

STERIC HINDRANCE TO ENERGY TRANSFER FROM $^3(n,\pi^*)$ AND $^3(\pi,\pi^*)$ STATES OF AROMATIC KETONES TO DIENES

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Summary

Efficiencies of excitation-resonance energy transfer in *n*-hexane from $^3(n,\pi^*)$ and $^3(\pi,\pi^*)$ states of seven aromatic ketones to *cis*-1,3-pentadiene (*c*-P) and 3 α ,24-dimethoxy- $\Delta^{7,9}$ -choladiene (D) were measured. The sterically hindered diene D is approximately 6 times less efficient as an acceptor than is *c*-P, regardless of the configuration of the sensitizer triplet state. A treatment of the energy transfer efficiencies which assumes no difference between n,π^* and π,π^* states and which includes only gross aspects of individual sensitizer-acceptor orientations accounts for *c*-P being no more than 4 times as efficient an acceptor as D. It is concluded that excitation energy migration within the benzoyl sensitizer is sufficiently rapid to make state differences of little importance during excitation-resonance energy transfer.

1. Introduction

Photophysical and photochemical studies have shown that n,π^* and π,π^* states of aromatic ketones behave quite differently. Most notable are the relatively slow rates of reactivity of π,π^* triplets in Norrish II processes [1 - 4] and the much shorter n,π^* triplet lifetimes [2, 4, 5]. In spite of the attention given to the differences between these states and to assessments of the steric requirements for quenching n,π^* states by α -diketones [6], amines [7] and alkenes [8, 9], no comparison of the steric requirements for excitation-resonance energy transfer [10] from n,π^* or π,π^* triplets of aromatic ketones has been reported. We conducted a set of experiments which demonstrates that in solution the efficiencies of excitation-resonance energy transfer from n,π^* or π,π^* triplet states of the aromatic ketones 1 - 7

