

A SEARCH FOR STERIC EFFECTS ON THE RATE CONSTANT FOR EXOTHERMIC SINGLET-SINGLET ELECTRONIC ENERGY TRANSFER IN FLUID SOLUTION†

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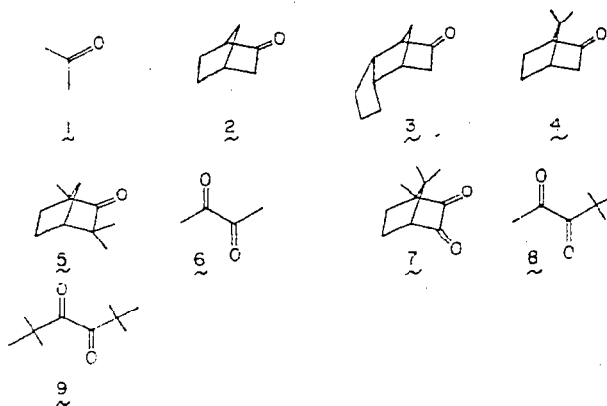
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A study of exchange singlet-singlet energy transfer was made between a series of sterically hindered ketones and α -diketones in fluid cyclohexane. The comparison of the measured rate constants of energy transfer shows them to be nearly diffusion controlled and insensitive to steric hindrance. This is argued to be a solvent cage effect. That is, the rate of energy transfer in a bimolecular collision may be sensitive to steric hindrance, but the many collisions within the cage result in a transfer efficiency of unity.

The processes of diffusion of reactive species together into a collision encounter and of reaction within the collision encounter aggregate are of general interest for the understanding of solution chemistry. There are many observations reported in the literature which are consistent with the rule that "electronic energy transfer in fluid solution occurs with near unit efficiency per collision encounter when the transfer is exothermic", i.e., such energy transfers are diffusion controlled [2]. This rule applies quite generally to singlet-singlet and to triplet-triplet energy transfer, with few, if any, documented exceptions. Focusing attention on singlet-singlet energy transfer, which can occur by both a resonance (long range dipole interaction) and an exchange (short range overlap of donor and acceptor electron bonds) mechanisms, we note that only the exchange mechanism is expected to show a sensitivity to steric effects on the rate constant for energy transfer. We are unaware of systematic studies directed toward elucidation of the question as to whether exothermic singlet energy transfer in solution is measurably sensitive to steric effects in the donor and acceptor molecules. We report such a study here, in which the fluorescence quenching of a series of alkanones by a series of α -diketones was chosen as

a model system, since long range dipole-dipole interaction has been shown to be negligible [2].



The ketones 1-5 allow a wide range of steric interactions to be explored during a solution collision encounter with one of the α -diketones 6, 7, 8 or 9. Electronic energy transfer is established conclusively by observation of quenching of alkanone fluorescence and simultaneous excitation of the α -diketone fluorescence. Acetone offers minimal steric interference to approach any α -diketone, while 2 possesses a relatively unhindered approach to the exo and endo carbonyl "faces" and to the "edges" of the carbonyl group. Ketones 3, 4, and 5, on the other hand, possess struc-

† Molecular photochemistry LIX. Paper LVIII, see ref. [1].

Table 1

Bimolecular rate constants^{a)} of ketone fluorescence quenching by α -diketones. Quenching by *cis*-diethoxyethylene 10, *trans*-dicyanoethylene 11, and 2,5-dimethyl-2,4-hexadiene 12 are included for comparison

Quencher	Ketone				
	1	2	3	4	5
6	9.4	8.4	8.0	7.6	6.1
7	8.2	6.5	6.5	6.7	4.9
8	7.1	5.3	5.6	5.6	5.5
9	—	1.8	2.3	2.5	1.4
10 b)	2.0	1.3	1.3	1.4	0.13
11 b)	2.5	5.2	5.6	1.0	1.7
12 c)	—	0.37	—	—	0.019

a) $k_q \times 10^{-9} \text{ M}^{-1} \text{ sec}^{-1}$ obtained from direct measurement of ketone fluorescence lifetimes in cyclohexane by the single photon counting technique except for acetone where emission quenching was studied with the assumption of $\tau_F^0 = 1.7 \times 10^{-9} \text{ sec}$.

b) See ref. [3]; c) see ref. [4].

tural features which should introduce predominant steric interference to approach of an α -diketone on the endo face, exo face and edges, respectively. The steric hindrance to ketone α -diketone interactions increases rapidly as one proceeds from 6 to 9. We are assured, that the singlet energy transfer step will be exothermic in all cases because the singlet energies of the ketones, as judged from their emission spectra, cannot be less than 70 kcal/mole, while the singlet energies of the α -diketones as judged by their absorption (and emission spectra) vary from 64 (55) kcal/mole for 6 to 60 (57) kcal/mole for 7 to 66 (60) kcal/mole for 8 to 77 (58) kcal/mole for 9, respectively.

Table 1 shows the bimolecular rate constants of exchange type singlet-singlet energy transfer between ketones 1-5 and the four α -diketones 6-9 in cyclohexane at 25°C. These were measured with an accuracy better than 20%, by obtaining the ketone fluorescence lifetime quenching as a function of α -diketone concentration by the single photon counting technique. The exception was for acetone where, with an accuracy better than 40%, the rate constant was calculated from emission quenching data assuming an excited singlet acetone lifetime of $1.7 \times 10^{-9} \text{ sec}$. Included in table 1 are also examples of chemical reaction ketone fluorescence quenching rate constants.

The results can be explained in terms of two general models.

