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 $\sim$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.

(11) Sigman, M. E.; Closs, G. L. *J. Phys. Chem.* **1991**, *95*, 5102.
(12) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 866.
(13) Wagner, P. J.; McGrath, J. M.; Zepp, R. G. *J. Am. Chem. Soc.* **1972**, *94*, 6883.
(14) Kobashi, H.; Morita, T.; Mataga, N. *Chem. Phys. Lett.* **1973**, *20*, 376.
(15) Wagner, P. J.; Kochevar, I. *J. Am. Chem. Soc.* **1968**, *90*, 2232.
(16) Saltiel, J.; Shannon, P. T.; Zafiriou, O. C.; Uriarte, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 6799.
(17) Anderson, R. W., Jr.; Hochstrasser, R. M.; Lutz, H.; Scott, G. W. *J. Chem. Phys.* **1974**, *61*, 2500.
(18) Wagner, P. J.; Giri, B. P.; Frerking, H. W.; De Francesco, J. *J. Am. Chem. Soc.*, following communication in this issue.

Spacer-Independent Intramolecular Triplet Energy Transfer in Diketones

Peter J. Wagner,* Brij. P. Giri, Harlan W. Frerking, Jr., and James DeFrancesco

*Chemistry Department, Michigan State University
East Lansing, Michigan 48824*

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]

(1) Wagner, P. J.; Nakahira, T. *J. Am. Chem. Soc.* **1973**, *95*, 8474.
(2) Wagner, P. J.; Nakahira, T. *J. Am. Chem. Soc.* **1974**, *96*, 3668.
(3) Frerking, H. F. Ph.D. Thesis, Michigan State University, East Lansing, MI, 1978.
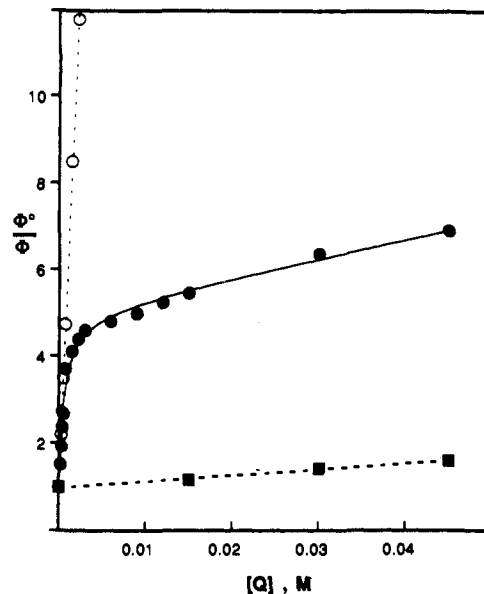(4) Wu, Z.-Z.; Morrison, H. *J. Am. Chem. Soc.* **1989**, *111*, 9267.

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

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.

We restrict our attention in this paper to the behavior of ω-(4-benzoylphenyl)alkanophenones **1a** and **1b** and ω-(4-o-toluyl-phenoxy)alkanophenones **3b–f**. Each of them has a phenone chromophore A with a triplet energy $\sim$72 kcal/mol[7] and a benzophenone chromophore B with a triplet energy $\sim$69 kcal/mol.[7] A undergoes Norrish type II photoelimination to produce
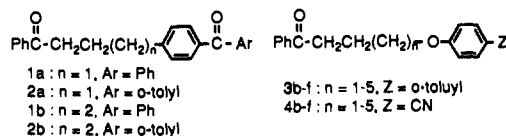
acetophenone,[8] the efficiency of which is lowered by exothermic energy transfer to B. In an inert solvent such as benzene, B is photostable and slowly transfers energy uphill to A. Figure 1 depicts quenching of this reversible energy transfer for **1b**, which forms acetophenone in quantum yields of 7% and 5% at 313 and
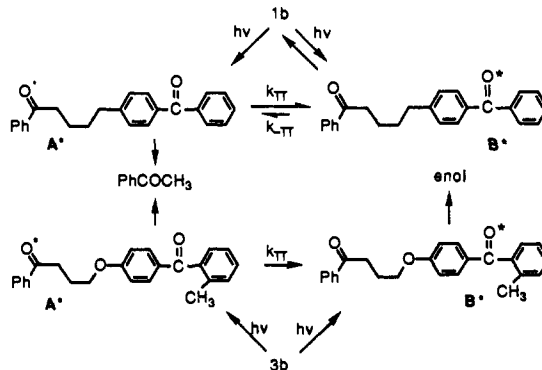
(5) Closs, G. L.; Johnson, M. D.; Miller, John R.; Piotrowiak, P. *J. Am. Chem. Soc.* **1989**, *111*, 3751.
(6) Encinas, M. V.; Funabashi, K.; Scaiano, J. C. *Macromolecules* **1979**, *12*, 1167. Scaiano, J. C.; Selwyn, J. C. *Macromolecules* **1981**, *14*, 1723. Das, P. K.; Scaiano, J. C. *Macromolecules* **1981**, *14*, 693.
(7) Kearns, D. R.; Case, W. A. *J. Am. Chem. Soc.* **1966**, *88*, 5087.
(8) Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168.

