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Intramolecular Triplet Energy Transfer in Bichromophores with Long Flexible Tethers

Petr Klán and Peter J. Wagner*

Chemistry Department, Michigan State University
East Lansing, Michigan 48824

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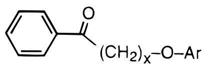
Triplet energy transfer has played a key role in mechanistic investigations of photochemistry for four decades. Many studies on intramolecular energy transfer have been undertaken to ascertain the effects of distance and relative orientation between donor and acceptor on rate constants.[1,2] Closs, Miller, and coworkers persuasively attributed energy transfer between benzophenone and naphthalene groups attached to cycloalkyl rings to through-bond interactions, with rate constants dropping an order of magnitude for each additional bond.[3] With a rigid steroid as spacer and the benzophenone separated by 10 atoms from the naphthalene, rate constants earlier had been found to be as low as 25 s^{-1}.[4] We recently described two systems in which donor and acceptor were connected by flexible 4-to-8 atom tethers: cinnamyl esters of ω-benzoylalkanoic acids[5] and α,ω-diaroylalkanes.[6] We concluded that in both systems intramolecular energy transfer occurs by a through-space mechanism for tethers longer than 4 atoms. We now wish to report measurements on intramolecular triplet energy transfer rates in molecules with polymethylene tethers as long as 15 atoms between the same chromophores that Closs studied.

Scheme 1 lists the bichromophoric ketones that we have studied. They were prepared by photoinduced ring opening of the hypochlorites of 1-phenylcycloalkanols,[7] followed by nucleophilic substitution reactions. Cyclohexane solutions 0.001 M in ketone were irradiated at 366 nm where the 2-naphthyloxy ($E_T \sim 62$ kcal/mol)[8] and 4-biphenyloxy ($E_T \sim 68$ kcal/mol)[9] chromophores do not absorb. The benzoyl chromophore ($E_T \sim 72$ kcal/mol)[10] has a n,π* lowest triplet state, which undergoes Norrish type II photoelimination to produce acetophenone.[11] The reaction efficiency is lowered by competing intramolecular triplet energy transfer to a naphthyl or a biphenyl chromophore. The model ω-phenoxyalkanophenones Bz-*x*-OPh provide measures of the quantum efficiencies and rate constants for the photoelimination reaction in the absence of energy transfer. Their triplet lifetimes depend only on γ-hydrogen abstraction,[12] because energy transfer to the phenoxy group ($E_T \sim 81$ kcal/mol)[13] is highly endothermic and charge-transfer quenching by anisole is slow.[14]

Acetophenone yields were determined by HPLC and converted to quantum yields by comparison to equally irradiated valerophenone actinometers.[15] Triplet lifetimes were determined by Stern−Volmer quenching of product formation with added 2,5-dimethyl-2,4-hexadiene. Tables 1 and 2 list the slopes of these linear plots as $k_q\tau$ values. Triplet lifetimes were calculated from the known k_q value of 8×10^9 M^{-1} s^{-1}.[16] Internal energy transfer rates were calculated by the equation $k_{ET} = 1/\tau - k_H - k_2[K]$, where τ is the triplet lifetime of the ketone, k_H is $1/\tau$ of the corresponding model ketone, k_2 is the rate constant for bimolecular energy transfer, and [K] is the ketone concentration. Since ketone concentrations were 0.001 M, bimolecular quenching (8×10^6 s^{-1} for Bz-*x*-ONp, 3×10^6 s^{-1} for Bz-*x*-OBp)[9] contributes less than 5% to the slowest triplet decay and could be neglected in our calculations. Calculation of k_H values from quantum yield variations produced nearly the same k_{ET} values.

