are required in this approach than by use of eq 2. The constant S must be determined for every acid in every solvent but then can be used for many different bases. The constant α must be determined for each acid–base pair and then reportedly can be used in many solvents. If the acid is to be varied in our procedure, acidic solvents which do not undergo specific interactions with the acid can be used with the base held constant. It should be emphasized that we make no claims for using our model to predict solvent effects on free energies. Furthermore, we anticipate it will fail when data in cyclohexane are employed if the adducts, acceptors, and/or donors are so polar that they are extensively associated in this solvent but not in the others that they are transferred to. Furthermore, our approach should not be employed when the adduct formed is itself a Lewis base that can undergo specific hydrogen bonding interactions with the solvent being employed. For these reasons, we have not considered the system $(CH_3)_3NSO_2$, which has been extensively studied.[10] These oxygens are expected to be at least as basic as those in an organic sulfone[22] and the adduct may be extensively associated in cyclohexane.

It would be of interest to apply eq 2 to those systems which we have considered ideal as far as the absence of specific interactions are concerned. The test of eq 2 is obtained by having data on a given adduct in widely different solvents. Since the test of ESP involves widely different bases in a given solvent, our effort has been directed along these latter lines and our data do not provide a good test of eq 2. Clearly, one must avoid systems which involve specific interactions in solving eq 2 for α. Otherwise, these complications get absorbed by the α value along with other effects making the interpretation of the α values difficult.

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Sterically Indifferent Triplet Energy Transfer[1]

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Abstract: Stern–Volmer $k_q\tau$ values for 2,5-dimethyl-2,4-hexadiene or 2-chloronaphthalene quenching of the type-II reactions of α,α-dimethylvalerophenone and for pyrene quenching of β,β-dimethyl-α-ketobutyrophenone show the same dependence on solvent viscosity as previously observed for the sterically unhindered valerophenone. This observation of "diffusion-controlled" quenching indicates that *tert*-alkyl groups do not significantly hinder energy transfer from carbonyl compounds. Comparison of these results with others in the literature suggests that the interaction distance between donor and acceptor in solution is on the order of 4 Å, long enough to preclude large steric effects.

The subject of steric hindrance in triplet energy transfer needs clarification. Hammond and his coworkers have concluded in several papers[3–6] that such steric hindrance can be important, presumably because of a decrease in the orbital overlap necessary for exchange interactions.[7] Nonetheless, several workers have performed standard Stern–Volmer quenching experiments in order to determine the excited state lifetimes of *tert*-alkyl ketones[8–10] and have decided against the possibility of steric hindrance by assuming "diffusion-controlled" rate constants for energy transfer. Since *tert*-alkyl ketones are well known to be highly resistant to nucleophilic attack on their carbonyl groups, conventional intuition added to Hammond's earlier conclusions surely would have predicted steric hindrance to energy transfer involving *tert*-alkyl ketones.

Since we also were interested in the photochemistry of some *tert*-alkyl ketones,[11] as well as in the topic of energy transfer, we have performed a few simple experiments which demonstrate that exothermic energy transfer from the triplets of *tert*-alkyl ketones remains diffusion controlled.

Results

We have utilized the type-II photocyclizations of α,α-dimethylvalerophenone (**1**)[9b,11] and of 3,3-dimethyl-1-phenyl-1,2-butanedione (**2**)[12] to monitor any steric hindrance to energy transfer. We performed standard quenching studies on the two reactions, using 2-chloronaphthalene and several dienes, particularly 2,5-dimethyl-2,4-hexadiene, to quench **1** and pyrene and anthracene to quench **2**. Linear Stern–Volmer plots

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[1] Triplet Energy Transfer. VIII.

[2] Alfred P. Sloan Fellow, 1968–1972.

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[11] P. J. Wagner and J. M. McGrath, *ibid.*, **94**, 3849 (1972).

