π^* state of the carbonyl compound and the ethylene moiety, followed by biradical formation and subsequent collapse to yield oxetanes and other products [2].

The intermediacy of an exciplex has been supported by the following observations.

(i) There is a small normal product isotope effect, contrary to the expectations for the direct formation of a biradical, whereas the change

in hybridization from sp^2 to sp^3 should yield an inverse product isotope effect [3].

(ii) The triplet state reaction is stereorandom, but the singlet reaction is stereoselective, which seems to be unacceptable for a direct addition to a biradical intermediate and can be rationalized in terms of the intermediacy of a charge transfer exciplex [4].

(iii) On the assumption that alkoxy radicals can model the n,π^* state reactivity, the rate constants k_q for interaction between carbonyl compounds and olefins are exceedingly fast for direct biradical formation. Although not inconceivably fast [3], they are about two orders of magnitude faster than expected [5].

(iv) The k_q values for the reaction of a given carbonyl compound with a series of olefins are correlated with the ionization potentials IP of electron-rich olefins or the reduction potentials $E_{1/2}^{red}$ of electron-poor olefins [6]. The first case is explained by charge transfer from the electron-rich highest occupied molecular orbital (HOMO) to the half-filled n orbital of the excited carbonyl, and the second case by charge transfer from the half-filled π^* orbital to the electron-poor olefin lowest unoccupied molecular orbital (LUMO) [4].

(v) The degree of regioselectivity in oxetane formation is smaller than would apparently be expected from the direct formation of a biradical [7, 8].

(vi) The sum of the quantum yields for product formation is significantly less than unity, whereas direct biradical formation is seen to allow for no such inefficiency [3].

(vii) Increasing the temperature of the reaction leads to only slight increases, or even decreases, in k_q [4].

Although all these observations are suggested to support the intermediacy of an exciplex, no such species has ever been observed and no direct evidence for exciplex formation ever reported. Furthermore, a recent study by Freilich and Peters [9] showed that the Paterno-Büchi reaction may involve a polar transition state, but does not contain a local minimum characterized as a charge transfer intermediate. These researchers were able to demonstrate that the mechanism of oxetane formation involves the direct attack of the excited ketone on the olefin to form a spin-protected biradical. As the biradical is spin protected, point (i) above can be rationalized without the intermediacy of an exciplex.

Spin protection can also explain point (ii). The triplet 1,4 biradical will be able to undergo rotations and lose memory of its initial stereochemistry, while the singlet biradical undergoes closure or β scission before rotations may occur [9]. We have attempted to formulate a model for the mechanism of this reaction, consistent with points (i) - (vii), which avoids the weaknesses of the alkoxy radical addition model and which does not require the intermediacy of a highly questionable exciplex.

For this, we have extended the tunnel effect mechanism, previously proposed to interpret hydrogen photoabstractions [10], α cleavages of

ketones [11] and photoketonization reactions [12, 13]. This mechanism is consistent with all the experimental observations and its application to this class of ketone reactions provides a unifying view of the overwhelming majority of known photochemical reactions of alkanones in solution [14].

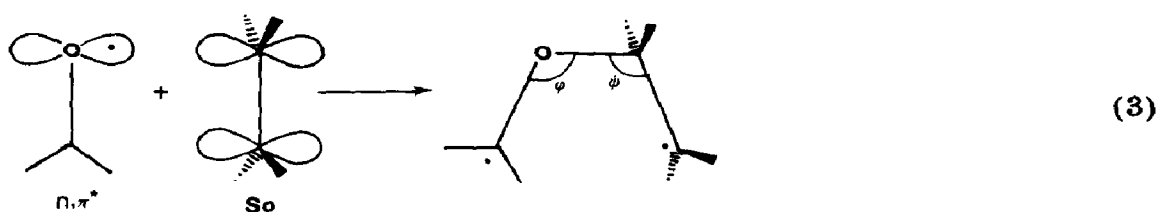
2. Model

The tunnel effect model interprets photochemical reactions as radiationless transitions between reactant and product potential energy surfaces. This model requires only the knowledge of the energy regions where the vibrational modes change significantly in frequency and/or geometry [15] and is most conveniently applied reducing these changes to a unidimensional reaction coordinate [16]. The reaction coordinate is defined using available experimental information. The radiationless transition rate through the reaction coordinate energy barrier is given by [16]

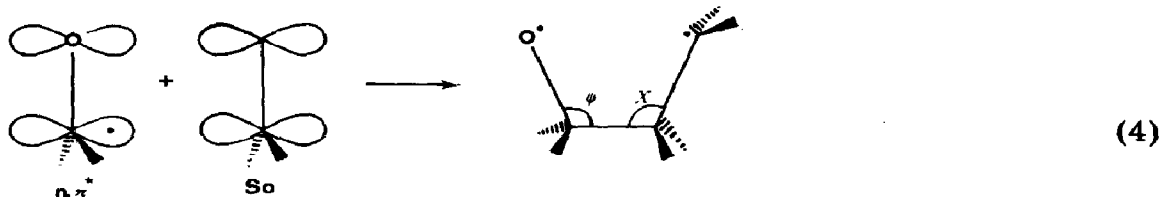
$$k_{nr} = \nu \exp \left[- \frac{2\pi}{h} \{ 2\mu(D - E_v) \}^{1/2} \Delta x \right] \quad (2)$$

where ν is the average frequency of the reactant vibrational models involved in the transition, μ is the oscillators' reduced mass, $D - E_v$ the energy barrier height and Δx is the energy barrier width. In our study ν ($= 10^{11} \text{ M}^{-1} \text{ s}^{-1}$) is taken as a collision frequency.

There are two clearly distinct reaction coordinates reported in the literature for the photocycloaddition of carbonyls to olefins [17]. The addition to electron-rich olefins proceeds through the attack of the carbonyl n orbital on the olefins, with the ketone and olefin π systems in a perpendicular conformation:



The addition to electron-poor olefins occurs via an interaction of the π^* systems of the ketone and of the olefin in a parallel configuration:



Olefin addition and hydrogen abstraction by ketones have the same basic state correlation diagram [18]. Therefore the reaction pathways of these two reactions must have similar features.

In hydrogen abstraction the reaction coordinate was defined by the contributions of the relevant vibrational motions along the line of the bonds being broken or formed. In the present case, the reaction coordinate is taken as collinear with the new bond being formed and the contributions of the relevant vibrational motions along this line are calculated. According to this formulation the angles in pathways (3) and (4) are $\phi = 111.8^\circ$, $\psi = 108.2^\circ$ and $\chi = 112.4^\circ$ [19]. The geometry of approach between the carbonyl group and the olefinic bond is assumed to be the same as the geometry of the biradical in pathway (3) or (4).