Scheme 1



Bz-x-OPh: Ar = Ph, x = 3-5, 7, 10, 11
Bz-x-ONp: Ar = 2-naphthyl, x = 3-7, 9-11,14
Bz-x-OBp: Ar = 4-biphenylyl, x = 3-7, 9-11,14

Table 1. Photokinetics of Model ω-Phenoxy Ketones[a]

Bz-x-OPh	Φ_{II}	$k_q\tau$, M^{-1}	$1/\tau$, 10^8 s^{-1}
Bz-3-OPh	0.48	30.7	2.6
Bz-4-OPh	0.48	232.4	0.34
Bz-5-OPh	0.38	89.6	0.89
Bz-6-OPh			1.0[b]
Bz-7-OPh	0.31	62.4	1.3
Bz-9-OPh			1.4[b]
Bz-10-OPh	0.30	57.3	1.4
Bz-11-OPh	0.30	58.2	1.4
Bz-14-OPh	0.26		1.4[b]

[a] Measured at 25 °C in cyclohexane; reproducibility ±5%. [b] Interpolated value.

Table 2. Photokinetics of ω-Aryloxyalkanophenones[a]

Bz-x-O-Ar	Φ_{II}	$k_q\tau$, M^{-1}	$1/\tau$, 10^8 s^{-1}	k_{ET}, 10^8 s^{-1}
Bz-3-ONp	0.14	4.2	19.0	16.3
Bz-4-ONp	0.04	16.3	4.9	4.5
Bz-5-ONp	0.17	19.5	4.1	3.1
Bz-6-ONp	0.17	22.2	3.6	2.5
Bz-7-ONp	0.18	23.2	3.4	2.0
Bz-9-ONp	0.12	15.0	5.3	3.8
Bz-10-ONp	0.15	13.6	5.9	4.4
Bz-11-ONp	0.21	24.7	3.2	1.7
Bz-14-ONp	0.18	30.8	2.6	1.1
Bz-3-OBp	0.18	7.7	10.4	7.8
Bz-4-OBp	0.06	20.7	3.9	3.5
Bz-5-OBp	0.14	27.3	2.9	2.0
Bz-6-OBp	0.15	30.4	2.6	1.6
Bz-7-OBp	0.18	32.5	2.5	1.2
Bz-9-OBp	0.14	20.5	3.9	2.5
Bz-10-OBp	0.08	23.3	3.4	2.0
Bz-11-OBp	0.22	33.4	2.4	1.0
Bz-14-OBp[b]	0.27	28.4	2.1	0.7

[a] Measured at 25 °C in cyclohexane; reproducibility ±5%. [b] In benzene; $k_q = 6 \times 10^9$ M^{-1} s^{-1} (ref 16).

Figure 1 compares our intramolecular energy transfer rate constants for Bz-*x*-ONp and Bz-*x*-OBp with those measured for rigid benzophenone−naphthalene bichromophoric systems.[3] We have plotted the fastest example from Closs' results for each value

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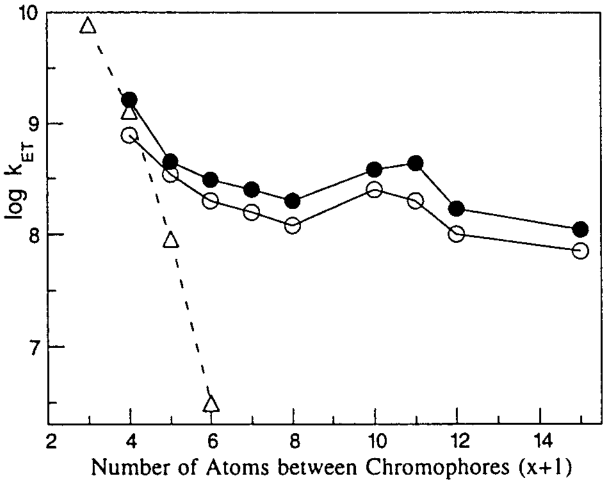

Figure 1. Energy transfer rate constants as a function of the number of atoms connecting donor and acceptor: (●) Bz-*x*-ONp; (○) Bz-*x*-OBp; (△) benzophenone−cycloalkane−naphthalene from ref 3.