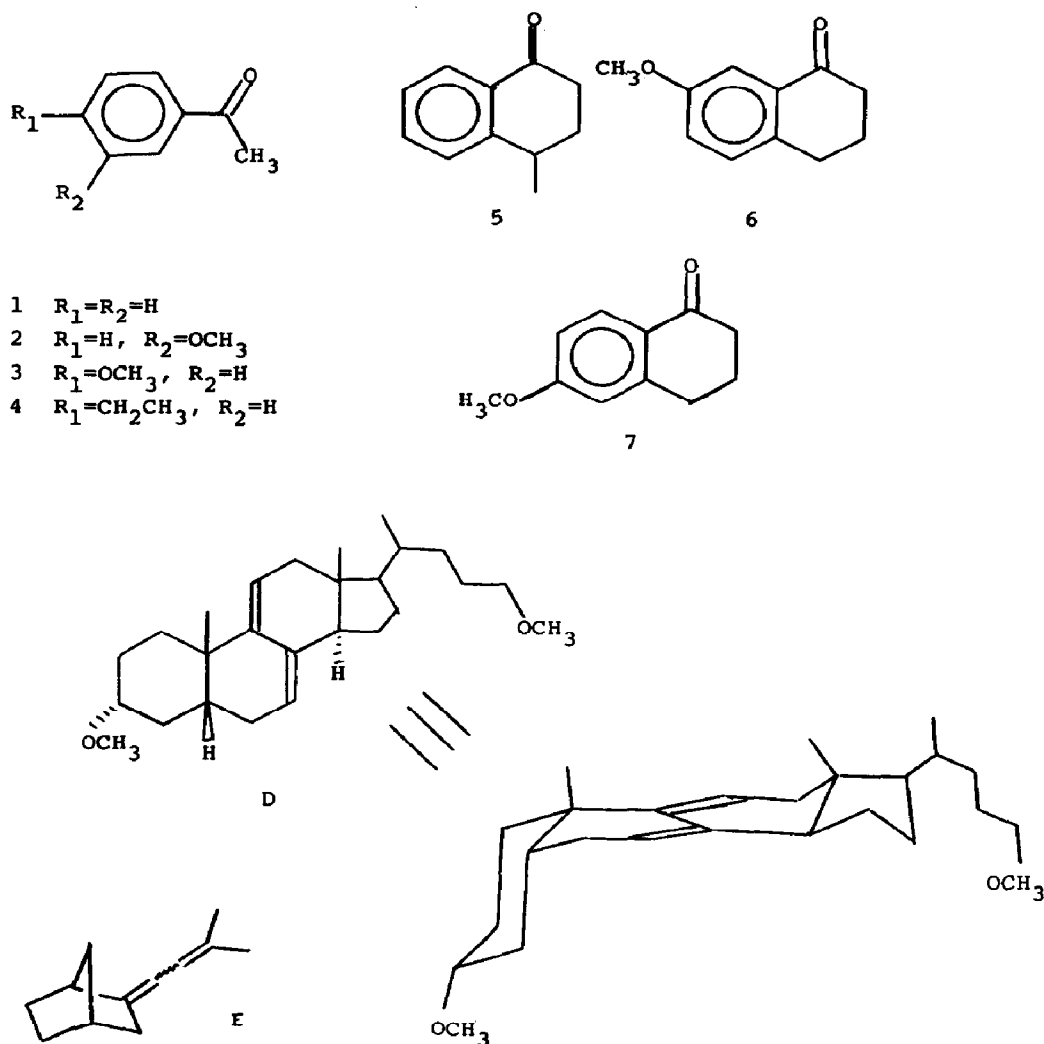


Fig. 1. The structures of the ketones 1 - 7 and of D and E.

(Fig. 1) to a sterically hindered diene 3 α ,24-dimethoxy- $\Delta^{7,9}$ -choladiene (D) are very similar. The same experiments were performed with the ketones 1, 2 and 3 as sensitizer and 2-(3-methyl-2-butenylidene)bicyclo[2.2.1]heptane (E) as a less sterically hindered quencher. The rates of energy transfer to *cis*-1,3-pentadiene (*c*-P) and E were found to be about equal in all three experiments.

2. Experimental

Spectra were determined on Zeiss DMR-10 and DMR-21 spectrophotometers (UV), on a Perkin-Elmer model 457 spectrophotometer (IR; KBr

pellets), on a Varian T-60 spectrometer (proton magnetic resonance) and on an Aminco-Bowman SPF-11 spectrophotofluorimeter (emission; uncorrected). Melting points, measured on a Kofler hot-stage microscope, were not corrected. Peaks from a Hewlett Packard 5750 or a Varian 1800 gas chromatograph, both with flame ionization detectors, were integrated either electronically or by weighing on a precision balance.

Acetophenone (Merck, boiling point 40 °C (5 mmHg)), *m*-methoxyacetophenone (Pfaltz and Bauer, boiling point 118 °C (2 mmHg)) and 4-methyl-1-tetralone (Aldrich, boiling point 111 °C (2 mmHg)) were vacuum distilled. *p*-Ethylacetophenone (Eastman) was vacuum distilled through a Nester-Faust Teflon spinning-band column and a center cut was collected. *p*-Methoxyacetophenone (Pfaltz and Bauer), after being recrystallized from petroleum ether and sublimed twice, yielded a melting point of 35.0 - 35.5 °C. 7-Methoxy-1-tetralone exhibited a melting point of 60.0 - 60.5 °C after sublimation. 6-Methoxy-1-tetralone (Aldrich) was recrystallized from methanol and was sublimed to give a melting point of 75.5 - 77.0 °C. Crysene (Pfaltz and Bauer) gave a melting point of 250.0 - 250.5 °C after recrystallization from benzene. Gas-liquid partition chromatography (GLPC) analyses on a 10% FFAP on Chromosorb W column (1.5 m × $\frac{1}{8}$ in) indicated that all the compounds except acetophenone (98.7%), 4-methyl-1-tetralone (98.4%), *m*-methoxyacetophenone (98.7%) and *p*-ethylacetophenone (98.6%) were greater than 99% pure. Purified samples were stored under nitrogen in the dark. *c*-P (Chemical Samples Co.; less than 0.4% *trans* by GLPC; boiling point 40 °C) was distilled from LiAlH₄ and was stored in sealed ampules in a refrigerator.

n-Hexane (Aldrich, spectro grade, boiling point 66 - 68 °C), fractionally distilled from calcium hydride under nitrogen, exhibited no discernible absorption from 220 to 360 nm.

