Fotochemia – *zagadnienia*

1. Spektroskopia UV/VIS – widma absorpcji i prawa absorpcji.

2. Stany elektronowo wzbudzone cząsteczek.

3. Wewnątrzcząsteczkowe i międzycząsteczkowe procesy fizycznej dezaktywacji stanów elektronowo wzbudzonych: fluorescencja i fosforescencja, wygaszanie stanów wzbudzonych.

4. Mechanizm przeniesienia energii wzbudzenia i przeniesienia elektronu.

5. Reakcje fotochemiczne – typy reakcji, wydajność kwantowa reakcji fotochemicznej.

6. Aparatura i metody stosowane w nowoczesnych badaniach fotochemicznych i fotofizycznych.

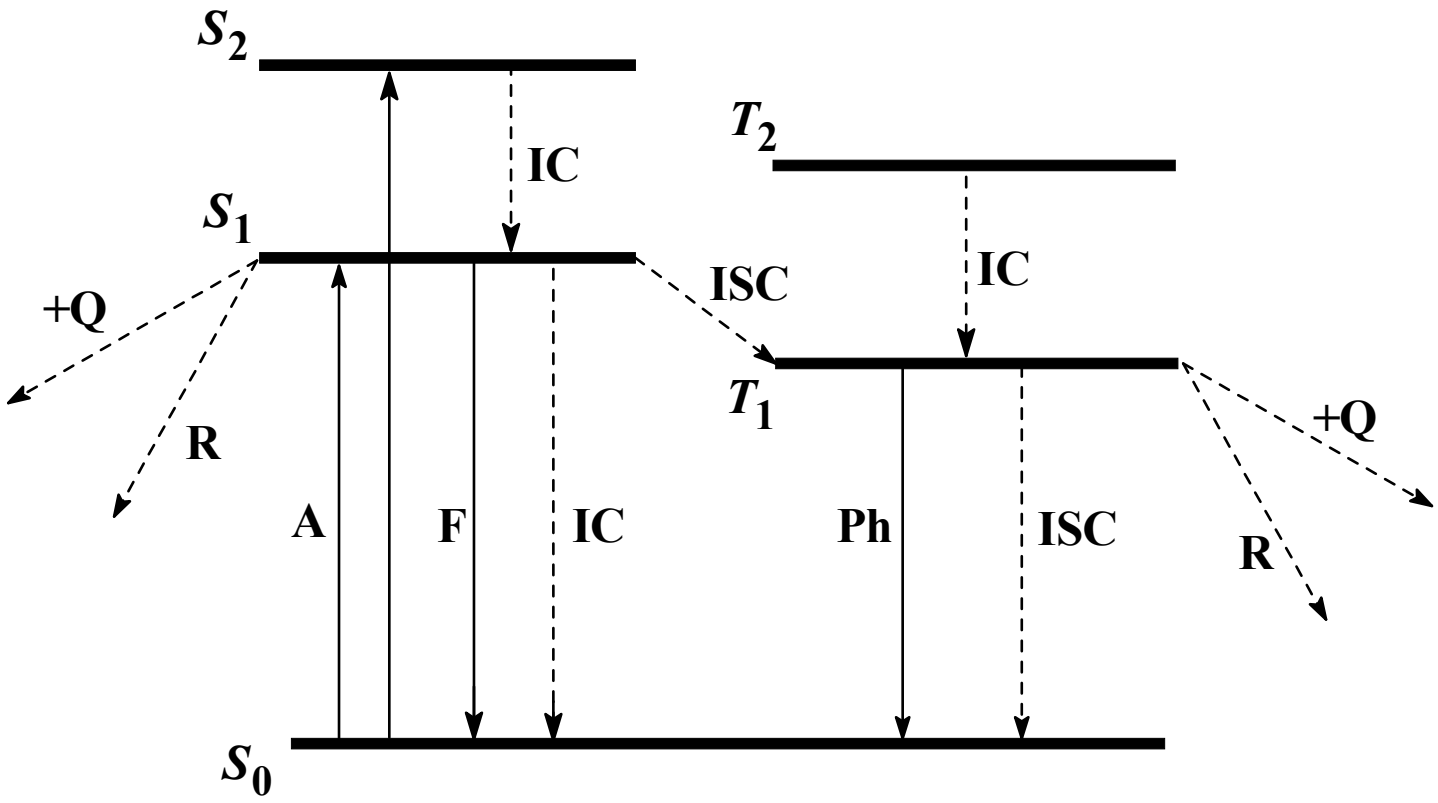
7. Mechanizmy wybranych reakcji fotochemicznych.

8. Zastosowanie procesów fotochemicznych.

PRZYKŁADY

Przeniesienie energii i przeniesienie elektronu

Jabłoński diagram



Intermolecular Excited-State Reactions

- Energy Transfer

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

- Electron Transfer

$$D^* + Q \rightarrow D^{+\bullet} + Q^{-\bullet}$$
$$D^* + Q \rightarrow D^{-\bullet} + Q^{+\bullet}$$

- Hydrogen Abstractions

Note:
Have to have excited states
that live long enough
to find quenching partner
by diffusion

Kinetic of quenching

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

Kinetic of quenching
Energy transfer

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

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)

