

- (17) ^1H NMR spectra at 90 MHz were of solutions of **6**, and **6D** dihydrochlorides in 0.2 M perdeuterioacetate buffer in deuterium oxide ($\text{pD} \sim 5.2$).
- (18) 3-[2- ^2H](3'-Aminopropyl)quinoline (**6D**) dihydrochloride was obtained in two steps from DL-[2- ^2H]lysine. Oxidation with *N*-bromosuccinimide gave Δ^1 -[2- ^2H]piperidine,¹⁹ in equilibrium with 5-[1- ^2H]aminopentanal, which was condensed with *o*-aminobenzaldehyde.¹⁵
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James C. Richards, Ian D. Spenser*

Department of Chemistry, McMaster University
Hamilton, Ontario, Canada L8S 4M1

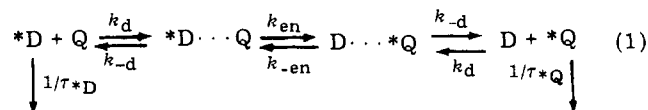
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Energy Transfer Processes Involving Distorted Excited States

Sir:

Some years ago, Weller^{1,2} extended the Marcus theory³⁻⁶ to electron-transfer quenching processes. Recent results concerning excited-state electron-transfer processes of organic^{7,8} and inorganic⁹⁻¹¹ molecules have confirmed the validity of that treatment.¹² We will show here that the same concepts can be used to treat collisional energy-transfer processes,¹³ and that in this way it is possible to obtain a unified view of "classical" and "nonclassical" energy-transfer behavior.¹⁴⁻²¹

For an energy-transfer quenching process involving a collisional (exchange) mechanism,¹⁴ this kinetic scheme 1 can be



used. Assuming that $1/\tau *Q \gg k_d[D]$ and using Stern-Volmer relationships and steady-state approximations, the experimental quenching constant k_q is given by

$$k_q = \frac{k_d}{1 + \frac{k_{-d}}{k_{en}} \left(1 + \frac{k_{-en}}{k_{-d}}\right)} \quad (2)$$

Scheme 1 and eq 2 are analogous to the scheme and the equation obtained for electron-transfer quenching.^{1,2,7-12} When at least one of the species involved is uncharged, no work is required to bring the reactants or products together at the separation distance of the encounter complex, and thus the free activation energy and the free-energy change of the whole process coincide with the analogous quantities (ΔG^\ddagger and ΔG) involved in the energy-transfer step. As $k_{-en}/k_{en} = \exp(\Delta G/RT)$ and $k_{en} = k_{en}^0 \exp(-\Delta G^\ddagger/RT)$, where k_{en}^0 is the frequency factor of the energy-transfer step, eq 2 can be transformed into

$$k_q = \frac{k_d}{1 + e^{\Delta G/RT} + \frac{k_{-d}}{k_{en}^0} e^{\Delta G^\ddagger/RT}} \quad (3)$$

The meaning of free energy in excited-state reactions and the relationships between spectroscopic and thermodynamic quantities have been thoroughly discussed by Grabowski.²² The free-energy difference of the energy-transfer process can be expressed by

$$\Delta G = -E^{0-0}(*D, D) + E^{0-0}(*Q, Q) + C(*D, D) + C(Q, *Q) \quad (4)$$

where E^{0-0} is the zero-zero excited-state energy and C is a

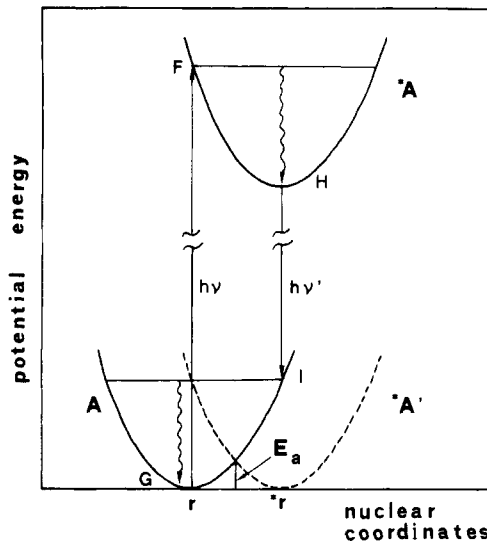


Figure 1. Schematic potential energy diagram for a molecule having the excited state with different nuclear coordinates. For the sake of simplicity, the two states are assumed to be described by the same harmonic function and the zero point energy is neglected. The Stokes shift (S) is given by $FG-HI$. In this very simple case, the "intrinsic barrier" to energy transfer caused by excited-state distortion, E_a , is equal to $1/8 S$.

