"Molecular Photochemistry - how to study mechanisms of photochemical reactions ?"

Bronislaw Marciniak

Faculty of Chemistry, Adam Mickiewicz University,
Poznan, Poland

2014/2015 - lecture 7

5. Examples illustrating the investigation of photoreaction mechanisms:

- photoinduced electron transfer and energy transfer processes

Kinetic of quenching

	rate
$A(S_0) \xrightarrow{h\nu} A(S_1)$	I_a (einstein dm^{-3} s^{-1})
$A(S_1) \rightarrow A(S_0) + h\nu_f$	$k_f[A(S_1)]$
$A(S_1) \rightarrow A(S_0) + \text{heat}$	$k_{IC}[A(S_1)]$
$A(S_1) \rightarrow A(T_1)$	$k_{ISC}[A(S_1)]$
$A(S_1) \rightarrow B + C$	$k_r[A(S_1)]$
$A(S_1) + Q \rightarrow \text{quenching}$	$k_q[A(S_1)][Q]$
$A(T_1) \rightarrow A(S_0) + h\nu_p$	$k_p[A(T_1)]$
$A(T_1) \rightarrow A(S_0) + \text{heat}$	$k'_{ISC}[A(T_1)]$
$A(T_1) \rightarrow B' + C'$	$k'_r[A(T_1)]$
$A(T_1) + Q \rightarrow \text{quenching}$	$k'_q[A(T_1)][Q]$

Kinetic of quenching
Energy transfer

	rate
$A(T_1) + Q \rightarrow A + Q^*$	$k'_q[A(T_1)][Q]$
$Q^* \rightarrow Q + h\nu_e$	$k''_e[Q^*]$
$Q^* \rightarrow Q + \text{heat}$	$k''_d[Q^*]$
$Q^* \rightarrow \text{products}$	$k''_r[Q^*]$

Stern-Volmer equation

for T_1

$$\frac{\Phi_p^0}{\Phi_p} = 1 + k_q' \tau_T^0 [Q]$$

$$\frac{\Phi'^0_R}{\Phi'_R} = 1 + k_q' \tau_T^0 [Q]$$

$$\frac{\tau_T^0}{\tau_T} = 1 + k_q' \tau_T^0 [Q]$$

$$\frac{1}{\tau_T} = \frac{1}{\tau_T^0} + k_q' [Q]$$

$$k_{obs} = k^0 + k_q'[Q]$$

$$\tau_T^0 = \frac{1}{k_p + k_{ISC}' + k_r'}$$

$$\tau_T = \frac{1}{k_p + k_{ISC}' + k_r' + k_q'[Q]}$$

Stern-Volmer equation

Sensitized emission of Q

$$\frac{1}{\Phi_Q} = \frac{1}{\eta_Q}\left(1 + \frac{1}{k_q' \tau_T^0 [Q]}\right)$$

modified Stern-Volmer equation

$$\eta_Q = k''_e/(k''_e + k''_d + k''_r)$$

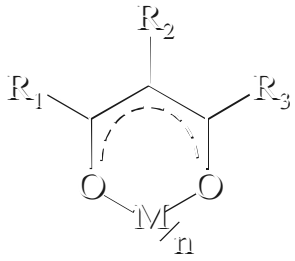
(observation of any process from Q* gives a direct evidence for the participation of energy transfer)

Quenching of triplet states of organic compoundes by lanthanide 1,3-diketonate chelates in solutions

1. B. Marciniak, M. Elbanowski, S. Lis,
   Monatsh. Chem. , **119**, 669-676 (1988)
   "Quenching of Triplet State of Benzophenone by Lanthanide 1,3-Diketonate Chelates in Solutions"

2. B. Marciniak, G. L. Hug
   J. Photochem. Photobiol. A: Chemistry, **78**, 7-13 (1994)
   "Energy Transfer Process in the Quenching Triplet States of Organic Compunds by 1,3-Diketonates of Lanthanides(III) and Magnesium(II) in Acetonitrile Solution. Laser Flash Photolysis Studies"