For electron-rich olefins, the carbonyl group and the olefinic bond approach along the reaction coordinate by the in-phase motion of the C=C stretching vibration (force constant $f_{C=C}^s$), the C=O stretching (force constant $f_{C=O}^s$) and the C=O in-plane wag (force constant $f_{C=O}^{bi}$) modes, which also change significantly along this coordinate. Therefore, these are the promoting modes for the reaction. The accepting modes are the C—O, O—C and C—C stretching vibrations (f_{C-O}^s , f_{O-C}^s and f_{C-C}^s , respectively); after the formation of the new O—C bond, the first and third vibrations are out of phase relative to the second vibration.

For the electron-poor olefins, one of the promoting modes is again the C=C stretching but now the C=O stretching cannot bring the reactant oscillators close together; however, in the quasi-parallel configuration we can expect a small in-phase contribution of the C=O out-of-plane wag ($f_{C=O}^{bo}$). For the products we can expect contributions from the out-of-phase C—C and C—C stretching vibrations (f_{C-C}^s , f_{C-C}^s), as well as from the distortion of the O—C—C angle (f_{OCC}^{da}), out of phase with C—C.

In Table 1 we present the force constants for the relevant vibrations collected from the literature. In order to obtain a unidimensional reaction coordinate, all force constants of each oscillator (C=O, C=C, C—O, O—C, C—C and O—C) are first weighted by their angles to the reaction coordinate

TABLE 1
Force constants

Force constant	Magnitude (N m ⁻¹)	Reference
$f_{C=C}^s$	901.5	20
$f_{C=O}^s$	1270.81 (S ₀)	11
	725 (T ₁ or S ₁)	11
$f_{C=O}^{bi}$	131.17	11
$f_{C=O}^{bo}$	33.19	11
f_{C-O}^s	509.0	21
f_{O-C}^s	426.1	21
f_{OCC}^{da}	60	22

and then added together. Afterwards, the force constants and displacements of all oscillators have to be reduced to those of a single diatomic molecule for the reactants and another for the products. For the reactants this can easily be done if it is assumed that the displacements of C=O and C=C are equal; the force constant for these motions in the reactants is then [16]

$$f_r = \{f_{C=O}^2 + f_{C=C}^2 + 2f_{C=O}f_{C=C} \cos \theta(\text{CO}, \text{CC})\}^{1/2} \quad (5)$$

with $\theta(\text{CO}, \text{CC}) = 68.6^\circ$ for electron-rich olefins and $\theta(\text{CO}, \text{CC}) = 72.5^\circ$ for electron-poor olefins, yielding $f_r = 559.0 \text{ N m}^{-1}$ and $f_r = 350.3 \text{ N m}^{-1}$ respectively. The ground state reactant force constant can be calculated in a similar way, yielding $f_{s_0} = 744.2 \text{ N m}^{-1}$ for electron-rich olefins and $f_{s_0} = 350.3 \text{ N m}^{-1}$ for electron-poor olefins.

However, for the products three oscillators have to be reduced to a single diatomic molecule. This can be done by reduction in the first place of the new bond, which contributes with a stretching vibration in a different direction from the coordinate of the reactants, to its contributions to the already existing CO and CC oscillators. This can be done using an expression similar to eqn. (5). For the electron-rich olefins we obtained

$$f_{C-O} = \{(f_{CO}^a \cos \phi)^2 + f_{CO}^a{}^2 + 2(f_{CO}^a \cos \phi)f_{CO}^a \cos \theta(\text{CO}, \text{OC})\}^{1/2} \quad (6)$$

$$f_{C-C} = \{(f_{CC}^a \cos \psi)^2 + f_{CC}^a{}^2 + 2(f_{CC}^a \cos \psi)f_{CO}^a \cos \theta(\text{CO}, \text{OC})\}^{1/2} \quad (7)$$

and for electron-poor olefins we obtained

$$f_{C-O} = \{(f_{OCC}^{da} \cos \psi)^2 + f_{CC}^a{}^2 + 2(f_{OCC}^{da} \cos \psi)f_{CC}^a \cos \theta(\text{OC}, \text{CC})\}^{1/2} \quad (8)$$

$$f_{C-C} = \{(f_{CC}^a \cos \chi)^2 + f_{CC}^a{}^2 + 2(f_{CC}^a \cos \chi)f_{CC}^a \cos \theta(\text{CC}, \text{CC})\}^{1/2} \quad (9)$$

These two oscillators can now be reduced to a single diatomic molecule for the products using again an expression similar to eqn. (5). The force constant for the products then becomes 754 N m^{-1} for electron-rich olefins and 636.2 N m^{-1} for electron-poor olefins.

We must note that the results obtained in this study are not critically dependent on these force constants. For simplicity we shall assume that the reactant and product oscillators have harmonic behaviour. To calculate k_{nr} it is necessary to know the horizontal displacement R and vertical displacement ΔH_r between the potential energy curves of the reactant and product.

The horizontal displacement involves the knowledge of a dissociative bond length and is difficult to estimate. Therefore R was treated as an adjustable parameter. The displacement between the potential energy curve of the ground state and of the reactant was taken as 0.012 nm , as in hydrogen abstraction reactions [10]. The contributions of the dissociative bond to the changes in the CO and CC bond lengths between the products and reactants (r_{CO} and r_{CC}) are similar. We estimated the change along the reaction coordinate in r_{CC} to be twice as large as in r_{CO} ; for example, in electron-rich olefins $r_{CC} = (0.1541 - 0.1337)(-\cos 108.2) = 0.00637 \text{ nm}$ [23], while

