Energy and electron transfer nomenclature

$D^+ + A \longrightarrow D + A^+$ **hole transfer**

$D^- + A \longrightarrow D + A^-$ **electron transfer**

$D^* + A \longrightarrow D + A^*$ **energy transfer**

Exothermic energy transfer

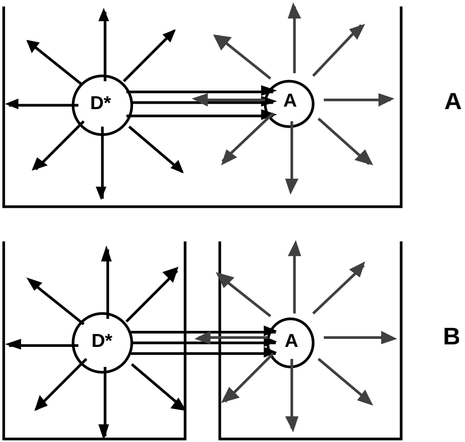
The rate constants for energy transfer processes which are exothermic by more than 3-4 kcal/mol and are spin allowed, frequently approach the diffusion controlled limit.

$$k_{diff} = \frac{8RT}{2000\eta} \qquad 2 \times 10^{5}\,\frac{T}{\eta}$$

Representative diffusion controlled rate constants in units of: $10^{10}\ M^{-1}\ s^{-1}$

isopentane	**4.6**
benzene	**1.6**
water	**1.1**

Trivial Mechanism for Energy Transfer



Trivial energy transfer between D* and A, with A* emitting following absorption of emission by D*. Part B emphasizes the independence of emission and absorption by noting that D and A could be in different containers.

$$D^* \longrightarrow D + h\nu \quad \text{(ee.11)}$$

$$h\nu + A \longrightarrow A^* \quad \text{(ee.12)}$$

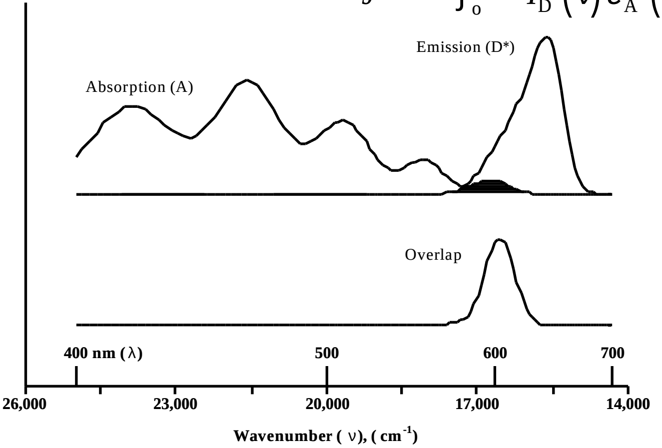
Conditions for trivial energy transfer

The "trivial" mechanism requires that D* emits photons which A is capable of absorbing. The rate or probability per unit time of energy transfer from D* to produce A* will depend on:

- The quantum yield (Φ_e^D) of emission by D*.
- The number of A molecules (concentration) in the path of photons emitted by D*.
- The light absorbing ability of A.
- The overlap of the emission spectrum of D* and the absorption spectrum of A, with consideration given to the extinction coefficient of A at the wavelength of overlap.

Representation of the overlap integral J between the emission spectrum of D* and absorption of A.

$$J = \int_0^\infty I_D(\bar{\nu})\, \varepsilon_A(\bar{\nu})\, d\bar{\nu}$$



Mechanism of electron transfer by electron ejection-electron capture (trivial mechanism)