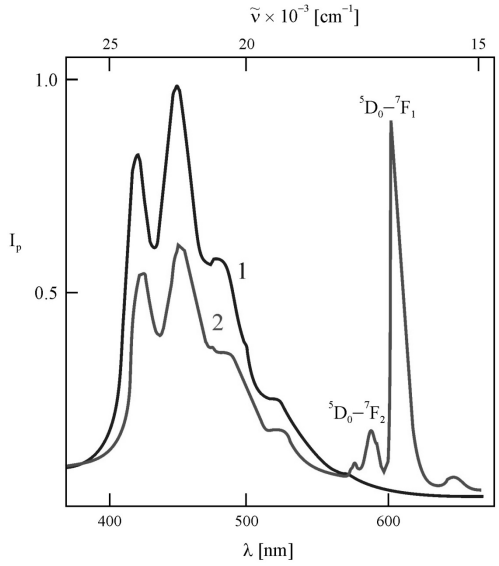
3. B. Marciniak, G. L. Hug
   Coord. Chem. Rev. , **159**, 55-74 (1997)
   "Quenching of Triplet States of Organic Compounds by 1,3-Diketonate Transition-Metal Chelates in Solution. Energy and/or Electron Transfer"



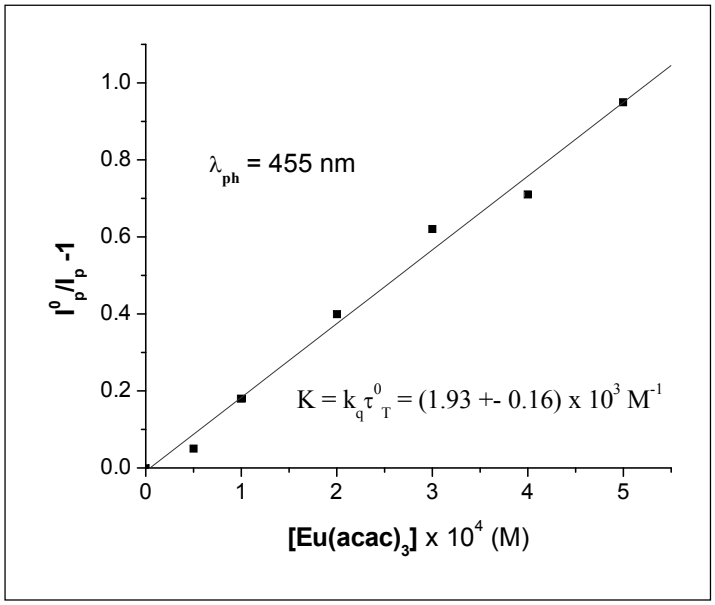
M = Ln (III) or Mg(II)

acac	hfac
$R_1 = R_3 = CH_3$	$R_1 = R_3 = CF_3$
$R_2 = H$	$R_2 = H$

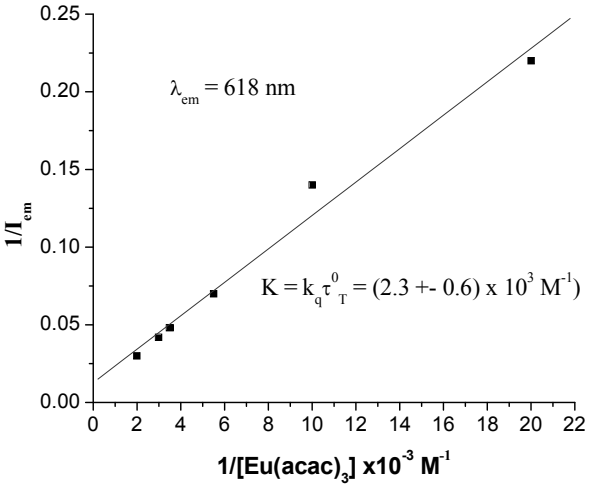
Benzophenone phoshorescence in the presence of $Eu(acac)_3$ (λ_{ph} = 455 nm)