$r_{CO} = (0.141 - 0.1307)(-\cos 111.8) = 0.00383$ nm [11, 23]. This result led to a distortion of the relative contribution of the CO and CC oscillators to the photocycloaddition which has to be accounted for by the reduced mass of the system. According to the criteria previously used [11], the reduced mass of the system was then

$$\mu = \left(\frac{\mu_{CO}^{1/2} + 2\mu_{CC}^{1/2}}{3} \right)^2 \quad (10)$$

Finally, it was necessary to calculate the photocycloaddition heats of reaction ΔH_r to be able to apply eqn. (2). ΔH_r was calculated from

$$-\Delta H_r = E_e + \Delta H_{\text{carbonyl}}^\circ + \Delta H_{\text{olefin}}^\circ - \Delta H_{\text{biradical}}^\circ \quad (11)$$

where E_e is the excited state energy and the other terms in the right-hand side of eqn. (11) are the standard heats of formation of the reactant carbonyl compound and olefin and of the product biradical. For these reactions $\Delta H_{\text{biradical}}^\circ$ was not known. However, it was still possible to calculate ΔH_r° using group additivity [24]. This type of calculation was very convenient because many group parameters cancel between reactants and products. The radical heats of formation have been continuously updated. Table 2 presents the radical group additivity parameters used in this work, as well as the radicals from where they were calculated, under the assumption that groups bonded to the radical centre are the same as the molecular groups [30]. Group additivity requires the calculation of steric effects. These were evaluated by addition of the correcting factor to the group parameters of the reactants:

$$S_r = \Delta H_{\text{reactants}}^\circ - \Delta H_{\text{reactants}}^{\text{add}} \quad (12)$$

where $\Delta H_{\text{reactants}}^\circ$ and $\Delta H_{\text{reactants}}^{\text{add}}$ are the experimental and group additivity calculated heats of formation. When the experimental value was not known, it was replaced by the value estimated from homodesmotic reactions [31]. The same was done for the products, where the radical free valence was replaced by a hydrogen atom. Given a coherent set of group parameters, the relative ΔH_r values for the reactions of a given carbonyl compound with a series of olefins are reasonable, since most of the errors involved are cancelled: generally it is not necessary to use more than six group parameters for each reaction and most of these parameters are common to the reactions within the series. The major shortcoming of these calculations is the difficulty in comparing the results among different series of reactions.

We compared the reaction rates calculated by the tunnel effect model with those given by the conventional thermal activation mechanism for the same energy barrier. The thermal activation rate is given by

$$k_{ta} = AC_0^{1-m} \exp\left(-\frac{D - E_v}{RT}\right) \quad (13)$$

TABLE 2
Group additivity parameters used in the calculations

Group parameter	Magnitude (kJ)	Source	Reference
$[\cdot\text{C}-(\text{C})_2(\text{H})]$	176.5	$\text{CH}_3-\dot{\text{C}}\text{H}-\text{CH}_3$ ^a	25
$[\cdot\text{C}-(\text{C})_3]$	179.5	$\text{CH}_3-\dot{\text{C}}\text{H}-\text{CH}_2-\text{CH}_3$ $\cdot\text{C}(\text{CH}_3)_3$ ^a	25
$[\cdot\text{C}-(\text{C}_d)(\text{C})(\text{H})]$	107.3	$(\text{CH}_3)_2-\dot{\text{C}}-\text{CH}_2-\text{CH}_3$	26
$[\cdot\text{C}-(\text{C}_d)(\text{C})_2]$	99.87	$\text{CH}_2=\text{CH}-\dot{\text{C}}\text{H}-\text{CH}_3$	26
$[\cdot\text{C}-(\text{CN})(\text{C})(\text{H})]$	251.5	$\text{CH}_2=\text{CH}-\dot{\text{C}}\text{H}(\text{CH})_3-\text{CH}_3$	26
$[\cdot\text{C}-(\text{CN})(\text{C})_2]$	251.2	$\text{CH}_2-\dot{\text{C}}\text{H}-\text{CN}$	26
$[\cdot\text{C}-(\text{Cl})_2(\text{C})]$	110.0	$(\text{CH}_3)_2-\dot{\text{C}}\text{H}-\text{CN}$	26
$[\text{C}-(\text{O}\cdot)(\text{C})_3]$	36.23	$\text{CHCl}_2-\dot{\text{C}}\text{Cl}_2$	23
$[\text{C}_d-(\text{C}_d)_2(\text{H})]$	28.598	$\cdot\text{O}-\text{C}(\text{CH}_3)$	26
$[\text{C}_d-(\text{C}_d)_2(\text{C})]$	37.26	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	24
$[\text{C}_d-(\text{C}_d)(\text{O})(\text{H})]$	8.66	$\text{CH}_2=\text{C}(\text{CH}_3)-\text{CH}=\text{CH}_2$	24
$[\cdot\text{C}-(\text{O})(\text{C})_2]$	129.8	$\text{CH}_2=\text{CH}-\text{O}-\text{CH}_2-\text{CH}_3$ ^b	27
$[\cdot\text{C}-(\text{C}_b)(\text{C})(\text{O})]$	81.34	$\cdot\text{CH}_2-\text{O}-\text{CH}_3$ ^c	26
$[\cdot\text{C}-(\text{O})(\text{C}_b)_2]$	61.92	$\text{CH}_3-\dot{\text{C}}\text{H}-\text{O}-\text{CH}_2-\text{CH}_3$	28
		$\cdot\text{C}(\text{CH}_3)_2\text{Ph}$ ^d	26
		$\cdot\text{C}(\text{Ph})_2\text{CH}_3$ ^e	29

^a Average of two possible values.

^b Setting $[\text{O}-(\text{C}_d)(\text{C})] \equiv [\text{O}-(\text{C})_2]$. Eventual error corrected as "steric effect".

^c On the assumption that changes in $[\cdot\text{C}-(\text{O})(\text{C})_x(\text{H})_y]$ are proportional to changes in $[\cdot\text{C}-(\text{OH})(\text{C})_x(\text{H})_y]$; $x, y = 0, 1, 2$. The values of $[\cdot\text{C}-(\text{OH})(\text{C})_x(\text{H})_y]$ were taken from ref. 26.

^d On the assumption that $[\cdot\text{C}-(\text{C}_b)(\text{C})_x(\text{O})_y]$ changes like $[\cdot\text{C}-(\text{C})_2(\text{C})_x(\text{O})_y]$; $x, y = 0, 1$.

^e On the assumption that $[\cdot\text{C}-(\text{C}_b)(\text{C})_x(\text{O})_y]$ changes like $[\cdot\text{C}-(\text{C})_2(\text{C})_x(\text{O})_y]$; $x, y = 0, 1$.

where A is the pre-exponential factor, $C_0 = 1 \text{ M}$ and m is the molecularity of the reaction. Although A has been claimed to be 10^8 s^{-1} for these reactions [2], in our calculations we used $A = 10^{11} \text{ s}^{-1}$, the collision frequency between neutral molecules in solution, which yields an upper limit to k_{ta} .