term which accounts for the difference in partition functions and entropy between ground and excited state. C can be either positive or negative and in favorable cases it is very small and can thus be neglected.^{2,22}

In order to understand the meaning of ΔG^\ddagger , consider a "self-exchange" energy-transfer reaction



between an excited state and a ground state having minima at different values of the nuclear coordinates (Figure 1). For the sake of simplicity, the two states are assumed to be described by the same harmonic function. A collision between $*A$ and A when both are in their zero vibrational levels cannot result in energy transfer because of Franck-Condon restrictions and energy conservation. The energy deficiency can be made up by vibrational excitation of $*A$ and/or A . The most convenient reaction path is that involving excitation of both $*A$ and A to vibrational levels which correspond to the crossing point between curves A and $*A'$ in Figure 1. For each molecule we can thus define a quantity (E_a in Figure 1) which is related to excited-state distortion and represents an "intrinsic barrier" to energy transfer. The free activation energy of a "self-exchange" energy-transfer reaction like that in eq 5 can thus be expressed by

$$\Delta G^\ddagger_A = 2(E_a + C^\ddagger) \quad (6)$$

where E_a is in some way related to the Stokes shift and C^\ddagger accounts for the difference in partition functions and entropy between reactants and transition state. When the donor-acceptor interaction is sufficiently weak, C^\ddagger can be neglected.^{2,4}

Using the Weller relationship^{1,2}

$$\Delta G^\ddagger = \frac{\Delta G}{2} + \left[\left(\frac{\Delta G}{2} \right)^2 + \left(\frac{\lambda}{4} \right)^2 \right]^{1/2} \quad (7)$$

eq 3 can be transformed into

$$k_q = \frac{k_d}{1 + e^{\Delta G/RT} + \frac{k_{-d}}{k_{en}^0} e^{[\Delta G/2 + \{(\Delta G/2)^2 + (\lambda/4)^2\}^{1/2}]/RT}} \quad (8)$$

where the reorganization parameter λ associated with energy transfer is given by the following equation^{5,6,12}

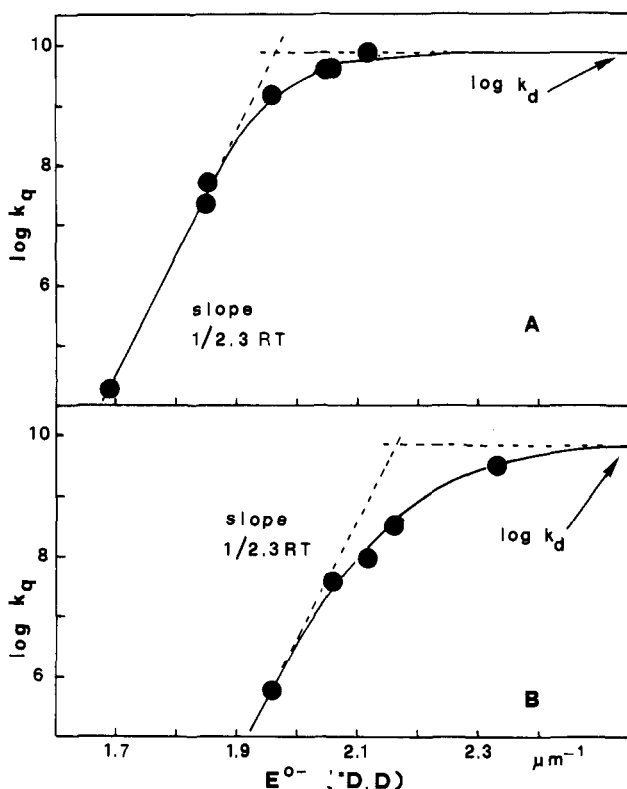


Figure 2. Plot of $\log k_q$ vs. $E^{0-0}(*D,D)$ for the energy-transfer quenching of aromatic triplets by biacetyl in benzene (A) and *o*-anisil in cyclohexane (B). The points represent the experimental data found in ref 23 and 16. The solid line is the best fitting curve according to eq 8 (see text).