Stern-Volmer plot for quenching of BP phosphorescence by $Eu(acac)_3$ in benzene



Modified Stern-Volmer plot for emission of $Eu(acac)_3$ in benzene



Results

for $Eu(acac)_3$:

quenching: $K = k_q \tau^0_T = (1.93 \pm 0.16) \times 10^3\ M^{-1}$

sensitization: $K = k_q \tau^0_T = (2.3 \pm 0.6) \times 10^3\ M^{-1}$

for $Tb(acac)_3$:

quenching: $K = k_q \tau^0_T = (1.70 \pm 0.15) \times 10^3\ M^{-1}$

sensitization: $K = k_q \tau^0_T = \sim 1.4 \times 10^3\ M^{-1}$

$$K_{quenching} = K_{sensitization}$$

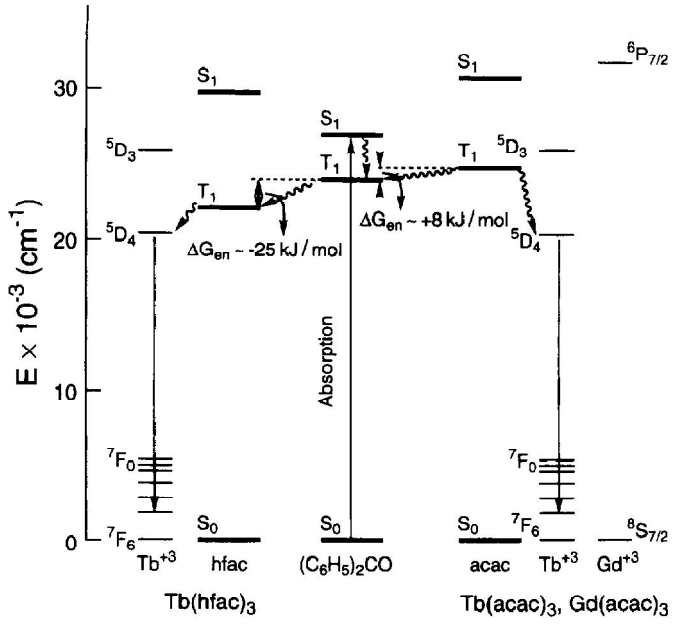
τ^0_T = constant

k_q (from quenching) $= k_q$ (from sensitized emission)

Conclusions

1. BP phosphorescence is quenched by $Ln(acac)_3$ (Ln= Sm, Eu, Gd, Tb, Dy) and $Mg(acac)_2$ with the rate constants $k_q \sim 9 \times 10^8\ M^{-1}s^{-1}$ (in acetonitrile).
2. k_q for quenching by Eu^{+3} and Tb^{+3} (perchlorates) are at least 5 times lower.
3. $k_q \sim 4 \times 10^9\ M^{-1}s^{-1}$ for quenching by $Eu(hfac)_3$
4. Similar k_q values obtained from the quenching and sensitization indicate the energy transfer process:

   $$A(T_1) + Q \rightarrow A + Q^*$$
5. Similar k_q values for all $Ln(acac)_3$ and $Mg(acac)_2$ used indicate the energy transfer from BP tiplet state to the ligand localized triplet state.



$$^3D^* + Q \rightarrow D + {}^3Q^*$$

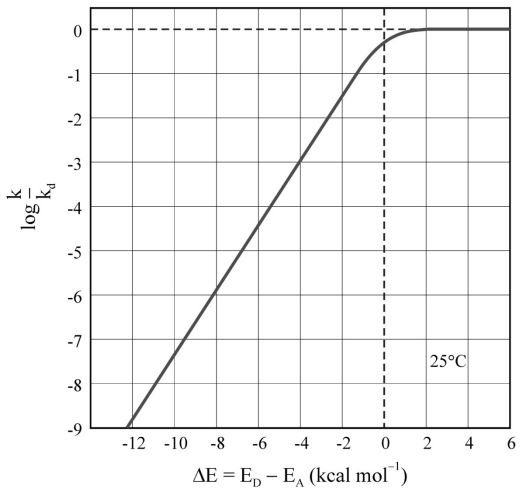
Energy transfer from BP tiplet state to the ligand localized triplet state