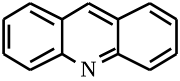
$$D \xrightarrow{h\nu} D^{+} + e^{-}_{\text{solv}}$$

$$e^{-}_{\text{solv}} + A \longrightarrow A^{\bullet -}$$

Electron trapping rate constants

Substrate	***k*** **(10^9 M^{-1} s^{-1})**	**Substrate**	***k*** **(10^9 M^{-1} s^{-1})**
Inorganic		*Olefins*	
Oxygen	20	styrene	3.0
N_2O	9.0	tetracyanoethylene	15
Cu^{2+}	39	butadiene	8.0
Aromatic		*Ketones*	
benzene	0.01	acetone	7.0
anisole	0.003	acetophenone	28
benzonitrile	19	benzophenone	28
naphthalene	5.0		

Two-photon trivial electron transfer

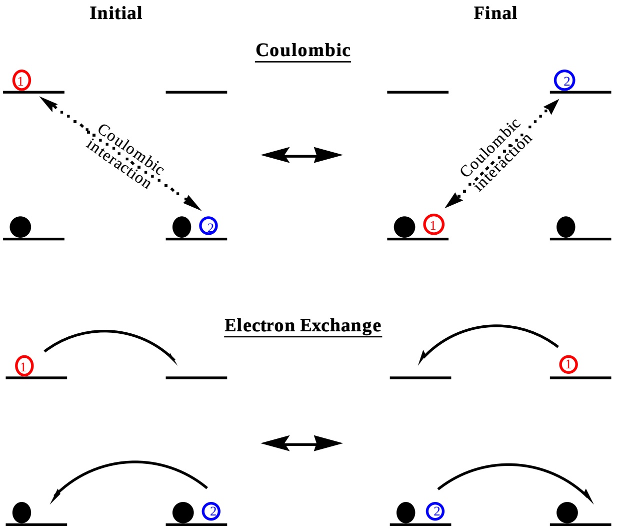


acridine

$$\text{acridine} \xrightarrow{\text{2-h}\nu} \text{acridine}^{+} + e^{-}_{\text{aq}} \qquad \text{(ee.18)}$$

$$e^{-}_{\text{aq}} + \text{acridine} \longrightarrow \text{acridine}^{-} \qquad \text{(ee.19)}$$

Comparison of the Coulombic and Exchange mechanisms of electronic energy transfer



Förster or Coulombic energy transfer

In Coulombic energy transfer no electrons "change molecules", but rather two transitions occur simultaneously in a process that could be described as the transfer of a "virtual photon"; Since no electrons are actually transferred in the Coulombic mechanism, it is clear that this process cannot have an analogy in the case of electron transfer.

There cannot be electron transfer if electrons are not exchanged between donor and acceptor

Förster mechanism

$$k_{ET}\ (total)\quad \alpha\Big[\big\langle \Psi(D^*)\Psi(A)\,\big|\,H_e\,\big|\,\Psi(D)\,\Psi(A^*)\big\rangle^2$$

Exchange

$$+\ \beta\big\langle \Psi(D^*)\Psi(A)\,\big|\,H_c\,\big|\,\Psi(D)\Psi(A^*)\big\rangle^2\Big]$$

Coulombic

$$k_{ET}(\text{Coulombic})\quad E^2 \approx \left(\frac{\mu_D\mu_A}{R_{DA}^3}\right)^2 = \frac{\mu_D^2\mu_A^2}{R_{DA}^6}$$

- •(a) The square of the transition dipole moment μD.
- •(b) The square of the transition dipole moment μA.
- •(c) The inverse sixth power of the separation between D* and A (i.e. 1/R6).