2.1. 3 α ,24-Dimethoxy- $\Delta^{7,9}$ -choladiene

The methyl ester of cholic acid, melting point 153 - 155 °C (literature [11] melting point 156 - 157 °C), was prepared from the acid and methanolic HCl by a standard method [11] in 95% yield. The 3 α ,7 α -diacetate of methyl cholate, melting point 184.5 - 186 °C (literature [12] melting point 185 - 187 °C), was prepared from methyl cholate and acetic anhydride in 80% yield as described in the literature [12]. Oxidation of the diacetate with chromium trioxide [12] yielded, after recrystallization from methanol, 84% of methyl 3 α ,7 α -diacetoxy-12-oxocholate, melting point 176 - 178 °C (literature [12] melting point 179 - 181 °C). Selenium dioxide treatment of the oxidation product [12] afforded an 80% yield after methanol recrystallization of methyl 3 α ,7 α -diacetoxy-12-oxo- $\Delta^{9(11)}$ -cholenate, melting point 153.5 - 156 °C (literature [12] melting point 159 - 161 °C).

Under a dry nitrogen atmosphere, 48.8 g (0.10 mol) of the cholenate was added to a previously prepared and chilled solution of 12 g of sodium in diethylene glycol and 50 ml of hydrazine hydrate [13]. The mixture was refluxed under nitrogen for 6 h at 160 °C and the distillate of boiling point

below 180 °C was removed. After 7 h further reflux at 180 °C, the distillate of boiling point less than 200 °C was removed. Following 8 h of reflux at 200 °C the solution was cooled, dilute acetic acid was added and the mixture was extracted with chloroform. Drying and evaporation of the organic layer left a white solid which, on recrystallization from methanol-ether, yielded 30.3 g (80%) of 3 α -hydroxy- $\Delta^{7,9}$ -choladienic acid (melting point 198 - 200 °C, $\lambda_{\max}^{\text{ethanol}} = 244 \text{ nm}$ ($\log \epsilon = 4.19$)) (literature [14] $\lambda_{\max}^{\text{ethanol}} = 244 \text{ nm}$ ($\log \epsilon = 4.24$)).

Under a dry nitrogen atmosphere a solution of 29.9 g (0.08 mol) of 3 α -hydroxy- $\Delta^{7,9}$ -choladienic acid in 400 ml of tetrahydrofuran was added dropwise to a stirred mixture of 11.5 g of LiAlH₄ and 300 ml of tetrahydrofuran [15]. The mixture was refluxed for 1 h and was cooled. Slowly and in sequence, 11.5 g of water, 11.5 g of 15% aqueous sodium hydroxide and 34 ml of water were added to the stirred mixture. Filtration was followed by copious washing of the solid with ether. The washes and the filtrate were combined, were dried (MgSO₄) and were evaporated to residue. The solid, recrystallized from acetone, was 26.2 g (91%) of 3 α ,24-dihydroxy- $\Delta^{7,9}$ -choladiene, melting point 160 - 163 °C.

Under nitrogen, 12.2 g (0.034 mol) of 3 α , 24-dihydroxy- $\Delta^{7,9}$ -choladiene in 300 ml of tetrahydrofuran were added slowly to a stirred mixture of 4 g of sodium hydride (57% in oil) and 50 ml of tetrahydrofuran. After no more gas was evolved (approximately 3 h), 30 ml of freshly distilled iodomethane were added and the solution was stirred at ambient temperature in the dark for 42 h. The mixture was filtered through Celite and the filter cake was washed with 500 ml of ether. The organic liquids, after being combined and evaporated, afforded a dark oil which was chromatographed on a 2 cm \times 30 cm silica gel column. After eluting with 1.5 l of petroleum ether, the first 30 ml of a 1:4 mixture of benzene-ethyl acetate (approximately 30 ml) contained 6.7 g (51%) of a white solid, melting point 55 - 59 °C.

The elemental analysis gave the following results: calculated (C₂₆H₂₄O₂), C, 80.77%; H, 10.95%; found, C, 80.91%; H, 11.30%. For the UV spectrum in methanol λ_{\max} values were 252.5, 244 ($\log \epsilon = 4.19$) and 238 nm (literature [14] λ_{\max} (ethanol) = 244 nm ($\log \epsilon = 4.24$)). The nuclear magnetic resonance (CDCl₃) δ values were 5.56 (1H, multiplet), 5.24 (1H, multiplet), 3.32 (2H, singlet), 3.35 (6H, singlet), 0.99 (6H, singlet) and 0.52 (3H, singlet).