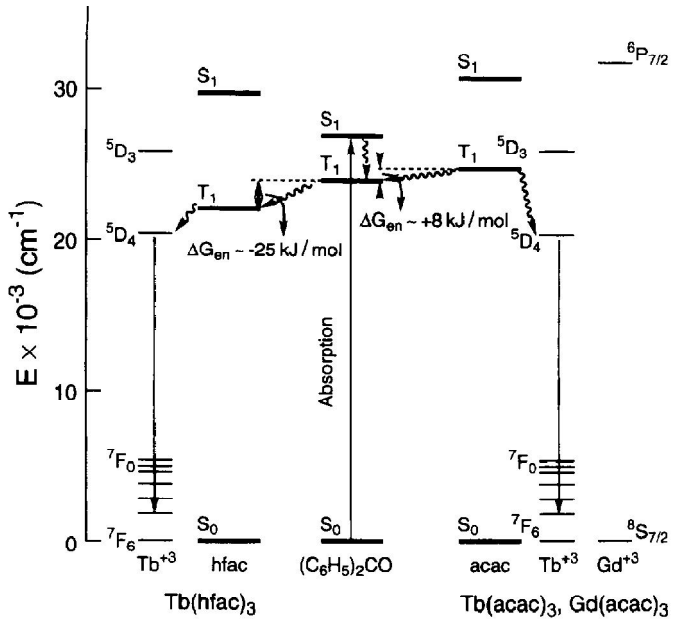
Sandros relation:

$$k_q/k_{dyf} = [1 + \exp -(E_T(D) - E_T(Q))/RT]^{-1}$$

Rates of energy transfer vs donor-aceeptor energy differences

$$k_q/k_{dyf} = [1 + \exp - \Delta E_T/RT]^{-1}$$

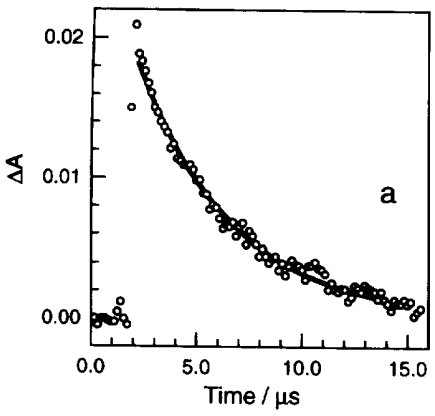


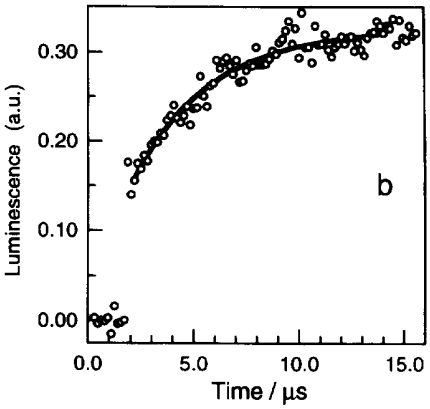


Quenching of triplet states of organic compoundes by lanthanide 1,3-diketonate chelates in solutions. Laser flash photolysis studies

Decay of BP triplet (λ_{TT}= 530 nm) and rise of Tb(III) emission (λ_e = 550 nm)

([BP] = 1 mM, [Tbacac)3 = 0.19 mM in MeCN)