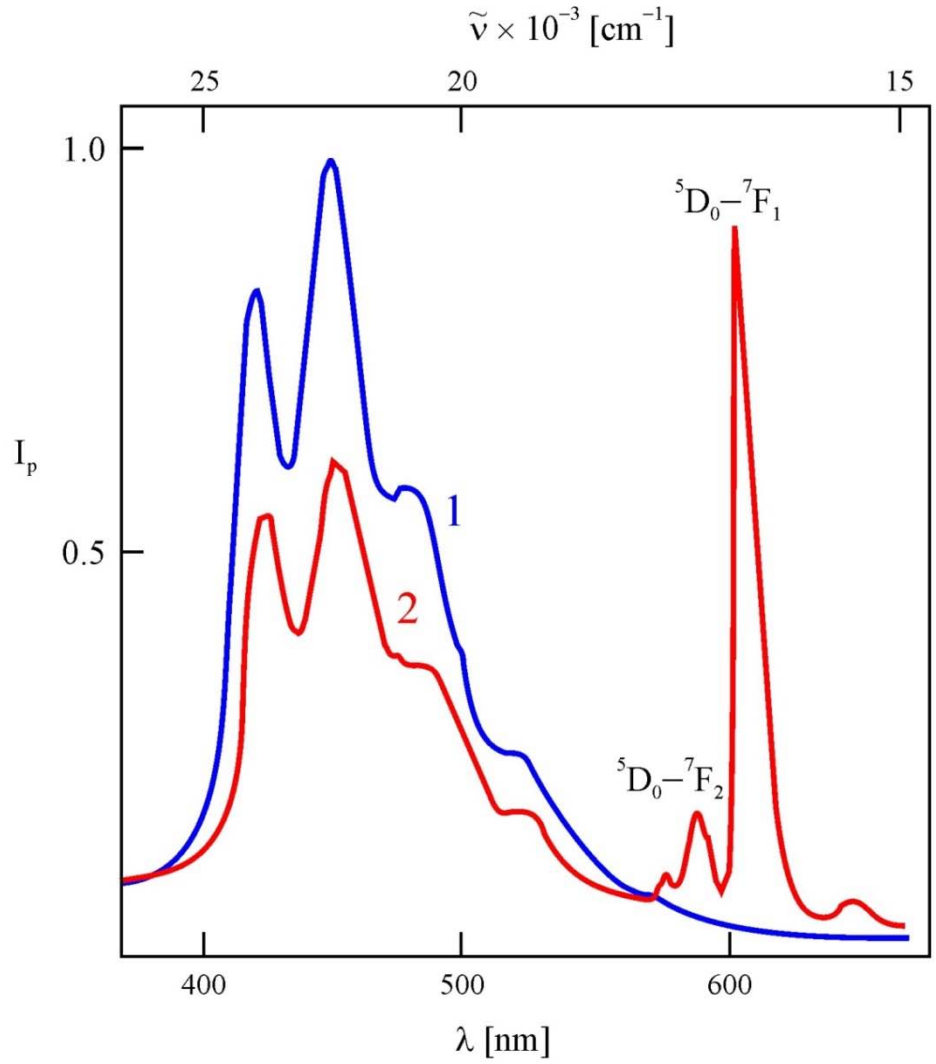
Energy transfer – example

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

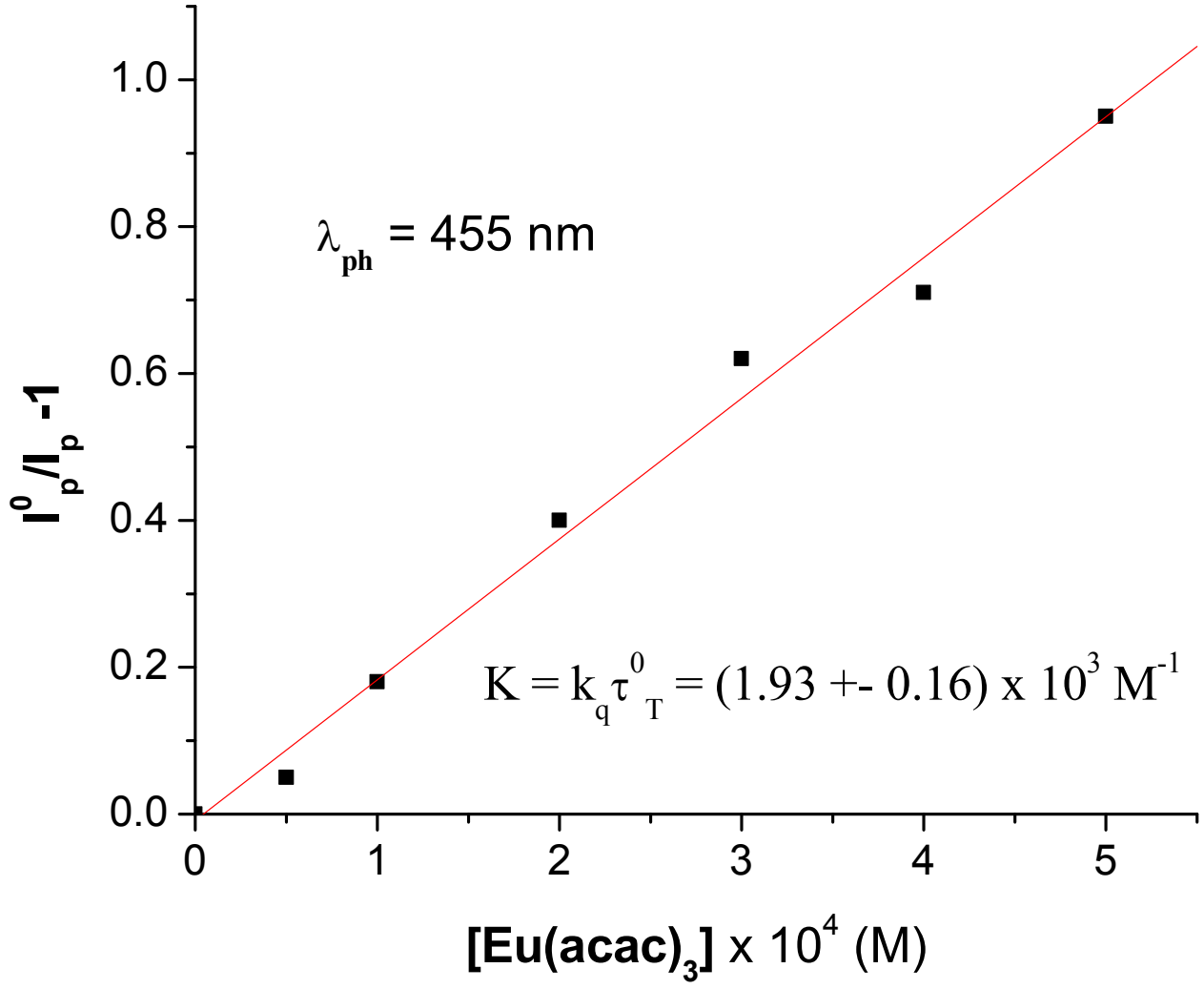
B. Marciniak, G. L. Hug, *J. Photochem. Photobiol. A: Chemistry*, **78**, 7-13 (1994)

