response lacks a fast inertial component, predict rates that are orders of magnitude slower than experiment.[3] Qualitatively, these results indicate that absolute ET rate theory is in good agreement with experiment for reaction 1, if vibrational modes and solvation dynamics are treated in a realistic fashion.

Acknowledgment. This work was supported by the NSF. We thank Prof. J. T. Hupp for guidance and assistance in many aspects of this research. D.A.V.K. is an NSF postdoctoral fellow.

Through-Space Intramolecular Triplet Energy Transfer: The Cinnamyl Esters of ω-Benzoyl Carboxylic Acids[†]

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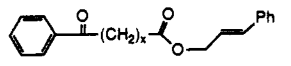
Received June 22, 1992

Closs has been very successful in recent years in interpreting intramolecular electron and energy transfer in relatively rigid cyclic "bichromophoric" molecules in terms of through-bond interactions.[1] Rate constants for triplet energy transfer drop approximately 1 order of magnitude for each additional bond between a benzophenone group and a naphthalene. In more flexible systems, it is to be expected that through-space transfer would become competitive as connecting chains become longer. We wish to report a clear example of this behavior that represents an extension to longer spacers of some of the earliest quantitative measurements on intramolecular energy transfer.[2]

Cowan and Baum reported sharp decreases in triplet energy transfer rate constants as the number of methylenes connecting a benzoyl group to the β-carbon of styrene increases from two to four.[2] In this case energy transfer from ketone (E_T = 72 kcal/mol[3]) to styrene (E_T = 62 kcal/mol[4]) is at least 10 kcal/mol exothermic, and the corresponding bimolecular reaction is diffusion limited.[5] We have extended the number of connecting atoms in a synthetically simple way by preparing the cinnamyl esters **1–4** of four ω-benzoylalkanoic acids.



1-4 : x = 1-4

Irradiation of the compounds at 365 nm, where the styrene group barely absorbs, produces efficient trans → cis isomerization, with quantum yields of 0.49–0.59 for **2–4**, just as was observed for the shorter analogs.[2] The cis compounds separate cleanly on GC columns and also give distinctive ^{1}H NMR signals for both the methylene and vinyl protons. Identical cis/trans ratios were measured by GC and by NMR. No other products were detectable by either analytical method except in the case of **4**, where a small amount of acetophenone was detected at high conversions.

Compound **1** is a special case, since it exists in a 2:1 equilibrium with its enol form **1′** in benzene. Its quantum yield of isomerization is only 0.06, since the enol absorbs more strongly than the ketone at 365 nm, but only the keto form undergoes trans → cis isomerization. NMR spectra at 10% conversion clearly show formation of the cis keto form with only a trace of cis enol. The cis ketone gradually is converted thermally to the cis enol until a 2:1 equilibrium is attained. The enol is a hydroxycinnamate with a lower excitation energy than the simple styrene, so that it is not surprising that excitation of the enol is not followed by triplet energy transfer to the styrene moiety.

1 **1′**

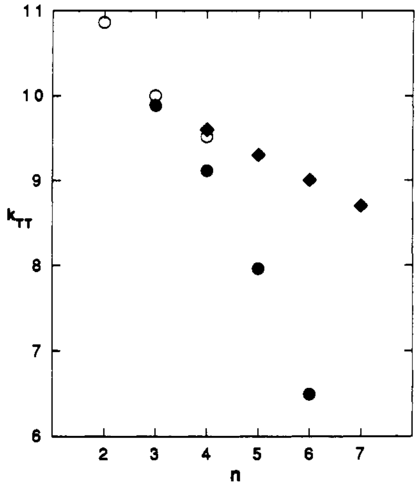


Figure 1. Rate constants for triplet energy transfer as a function of the number of atoms connecting the donor triplet benzoyl group and the acceptor: ●, ref 1; ○, ref 2; ◆, compounds **1–4**.