Communications to the Editor

J. Am. Chem. Soc., Vol. 114, No. 21, 1992 8327

Table I. Photokinetics Data in Benzene for
$PhCOCH_2CH_2(CH_2)_nXC_6H_4Z$

ketone	$\Phi_{II}^{max\ a}$	$k_q\tau$, $M^{-1\ b}$	$1/\tau$, $\times 10^{-7}$ s^{-1}	k_{TT},^{c} $\times 10^{-7}$ s^{-1}
4b	0.56	81	7.4	
4c	0.53	404	1.5	
4d	0.36	77	7.8	
4e	0.25	46	13	
4f	0.32	38	16	
3b	0.011	15	40	30
3c	0.01	34	18	13
3d	0.02	25	24	13
3e	0.06	20	30	14
3f	0.04	16	37	18
2a	0.02	6	100	~82^d
2b	0.03	12	50	~43^e

^{a} Maximum acetophenone yields in the presence of 2–3 M dioxane, 313-nm irradiation. Another 15–20% of cyclobutanols were also formed. ^{b} Quencher = 2,5-dimethyl-2,4-hexadiene; $k_q = 6 \times 10^9$ M^{-1} s^{-1}. ^{c} $k_{TT} = 1/\tau - k_H - (3 \times 10^7)$, where $k_H = 1/\tau$ (cyano ketone) and 3×10^7 is the calculated rate for intermolecular energy transfers. ^{d} $k_H \approx 1.5 \times 10^8$ s^{-1}, refs 3 and 20. ^{e} $k_H \approx 4 \times 10^7$ s^{-1}, refs 3 and 20.

366 nm excitation, respectively. At the former wavelength, A absorbs 37% of the light, and at the latter, only 6%. The Stern–Volmer plot at 366 nm is linear and reflects the long (1 μs) lifetime of unreactive B. The plot at 313 nm is curved, since both the reaction of A and the interconversion of B to A are quenched until at high quencher concentration reaction occurs only from the short-lived A triplets initially excited.[1,9,10] Both plots demonstrate that excitation of B produces reaction of A, necessarily by uphill energy transfer.

Such curved quenching plots can be analyzed to extract rate constants for energy transfer in both directions when rate constants for the other decay paths of each chromophore are known;[2,38] k_{TT} values of 6×10^8 and 2×10^6 s^{-1} best fit the data. However, it is far simpler to make the A $\rightarrow$ B energy tranfer effectively irreversible by modifying B to an *o*-methylbenzophenone structure.[11] Extremely rapid enolization[12–14] shortens the triplet's lifetime such that uphill energy transfer to A cannot compete.[11] The ortho-methylated **2b** does not react at 366 nm; it does react at 313 nm with $\Phi = 0.03$ and provides the linear Stern–Volmer plot shown at the bottom of Figure 1. The slope of 12 M^{-1} and a k_q value of 6×10^9 M^{-1} s^{-1} [15] indicate a triplet decay rate of 5×10^8 s^{-1}. Since the rate constant for γ-hydrogen abstraction is only ~5×10^7 s^{-1},[3] the rate constant for energy transfer is 4.3×10^8 s^{-1}. This value compares to the value 3×10^9 s^{-1} measured for δ-styrenylvalerophenone[16] and provides another example that energy transfer to quenchers with n,π^* triplets is slower than to those with π,π^* triplets.[11,17–19]

The various ω-(toluylphenoxy) ketones **3** and ω-(*p*-cyanophenoxy) ketones **4** were synthesized by straightforward S_N2 and Friedel–Crafts substitutions. A 313-nm excitation of 0.01 M benzene solutions of diketones **3** produces acetophenone in low quantum yields. (A now absorbs only 12% of the light.)

Quenching plots are all linear; the data are presented in Table I. Since remote substituents depress rate constants for γ-hydrogen abstraction, the cyanophenoxy ketones **4** were used as models for hydrogen abstraction[20,21] in **3**. The triplet decay rates of **4** grow with increasing n exactly as expected for γ-hydrogen abstraction[20] and thus were used to calculate, from the triplet lifetimes of **3**, the listed rate constants for irreversible[22] A $\rightarrow$ B energy transfer. Separate experiments indicated that 4-methoxy-2'-methylbenzophenone quenches triplet butyrophenone with a rate constant of 3×10^9 M^{-1} s^{-1}; therefore, the intermolecular contribution to $1/\tau$ values is 3×10^7 s^{-1}, only 20% of the lowest k_{TT} values.