B. Marciniak, G. L. Hug *Coord. Chem. Rev.* , **159**, 55-74 (1997)

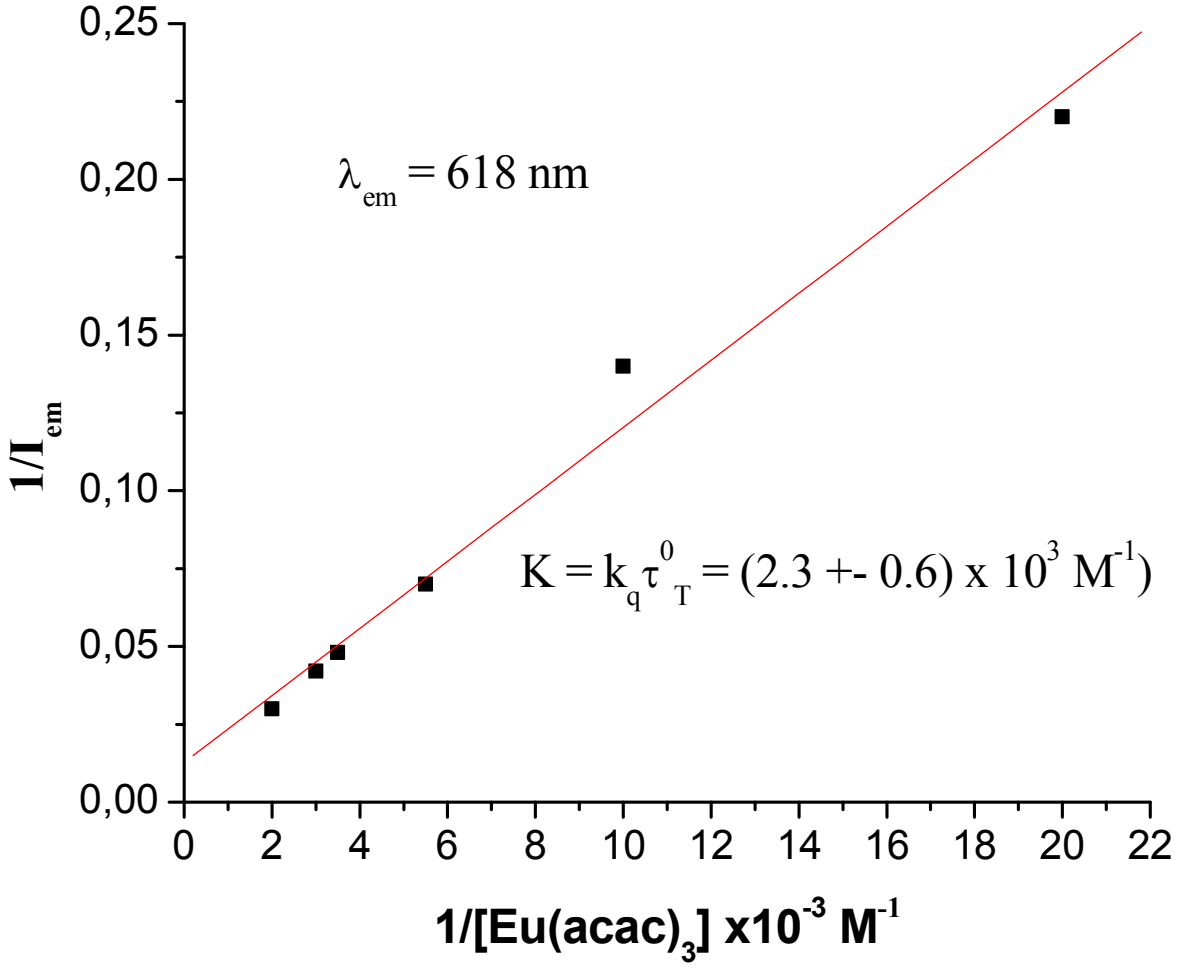
Benzophenone phoshorescence in the presence of $Eu(acac)_3$ (λ_{ph} = 455 nm)