2.2. Relative quantum yields for isomerization of *cis*-1,3-pentadiene

For each sensitizer a series of eight 13 mm \times 100 mm constricted Pyrex test tubes were filled with 3.0 ml of *n*-hexane solution containing a fixed total concentration of *c*-P and D (6×10^{-2} M, varying in the ratios 1:0, 3:1, 2:1, 1:1, 1:2, 1:3, 1:4 and 1:5) and fixed concentrations of sensitizer and *n*-nonane (10^{-2} M; internal standard). The tubes were degassed (three freeze-pump-thaw cycles) on a mercury-free vacuum line at less than about 2×10^{-4} Torr and were sealed. The tubes were irradiated in a "merry-go-round" apparatus [16] with the filtered (Pyrex and 318 nm Jena interference

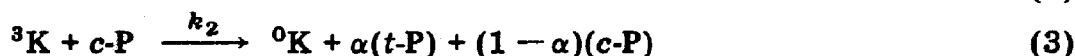
filters) output of a Hanovia 450 W medium pressure mercury lamp such that only the sensitizer absorbed the light. The irradiation times were chosen to effect approximately 3% isomerization of *c*-P in the tubes with no D.

The ratios of pentadiene isomers to *n*-nonane in each tube were determined 3 - 5 times before and after irradiation by GLPC (25% β,β' -oxydi-propionitrile on a 60/80 acid-washed Chromosorb W column (6 m \times $\frac{1}{8}$ in) at 35 °C). Experiments in which the concentrations of the sensitizers were varied were conducted similarly. All the sample tubes contained 2×10^{-2} M *c*-P.

3. Method and results

3.1. Method

"Exothermic" excitation-resonance energy transfer from unhindered triplet states to unhindered dienes is known to proceed at diffusion-controlled rates [17]. Scheme 1 (reactions (1) - (5)) describes the important steps leading to energy transfer from a ketone triplet (^3K) and to *trans*-1,3-pentadiene (*t*-P) formation.



Scheme 1.

The extremely short lifetimes of ketone singlets and diene triplets [18] allow experimental conditions to be selected (dilute concentrations of K, *c*-P and D) which minimize the importance of $^1\text{K}-^0\text{K}$ interactions and diene triplet reactions with ground state dienes.

Self-quenching of ^3K by K (eqn. (6)) has been shown to be important in several types of aromatic ketones [19]. Equation (7), in which Φ_{S}^0 and Φ_{T}^0 are the quantum yields for self-quenching and pentadiene triplet formation respectively in the absence of D and in which Φ_{ST} is near unity (*vide infra*), allows the contribution of self-quenching to be estimated for several of the ketones employed.



$$\frac{\Phi_{\text{S}}^0}{\Phi_{\text{T}}^0} = \frac{k_6[\text{K}]}{k_2[\text{c-P}]} \quad (7)$$

TABLE 1

Quantum yields for 318-nm-sensitized isomerizations of *t*-P to *c*-P^a

Sensitizer	Concentration $\times 10^2$ (M) ^b	Φ_{t-P}^0 ^c
Acetophenone (1)	4.51	(0.55)
<i>m</i> -Methoxyacetophenone (2)	0.21	0.50 \pm 0.02
	0.20	0.48 \pm 0.01
	0.15	0.47 \pm 0.03
<i>p</i> -Methoxyacetophenone (3)	1.94	0.52 \pm 0.02
	1.74	0.54 \pm 0.02
	1.34	0.51 \pm 0.02
<i>p</i> -Ethylacetophenone (4)	3.33	0.58 \pm 0.02
	3.06	0.50 \pm 0.02
	2.35	0.51 \pm 0.01
4-Methyl-1-tetralone (5)	5.70	0.59 \pm 0.01
	4.96	0.58 \pm 0.02
	3.90	0.59 \pm 0.07
7-Methoxy-1-tetralone (6)	0.07	0.45 \pm 0.02
	0.06	0.46 \pm 0.02
	0.05	0.46 \pm 0.01
6-Methoxy-1-tetralone (7)	2.16	0.56 \pm 0.05
	1.60	0.54 \pm 0.03

^aThe initial concentration of *c*-P was 2×10^{-2} M in all runs; the percentage conversions were corrected for back reactions [21].

^bThe quantum yields were corrected to account for partial transmission of light in some samples.