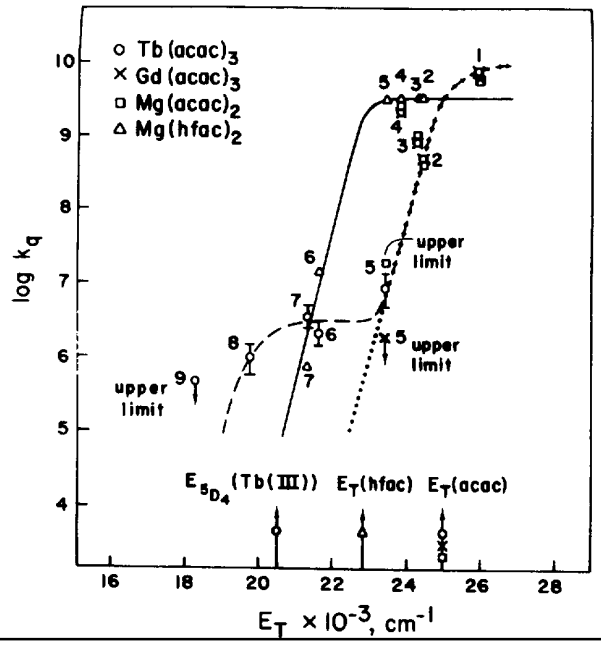
$k_{decay}=2.2\times10^5\ s^{-1}$ $k_{rise}=2.7\times10^5\ s^{-1}$

$$^3D^* + Q \rightarrow D + Q^*$$

Table 2
Rate constants for quenching of the triplet states of organic molecules by metal complexes in deoxygenated acetonitrile solution at room temperature (from [10])

No.	Molecule	$k_q \times 10^{-9}/M^{-1}\ s^{-1}$ [a]			
		$Tb(acac)_3$	$Gd(acac)_3$	$Mg(acac)_2$	$Mg(hfac)_2$
1	Xanthone	7.6	7.4	5.5	5.4
2	4,4′-Dimethoxybenzophenone	0.47	0.44	0.44	3.2
3	Benzophenone	0.92	0.86[b]	1.1	3.3
4	4-Trifluoromethylbenzophenone	2.2	2.2	2.7	3.2
5	Triphenylene	0.01[c]	≤0.002	≤0.02	3.1
6	Phenanthrene	0.002[c]	≤0.001	–	0.015
7	Naphthalene[d]	0.003[c]	≤0.001	–	0.0008[c]
8	Chrysene	0.001[c]	–	–	–
9	Dibenz[*a*,*h*]anthracene	≤0.0005	–	–	–

Dependence of k_q on E_T



$$^3D^* + {}^mQ \underset{k_{-d}}{\overset{sk_d}{\rightleftarrows}} {}^n(D^*...Q) \underset{k_{-en}}{\overset{k_{en}}{\rightleftarrows}} {}^n(D...Q^*) \xrightarrow{k_{-d}} {}^1D^* + {}^nQ^*$$

s = n/3m (spin statistical factor)

$$\ln(k_{en}/k_{-en}) = -\Delta G_{en}/RT$$

$$\boxed{\Delta G_{en} = -\,Nhc\,[\bar{\nu}_{0\text{-}0}(^3D^*) - \bar{\nu}_{0\text{-}0}(^nQ^*)\,]}$$

$$k_q^{en} = sk_d\left[1 + \frac{k_{-d}}{k_{en}^0}\exp\left(\frac{\Delta G_{en}^{\neq}}{RT}\right) + \exp\left(\frac{\Delta G_{en}}{RT}\right)\right]^{-1}$$

ΔG_{en} and ΔG_{el} - the standarg free-energy changes for energy- and electron transfer processes