This dipole-dipole coupling mechanism, frequently called the "Förster mechanism" can only be effective in singlet-singlet energy transfer because only multiplicity-conserving transitions have large transition dipoles

Electron exchange mechanisms

- **Energy transfer in some cases**
    - **always in the case of triplet-triplet energy transfer**
- **Triplet-triplet annihilation**
- **Charge transfer**
- **Charge translocation**

A theory of energy transfer by electron exchange was worked out by Dexter:

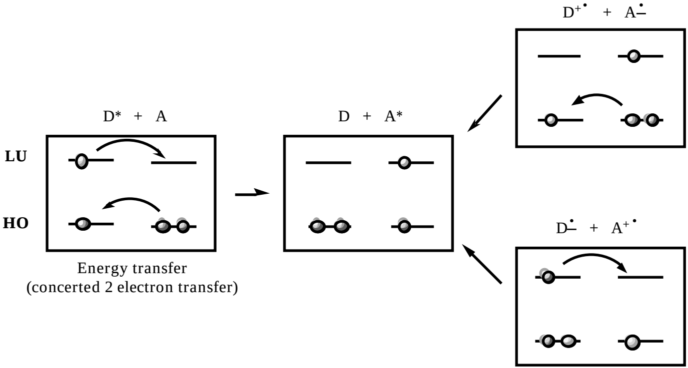
$$k_{ET} \text{ (exchange)} = KJ \exp(-2\, r_{DA}/L)$$

- K is related to specific orbital interactions.
- J is the normalized spectral overlap integral, where normalized means that both the emission intensity (I_D) and extinction coefficient (ε_A) have been normalized to unit area on the wavenumber scale.
    - J, by being normalized does not depend on the actual magnitude of ε_A.
- rDA is the donor-acceptor separation relative to their van der Waals radii, L.
    - By being defined in this manner r_{DA} corresponds to the edge-to-edge separation

Förster (Coulombic) vs. Dexter (exchange)

- The rate of dipole-induced energy transfer decreases as R^{-6} whereas the rate of exchange-induced transfer decreases as exp–(2r/L). This means that k_{ET}(exchange) drops to negligibly small values (relative to the donor lifetime) as the intermolecular (edge-to-edge) distance increases more than on the order of one or two molecular diameters (5-10Å).
- The rate of dipole-induced transfer depends on the oscillator strength of the D* → D and A → A* radiative transitions, but the rate of the exchange-induced transfer is independent of the oscillator strength of the D* → D and A → A* transitions.
- The efficiency of energy transfer (fraction of transfers per donor lifetime ~ k_{ET}/k_D) by the dipole mechanism depends mainly on the oscillator strength of the A → A* transition (since a smaller oscillator strength for D* → D is compensated by a slower radiative rate constant), whereas the efficiency of energy transfer by the exchange interaction cannot be directly related an experimental quantity.

Exchange mechanisms for excited state formation



$D^{+\bullet} + A^{\bullet-}$

$D^* + A$

$D + A^*$

LU

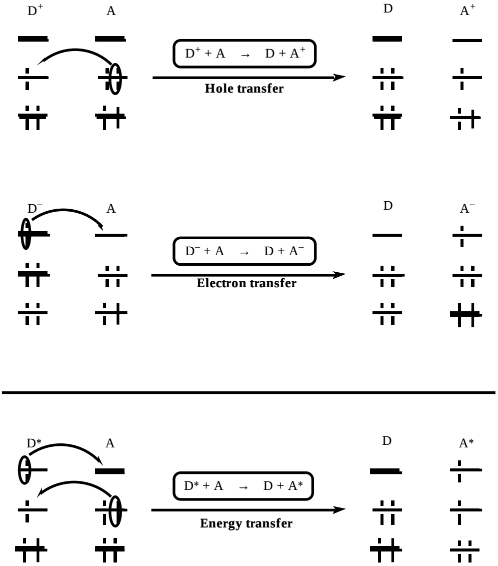
HO

$D^{\bullet-} + A^{+\bullet}$

Energy transfer
(concerted 2 electron transfer)

Charge transfer
recombination

Why examine energy and electron transfer together?