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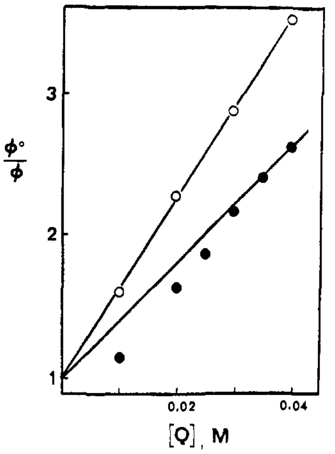
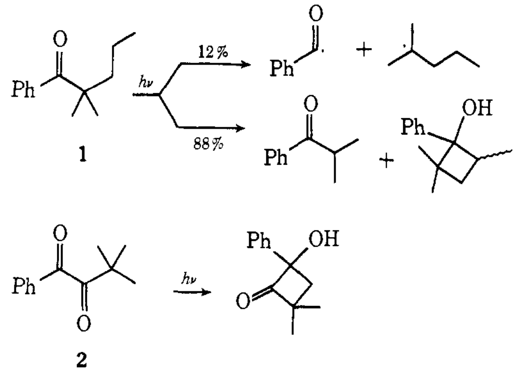


Figure 1. Stern–Volmer plots for quenching of cyclobutanol formation from α,α-dimethylvalerophenone by 2-chloronaphthalene (○) and by 2,3-dimethyl-1,3-butadiene (●), both in benzene.



of Φ^0/Φ values *vs.* quencher concentration yielded the $k_q\tau$ values listed in Table I.

Table I. Stern–Volmer Quenching Constants (M^{-1}) for Quenching of the Photocyclizations of **1** and **2** in Different Solvents[a]

Solvent (η, cP)	1- $C_{10}H_7Cl$[b]	1- diene[c]	2- pyrene[d]	VP- diene[e]
Pentane (0.33)			2900	95
Hexane (0.33)	150	97		79
Decane (0.92)			1500	51
Benzene (0.63)	63	48[f]	1000[g]	36
Cyclooctane (2.2)	56	50	900	31
1-Propanol (1.9)		46		52
1-Pentanol (3.1)		28		36
1-Heptanol (5.5)		22		23

[a] Quenching studies performed on 0.1 *M* ketone solutions; reproducibility of duplicate $k_q\tau$ values averaged 5%. [b] 2-Chloronaphthalene quencher, 365-nm radiation. [c] 2,5-Dimethyl-2,4-hexadiene quencher, 313-nm radiation. [d] 436-nm radiation. [e] Valerophenone-2,5-dimethyl-2,4-hexadiene, ref 13. [f] The values were 61 with 1,3-pentadiene and 40 with 2,3-dimethyl-1,3-butadiene. [g] Same value obtained with anthracene as quencher.

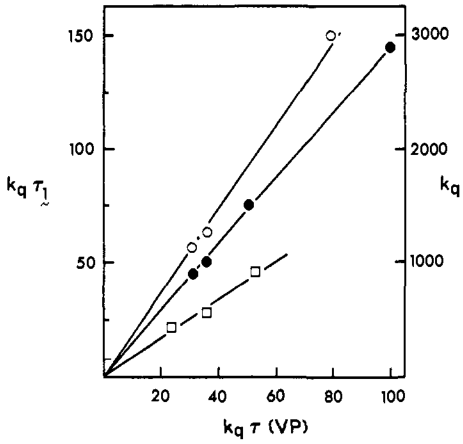


Figure 2. $K_q\tau$ values for hindered ketones *vs.* $k_q\tau$ values for valerophenone–2,5-dimethyl-2,4-hexadiene in the same solvent: (○) **1**, 2-chloronaphthalene, hydrocarbon solvents; (□) **1**, 2,5-dimethyl-2,4-hexadiene, alcohol solvents; (●, right ordinate) **2**, pyrene, hydrocarbon solvents.

Since the *tert*-alkyl groups in **1** and **2** might affect τ as well as k_q, we needed an adjustable parameter independent of either k_q or τ. As in our previous study of diffusion-controlled energy transfer,[13] we measured $k_q\tau$ values in several similar solvents of differing viscosities, reasoning that τ (which is determined entirely by the rate of intramolecular reaction) should be independent of solvent viscosity while k_q would decrease with increasing solvent viscosity *if energy transfer is diffusion controlled.* As Table I clearly shows, $k_q\tau$ values do decrease significantly with increasing solvent viscosity. We did not study more solvents because the viscosity effects on quenching of **1** and **2** so closely parallel those on quenching of valerophenone. Both anthracene (E_T = 43 kcal)[14] and pyrene (E_T = 48 kcal)[14] are equally effective quenchers of triplet **2** (E_T = 51 kcal). There is a small but reproducible variation among the quenching efficiencies of the different quenchers toward triplet **1** (E_T = 72 kcal)[15] in benzene, chloronaphthalene (E_T = 60 kcal)[14] and 1,3-pentadiene being 30–50% better quenchers than the more heavily substituted dienes (E_T = 58–60 kcal).[16] The $k_q\tau$ values for 1,3-pentadiene and 2,3-dimethyl-1,3-butadiene were determined from the highest concentration points (Figure 1) since efficient radical formation at low diene concentrations results in loss of diene. Such problems do not occur with naphthalene or 2,5-dimethyl-2,4-hexadiene which are both poor radical traps.