^cAll quantum yields are relative to acetophenone as sensitizer [22] and represent the average of three determinations; absolute errors are estimated to be $\pm 10\%$.

Using the k_6 value of Chapman and Wampfler [19] and k_2 equal to $k_{\text{diffusion}}$ ($1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ †), the total contribution from self-quenching is found to be less than our experimental error. In addition, the quantum yields Φ_{t-P}^0 for sensitized isomerization of *c*-P to *t*-P in the absence of D were measured for different concentrations of several of the sensitizers [21]. The results, summarized in Table 1, support those obtained with eqn. (7). If self-quenching were important, Φ_{t-P}^0 would have decreased drastically as the concentrations of the ketones were increased. (The larger differences in Φ_{t-P}^0 among the sensitizers may be due to unaccounted-for variables. They would affect only slightly our determination of k_3 relative to that of k_2 .) It can be seen that Φ_{t-P}^0 for each sensitizer is nearly constant in the concentration ranges explored.

†The value cited is less than that predicted for $k_{\text{diffusion}}$ in hexane, the solvent employed, but reflects the correction necessary to account for inefficient ^3K -diene encounters [20].

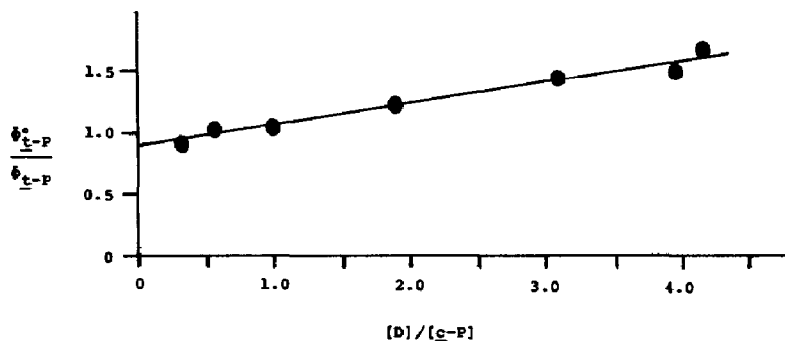


Fig. 2. A Stern-Volmer plot for the acetophenone-sensitized isomerization of *c*-P to *t*-P in the presence of D.

Stern-Volmer analysis of Scheme 1 yields eqn. (8), in which Φ_{t-P}^0 is the quantum yield for the formation of *t*-P in the presence of D.

$$\frac{\Phi_{t-P}^0}{\Phi_{t-P}} = \frac{k_3 [D]}{k_1 + k_2 [c-P]} + 1 \quad (8)$$

If $k_2 [c-P] \gg k_1^\ddagger$, plots of $\Phi_{t-P}^0 / \Phi_{t-P}$ versus $[D] / [c-P]$ should be linear with intercepts of unity. A representative plot for acetophenone is shown in Fig. 2. For all sensitizers the extrapolated intercepts were 1.0 ± 0.1 and the data points were fitted easily to straight lines. The k_2/k_3 ratios, taken as the reciprocals of the slopes of the graphs, are summarized in Table 2.

3.2. Nature of the lowest triplet states

Aromatic ketones are capable of exhibiting predominantly n, π^* (eqn. (9), $a \gg b$), π, π^* (eqn. (9), $b \gg a$) or strongly mixed lowest triplet states (eqn. (9), $a \approx b$) [26]. In fact, the state order can be altered by varying the solvents [2, 26] or the substituents [27] on the aromatic ring. The energy of the π, π^* (3L_a) state localized on the phenyl ring is much more sensitive to substituents than is the n, π^* state localized on the carbonyl group [28 - 30].

$$\psi_T = a\psi_{n, \pi^*} + b\psi_{\pi, \pi^*} \quad (9)$$

Although the contributions of a and b in eqn. (9) can be calculated [3] for some aromatic ketones, the requisite information is lacking for several of our sensitizers. An alternate approach, based on triplet state lifetimes, reactivity and other properties [31], leads to the designations in Table 2. We assume that the only reasonable description of the excited states requires the inclusion of both the phenyl and the carbonyl groups since there is no hindrance to overlap of their π systems.

[‡] Triplet lifetimes of aromatic ketones incapable of undergoing Norrish II reactions are at least in the microsecond range in hydrocarbon solutions [2, 4, 5, 23].