Triplet lifetimes of the ketones were determined by Stern–Volmer quenching of the trans → cis isomerization with added 2,5-dimethyl-2,4-hexadiene. Quantum yields of cis formation were first corrected for reversibility;[6,7] the slopes of the linear Stern–Volmer plots provided $k_q\tau$ values. Reciprocal lifetimes were calculated from the known k_q value of 6×10^9 M^{-1} s^{-1}.[8] The ester functionality near the γ-carbon in **3** and **4** is known to markedly depress rate constants for γ-hydrogen abstraction.[9] This fact and the lack of competing reaction allow us to equate k_{TT} with $1/\tau$ for these compounds: $k_{TT} = 4 \times 10^9$, 2×10^9, 1×10^9, and 5×10^8 s^{-1} for x = 1–4, respectively. Any contribution of bimolecular energy transfer to the observed decay rates is $<5 \times 10^7$ s^{-1} since the ketone concentrations were kept below 10^{-2} M.

Figure 1 compares our results with those of Cowan[10] and Closs. Energy-transfer rate constants are plotted as a function of the number of atoms in the chain linking the two chromophores. We have chosen Closs' data only for benzophenone and naphthalene occupying equatorial positions on cyclohexane or decalin so that all of the connecting bonds have staggered conformations. This arrangement results in the fastest energy transfer in Closs' system and should correspond to the most stable conformation of the short polymethylene links in **1–4**, where $n = x + 3$. Closs' cyclic compounds of course are constrained to transfer energy through the intervening bonds, whereas the flexible acyclic tethers that we and Cowan studied potentially allow through-space transfer from partially coiled conformations to compete with through-bond transfer from stretched out conformations.

Considering Cowan's data first, we see that only the $n = 2/n = 3$ pair lies on the same curve as Closs' results and shows the order of magnitude decrease observed for each additional intervening bond in the Closs system. The similarity of actual rate constants in the two systems is not surprising, given that they both represent highly exothermic energy transfer to conjugated π-

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[†] This paper is dedicated to the memory of Gerhard Closs, whose lively brilliance made things easier for the rest of us.

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(10) Cowan and Baum used a k_q value of 5×10^9 M^{-1} s^{-1}; we have corrected their k_{TT} values upward by 20%.

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systems, but identical electronic and Frank–Condon factors for the two systems cannot be assumed.[11] The mere 3-fold drop in k_{TT} upon changing from $n = 3$ to $n = 4$ in both the Cowan ketone and our keto ester suggests that another mechanism is beginning to contribute. The mere factor of 2 decrease for each additional methylene in our longest three compounds **2–4** dramatically confirms the suspicion aroused by the $n = 4$ compounds that through-bond coupling no longer dominates energy transfer for medium-length tethers. A simple through-space (solvent) mechanism from the ensemble of partially coiled conformations seems the most likely explanation.

The k_{TT} values around 10^9 M^{-1} s^{-1} for our $n = 5$–7 compounds indicate an average distance between chromophores of ~6 Å in these compounds. This estimate comes from evaluations of the distance dependence of triplet energy transfer according to the standard Dexter inverse exponential formulation,[12] in which a 1-Å increase corresponds to a 1 order of magnitude decrease in k_{TT}.[13,14] A key element of this estimate is that the pseudo-unimolecular k_{TT} value that describes bimolecular energy transfer between a triplet ketone and a conjugated π-acceptor in a solution encounter pair is on the order of 10^{11} s^{-1}.[15–17] The longest distance between the ketone carbon and the styrene β-carbon in fully stretched **4** is a little over 9 Å. A single gauche conformer brings the two ends 7 Å apart, close to the "average" distance.

It is possible that the presence of the ester carbonyl might enhance through-bond coupling by providing a π^*-orbital along the path. Likewise, the ester group is well-known to impose limitations on conformational freedom around it. The similar k_{TT} values for our compound **1** and Cowan's $n = 4$ compound probably reflect the absence of such effects rather than their counteracting each other, and more importantly, validate our present comparison. The following communication[18] in this issue describes another example of this leveling of k_{TT} values in a bichromophore separated purely by a polymethylene chain.