3. Results

Tables 3 - 7 show the results of our calculations for the reactions of singlet and triplet acetone, butyrophenone, benzophenone and 4-carboxymethylbenzophenone with a series of over 30 different olefins. We optimized R so that the tunnelling rate constants reproduce the experimental rate constants. The thermal activation rate constants calculated with the same energy barrier are from 30 to 10^5 times smaller than the corresponding tunnelling rate constants. These calculations show that the rate constants for direct biradical formation can be accounted for by the tunnel effect model, explaining point (iii) of Section 1.

TABLE 3

Cycloadditions of singlet acetone to olefins

Cyclo-addition	Olefin	log k_q	ΔH_r (kJ mol ⁻¹)	ϕ	IP (eV)	R (nm)
1	2,5-Dimethyl-2,4-hexadiene	8.8 ^a	159.8	0.1 ^a	7.46 ^b	0.0392
2	1,3-Cyclohexadiene	8.6 ^a	172.2	0.05 ^a	7.88 ^b	0.0406
3	<i>trans</i> -1,3-Pentadiene	8.0 ^a	158.8		8.42 ^b	0.0420
4	<i>cis</i> -1,3-Pentadiene	8.0 ^a	163.1		8.45 ^b	0.0423
5	2-Methyl-1,3-butadiene	7.9 ^a	173.1		8.60 ^b	0.0431
6	<i>cis</i> -1,2-Diethoxyethylene	9.5 ^c	134.3		7.38 ^c	0.0346
7	<i>trans</i> -1,2-Diethoxyethylene	9.3 ^c	134.3		7.40 ^c	0.0350
8	<i>cis</i> -1,2-Dimethoxyethylene	9.5 ^c	137.4		7.63 ^c	0.0347
9	1-Methoxy-2-methylpropene	8.9 ^c	118.5		7.65 ^c	0.0358
10	1-Ethoxy-2-methylpropene	8.8 ^c	126.2		7.70 ^c	0.0365
11	<i>cis</i> -1-Methoxy-1-butene	8.5 ^d	126.4	0.04 ^d		0.0378
12	<i>tert</i> -Butyl vinyl ether	7.9 ^c	120.9		8.19 ^c	0.0393
13	Isopropyl vinyl ether	7.7 ^c	120.9		8.36 ^c	0.0402
14	Ethyl vinyl ether	7.4 ^c	120.9		8.49 ^c	0.0412
15	2,3-Dimethyl-2-butene	8.1 ^a	127.7		8.27 ^e	0.0392
16	2-Methyl-2-butene	7.7 ^a	115.1		8.68 ^e	0.0398
17	<i>cis</i> -3-Hexene	7.6 ^a	112.2		8.95 ^e	0.0399
18	1-Hexene	6.9 ^a	105.2		9.48 ^e	0.0412
19	β,β -Dimethylacrylonitrile	< 7 ^f	127.8	$\approx 0^f$		> 0.0506
20	Crotononitrile	7.2 ^f	131.7	0.050 ^f	10.23 ^g	0.0501
21	Acrylonitrile	8.2 ^f	133.9	0.20 ^f	10.92 ^g	0.0467
22	Fumaronitrile	9.4 ^h	158.9	0.076 ^h	11.15 ^g	0.0437
23	Maleonitrile	9.7 ^h	158.9	0.086 ^h	11.15 ^g	0.0426

^aSee ref. 4.^bSee ref. 32.^cSee ref. 33.^dSee ref. 8.^eSee ref. 34.^fSee ref. 17.^gSee ref. 35.^hSee ref. 36.

The values of R are consistent with corresponding values used in previous applications of the tunnel effect theory and can be compared with the predictions of the general intersecting-state model (ISM) reaction energy barriers [40]. This model shows that

$$R = \eta(l_r + l_p) \quad (14)$$

where l_r and l_p are the equilibrium bond lengths of the reactants and products and η is the reduced bond extension

$$\eta = \frac{a' \ln 2}{n^+} + \frac{a'}{2\lambda^2} (\Delta H_r)^2 \quad (15)$$

TABLE 4
Cycloadditions of triplet acetone to olefins

Cyclo-addition	Olefin	$\log k_q$	ΔH_r (kJ mol ⁻¹)	ϕ	IP (eV)	R (nm)
24	<i>cis</i> -1,2-Diethoxyethylene	9.1 ^a	109.2		7.38 ^a	0.0342
25	<i>trans</i> -1,2-Diethoxyethylene	8.8 ^a	109.2		7.40 ^a	0.0351
26	1-Ethoxy-2-methylpropene	8.5 ^a	101.1		7.70 ^a	0.0359
27	<i>trans</i> -1-Ethoxy-1-butene	8.0 ^b	95.02			0.0369
28	<i>cis</i> -1-Methoxy-1-butene	8.2 ^c	101.3	0.08 ^c		0.0367
29	Ethyl vinyl ether	7.3 ^a	95.81		8.49 ^a	0.0394
30	2,3-Dimethyl-2-butene	7.7 ^b	102.6		8.27 ^d	0.0385
31	2-Methyl-2-butene	7.4 ^b	90.00		8.68 ^d	0.0386
32	Cyclohexene	7.0 ^b	85.94		8.72 ^e	0.0393
33	<i>cis</i> -2-Pentene	7.0 ^b	84.22		9.04 ^d	0.0392

^aSee ref. 33.

^bSee ref. 37.

^cSee ref. 8.

^dSee ref. 34.

^eSee ref. 38.

TABLE 5
Cycloadditions of butyrophenone to olefins

Cyclo-addition	Olefin	$\log k_q$ ^a	ΔH_r (kJ mol ⁻¹)	ϕ ^a	IP (eV)	R (nm)
34	2,3-Dimethyl-2-butene	8.7	120.7		8.27 ^b	0.0367
35	2-Methyl-2-butene	8.1	108.1	0.04	8.68 ^b	0.0379
36	Cyclohexene	7.6	104.1	0.05	8.72 ^c	0.0390
37	<i>cis</i> -3-Hexene	7.6	105.2		8.95 ^b	0.0392
38	<i>trans</i> -3-Hexene	7.0	99.16		8.96 ^b	0.0404
39	<i>cis</i> -2-Pentene	7.7	102.3		9.04 ^b	0.0387
40	<i>trans</i> -2-Pentene	7.3	98.45		9.04 ^b	0.0395
41	2-Methyl-1-butene	7.4	100.3		9.15 ^b	0.0395
42	1-Pentene	6.9	98.24		9.52 ^b	0.0409

^aSee ref. 39.