$$\lambda = 2(\Delta G^{\ddagger}_D + \Delta G^{\ddagger}_Q) \quad (9)$$

where ΔG^{\ddagger}_D and ΔG^{\ddagger}_Q are the free activation energies of the corresponding "self-exchange" energy-transfer reactions. In the energy-transfer quenching of a homogeneous family of donors having variable excited-state energies by a single quencher, k_d , k_{-d} , k_{en}^0 , λ , $E^{0-0}(*Q,Q)$, $C(*D,D)$, and $C(Q,*Q)$ are constant and eq 4 reduces to

$$\Delta G = -E^{0-0}(*D,D) + \text{constant} \quad (10)$$

Thus according to eq 8, for low $E^{0-0}(*D,D)$ values, $\log k_q$ increases linearly (slope $1/2.3RT$) as $E^{0-0}(*D,D)$ increases, while for high $E^{0-0}(*D,D)$ values $\log k_q$ reaches a plateau value equal to $\log k_d$. Using different quenchers, the $E^{0-0}(*D,D)$ range covered by the intermediate nonlinear region becomes broader and broader as λ increases. From the best fitting procedure of eq 8 to experimental results, it is possible to obtain λ and the $E^{0-0}(*D,D)$ value which makes $\Delta G = 0$. For example, using Sandros' data for energy transfer from aromatic triplets to biacetyl ("classical" acceptor)²³ and *o*-anisil ("nonclassical" acceptor),¹⁶ the best fitting procedure (Figure 2)²⁴ gives $\lambda = 0.3 \mu\text{m}^{-1}$ and $\Delta G = 0$ for $E^{0-0}(*D,D) = 1.95 \mu\text{m}^{-1}$ in the case of biacetyl and $\lambda = 0.5 \mu\text{m}^{-1}$ and $\Delta G = 0$ for $E^{0-0}(*D,D) = 2.14 \mu\text{m}^{-1}$ for *o*-anisil. For biacetyl, E^{0-0} is known²³ to be $1.97 \mu\text{m}^{-1}$, which means that in this case the C terms in eq 4 are negligible. Assuming that this is also approximately true for *o*-anisil, we obtain a value of $\sim 2.14 \mu\text{m}^{-1}$ for its unknown E^{0-0} energy. The much higher λ value obtained for *o*-anisil is in agreement with the fact that its triplet is much more distorted than triplet biacetyl.¹⁶

A more detailed discussion and the application of this treatment to other "classical" and "nonclassical" energy-transfer processes^{14,15,17-21} will be reported elsewhere.

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V. Balzani*

*Istituto Chimico "G. Ciamician" dell'Università
and Laboratorio di Fotochimica e Radiazioni d'Alta
Energia del C.N.R., Bologna, Italy*

F. Bolletta

*Istituto Chimico "G. Ciamician" dell'Università
Bologna, Italy*

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Bifunctional Activation of Carbon Dioxide. Synthesis and Structure of a Reversible CO₂ Carrier

Sir:

Unlike many other small molecules, CO₂ very rarely forms adducts with transition metals.^{1,2} Formation of elusive CO₂ complexes is normally followed by ready metal-promoted elementary transformations, which include dimerization,³ disproportionation,^{3,4} and deoxygenation of CO₂.⁵ So far, the presence of intact CO₂ has only been structurally verified in (Cy₃P)₂Ni(CO₂) (Cy = cyclohexyl).¹

Although it was variously suggested that metal basicity^{1,2,6} is an important prerequisite to CO₂-metal adducts formation, we feel that the bifunctional nature of some metal complexes which contain transition metals in low oxidation states, along with alkali cations, could be taken into account as playing an unexpected role in CO₂ fixation. This hypothesis comes from the fact that in many simple reactions CO₂ seems to require for its activation, in addition to a basic center, the assistance of an acidic⁷ partner. With this in mind, we looked for an acid-base partnership between transition and alkali ions in bimetallic complexes.

Reducing *N,N'*-ethylenebis(salicylideneiminato)cobalt(II), Co(salen), or a substituted Co(salen), with alkali metals (M), we generated a bifunctional complex, Co(salen)M, in which