(a) The distance required for effective transfer of energy is so long that the stereochemical barriers imposed on the ketones do not matter. Models show that the introduction of methyl groups increases the closest approach distance to the center of the carbonyl by about 4 Å.

(b) The reactions being diffusion controlled, show no structural sensitivity because, in the encounter complex, reaction occurs with unit efficiency.

The rate constants for singlet-singlet energy transfer are found to be relatively insensitive to ketone structure when compared to the cases of chemical quenching. Other important observations are that for the alkanone-biacetyl (6) systems, the alkanone-camphorquinone (7) systems and the alkanone-methyl-*t*-butyl-diketone (8) system, the maximum variation in k_q is very small (much less than a factor of 2 if the acetone-biacetyl system is ignored). Similarly, transfer of singlet energy from alkanones to 9, show only a small variation in k_q ; however, in comparing the k_q value for 9 as a quencher to those for 6, 7 and 8 quenchers, a clear cut factor of 3 to 5 fold difference in k_q is found.

Since k_{diff} in cyclohexane is calculated [5] to be $7 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$, we conclude that the quenching of alkanone singlets by 6, 7 and 8 is very probably diffusion controlled. This conclusion is consistent with the facts that (1) the k_q 's reported in table 1 for 6, 7 and 8 are as large as ever reported for cyclohexane solution; (2) k_q is insensitive to the wide variation in structures of 1 through 5, which indicates that common, rate-limiting feature that is structure independent (i.e., diffusion) determines the value of k_q .

It should be noted that even if the stereochemical barriers should reduce the probability of energy transfer per pair-collision, the probability of energy transfer within a solvent cage of many collisions might retain a value close to unity†. That is, despite the stereochemical barriers, the measured rate constants only reflect the rate of diffusion controlled encounters.

Let us now use the equations

† A rough estimate of the number of pair-collisions can be made by noting that the cage lifetime is about 10^{-10} sec , while the period of a collision is about 10^{-13} sec [6].

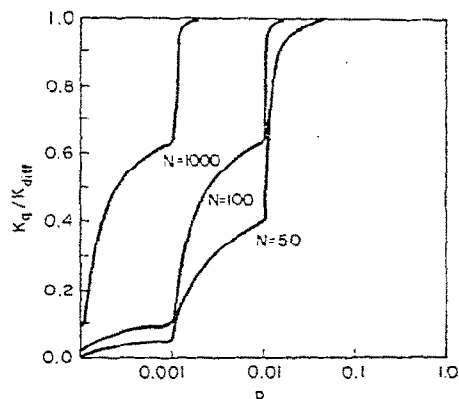


Fig. 1. Probability of energy transfer per cage as a function of the probability of energy transfer per pair-collision.



to consider the problems of deriving kinetic information for an efficient reaction within a collision complex. The measured rate constant, k_q , is the product of the rate of formation of collision complexes times the probability of reaction within the lifetime of a collision complex, i.e.,

$$k_q = k_{diff} \left(\frac{k_q'}{k_{-diff} + k_q'} \right). \quad (3)$$

Thus, the average probability of reaction within a collision complex is k_q/k_{diff} .

Using a simple model of the solvent cage, we can restate the above argument mathematically. The average probability of reaction per solvent cage can be defined as k_q/k_{diff} , when k_{diff} is the rate constant of diffusion and k_q is the experimentally measured rate constant. If the probability of reaction per pair-collision is p , then in a solvent cage of N collisions $k_q/k_{diff} = 1 - (1-p)^N$.

Given a high value of p , fig. 1 shows that there is no significant change in the measured values of k_q even if the stereochemical barriers should reduce p by an order of magnitude, while the reverse is true if the original value of p is low to begin with.

Table 1 shows that quenching by α -diketone 9 is

slow and seemingly not diffusion controlled. In analogy with the recent work of Watts and Ingold [7] on radical recombination rates, one could assign the smaller rate constants to slower diffusion of diketone 9. Yet comparison with diketones 6, 7 and 8 shows that this is probably not the case. These smaller rate constants combined with the fact that there is no significant variation of the rate constant with the structure would seem to rule out the second model (model above). However, if the only effective α -diketone quencher molecules are those that have nearly coplanar carbonyl systems, then, since there are many rotational conformers available [8] to the ground state of α -diketone 9, the effective quencher concentration may have been lower than assumed. This may also be an indication that, in the α -diketone 9, the period of rotation about the bond joining the carbonyl groups is longer than the cage lifetime. It is also interesting to note that of the α -diketones studied, 9 has the greatest overlap integral of absorption-ketone emission spectra and would be expected to have the highest long-range dipole-dipole energy transfer rate constant. The recent vapor-phase work of Wettack and Janda [9] shows that steric factors can be important in reducing the cross section of exchange singlet-singlet energy transfer from excited benzene to ketones. Further investigations in our laboratories on rigid molecules should elucidate the distance dependence involved in the exchange singlet-singlet electronic energy transfer between ketones and α -diketones.

In conclusion, for the first time an extensive systematic study of the variation of highly exothermic exchange energy transfer is reported. Except in cases where steric congestion severely inhibits approach of both excited donor and ground state acceptor (e.g., the pair 5*–9), the measured rate constants in cyclohexane are close to the value expected for diffusion controlled quenching. Effects other than steric factors, e.g., stabilities of cage complexes and rotameric populations of effective quenchers, may contribute to the lower rate constant in the latter example. Perhaps, the most remarkable result derived from this work is an experimental demonstration of the relative insensitivity of exchange energy transfer to extensive steric effects.

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