$D^+ + A \rightarrow D + A^+$

Hole transfer

$D^- + A \rightarrow D + A^-$

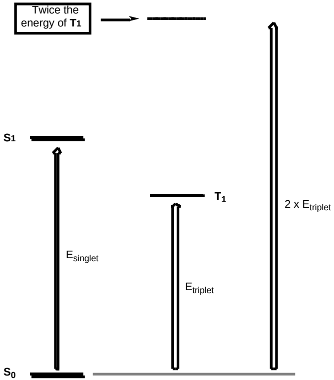
Electron transfer

$D^* + A \rightarrow D + A^*$

Energy transfer

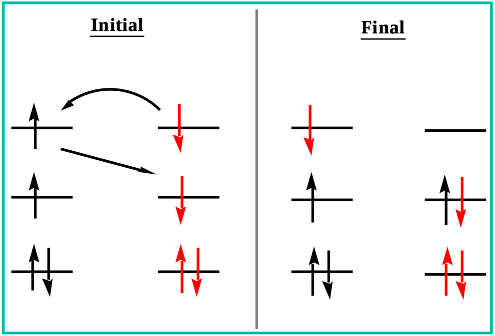
Triplet-Triplet Annihilation (TTA):

a Special Case of Energy Transfer via Electron Exchange Interactions



$$D^*(T_1) + D^*(T_1) \xrightarrow{k_{TTA}} D^*(S_1) + D(S_0)$$

with $\Delta H < 0$



Properties of TTA in solution

- The rate constants for TTA, k_{TTA}, are generally very large.
- With lasers triplet state concentrations in excess of 10–5 M are common. Typical products $k_{TTA}[D^*(T1)]$ may then be around or over 10^5 s^{-1}. Thus, any triplet with lifetime of a few microseconds (a common situation) will undergo at least some TTA in fluid solution.
- The high sensitivity with which fluorescence can be detected makes TTA an easily observable process even when it is not the major mechanism for triplet decay.

Substrate	**Solvent**	**T, (K)**	**k_{TTA} ($10^9 M^{-1} s^{-1}$**
Anthracene[15]	toluene	258	2.74
Anthracene[15]	toluene	298	4.10
1,2-Benzanthracene[16]	n-hexane	296	20.3
Pyrene[17]	cyclohexane	room T	7 ± 2
Pyrene[17]	dodecane	room T	5 ± 1
Pyrene[17]	hexadecane	room T	1.9 ± 0.2

Types of electron transfer

Charge transfer

$$D^* + A \longrightarrow D^{+\bullet} + A^{\overset{\bullet}{-}}$$

or

$$D^* + A \longrightarrow D^{\overset{\bullet}{-}} + A^{+\bullet}$$

Electron translocation or transfer

$$D^{\overset{\bullet}{-}} + A \longrightarrow D + A^{\overset{\bullet}{-}}$$

Hole translocation or transfer

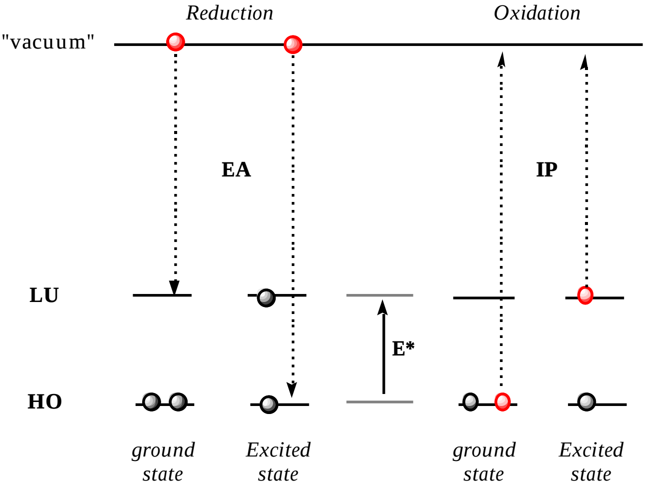
$$D^{+\bullet} + A \longrightarrow D + A^{+\bullet}$$

Redox properties of excited states

Excited states of diamagnetic molecules with closed shell ground states are always better oxidizing and reducing agents than their corresponding ground states

This is not necessarily true of species with open shell ground states

Redox properties of excited states



Gas phase vs. solution redox properties

From the point of view of organic photochemistry, we will frequently be interested in charge transfer processes in solution. To determine the energetics associated with these processes, we could follow two distinct approaches:

(a) We could calculate ΔG for the gas phase reaction and then correct ΔG to take into account the solvation energies for all the participants (i.e. D*, A, D+• and A•) in the reaction.