^bSee ref. 34.

^cSee ref. 38.

where n^\ddagger is the average bond order of the transition state, λ is the configuration entropy and $a' = 0.156$. The second term of eqn. (15) is not relevant for these reactions.

We apply here the procedure used to calculate R for hydrogen abstractions to the calculation of R for olefin cycloadditions. In the case of electron-rich olefins, for the C—O bond we have the same $d_{CO} = 0.0308$ nm. For the XH modes we have $l_r = l_{C=C} = 0.1375$ nm and $l_p = (l_{C-C} + l_{C-O})/2 =$

TABLE 6

Cycloadditions of benzophenone to olefins

Cyclo-addition	Olefin	$\log k_d$	ΔH_r (kJ mol ⁻¹)	ϕ	IP (eV)	<i>R</i> (nm)
43	<i>cis</i> -1,2-Diethoxyethylene	9.6 ^a	149.2		7.38 ^a	0.0349
44	1-Ethoxy-2-methylpropene	9.0 ^a	138.1		7.70 ^a	0.0366
45	1-Butyl vinyl ether	8.4 ^a	132.8		8.19 ^a	0.0388
46	Isopropyl vinyl ether	8.1 ^a	132.8		8.36 ^a	0.0397
47	Ethyl vinyl ether	7.9 ^a	132.8		8.49 ^a	0.0405
48	2,3-Dimethyl-2-butene	8.7 ^b	139.5		8.27 ^c	0.0367
49	2-Methyl-2-butene	8.1 ^b	127.0		8.68 ^c	0.0376
50	Cyclohexene	7.6 ^b	123.0		8.72 ^d	0.0398
51	<i>cis</i> -2-Pentene	7.9 ^b	121.2		9.04 ^c	0.0396
52	<i>cis</i> -2-Butene	7.8 ^e	121.8	0.1 ^e	9.12 ^c	0.0400
53	2-Methylpropene	7.5 ^e	116.3	0.091 ^e	9.24 ^c	0.0405

^aSee ref. 33.^bSee ref. 37.^cSee ref. 34.^dSee ref. 38.^eSee ref. 3.

TABLE 7

Cycloadditions of 4-carboxymethylbenzophenone to olefins

Cyclo-addition	Olefin	$\log k_d$ ^a	ΔH_r (kJ mol ⁻¹)	IP ^b (eV)	<i>R</i> (nm)
54	2,3-Dimethyl-2-butene	9.2	127.4	8.27	0.0349
55	2-Methyl-2-butene	8.7	114.9	8.68	0.0363
56	<i>trans</i> -2-Pentene	7.7	105.2	9.04	0.0387
57	<i>cis</i> -2-Pentene	8.0	109.1	9.04	0.0383
58	2-Methyl-1-butene	7.9	107.0	9.15	0.0385
59	1-Hexene	6.9	105.0	9.48	0.0412

^aSee ref. 2.^bSee ref. 34.

0.1500; therefore $d_{XC} = 0.0622$ nm. On the assumption of no charge transfer, *R* must be the average of the two displacements, 0.046 nm, in reasonable agreement with the *R* expected in our calculations in the absence of charge transfer (acetone vertical IP = 9.7 eV [41]).

In the hydrogen abstraction reactions we found that, for a given ketone and a series of substrates, *R* increases with increasing IP of the substrate for charge transfer abstractions and remains constant for the other cases. We can expect a similar result for olefin cycloaddition. In Figs. 1 to 3 we plotted *R* against IP. We excluded cyclohexene data from these figures

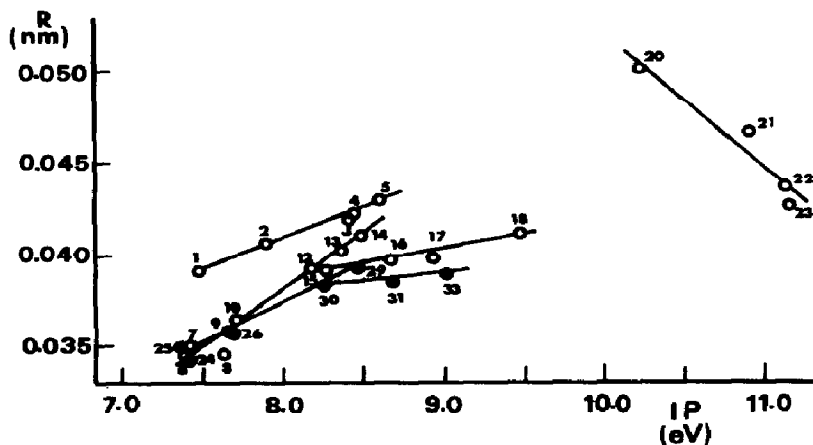


Fig. 1. Correlation between R and IP for $^1(n,\pi^*)$ acetone (\circ) and $^3(n,\pi^*)$ acetone (\bullet). The correlation coefficients r and slopes m are as follows: cycloadditions 1 - 5, $r = 0.99$ and $m = 0.00321$; cycloadditions 6 - 14, $r = 0.98$ and $m = 0.00606$; cycloadditions 15 - 18, $r = 0.97$ and $m = 0.00161$; cycloadditions 20 - 23, $r = -0.95$ and $m = -0.00737$; cycloadditions 24 - 29, $r = 0.99$ and $m = 0.00433$; cycloadditions 30 - 33, $r = 0.91$ and $m = 0.00089$.

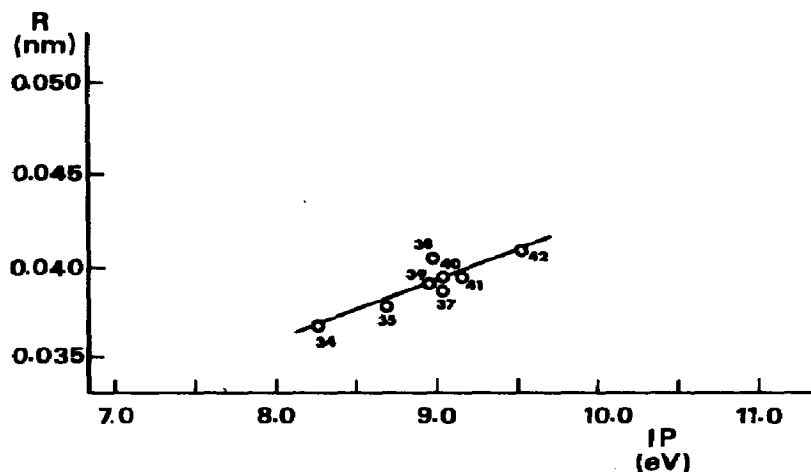


Fig. 2. Correlation between R and IP for $^3(n,\pi^*)$ butyrophenone. The correlation coefficient is 0.90 and the slope 0.00336.

because its IP was obtained in a different study from the other alkyl-substituted ethylenes and is not consistent with their IP values. Three remarkable features are evident in these figures.