TABLE 2

Energy transfer ratios for aromatic ketone sensitizers, irradiated at 318 nm in *n*-hexane

Sensitizer	Concentration $\times 10^2$ (M)	Lowest triplet configuration [23]	k_2/k_3 ^a
1	5.2 ^b	n, π^*	6.3 ± 0.3
1	4.5	n, π^*	5.9 ± 0.3
1	4.5 ^c	n, π^*	6.5 ± 0.6
2	0.036	π, π^*	8.6 ± 0.7
2	0.3	π, π^*	6.5 ± 0.4
3	1.8	π, π^*	8.0 ± 0.5
4	3.0	π, π^* ^d	6.3 ± 0.3
5	5.5	π, π^* ^e	4.8 ± 0.5
6	0.062	π, π^* ^e	7.4 ± 0.3
7	2.3	π, π^* ^e	4.9 ± 0.2

^aCalculated with a non-linear least-squares program [24]; absolute errors are estimated to vary from 15% to 20%, depending on the sensitizer and the percentage of *c*-P converted.

^bPyrex filter only ($\lambda > 300$ nm).

^cDodecane as solvent.

^dProbably strongly mixed with n, π^* [2, 25].

^eAssignment based on aromatic ketones with similar substituents.

3.3. Energies of sensitizers and quenchers

The energies of the lowest triplet states of 1, 2 and 3 as well as of *p*-methylacetophenone (a good model for 4) are known [4] to be more than 290 kJ mol^{-1} above their ground states. Each alkyl or alkoxy group reduces the π, π^* triplet energy of acetophenone by approximately 8 - 15 kJ mol^{-1} . By analogy, the lowest triplets of 5, 6 and 7 are estimated to be greater than about 290 kJ mol^{-1} . (The triplet energy E_T of 1-tetralone is 304 kJ mol^{-1} [32].)

The triplet energy of *c*-P, 240 kJ mol^{-1} , has been well defined by several investigators [9]. The triplet energy of D was approximated to lie between 240 and 253 kJ mol^{-1} ; D quenches the phosphorescence of naphthalene but not that of crysene.

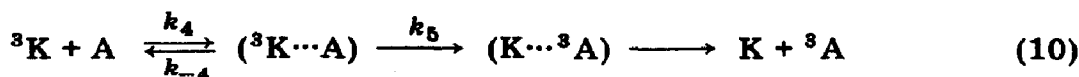
Thus, the exothermicity of energy transfer from the sensitizer triplets to D, in the absence of steric effects, should be diffusion controlled and irreversible [33].

4. Discussion

It is apparent from the data in Table 2 that the difference in any steric factors for energy transfer from $^3(n, \pi^*)$ or $^3(\pi, \pi^*)$ states of the aromatic ketones to D must be small. In fact, virtually all the rate constant ratios are

within experimental error. In part, the lack of an observed steric effect may be due to the multiple collisions per encounter suffered by the sensitizers and D even in a solvent of very low viscosity such as *n*-hexane ($\eta = 3.3 \times 10^{-3}$ P). Presumably the sensitizer and D are able to explore a myriad of orientations during each encounter, finding one which is suitable for transfer to occur.

A crude calculation of diffusional effects accounts for a part of the difference in the energy transfer rates from one sensitizer to *c*-P or D. Assuming the simple scheme for energy transfer shown in eqn. (10), where ($^3\text{K}\cdots\text{A}$) and ($\text{K}\cdots^3\text{A}$) represent the encounter complexes between a sensitizer and an acceptor (A) before and after energy transfer respectively, the overall rate constant k_{obs} for energy transfer is given by eqn. (11). The k_{obs} values are k_2 (A \equiv *c*-P) and k_3 (A \equiv D) (see Scheme 1). The absence of ground state complexes between K and A, which would complicate the kinetic treatment, is indicated by the fact that no changes in the absorption spectra (above 300 nm) of the aromatic ketones were detected when *c*-P and D were added. The exothermicity of the net energy transfer processes allows reverse energy transfer (eqn. (12)) to be neglected [33].



$$k_{\text{obs}} = \frac{k_4 k_5}{k_{-4} + k_5} \quad (11)$$



In terms of Scheme 1, two boundary conditions for k_{obs} will determine whether steric effects, should they exist, are capable of being detected in the k_2/k_3 ratios.