(b) We could employ the electrochemical potentials for the oxidation of reductions involved to calculate free energy changes directly in solution.

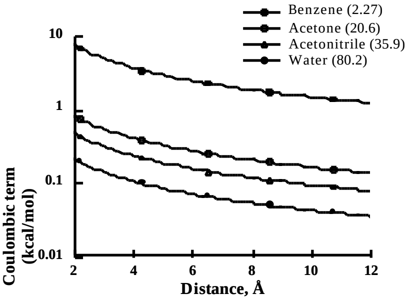
Gas phase vs. solution

Gas Phase

$$\Delta G = (IP)_D - (EA)_A - E_D^*$$

Solution

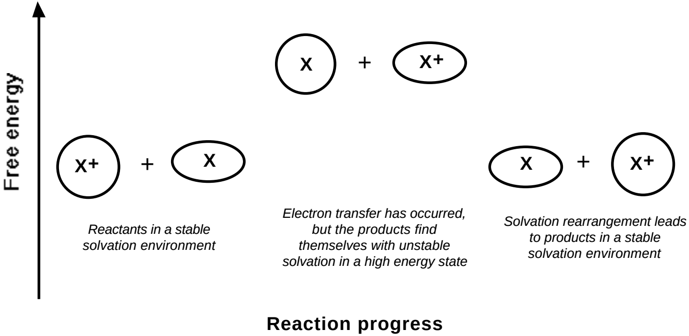
$$\Delta G \approx E^o_{D^{+\cdot}/D} - E^o_{A/A^{-\cdot}} - E_D^*$$



Solution (with Coulombic correction)

$$\Delta G \approx E^o_{D^{+\cdot}/D} - E^o_{A/A^{-\cdot}} - E_D^* - N_A \frac{e^2}{4\pi\varepsilon^o \varepsilon r}$$

Marcus vs Libby Theory of Electron Transfer

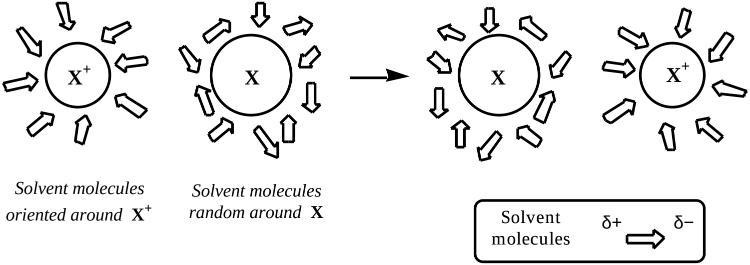


Reactants in a stable solvation environment

Electron transfer has occurred, but the products find themselves with unstable solvation in a high energy state

Solvation rearrangement leads to products in a stable solvation environment

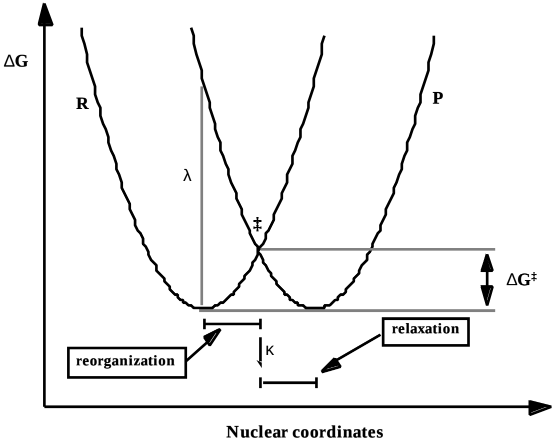
Visualization of the inner (note size change) and outer (note solvent reorganization) changes