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



for $Eu(acac)_3$:

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

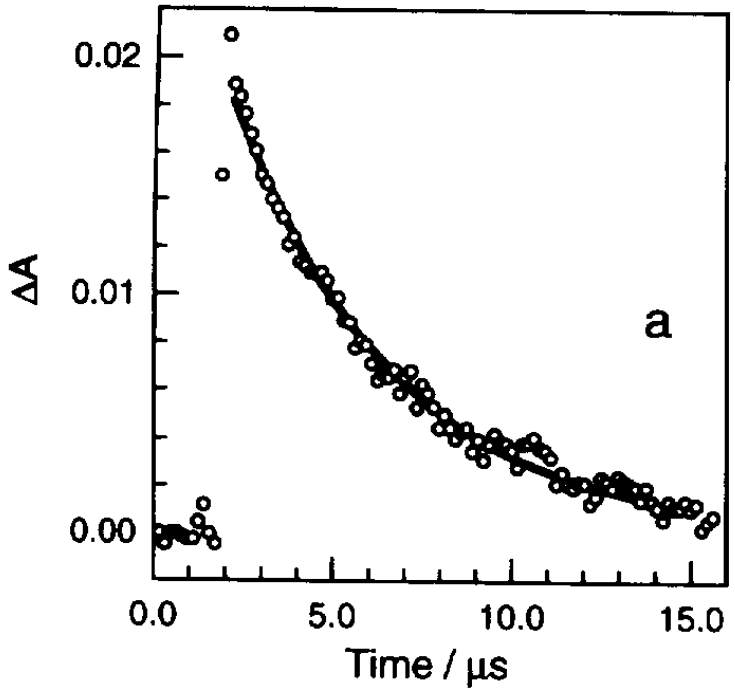
sensitization: $K = k_q \tau^0_T = (2.3 \pm 0.6) \times 10^3\ M^{-1}$

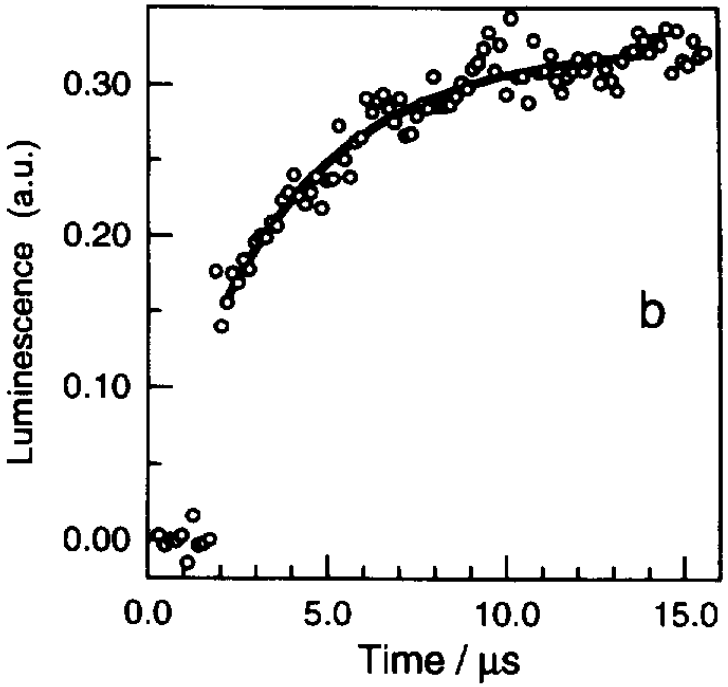
$$K_{quenching} = K_{sensitization}$$

$$\tau^0_T = \text{constant}$$

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

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





$k_{decay} = 2.2 \times 10^5\ s^{-1}$

$k_{rise} = 2.7 \times 10^5\ s^{-1}$

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

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

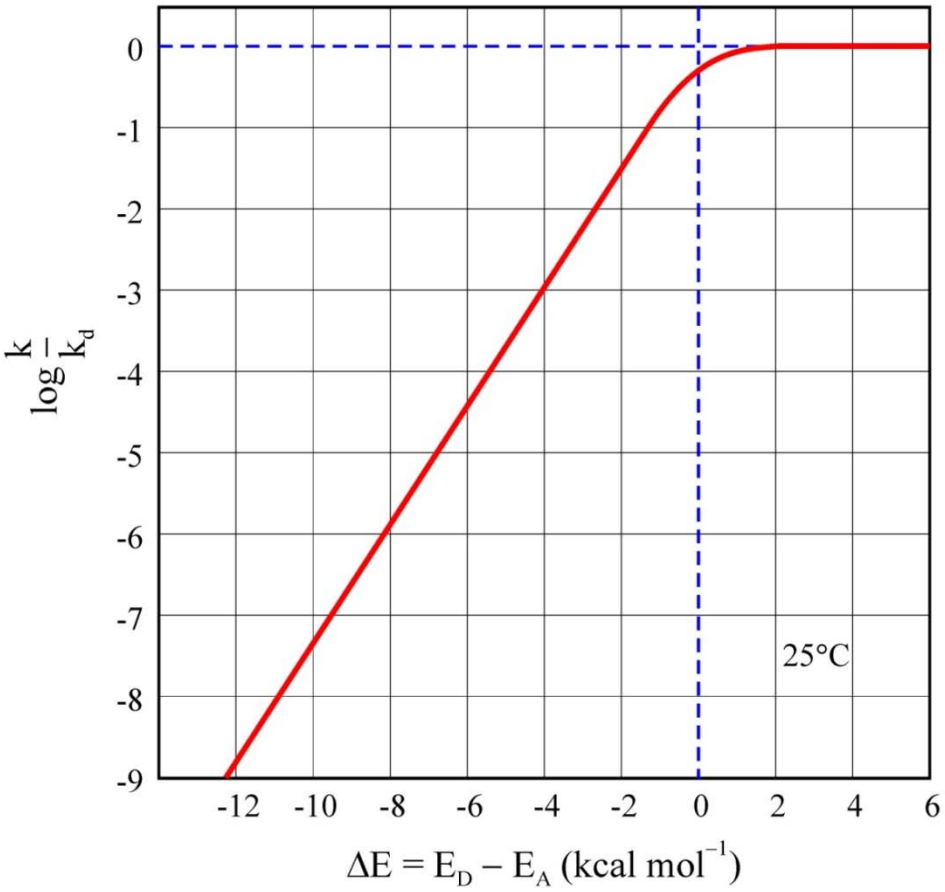
Energy transfer from benzophenone tiplet state to the ligand localized triplet state