(i) For the series of alkyl-substituted ethylenes the slopes increase with increasing ketone-accepting ability, defined by $E_{1/2}^{ox} + E_{1/2}^{red}$ where $E_{1/2}^{ox}$ and $E_{1/2}^{red}$ are the ketone half-wave oxidation and reduction potentials [37]. This is better seen in Table 8. Such a relation means that reactions involving ketones with a larger accepting ability have a larger degree of charge transfer from the olefin to the ketone, consistent with previous observations [4].

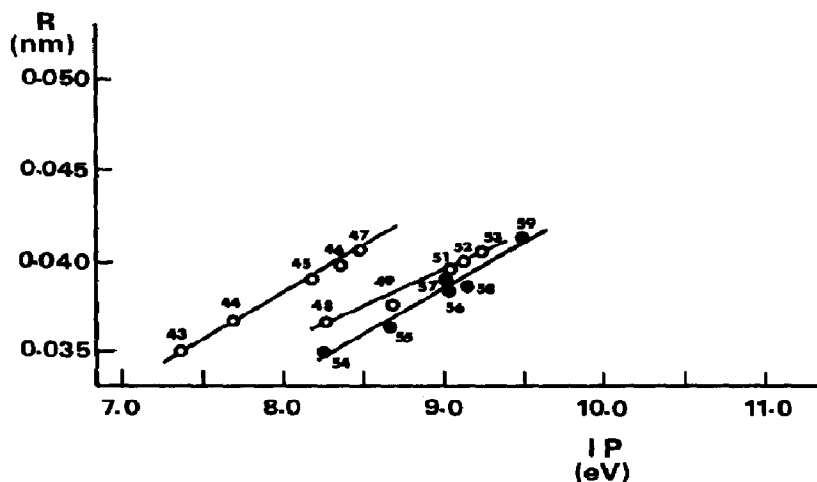


Fig. 3. Correlation between R and IP for $^3(n,\pi^*)$ benzophenone (\circ) and 4-carboxymethylbenzophenone (\bullet). The correlation coefficients r and slopes m are as follows: cycloadditions 43 - 47, $r = 0.999$ and $m = 0.00492$; cycloadditions 48 - 53, $r = 0.98$ and $m = 0.00409$; cycloadditions 54 - 59, $r = 0.98$ and $m = 0.00511$.

TABLE 8

Ketone accepting ability and degree of charge transfer

Ketone	$E_{1/2}^{\text{ox}}$ ^a (V)	$E_{1/2}^{\text{red}}$ (V)	$E_{1/2}^{\text{ox}} + E_{1/2}^{\text{red}}$ (V)	Slope (nm eV ⁻¹)
Acetone triplet	2.59	-2.31 ^b	0.28	0.00089
Acetone singlet	2.59	-2.31 ^b	0.28	0.00161
Butyrophenone	2.34	-2.03 ^b	0.31	0.00336
Benzophenone	2.37	-1.84 ^b	0.53	0.00409
4-Carboxymethyl- benzophenone		-1.66 ^c		0.00511

^aSee ref. 37.^bSee ref. 6.^cValue from ref. 42.

(ii) Singlet acetone undergoes cycloaddition with a more complete set of olefins, because the triplet reactions with electron-poor olefins proceed through triplet energy transfer and do not yield oxetanes. For this ketone, the degree of charge transfer from the olefin to the ketone, as measured by the slopes of the curves plotted in Fig. 1, decreases when the IP of the olefin approaches the IP of acetone. When the IP of the olefin (which is linearly related to $E_{1/2}^{\text{ox}}$) becomes larger than the IP of acetone and the corresponding $E_{1/2}^{\text{red}}$ values increase [35], the direction of charge transfer is reversed. Again, this agrees with previous reports [4, 37], although such a clear picture of this change has never been observed before.

(iii) When all the approximations involved in these calculations are recalled, the correlation coefficients obtained, which are always larger than 0.9, must be considered to be quite good.

The above features explain in depth the relation between the rate constants for cycloaddition and the IP or $E_{1/2}^{\text{red}}$ of the olefins. The correlations between k_q and IP very often found in the literature [6] must be interpreted with care because the more substituted (electron-rich) olefins do have lower IP values but also have stronger steric effects [2].

We shall refrain from drawing conclusions out of relative changes in R among the several ketones for the same olefin. These changes may be affected by significant errors in their ΔH_r values, because they involve different reaction series. However, we can compare R between singlet and triplet acetone.

The reactions of acetone in its $^1(n,\pi^*)$ state show a significantly higher R value than the corresponding $^3(n,\pi^*)$ state reaction. This can be rationalized on the assumption that in the singlet biradical there is sufficient interaction between the spin-paired but space-separated free valence electrons so that the cisoid conformation is favoured over the transoid conformation [43] (Fig. 4). In the cisoid conformation steric effects operate to keep the olefin moiety away from the carbonyl group, therefore increasing R for the singlet reaction. For the triplet we note that even in the cisoid conformation the C=O and C=C oscillators can come close together, because the polarization induced by the triplet state on the π system of the olefin may distort its planarity and favour the approach [8]. A twisted cisoid triplet biradical or a transoid triplet biradical are expected to yield stereorandom cycloadditions as has been experimentally observed. However, only a cisoid singlet biradical can yield the stereospecific cycloadditions reported in the literature. This interpretation of the reaction conformation of the cycloadditions is further emphasized by the observation that bond rotations are faster than intersystem crossing in the triplet biradical, while the singlet biradical collapses within a few picoseconds after its formation [9].

It is interesting to note that the difference in R between singlet and triplet acetone is reduced with increasing substitution. This can be explained when it is considered that the distortion of the olefin planarity induced by the triplet acetone is no longer dominant over the increased steric effects.

The larger R value of the conjugated dienes relative to that of the other olefins can be explained by the ISM.

The model predicts that, in reactions with conjugated dienes, where the double bonds have some single bond character, the contribution of the XH mode to R should be calculated with $l_x = (l_{\text{C=C}} + l_{\text{C-C}})/2$ and n^+ should be smaller. This yields a larger value of R than that for ethylenes, as observed in our studies.