Solvent molecules oriented around $\mathbf{X}^+$

Solvent molecules random around **X**

Potential energy description of an electron transfer reaction with ΔG = 0

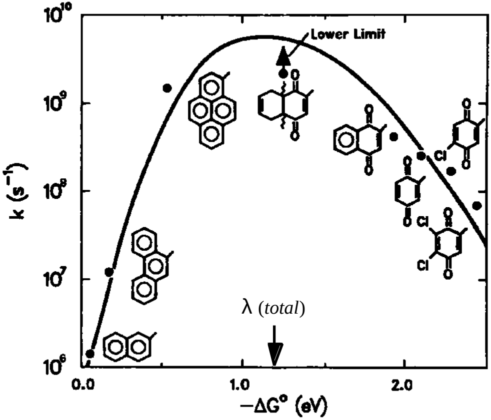


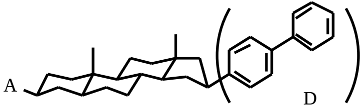
$$k_{et} = nN\,k\,\exp(-\Delta G^{\ddagger}/RT)$$

$$\Delta G^{\ddagger} = \frac{\lambda}{4}\left(1 + \frac{\Delta G^{o}}{\lambda}\right)^{2}$$

In theatomic configuration. at the crossing, a hypothetical system possessing the electronic wave function (and therefore the ionic charges) of the reactants must have the same energy as that of a hypothetical system possessing the electronic wave function of the products in the same configuration

Marcus Inverted Region: Experimental Verification



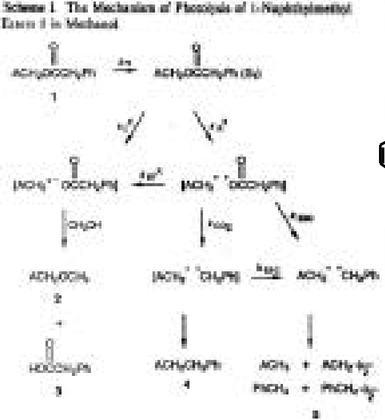


A–Sp–D

Intramolecular electron transfer rate constants as a function of ΔG° in methyltetrahydrofuran solution at 206 K. From: Closs, G. L.; Calcaterra, L. T.; Green, H. J.; Penfield, K. W.; Miller J. R., J. Phys. Chem. 1986, 90, 3673

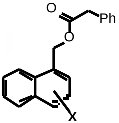
Chemical Spectroscopy:

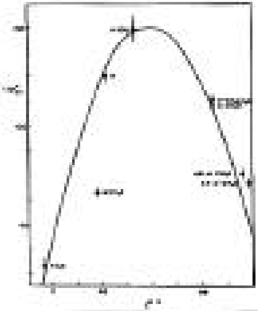
Application of Marcus Theory to the Interpretation of Electron-Transfer control of Product distributions



Scheme I. The Mechanism of Photolysis of 1-Naphthylmethyl Esters 1 in Methanol

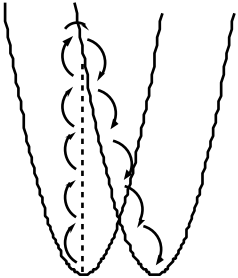
from J. Am. Chem. Soc. 1989, 111, 8948.