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

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

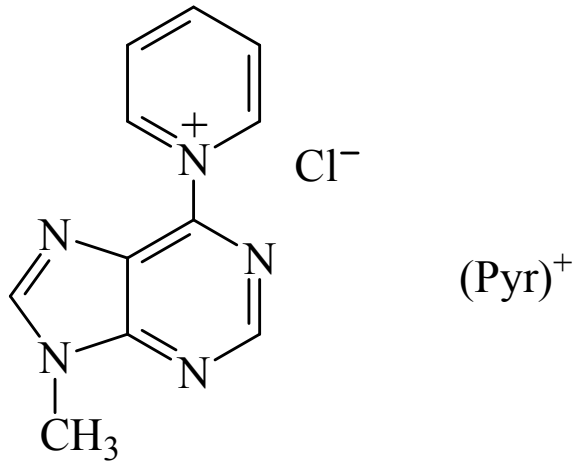


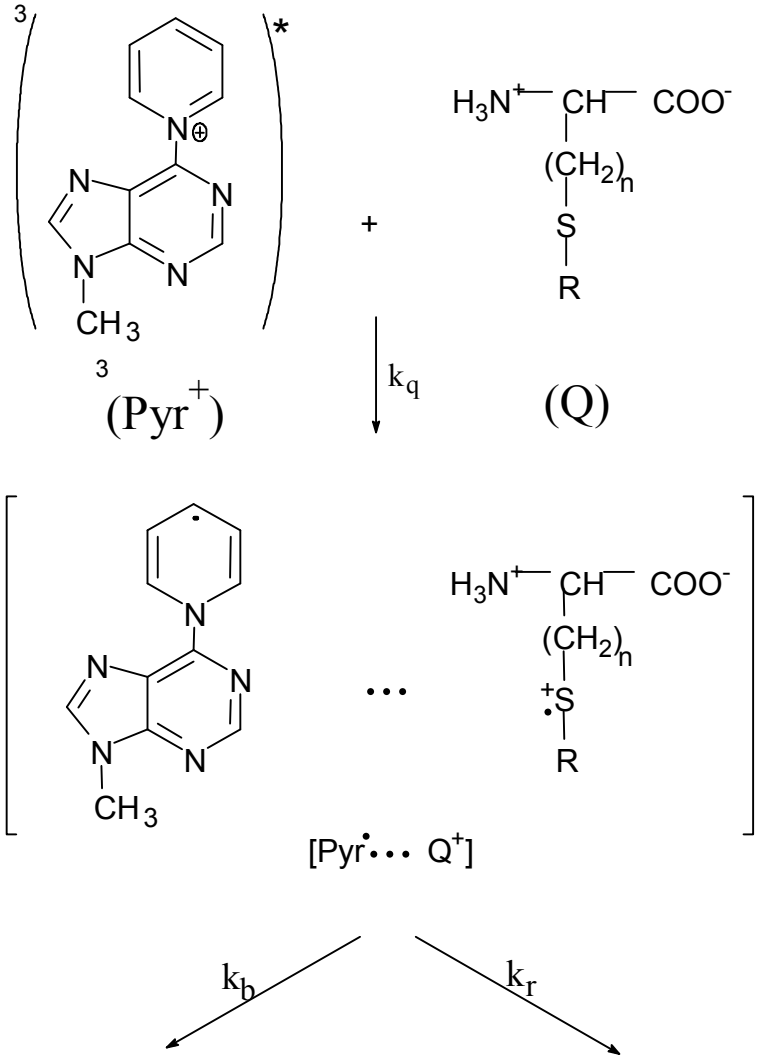
Electron transfer – example

$$D^* + Q \rightarrow D^{-\bullet} + Q^{+\bullet}$$

Excited Tripet State of N-(9-Methylpurin-6-yl)pyridinium Cation as an Efficient Photosensitizer in the Oxidation of Sulfur-Containing Amino Acids

(B. Marciniak, G.L. Hug, J. Rozwadowski, K. Bobrowski, *J. Am. Chem. Soc.*, **117**, 127 (1995))