(3−6) of the number of connecting atoms. For the cases in which donor and acceptor are separated by four atoms, rate constants are nearly identical for both rigid and flexible spacers; we conclude that the through-bond mechanism predominates, with some through-space contribution from gauche conformers. For systems with longer polymethylene chains, rate constants no longer fall an order of magnitude per additional bond, as they do for molecules with cyclic spacers. Molecular flexibility provides some conformations in which the two chromophores are close enough that through-space interactions contribute, thus raising the overall rate constants from those predicted for pure through-bond interactions. The plot suggests that for Bz-4-ONp some 75% of the total energy transfer occurs through space; for longer tethers, >99%. For 10 atom spacer systems, the polymethylene chain allows energy transfer to be 10^6 times faster than does a rigid steroid spacer.[4] Rate constants for $x = 14$ are only 1 order of magnitude lower than those for molecules with four atoms between the chromophores. Since k_{ET} values pretty much level off for molecules with seven or more tether atoms, we conclude that conformational factors produce a nearly constant percentage of molecules with the two chromophores close enough for through-space energy transfer. Similar leveling observations have been described in studies on electron transfer in bifunctional radical anions[17] and on spin−orbit exchange interactions in biradicals.[18]

The shape of the plots in Figure 1 is very different from those associated with chemical reaction of,[19] or excimer formation between,[20] two functional groups at opposite ends of a molecular chain. This is not surprising, since energy transfer occurs over longer distances than does either bond or excimer formation. Moreover, the bimolecular versions of the energy transfer occurring in these bichromophores have rate constants close to diffusion controlled. The efficiency of correspondingly fast intramolecular processes can be controlled by bond rotation rates and/or by ground state conformational distribution.[21,22] Thus the ratios of intramolecular/bimolecular energy transfer rate constants are not measures of "effective molarity" such as one observes with slow ground state reactions under conditions of conformational equilibrium. Excitation of the carbonyl chromophore is unlikely to significantly alter the conformational equilibria of the triplet bichromophores from that already established in their ground states. All molecules whose chain ends are ≤ 6 Å apart, where $k_{ET} \geq 10^8$ s^{-1},[23] should contribute directly to the observed value of k_{ET}, which is a weighted average over all conformations.[24] Conformers in which the chromophores are within 3−4 Å of each other should undergo energy transfer in 100 ps or less,[14,25,26] as observed for *in-cage* bimolecular energy transfer, where chromophores presumably approach van der Waals separation. Whatever fraction of molecules possess such equilibrium geometries would undergo the intramolecular equivalent of static quenching. Monte Carlo[27] and exact enumeration calculations[28] predict that long molecules with 10 to 25 atom chains contain a similar but small fraction of conformations allowing proximity of the two ends. Since the quantum efficiency of energy transfer in our longer bichromophores (30 to 60%) is quite high, only a few percent could be attributed to such static quenching (ground-state control). The major portion of the energy transfer must be provided by a combination of other conformers rotating into such static quenching geometries within the lifetime of the triplet ketone and by conformers with their ends 5−6 Å apart undergoing direct energy transfer with rate constants of 10^8−10^9 s^{-1}. Both of these processes can be viewed as being controlled by rapid conformational equilibrium, but with a bond rotation being rate determining in the former case, energy transfer in the latter. The overall efficiency of energy transfer thus is determined by a combination of ground-state control, rotational control, and conformational equilibrium.

Our k_{ET} values are consistently lower for biphenyl than for naphthalene as an acceptor, by a factor of ca. 2, as was observed previously for both bimolecular[9] and intramolecular energy transfer.[29] This effect, known to reflect an increase in reorganizational energy because of the large change in biphenyl's geometry upon excitation,[9,30] appears to be independent of whether through-bond or through-space interactions predominate.

The hump in the k_{ET} plots for $x = 10$ and 11 indicates that these chain lengths provide, compared to $x < 10$ and $x > 11$, roughly double the number of conformations that bring the two ends close enough to allow through-space energy transfer. There is precedent for such behavior in other intramolecular processes.[17]

In summary, our kinetic measurements reveal that triplet energy transfer occurs primarily by through-space interactions in flexible bichromophoric systems and remains efficient even for long tethers. In 10 ns, conformational dynamics move a significant fraction of the molecules into geometries with the two end chromophores close enough to exchange electrons very rapidly. A full paper will expand the discussion of what conformational factors produce the observed behavior and will describe some additional effects involving changes in the donor's excitation type, the acceptor's steric and conjugative demands, and the tether.

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