(1) When k_{obs} is limited by the rates of diffusion ($k_5 \gg k_{-4}$)

$$\frac{k_2}{k_3} \approx \frac{k_4(\text{c-P})}{k_4(\text{D})}$$

and no steric effect is expected.

(2) When excitation transfer is slower than back diffusion ($k_5 \ll k_{-4}$)

$$\frac{k_2}{k_3} \approx \frac{k_4(\text{c-P})k_{-4}(\text{D})k_5(\text{c-P})}{k_{-4}(\text{c-P})k_4(\text{D})k_5(\text{D})}$$

and the observation of a steric effect is possible.

k_5 can be approximated by the well-known equation (eqn. (13)) of Dexter [33]. Using the data and the variational method developed by Doi [34] for bimolecular reactions in solution, k_4 and k_{-4} were estimated (see also eqns. (14) and (15)). (The treatment of Doi [34] actually allows calculation of $k_{\text{eq}} = k_4/k_{-4}k_5$ from which k_{-4} is obtained.) Substituting eqns. (13)

- (15) into eqn. (11) yields eqn. (16) in which no assumptions concerning the relative magnitudes of k_{-4} and k_5 are made. Since K and J are dependent only on the chromophores, it is assumed that they vary with the nature of the sensitizer but are independent of the acceptor. Thus, when either of the limiting rate conditions applies, K and J need not be calculated. The coefficients D of diffusion were calculated by the method of Arnold [35] while the estimates of R were according to Edward [36]. The values of r , taken to be the distance of closest approach of the π clouds of the sensitizer and acceptor, were evaluated from the values listed by Bondi [37]. R is the distance of closest approach between the centers of the molecules. The numbers assigned to σ (approximately 0.6 for *c*-P and approximately 0.35 for D) are taken to be the ratios r/R for each of the acceptors. L , the average effective Bohr radius, is assumed to be about 1 Å [38].

$$k_5 = K^2 J \exp(-2r_{K-A}/L) \quad (13)$$

$$k_4 = 4\pi D_{K-A} r_{K-A} \sigma_A \quad (14)$$

$$k_{-4} = 4\pi D_{K-A} \frac{R_{K-A}^2}{r_{K-A}^4} \sigma_A \quad (15)$$

$$\frac{k_2}{k_3} = \frac{4\pi D_{K-D} R_{K-D} \sigma_D + K^2 J \exp(-2r_{K-D}/L) r_{K-D}^5 / R_{K-D}^2}{4\pi D_{K-c-P} r_{K-c-P} \sigma_{c-P} + K^2 J \exp(-2r_{K-c-P}/L) r_{K-c-P}^5 / R_{K-c-P}^2} \times \quad (16)$$

$$\times \frac{\exp(-2r_{K-c-P}/L) r_{K-c-P}^5 / R_{K-c-P}^2}{\exp(-2r_{K-D}/L) r_{K-D}^5 / R_{K-D}^2} \frac{D_{K-c-P} r_{K-c-P} \sigma_{c-P}}{D_{K-D} r_{K-D} \sigma_D}$$

Energy transfer ratios k_2/k_3 were calculated in this way for orientations with the aromatic ketones and *c*-P or D either in parallel or in perpendicular planes. For no sensitizer did the k_2/k_3 ratios vary by more than ± 0.2 from the average values reported in Table 3. Thus, the model employed (which assumes no difference in the efficiency of energy transfer for $^3(n, \pi^*)$ and $^3(\pi, \pi^*)$ states of aromatic ketones) and the experiments yield the same conclusion: reorganization of excitation energy within the extended chromophores is much more rapid than the movement of the molecules. The difference between the calculated and the observed ratios suggests that steric effects, in addition to those considered here, exist but that they are about equally manifested in all the sensitizers. (We note that the assumptions attendant to the calculations make their absolute magnitude of lesser importance than their relative differences.) Considering the rather small magnitude of the observed effect, a detailed analysis of the restrictions is unwarranted. Yet, a spatial representation of D clearly shows that at least the β side of D is quite shielded.

A more accurate assessment of these steric effects will probably be obtained only from gas phase experiments in which the number of collisions per encounter is one [39].

TABLE 3

Calculated k_2/k_3 ratios

	k_2/k_3	
	Parallel planes	Perpendicular planes
$k_5 > k_{-4}$	2.0	2.0
$k_5 < k_{-4}$	3.8	3.9

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