3
*
N⊕
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3
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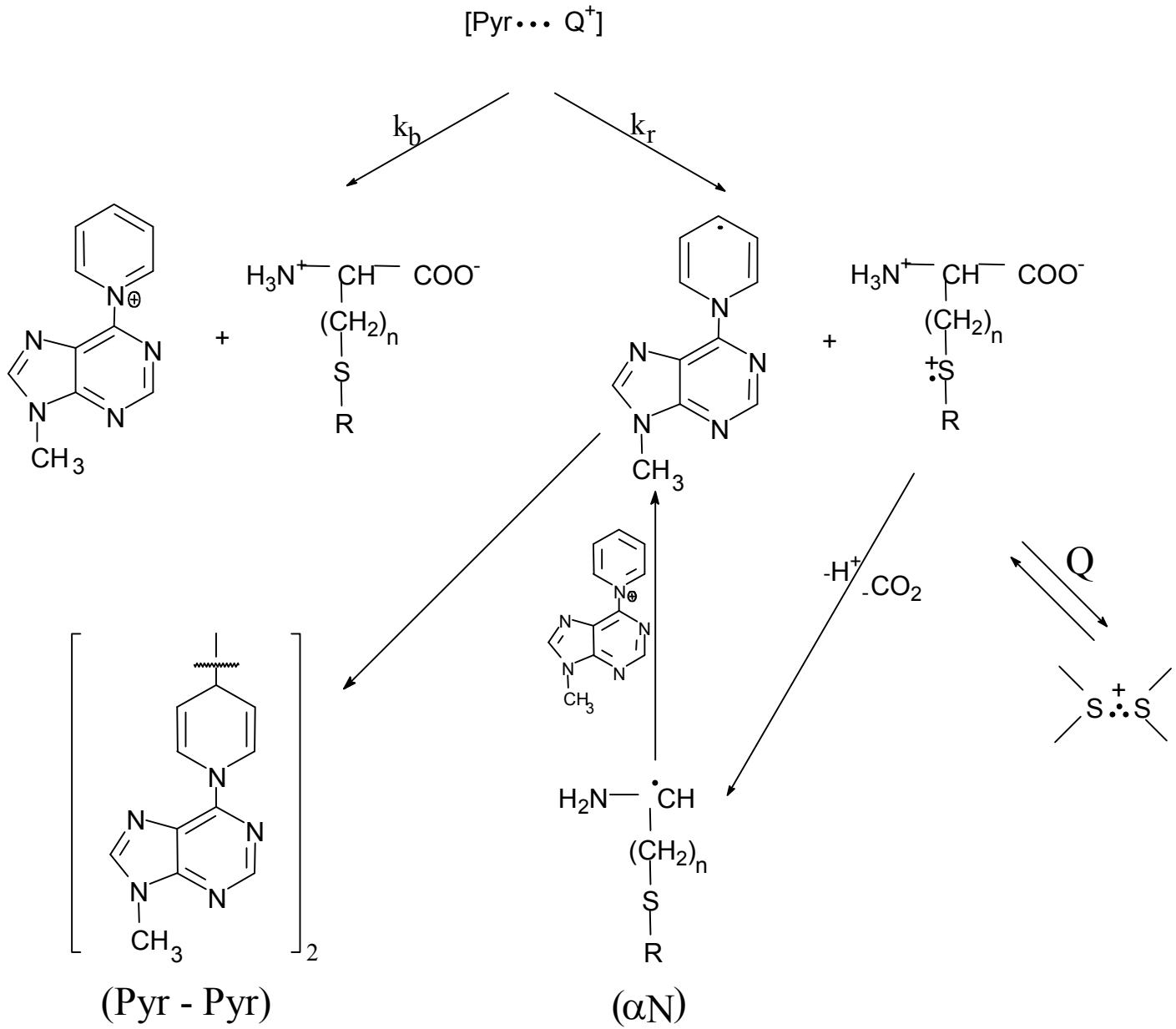

[Pyr••• Q+]
kb
kr
H3N+ CH COO-
(CH2)n
S
R
N⊕
N
CH3
+
-H+
-CO2
Q
S∴S+
H2N CH
(Pyr - Pyr)
(αN)