First, we note that **2b** and **3b** have nearly the same k_{TT} value. This fact shows that replacement of a methylene with an oxygen atom produces no large change in the energy-transfer rate. Second, k_{TT} values drop as expected in proceeding from three connecting atoms (**2a**) to four (**2b** and **3b**) and then to five, although the decrease per intervening bond is not the factor of 10 that Closs found for cycloalkane spacers.[5] Finally, k_{TT} reaches a constant value for five to eight connecting atoms. Such behavior rules out a through-bond mechanism for this long-range energy transfer and implicates a through-space process. With the flexible methylene chain as a spacer, the molecules adopt a variety of geometries with different mixtures of staggered and gauche conformations about individual bonds. Thus each compound exists in a mixture of geometries with the two ketone chromophores different distances apart. The observed rate constant for each compound reflects the sum of population-averaged, distance-dependent rate constants for each molecular geometry. Apparently, these values coincidentally provide similar summations for the spacer lengths that we have studied. It will require careful molecular dynamics simulations to confirm this assessment.

We provide another example of this phenomenon in the preceding communication in this issue. We note here that the near-diffusion-controlled rate constants for bimolecular triplet energy transfer[15,23–25] necessitate that through-space (solvent) mechanisms must compete with through-bond mechanisms in any given compound that has sufficient conformational flexibility. This reality has been recognized in the case of metal-to-metal electron tranfser in proteins.[26] It is also interesting to compare these results to the behavior of triplet benzophenones with long alkyl tails on the para carbon.[27] Groups on the end of the tail cannot interact *chemically* with the excited carbonyl group unless the tail is over 10 atoms long. The rapid energy transfer from a remote benzoyl group on the 3–8-atom tethers that we have measured indicates that close contact with the carbonyl itself is not necessary, even though triplet excitation is known to be highly localized on the carbonyl. There is sufficient delocalization of both the n[28] and π^* [29] orbitals onto the benzene ring to allow the orbital overlap required for an exchange interaction.

(9) Zimmerman, H. E.; Lynch, D. C. *J. Am. Chem. Soc.* **1985**, *107*, 7745.
(10) Wagner, P. J. In *Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. II, p 251.
(11) Bays, J. P.; Encinas, M. V.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 727.
(12) Wagner, P. J. *Pure Appl. Chem.* **1977**, *49*, 259.
(13) Wagner, P. J.; Chen, C.-P. *J. Am. Chem. Soc.* **1976**, *98*, 239.
(14) Das, P. K.; Encinas, M. V.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 6965.
(15) Scaiano, J. C.; Leigh, W. J.; Meador, M. W.; Wagner, P. J. *J. Am. Chem. Soc.* **1985**, *107*, 5806.
(16) Cowan, D. O.; Baum, A. A. *J. Am. Chem. Soc.* **1971**, *93*, 1153.
(17) Wagner, P. J.; Kochevar, I. E.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 7489.
(18) Lechtken, P.; Turro, N. J. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 314.
(19) Mirbach, M. F.; Ramamurthy, V.; Mirbach, M. J.; Turro, N. J.; Wagner, P. J. *Nouv. J. Chim.* **1980**, *4*, 471.

(20) Wagner, P. J.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 7495.
(21) Wagner, P. J. *Org. Photochem.* **1991**, *11*, 227.
(22) Technically there is a few percent uphill energy transfer from the minor amount of relatively long-lived anti conformers of B.[12,13] This causes the Stern–Volmer plots for **2b,c** to intercept the *y*-axis at 1.05–1.10 instead of at 1.00 but does not otherwise affect the slope. The full kinetics treatment for three interconverting states will be presented in a full paper.
(23) Herkstroeter, W. G.; Hammond, G. S. *J. Am. Chem. Soc.* **1966**, *88*, 4769.
(24) Wagner, P. J.; Kochevar, I. *J. Am. Chem. Soc.* **1968**, *90*, 2232.
(25) Saltiel, J.; Shannon, P. T.; Zafiriou, O. C.; Uriarte, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 6799.
(26) Jacobs, B. A.; Mauk, M. R.; Funk, W. D.; MacGillivray, R. T. A.; Mauk, A. G.; Gray, H. B. *J. Am. Chem. Soc.* **1991**, *113*, 4390.
(27) Winnik, M. A.; Lee, C. K.; Basu, S.; Saunders, D. S. *J. Am. Chem. Soc.* **1974**, *96*, 6182.
(28) Hochstrasser, R. M.; Scott, G. W.; Zewail, A. H. *J. Chem. Phys.* **1973**, *58*, 393; *Mol. Phys.* **1978**, *36*, 475.
(29) Mucha, J. A.; Pratt, D. W. *J. Chem. Phys.* **1977**, *66*, 5339. Brode, P. F.; Pratt, D. W. *Chem. Phys. Lett.* **1978**, *59*, 334.