Finally, for electron-poor olefins, ISM predicts $R = 0.047$ nm. However, for these olefins the CO bond contribution to R is just given by its small out-of-plane wag. Under the extreme condition of neglecting this contribution, we obtained $R = d_{\text{XC}} = 0.063$ nm. This shows that the R values for

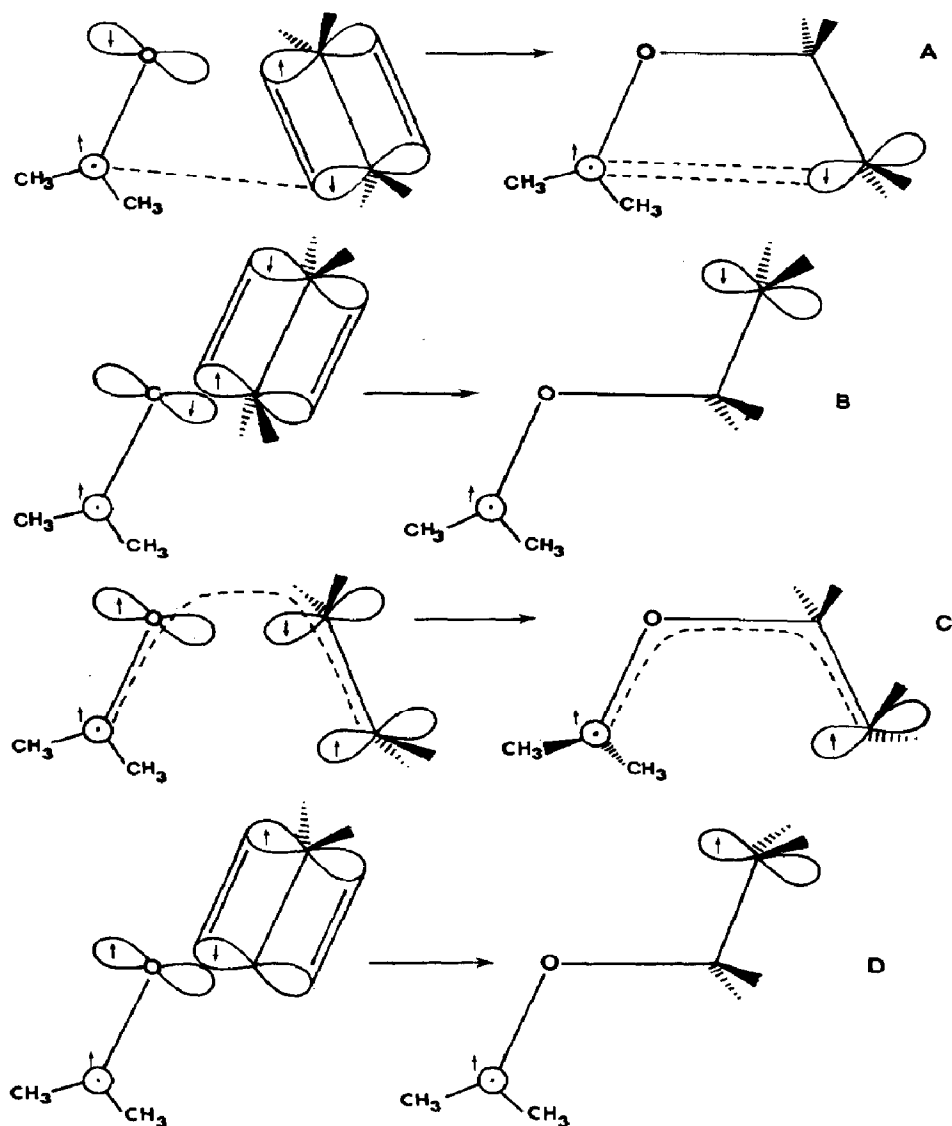


Fig. 4. Possible geometries of attack of S_1 on an ethylene to yield a cisoid or a transoid singlet biradical, A or B. The ketone T_1 attack on an ethylene might polarize its π system and twist it, to yield a twisted cisoid biradical, C; the interaction may also lead to a transoid biradical, D.

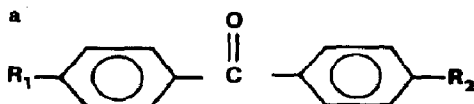
electron-poor olefins must be larger than those for their electron-rich counterparts, as observed.

We can study more quantitatively how R changes for a given olefin with a series of ketones using substituted benzophenones. In the reactions of a series of benzophenones with a given olefin, the changes in ΔH_r are due solely to the different excited state energies of the benzophenone, which are reported in the literature. Table 9 shows the results of calculations for the

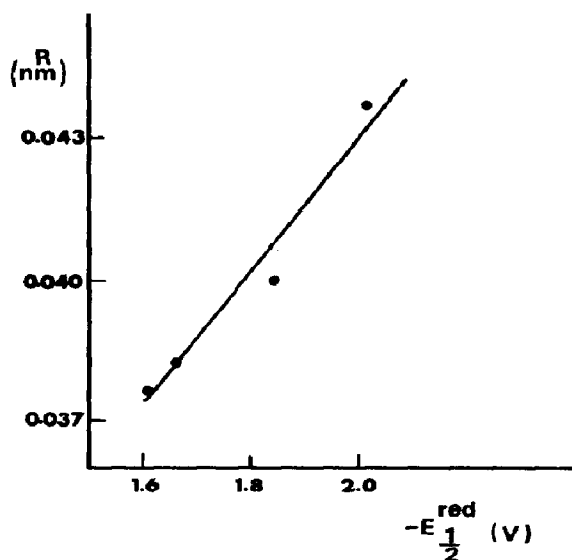
TABLE 9

Substituent effects^a

R_1	R_2	$E_T(n,\pi^*)$ (kJ mol ⁻¹)	$E_{1/2}^{\text{red}}$ (eV)	$\log k_q$ ^b	R (nm)
CF ₃	H	283 [44]	-1.61 [44]	8.3 [3]	0.0377
CO ₂ CH ₃	H	270 [45]	-1.66 ^c	8.0 [2] ^d	0.0383
H	H	270 [44]	-1.84 [44]	7.8 [3]	0.0400
OCH ₃	OCH ₃	290 [44]	-2.01 [44]	6.6 [3]	0.0437

^bAddition to *cis*-2-butene, except where noted.^cValue of ref. 42 corrected for the experimental conditions of ref. 44.^dAddition to *cis*-2-pentene.

reactions of 4-trifluoromethylbenzophenone, 4,4'-dimethoxybenzophenone and benzophenone with *cis*-2-butene, together with the reaction of 4-carboxybenzophenone with *cis*-2-pentene. As we were unable to find the experimental reaction rate for the addition of 4-carboxybenzophenone to *cis*-2-butene, the value for the addition to *cis*-2-pentene was used. The decrease in R with increase in $E_{1/2}^{\text{red}}$ is consistent with the previous findings for hydrogen abstractions [16] and can easily be interpreted in terms of a better accepting ability of the ketones in the charge transfer interaction (Fig. 5). It is well known [46] that, for example, the trifluoromethyl-

Fig. 5. Correlation between R and $E_{1/2}^{\text{red}}$.

substituted ketone has an enhanced electrophilicity over the other substituted ketones.