Steady-state Photolysis

1. Identification of stable products:

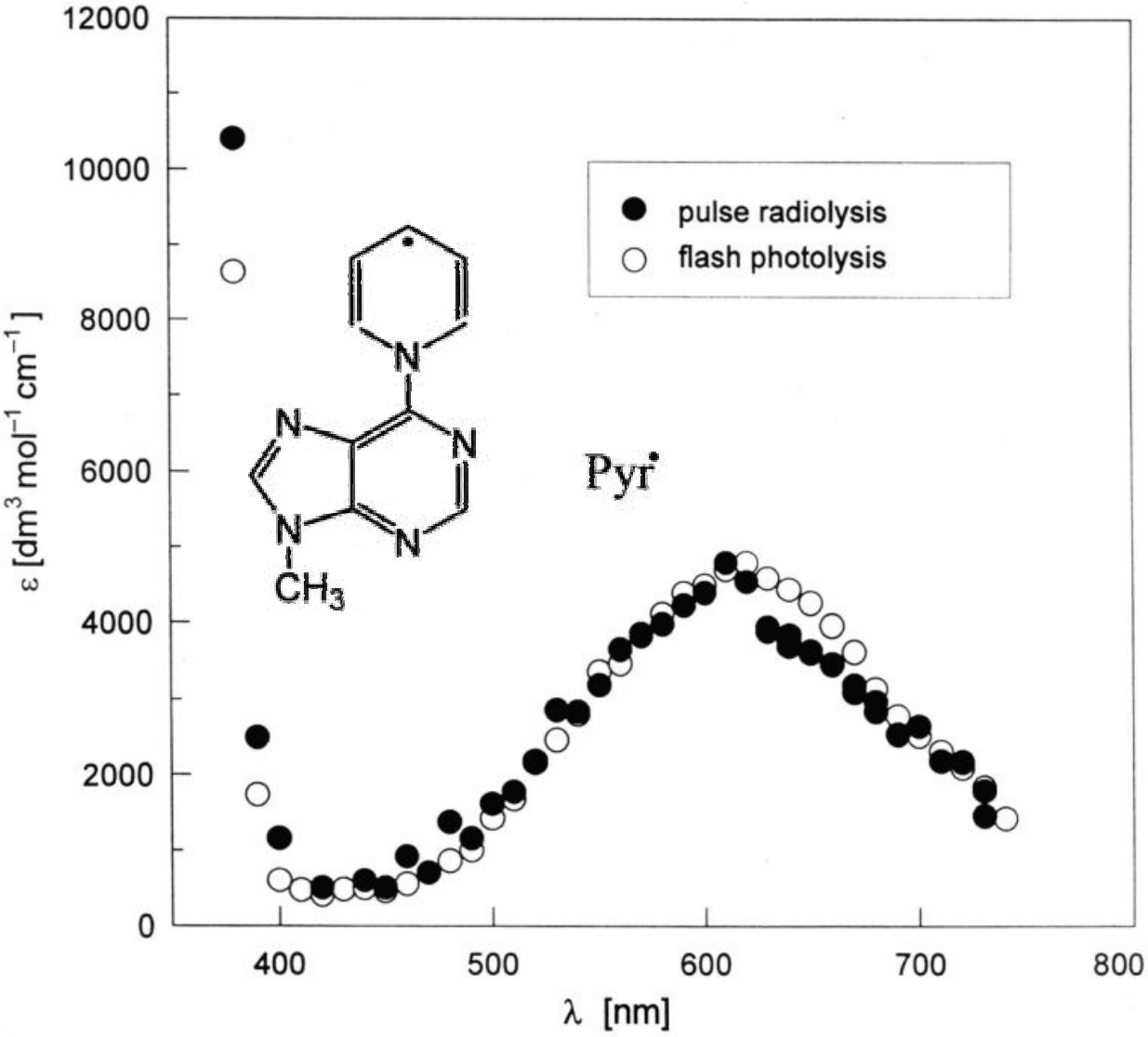
   Pyr-Pyr dimer

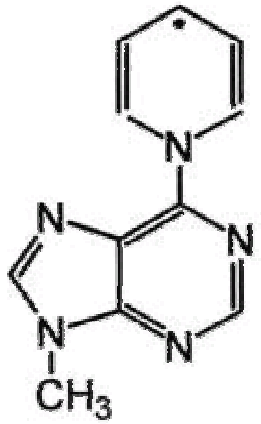
   CO_2

2. Quantum yields:

   Φ_{Pyr^+} and Φ_{CO_2}

Short-lived reactive itermediate Pyr•





Pyr•

1) Flash photolysis:

([Pyr^+] = 2×10^{-4} M, [Q] = 0.01 M, pH = 6.5)

λ_{max} = 610 nm

$\varepsilon_{max} = 5.4 \times 10^3\ M^{-1}cm^{-1}$

(el. transfer quenching by DMA
for DMA^+ e_{470} = 4 500 $M^{-1}cm^{-1}$
Holcman et al. 1977)

2) Pulse radiolysis:

$Pyr^+ + e_{aq} \rightarrow Pyr^\bullet$ ($k = 4 \times 10^{10}\ M^{-1}s^{-1}$)