$\Delta G^{\neq}_{en}$ and $\Delta G^{\neq}_{el}$ - thre free energy of activation for energy- and electron transfer processes

k_d - the diffusion rate constant

k_{-d} - the dissociation rate constant for the encounter complex

$$k_{en(el)} = k^0_{en(el)} \exp\left(\frac{-\Delta G^{\neq}_{en(el)}}{RT}\right)$$

$$k^0_{en(el)} = \kappa_{en(el)} k_B T/h$$

κ_{en} and κ_{el} - transmission coefficients

k^0_{en} and k^0_{en} - preexponential factors

Limiting value of k_q (plateau value):

$$k_q^{pl} = \frac{s k_d k^0_{en(el)}}{k^0_{en(el)} + k_{-d}}$$

k_d is the diffusion rate constant

$\boxed{k_d = 8000RT/3\eta}$ (Debye equation)

k_{-d} is the dissociation rate constant for the encounter complex

$\boxed{k_{-d} = 3000k_d/4\pi r^3 N_0}$ (Eigen equation)

for CH_3CN at room temperature:

$k_d = 1.9 \times 10^{10}\ M^{-1}\ s^{-1}$

$k_{-d} = 2.2 \times 10^{10}\ s^{-1}$ (r = 7A)

Energy transfer
to ligand-localized triplet states of $Tb(acac)_3$, $Gd(acac)_3$, $Mg(acac)_2$, and $Mg(hfac)_3$

taking:

$k_q^{pl} = (3\text{-}7) \times 10^9\ M^{-1}\ s^{-1}$
(for energy transfer to acac or hfac triplet states)

$s = 1$ (^1Q and $^3Q^*$)

$k^0_{en} \sim 5 \times 10^9\ s^{-1}$

$\kappa_{en} \sim 1 \times 10^{-3}$

Energy transfer to ff level of $Tb(acac)_3$*

taking:

$k_q^{pl} = 3 \times 10^6\ M^{-1}\ s^{-1}$

(for energy transfer to Tb(III) $^5D_4$ level)

$s = 5/21$

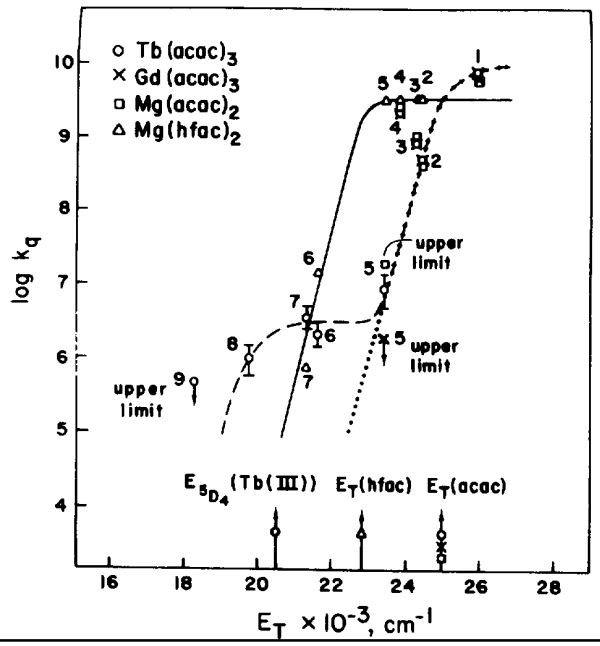
(Q and Q* are $^7F_6$ and $^5D_4$ level)

$k^0_{en} = 1.5 \times 10^7\ s^{-1}$

$\kappa_{en} = 2.4 \times 10^{-6}$

(three order of magnitude lower than for energy transfer to ligand-localized triplet states)

Dependence of k_q on E_T



Conclusions

1. Quenching of the triplet states of organic compounds by by lanthanide(III) and magnesium(II) 1,3-diketonates in MeCN is adequately described by energy transfer to the excited ff states of lanthanide complexes or by energy transer to the ligand-localized triplet states.

2. The values of transmission coefficients for energy transfer to the ff* states are in the range of 10^{-6}, and are three order of magnitude lower than those for energy transfer to ligand-localized triplets.

3. In the case of BP derivatives, an additional quenching process, *i.e.* electron transfer from acac ligand to the BP triplet may occur.