Discussion

As Figure 2 shows, $k_q\tau$ values for the two "hindered" *tert*-alkyl ketones and for the unhindered valerophenone vary with solvent viscosity in parallel fashions. Consequently, we must conclude that energy transfer from the "hindered" ketone triplets is just as "diffusion controlled" as energy transfer from the unhindered ketone triplet. We have already stressed[13] that such energy transfer is not completely diffusion controlled in light hydrocarbon solvents but approaches being so in the more viscous alcohols. In terms of our earlier analysis,[13] energy transfer within an encounter pair and diffusion apart compete so that α decreases with decreasing solvent viscosity.

$$k_q = \alpha k_{\mathrm{dif}} \qquad (1)$$

$$\alpha \approx k_{\mathrm{et}}/(k_{\mathrm{et}} + k_{-\mathrm{dif}}) \qquad (2)$$

---

(13) P. J. Wagner and I. Kochevar, *J. Amer. Chem. Soc.*, **90**, 2232 (1968).

(14) S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs, N. J., 1969, Table 4.12, p 159.

(15) P. J. Wagner, M. J. May, A. Haug, and D. R. Graber, *J. Amer. Chem. Soc.*, **92**, 5268 (1970).

(16) R. E. Kellogg and W. T. Simpson, *ibid.*, **87**, 4230 (1965).

Our current study is critically dependent on the fact that even unhindered triplet energy transfer is only partially diffusion controlled in light solvents (*i.e.*, $k_{\mathrm{et}} \sim k_{-\mathrm{dif}}$). If k_{et} were much larger than $k_{-\mathrm{dif}}$, so that a plot of $k_{\mathrm{q}}\tau$ *vs.* $1/\eta$ were linear, a sterically induced decrease in k_{et} could have gone unnoticed. On the other hand, if k_{et} were much smaller than $k_{-\mathrm{dif}}$, $k_{\mathrm{q}}\tau$ values would not vary with solvent viscosity and substitution-induced changes in τ could not be detected. Since $k_{\mathrm{q}}\tau$ values show a parallel dependence on solvent viscosity for both the hindered and unhindered ketones, k_{et}, the rate of energy transfer between nearest-neighbor donor and acceptor molecules, cannot be subject to significant steric hindrance. The slightly different quenching efficiencies of several different dienes toward **1** presumably indicate a very small amount of steric hindrance, since no such difference occurs in quenching of unhindered phenyl ketones.

It might be argued that quenching of **1** shows no steric effect because the π^* orbital includes the benzene ring, so that the quenchers need overlap only with the benzene π system. However, n,π^* triplet excitation in **2** is much more localized on the α-dicarbonyl chromophore, yet quenching of **2** is not subject to any steric effects either. Assumption of diffusion-controlled quenching of several aliphatic *tert*-alkyl ketones results in triplet lifetimes consistent with known rates of intramolecular hydrogen abstraction[17] and singlet lifetimes identical with those measured directly by single-photon counting techniques.[10b] Consequently we conclude that partial delocalization of electronic excitation onto the benzene ring is not what prevents steric hindrance in the quenching of triplets **1** and **2**.

The search for steric effects in triplet energy transfer is motivated by a lack of clear theoretical predictions of just how close donor and acceptor must come to promote the exchange interaction required for transfer. A *tert*-alkyl group clearly slows the approach of any moderate-sized reagent to within covalent bonding distance of the carbonyl in ketones such as **1**. Not only are *tert*-alkyl ketones resistant to nucleophilic addition, but triplet phenyl *tert*-butyl ketone abstracts hydrogen from 2-propanol only $^{1}/_{30}$th as fast as does triplet acetophenone.[9a,19] Since our results demonstrate that the bulky *tert*-alkyl group does not interfere significantly with energy transfer from triplet carbonyl compounds, donor and acceptor must not have to approach within bonding distance in order to achieve the requisite orbital overlap.

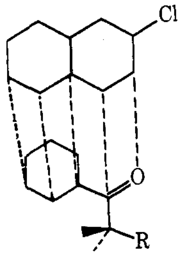
Equation 3 describes the theoretical dependence of rates of exchange-induced energy transfer on the distance R between donor and acceptor.[7] L is a fixed distance akin to an "average effective Bohr radius." Its value has never been specified. Y includes several parameters such as spin statistics and orbital overlap.