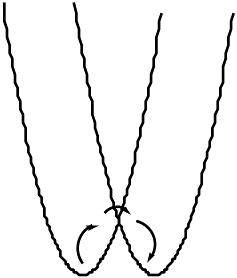


Plot of log ket versus E˚ of electron transfer for the conversion of the radical pair to the ion pair. The curve is a fit according to the Marcus Theory using λ = 0.39 eV. From J. Am. Chem. Soc. 1989, 111, 8948

Free energy requirements of the electron transfer pathways in the Libby and Marcus models

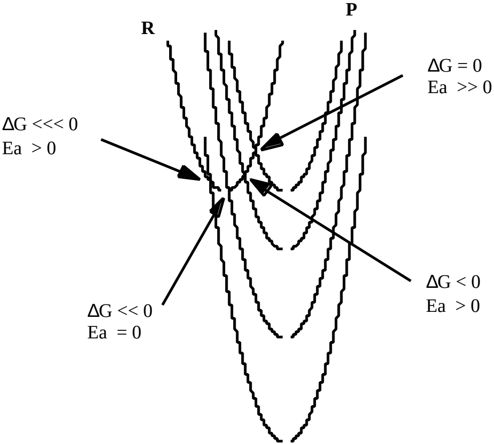


Libby



Marcus

Marcus theory: the breakdown of conventional thinking in terms of free energy relationships



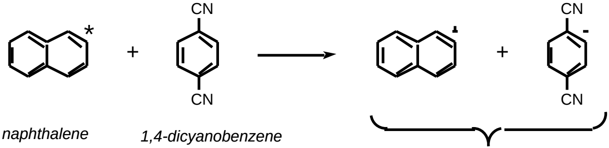
ΔG = 0
Ea >> 0

ΔG <<< 0
Ea > 0

ΔG << 0
Ea = 0

ΔG < 0
Ea > 0

Thermodynamics and kinetics of electron transfer: an example



naphthalene

1,4-dicyanobenzene

radical ions

$E^0_{D^+/D} = +1.60$ V

$E^0_{A/A^-} = -1.64$ V

$E(S_1) = 3.94$ eV = 90.9 kcal/mol

$$\Delta G = FE^0_{D^+/D} - FE^0_{A/A^-} - E^0_D - 0.2$$

$$\Delta G = 36.9 - (-37.8) - 92.1 - 0.2 = -17.6 \ kcal/mol$$

$$k(electron\ transfer) \approx 1.8 \ x \ 10^{10} \quad M^{-1}s^{-1}$$

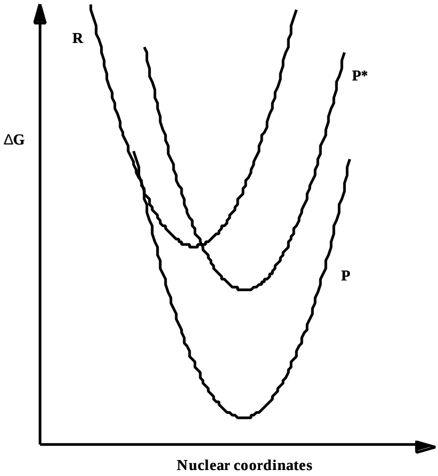
from: Rehm, D.; Weller, A. Isr. J. Chem. 1970, 8, 259

Contact and solvent-separated radical ion pairs

$$\mathrm{D}^* + \mathrm{A} \rightleftharpoons \mathrm{D}^*(\mathrm{S})\mathrm{A} \rightleftharpoons \mathrm{D}^*,\mathrm{A} \longrightarrow \underset{\text{"CRIP"}}{\overline{\mathrm{D}^+,\mathrm{A}^-}} \qquad \text{(ee.63)}$$

$$\mathrm{D}^* + \mathrm{A} \rightleftharpoons \mathrm{D}^*(\mathrm{S})\mathrm{A} \longrightarrow \underset{\text{"SSRIP"}}{\mathrm{D}^+(\mathrm{S})\mathrm{A}^-} \qquad \text{(ee.64)}$$

Chemiluminescent Ion Recombination



When is it plausible?

- When reaction to the ground state takes place in the Marcus inverted region, the smaller DG change to the excited products may be kinetically preferred.
- A triplet radical ion pair can populate an excited triplet state of D or A, but formation of ground state products is spin forbidden.