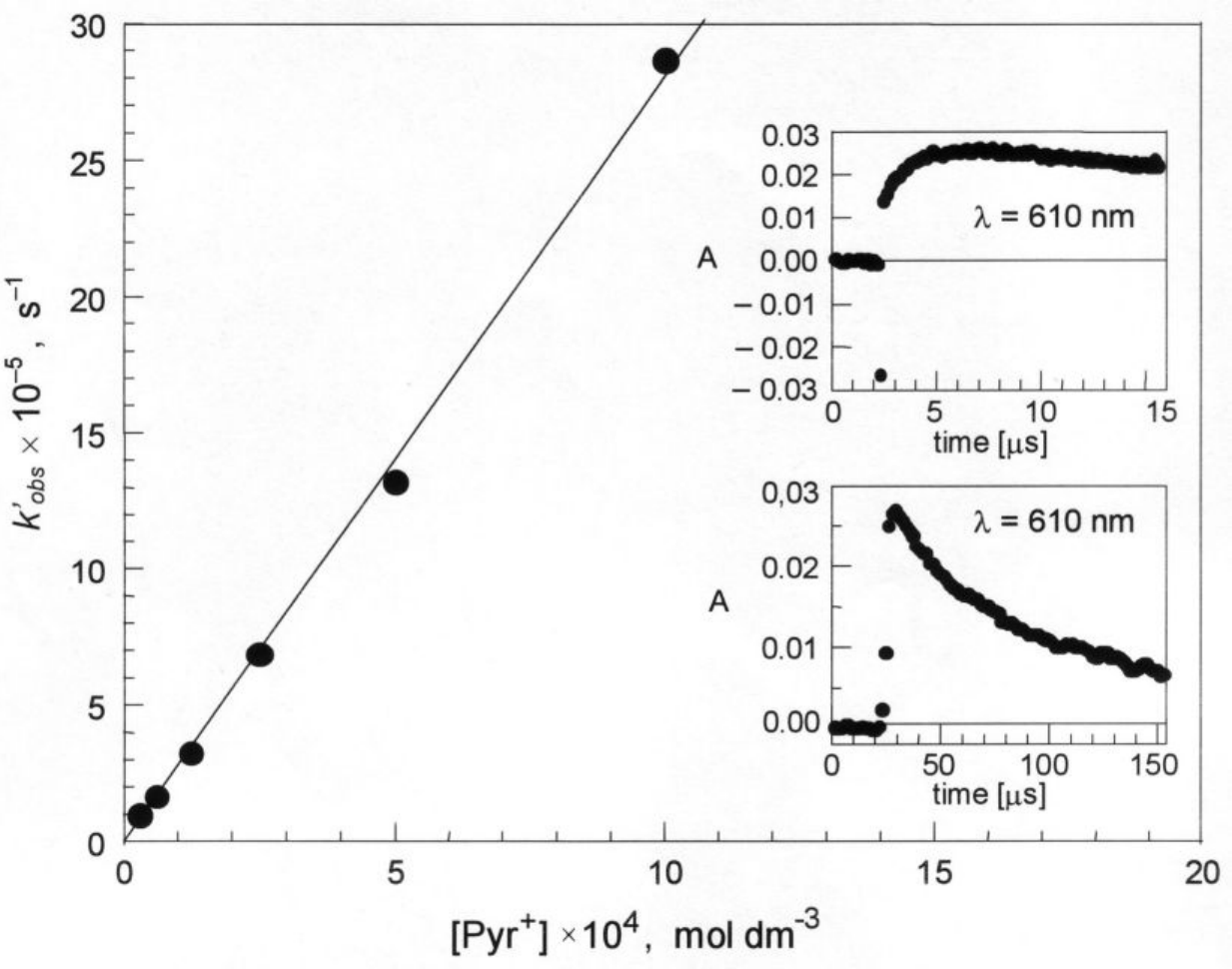
λ_{max} = 610 nm

$\varepsilon_{max} = 4.8 \times 10^3\ M^{-1}cm^{-1}$

Secondary reactions of Pyr^+

$$Pyr^+ + \alpha N \rightarrow Pyr^{\bullet} + Products$$

For thiaproline: $Pyr^+ + \alpha N \rightarrow Pyr^\bullet$ + Products



$$H_2N{-}\dot{C}H{-}R + Pyr^+ \longrightarrow H_2\overset{+}{N}{=}CH{-}R + Pyr^\bullet$$

$$H_2N{=}CH{-}R \xrightarrow{H_2O} \text{Products}$$

Table
Quantum yields for $Pyr^{\bullet}$ formation and Pyr^{+} disappearance

	flash photolysis			steady-state photolysis	
quencher	$\Phi_{Pyr^{\bullet}}$ a)	$\Phi'_{Pyr^{\bullet}}$ a)	$\Phi_{Pyr^{\bullet}}$ sum b)	$\Phi_{Pyr^{+}}$	$\Phi_{Pyr^{+}}/\Phi_{CO_2}$
thiaproline	0.31	0.32	0.63	0.61 a)	1.8
methionine	0.27	d)	0.27	0.20 b)	2.5
2,2'-thiodi-ethanoic acid	–	–	–	0.15 c)	1.1

a) experimental error ±10%
b) sum $\Phi_{Pyr^{\bullet}} + \Phi'_{Pyr^{\bullet}}$
c) experimental error ±10%
d) not observed

Conclusions

1. The electron transfer from the sulfur atom to the triplet state of Pyr^+ was a primary photochemical reaction:

   - direct observation of electron transfer intermediates $Pyr^{\bullet}$ and $(S\therefore S)^+$ dimer
   - detection of Pyr-Pyr (stable product)
   - $k_q \sim 2\times10^9\ M^{-1}s^{-1}$ for quenching by sulfur-contaiting amino acids
   - $k_q \sim 10^6\ M^{-1}s^{-1}$ for quenching by alanine
   - $\Delta G_{el} \sim -100$ kJ/mol

Conclusions

2. The slow formation of $Pyr^{\bullet}$ radicals (on microsecond time scale) was assigned to the one-electron reduction of Pyr^{+} by the α-aminoalkyl radicals (αN) produced in the decarboxylation of $S^{+\bullet}$ radicals

$$Pyr^{+} + \alpha N \rightarrow Pyr^{\bullet} + \text{products}$$

- linear dependence of pseudo-first order rate constant k_{obs} vs. $[Pyr^{+}]$
- generation of αN radicals and their kinetic studies in the complementary pulse radiolysis experiments

Standard free energy change for electron transfer (the driving force for the process)

$$\Delta G_{el} = F(E_{ox} - E_{red}) - E_T + \Delta w$$

for Pyr^+ : $E_{red} = -0.57$ V

$E_T = 268$ kJ/mol (64 kcal/mol)

for methionine: $E_{ox} = 1.1$ V

$\Delta w = 0$

$\Delta G_{el} = -107$ kJ/mol