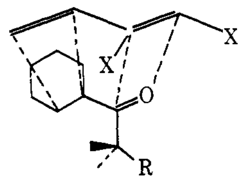
$$k_{\mathrm{et}} = Y \exp(-2R/L) \qquad (3)$$

We have previously estimated a value of 8×10^{10} sec^{-1} for k_{et} when energy transfer between triplet ketone and diene molecules in a solvent cage is involved.[13] Under such conditions, R must be close to the sum of the van der Waals radii of the molecules, 3.5–4 Å. Cowan has measured k_{et} from 3×10^{9} to 10^{11} sec^{-1} for intramolecular energy transfer in several ketones where the average distance between donor and acceptor varies from 3 to 5 Å.[20] At the other extreme, Keller and Dolby have measured a k_{et} value of 25 sec^{-1} for intramolecular transfer from a benzophenone at C_{17} on a steroid skeleton to a naphthalene at C_3, where R = 14–15 Å.[21] In the earliest work on triplet energy transfer, Terenin and Ermolaev determined a pseudo-unimolecular rate constant of 200 sec^{-1} for static energy transfer between the same two chromophores held 13 Å apart in a rigid matrix.[22] Since in all four cases donor and acceptor can freely rotate with respect to one another, we assume that Y values are similar and can solve eq 3 for L. A value of 1.0 Å fits the observed rates of both short-range and medium-range triplet energy transfer.[23] Every 1.2 Å increase in R results in an order of magnitude decrease in k_{et}.

As we have already pointed out, the fact that every collision between donor and acceptor does not produce energy transfer,[24] even when transfer is highly exothermic, may indicate an orientational requirement for orbital overlap. Ullman has reasoned along the same lines in proposing orbital symmetry requirements for triplet energy transfer.[25] Dexter's original formulation of exchange-induced energy transfer[7] in fact contains a factor (presumed to be much lower than unity) to account for orbital symmetry and therefore presumes an orientational requirement. Attempts to establish such a requirement by spectroscopic techniques unfortunately have not been conclusive.[26]

Presumption of maximum π overlap, preferred orientation, and an R close to the sum of the van der Waals radii of the donor and acceptor π systems provides a geometric model which is consistent with all the known experimental facts concerning steric effects in triplet energy transfer. The drawings below portray maximum π overlap between **1** and both chloronaphthalene and a diene. In the case of naphthalene or 1,3-pentadiene, only hydrogen atoms need lie above the *tert*-alkyl group. For the dienes which exhibit lower k_{q} values, a methyl group must lie there.





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[17] *I.e.*, the rate of triplet state γ-hydrogen abstraction in *tert*-butyl *n*-butyl ketone is calculated to be 1×10^{8} sec^{-1},[10a] the same measured for 2-hexanone.[18]

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[22] A. Terenin and V. Ermolaev, *Trans. Faraday Soc.*, **52**, 1042 (1956).

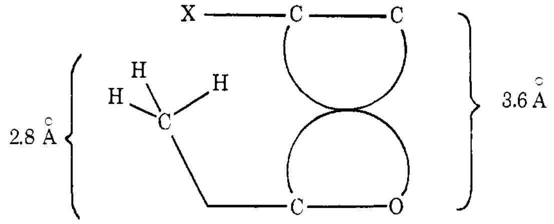
[23] This calculation ignores σ-bond participation in the exchange interaction, as the experiments seem to dictate.

[24] In the gas phase, 50–100 collisions are required for triplet energy transfer from ketones to dienes: (a) R. E. Rebbert and P. Ausloos, *J. Amer. Chem. Soc.*, **87**, 1847, 5569 (1965); (b) G. R. DeMare, M.-C. Fontaine, and M. Termonia, *Chem. Phys. Lett.*, 11, 617 (1971).

[25] E. F. Ullman and N. Baumann, *J. Amer. Chem. Soc.*, **90**, 4158 (1968).

[26] (a) J. K. Roy and M. A. El-Sayed, *J. Chem. Phys.*, **40**, 3442 (1964); (b) S. Siegel and L. Goldstein, *ibid.*, **43**, 4185 (1965).

