

Direct Chemical Evidence for Energy Transfer between Identical Molecules^[**]

By Peter Lechtken and Nicholas J. Turro^[*]

Energy transfer in the solid state, especially in crystals, is a well-known and well-studied phenomenon^[1]. However, with the sole exception of some studies employing the indirect technique of fluorescence depolarization^[2], there exists little information in the literature concerning energy transfer between identical molecules in fluid solution at room temperature^[3]. The difficulty in studying energy transfer between identical molecules in fluid solution resides in the absolute identity of the reactants and the products [Reaction (1)].

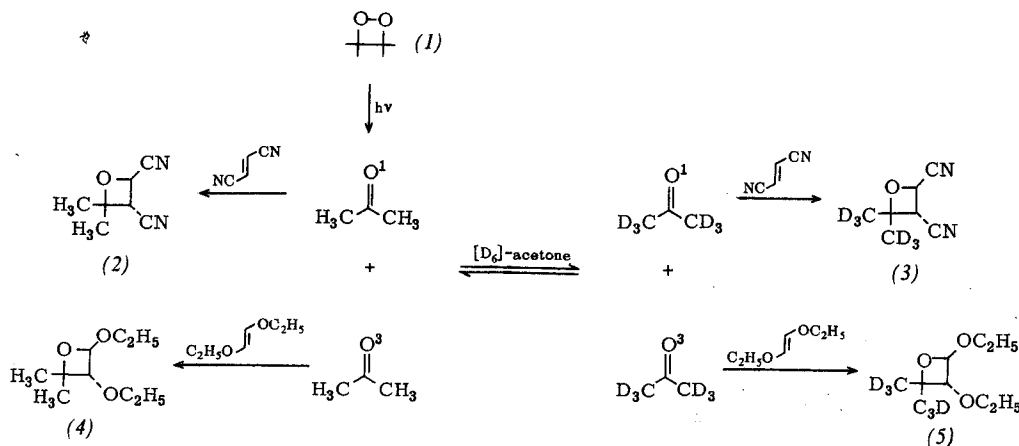


Fig. 1. Reaction scheme of energy transfer.

(Even if some anisotropy were involved in the reaction, say, initiated by excitation with polarized light, the rapid rate of tumbling of molecules in fluid solution converts the system into an isotropic one much faster than most physical measurements can be made).

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Evidence for the occurrence of such an "energy hopping" between identical molecules is of great interest for:

- unraveling the question of whether excimers^[4] of ketones exist [(AA)*; Reaction (2)];
- providing a novel mechanism for "long range" energy transfer;
- understanding the factors which determine the duration of electronic excitation in a molecule.

The ability of tetramethyl-1,2-dioxetane (1) to produce high yields of excited singlet and triplet acetone upon photolysis^[5] provides a unique opportunity to demonstrate electronic excitation transfer between identical molecules by a direct chemical method of analysis. Indeed, (1) may be considered as a stable, "masked" electronically excited acetone molecule. Irradiation of (1) in deuterioacetone, under conditions such that acetone^[6] is not excited by direct absorption of light (high pressure Hg lamp, 365 nm line), effects the reaction scheme shown.

The acetone singlets and triplets generated from photolysis of (1) were trapped with dicyanoethylene and diethoxyethylene, respectively, to give the corresponding oxetanes (2) and (4)^[7]. Since the excitation energy must originally reside on a [H₆]-acetone (A-H₆) molecule, one can determine the extent of energy transfer to [D₆]-acetone (A-D₆) by simply measuring the ratio of (2) to (3) and/or (4) to (5) in the reaction products.

The analysis of the reaction mixture was executed by a combination of gas chromatography and mass spectrometry. The relative amounts of (2) and (3), or (4) and (5), were determined from the intensities of the relevant masses (Table 1). As standard controls, authentic mixtures

of (2) and (3) [or (4) and (5)] were prepared and analyzed.

Table 1. Mass numbers for analysis of deuterium contents [8].

Fragment X=H, D	Oxetane			
	(2)	(3)	(4)	(5)
CX ₃ CO	43	46	43	46
CX ₃ COCX ₃	58	64	58	64
(CX ₃) ₂ CCHCN	81	86	—	—
(CX ₃) ₂ CCHOC ₂ H ₅	—	—	100	106
(M-15)	121	124	—	—

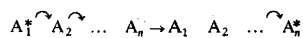
Analysis of the oxetanes from addition of singlet acetone to dicyanoethylene revealed 5 ± 2% deuteriooxetane (3)

in the total oxetane mixture, while the corresponding deuterated oxetane (5) from addition of triplet acetone to diethoxyethylene accounted for $10 \pm 5\%$ of the total oxetane mixture.

Application of Stern-Volmer kinetics^[9] leads to the following rate constants for energy transfer:

$$\begin{aligned} \text{Singlet-Singlet: } & k_q^1 = 3.5 \times 10^6 \text{ mol}^{-1} \text{ s}^{-1} \\ \text{Triplet-Triplet: } & k_q^3 = 2.8 \times 10^6 \text{ mol}^{-1} \text{ s}^{-1} \end{aligned}$$

Thus, within the experimental error of $\pm 50\%$, the two energy transfer rate constants are equal and about three orders of magnitude smaller than the value for diffusion in acetone ($\approx 5 \times 10^9 \text{ mol}^{-1} \text{ s}^{-1}$).



$$\Phi_{\text{HOP}} = \frac{k_q}{k_q + \sum k_d} [A] \quad \begin{array}{l} n^1 \approx 1 \\ n^3 \approx 14 \end{array}$$

The number of energy hopping events, Φ_{HOP} , depends on the ratio of the rates of hopping to the sum of all deactivation rates ($\sum k_d$). In pure acetone at room temperature ($[A] = 14 \text{ M}$, $\sum k_d^1 \approx 0.6 \times 10^9 \text{ s}^{-1}$, $\sum k_d^3 \approx 2 \times 10^5 \text{ s}^{-1}$)^[10] the singlet makes only one hop per lifetime, while the triplet makes about 14 hops per lifetime.

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