The tunnel effect model can also account for the regioselectivity of oxetane formation. For example, the addition of acetone singlets (triplets) to *cis*-1-methoxy-1-butene produces 3-methoxyoxetanes and 2-methoxyoxetanes in the ratio 1.2:1 (1.3:1) [8]. Optimization of R to reproduce the observed rate constant, $k_1 = 3.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ($1.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$), for the formation of the most stable radical products, $\Delta H_r = 126.4 \text{ kJ mol}^{-1}$ ($101.3 \text{ kJ mol}^{-1}$), gives $R = 0.0378 \text{ nm}$ (0.0367 nm). Calculating, for the same R , the rate of reaction to yield the less stable biradical, $\Delta H_r = 123.3 \text{ kJ mol}^{-1}$ ($98.20 \text{ kJ mol}^{-1}$), we obtained $k_2 = 2.7 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ ($1.4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$). Therefore, the calculated regioselectivity is 1.2:1 (1.2:1). This is in excellent agreement with the experimental data. A similar calculation for the addition of singlet acetone to *trans*-1-methoxy-1-butene yields $k_1/k_2 = 1.2$, with $R = 0.0374 \text{ nm}$, in reasonable agreement with the reported regioselectivity of 1.5:1 [8, 43]. Another example of the prediction of the correct regioselectivity is the addition of triplet acetone to 2-methyl-2-butene. For this reaction $k_q = 2.8 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ [37] which is exactly reproduced with $R = 0.0384$. Calculating k_q for the reaction to yield the less stable biradical ($\Delta H_r = 89.12 \text{ kJ mol}^{-1}$), we obtain a stereoselectivity of 1.1:1, in line with the reported 1.2:1 [47]. These calculations show that the degree of regioselectivity in oxetane formation is not smaller than expected from the direct formation of a biradical, as mentioned in point (v) of Section 1.

In hydrogen abstractions the dominance of the tunnel effect mechanism over thermal activation could be shown when the energy ω of the crossing between the ground state potential energy curve of the reactant and the primary photoproduct curve was higher in energy than E_e [10]. For the cases when $\omega > E_e$ the efficiency for the primary photoproduct formation should be unity if the reaction proceeds according to the tunnel effect mechanism, and less than unity if it goes through thermal activation. This difference is due to the necessary passage of the system by the crossing ω , where it can convert to the ground state potential energy curve, reducing the efficiency of the reaction. For $\omega < E_e$ the cycloaddition efficiency must then be less than unity for both mechanisms. As olefin additions and hydrogen abstractions can be treated with similar state correlation diagrams [18], we can expect a similar structure-efficiency relationship in both types of reaction. Therefore, olefin additions must also be sensitive to the relative positions of ω and E_e . Turro and Ramamurthy [48] also pointed out that the inefficiency of cycloadditions involving n, π^* states could occur on the way to the primary intermediate.

In the cycloadditions mentioned so far, ω is always below E_e . This explains the low product quantum yields observed in these reactions. The reaction where ω is almost isoenergetic with E_e is the cycloaddition of 4-carboxymethylbenzophenone to 1-hexene ($\omega = 101.5 \text{ kJ}$, $E_e = 105.0 \text{ kJ}$), as a result of a low value of E_e and a large R value. This led us to search

for reported quantum yields for similar reactions. A very interesting study has been presented by Winnik and Hsiao [45] on the intramolecular quenching of benzophenone-4-CO₂(CH₂)₉CH=CH₂ where the quantum yield of such a process was estimated to be unity, within experimental error. The chemical yield of oxetane formation is 83% [49]. The reported k_q value is $5.2 \times 10^5 \text{ s}^{-1}$ and the quenching step is likely to yield the same intermediate as oxetane formation, *i.e.* the corresponding biradical. We assumed no significant strain in this intramolecular reaction and used the same ΔH_r as for the reaction between 4-carboxymethylbenzophenone and 1-hexene. Setting $R = 0.0446 \text{ nm}$ we can reproduce k_q . This slightly larger R value than that found for intermolecular reactions can be assigned to the less favourable configuration of approach for intermolecular reactions. Using these values for ΔH_r and R , then $\omega = 124.3 \text{ kJ mol}^{-1}$ gives the quantum yield as unity.

The explanation of the cycloaddition efficiency is not only in agreement with point (vi) of Section 1. It also provides strong evidence that these photochemical reactions proceed through the tunnel effect mechanism and not through some sort of thermal activation, which always predicts inefficient cycloadditions.

Finally, temperature dependence must be considered. In thermal activation the temperature dependence is simply given by the Arrhenius law. For a tunnel effect mechanism the temperature dependence is more complex. We can expect that higher vibrational modes are more populated at higher temperatures; however, higher average bond lengths may lead to radiationless transitions involving larger displacements. Then, the increase in the energy of the reactants could be compensated by the increase in R and the resulting rate constant would show a complex dependence on the temperature.

4. Conclusions

Our study of about 70 cycloadditions of ketones to electron-rich and electron-poor olefins, with reactivities differing by four orders of magnitude, shows that the tunnel effect model provides a unifying explanation for the characteristics of such reactions.

The tunnel effect model can explain the observed stereospecificity, reactivity, substituent effects, regioselectivity and efficiency, without postulation of the intermediacy of an exciplex. The extended tunnelling model explains the reactivity of carbonyl cycloadditions to olefins in terms of the stability of the biradical products and charge transfer interactions.

The present study and the previous applications of the tunnel effect model provide a general explanation of the reactivity of the ketone n, π^* states within the framework of the general intersecting-state model.

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