We can also view the two molecules edge-on, such that the two molecular planes are perpendicular to the paper. Consideration of bond lengths, bond angles, and atomic van der Waals radii indicates that the α-methyls extend 2.8 Å above the carbonyl plane. When X is H, ketone and quencher can approach to within 3.8–4.0 Å, very close to the van der Waals diameter of a π system. When X is methyl, with its 2-Å van der Waals radius, either R must increase or, more likely, the two molecules must tilt somewhat, decreasing k_{et} by a $\cos^2 \varphi$ factor. Of course, this description of steric effects has been applied to that mutual orientation of donor and acceptor molecules which presumably produces the greatest value of k_{et}. Energy transfer also occurs at greater R's and less favorable φ's, where steric effects would be even less significant.



The above picture must surely be tested further, but it does explain nicely the one published example of significant steric hindrance. The less efficient quenching by stilbene of a 2,6-diisopropylphenyl ketone triplet relative to the 2,6-dimethyl analog indicates a steric effect on the order of 15.[5] In this system, the large ortho substituents force the phenyl ring out of planarity with the carbonyl, ending up above and below the carbonyl, and surely prevent approach of a quencher to within van der Waals distance of the carbonyl π system.

Experimental Section

The preparations of **1** and **2** are described elsewhere.[11,12] Solvents were purified and distilled as usual.[13] Quenching studies were performed as described previously,[13] by parallel irradiation of degassed samples containing varying concentrations of quencher in a rotating turntable assembly. Relative quantum yields of cyclobutanol products at low conversion were monitored by vpc analysis. In samples containing **1** and low concentrations of either 1,3-pentadiene or 2,3-dimethyl-1,3-butadiene, irradiation resulted in decreases in the diene concentration and formation of several unidentified products not formed with other quenchers or ketones, as judged from vpc traces of the photolyzed samples. At higher diene concentrations, where most of the reaction of **1** is quenched, there was no evidence for a decrease in diene concentration.

Acknowledgment. We wish to thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Rate Constants for Radical Recombination. IV. The Activation Energy for Ethyl Radical Recombination[1a]

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Received December 3, 1971

Abstract: Products from the thermal decomposition of propionyl peroxide in MeI–EtI mixtures at 81° in the vapor phase have been determined. Those from radical recombination, governed by the buffer equilibrium $\mathrm{Me\cdot} + \mathrm{EtI} \rightleftarrows \mathrm{MeI} + \mathrm{Et\cdot}$, and the rate constants for radical recombination have been compared with analogous results at 142° to give an activation energy for $\mathrm{Et\cdot} + \mathrm{Et\cdot}$ recombination of 0 ± 0.2 kcal if the absolute rate is taken as $k_E = 10^{8.6}\ M^{-1}\ \mathrm{sec}^{-1}$. If the thermochemistry of the buffer reaction $\mathrm{Me} + \mathrm{EtI} \rightleftarrows \mathrm{Et} + \mathrm{MeI}$ is adjusted to give k_E (441°K) $= 10^{9.6}\ M^{-1}\ \mathrm{sec}^{-1}$, then it requires a negative activation energy for Et recombination of 2 kcal.

Previous measurements of the absolute rate for ethyl radical recombination, by sector methods,[2] or by esr spectroscopy,[3] have indicated an activation energy for the reaction of 1–2 kcal.[4] While it seems unlikely that the reaction should have an activation energy,[5] no experimental evidence has yet been adduced in favor of this supposition.

We have been encouraged to apply the method of free radical buffers[6] to this problem since the products from the sequence

$$\mathrm{Me\cdot} + \mathrm{EtI} \underset{}{\overset{K_{ME}}{\rightleftarrows}} \mathrm{MeI} + \mathrm{Et\cdot} \qquad (1)$$

$$2\mathrm{Me\cdot} \xrightarrow{k_M} \mathrm{EtH} \qquad (2)$$

$$\mathrm{Me\cdot} + \mathrm{Et\cdot} \xrightarrow{k_{ME}} \mathrm{PrH} \qquad (3)$$

$$\mathrm{Et\cdot} + \mathrm{Et\cdot} \xrightarrow{k_E} \mathrm{BuH} \qquad (4)$$

can be determined with fair precision. The only seri-

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(1) (a) This work has been supported, in part, by Contract No. F44620-71-C-0103 of the Air Force Office of Scientific Research and, in part, by an ACS-PRF, Type D, grant. (b) On sabbatical leave from the Department of Chemistry, Brock University, St. Catharines, Ontario, Canada.

(2) A. Shepp and K. O. Kutsche, *J. Chem. Phys.*, 26, 1020 (1957).

(3) R. W. Fessenden, *J. Phys. Chem.*, **68**, 1508 (1964).

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(6) R. Hiatt and S. W. Benson, *J. Amer. Chem. Soc.*, **94**, 25 (1972).