Acknowledgment. This work was supported by NSF Grants Nos. CHE88-15052 and CHE91-20931. The NMR spectrometer was funded by NSF Grant CHE88-00770.

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Spacer-Independent Intramolecular Triplet Energy Transfer in Diketones

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We have been investigating the effect of reversible intramolecular energy transfer on the photochemistry of diketones,[1–3] typically diketones connected by short methylene chains, for some time. Recent interest in the selective photochemistry of diketones[4] and the details of intramolecular energy transfer, especially the apparent predominance of through-bond effects,[5] together with questions about energy migration in polymers[6] prompted us to look at diketones held together by progressively longer tethers. We report here that triplet energy transfer in such systems proceeds predominantly through space rather than through bonds when the number of connecting atoms exceeds five.

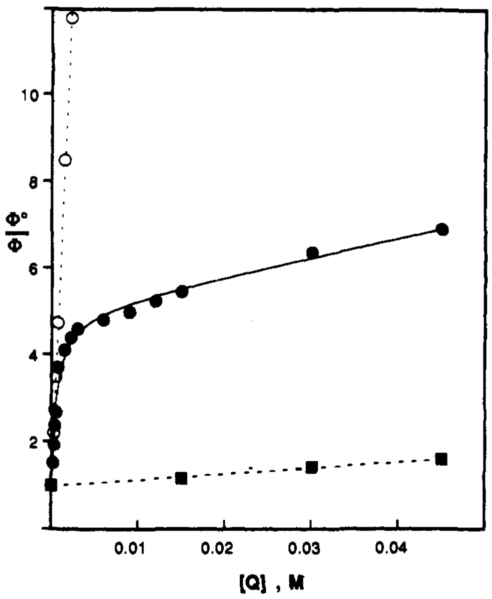
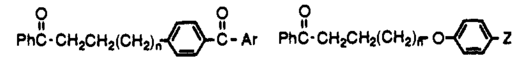


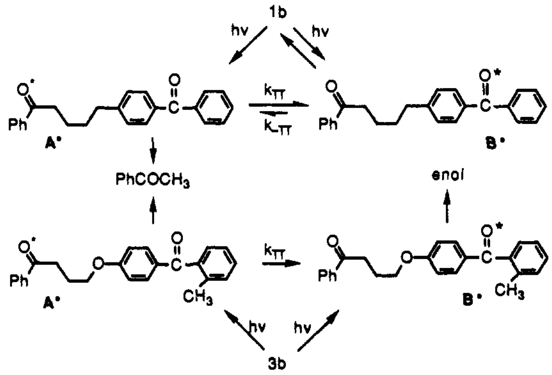
Figure 1. Stern–Volmer quenching of acetophenone formation from (○) **1b** at 366 nm, (●) **1b** at 313 nm, and (■) **2b** at 313 nm.

We restrict our attention in this paper to the behavior of ω-(4-benzoylphenyl)alkanophenones **1a** and **1b** and ω-(4-*o*-toluylphenoxy)alkanophenones **3b–f**. Each of them has a phenone chromophore A with a triplet energy ~72 kcal/mol[7] and a benzophenone chromophore B with a triplet energy ~69 kcal/mol.[7] A undergoes Norrish type II photoelimination to produce acetophenone,[8] the efficiency of which is lowered by exothermic energy transfer to B. In an inert solvent such as benzene, B is photostable and slowly transfers energy uphill to A. Figure 1 depicts quenching of this reversible energy transfer for **1b**, which forms acetophenone in quantum yields of 7% and 5% at 313 and



1a : n = 1, Ar = Ph
2a : n = 1, Ar = o-tolyl
1b : n = 2, Ar = Ph
2b : n = 2, Ar = o-tolyl

3b-f : n = 1-5, Z = o-toluyl
4b-f : n = 1-5, Z = CN



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