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

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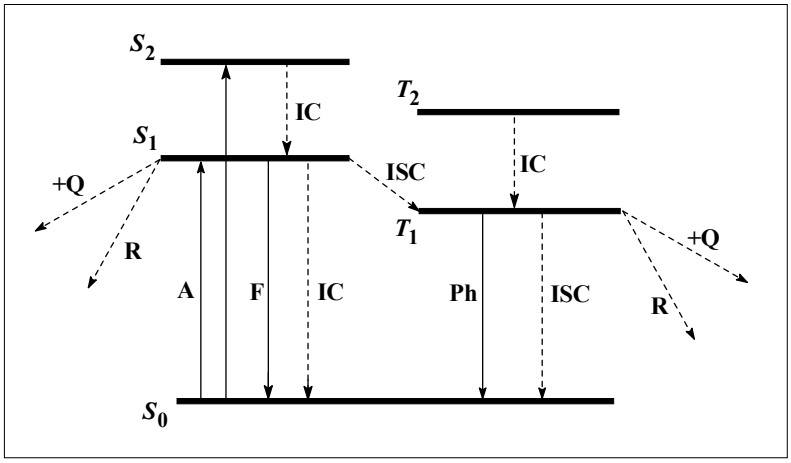
4. Example illustrating the investigation of photoreaction mechanisms:
   - sensitized photooxidation of sulfur (II)-containing organic compounds.

2. Qualitative investigation of photoreaction mechanisms - steady-state and time resolved methods

- analysis of stable products
- identification of short-lived reactive intermediates
- identification of the excited states responsible for photochemical reactions

Jablonski diagram



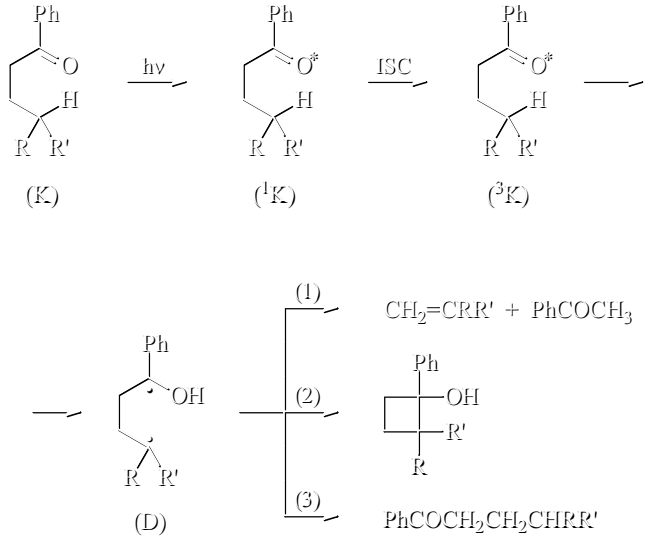
Scheme of photochemical reaction

$$A \xrightarrow{h\nu} A^* \longrightarrow I \longrightarrow B + C$$

Intermediates — *Stable products*

- analysis of stable products
- identification of short-lived reactive intermediates
- identification of the excited states responsible for photochemical reactions

Norrish type II Photoreaction



Analysis of stable products

$$A \xrightarrow{h\nu} A^* \longrightarrow I \longrightarrow B + C$$

1. Preparative irradiations
2. Product analysis: GC, HPLC, TLC, GCMS, LCMS, spectroscopic methods etc.
3. Separation of products from the reaction mixture:
   - prepartative GC, HPLC, TLC,
   - column chromatography
   - other methods
4. Identification of separated products: spectroscopic methods: IR, NMR, UV-Vis, Fl, MS, elemental analysis etc.

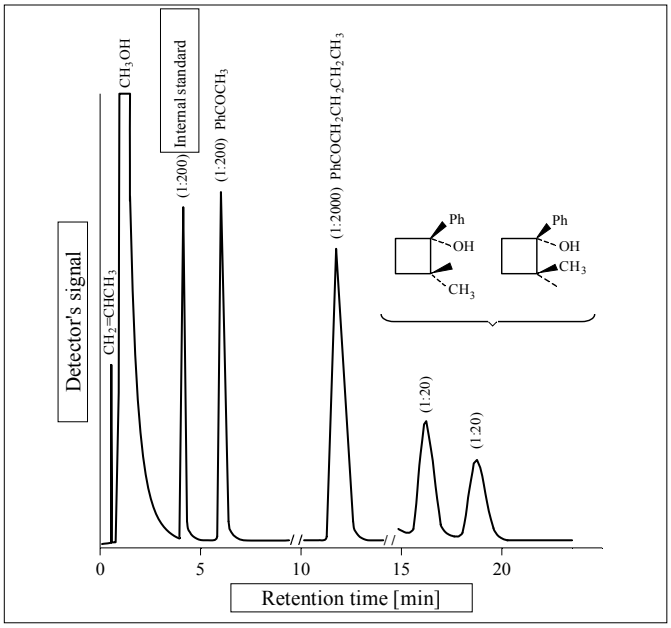
Note:

Separated products can be used as reference samples in the quantitative analysis

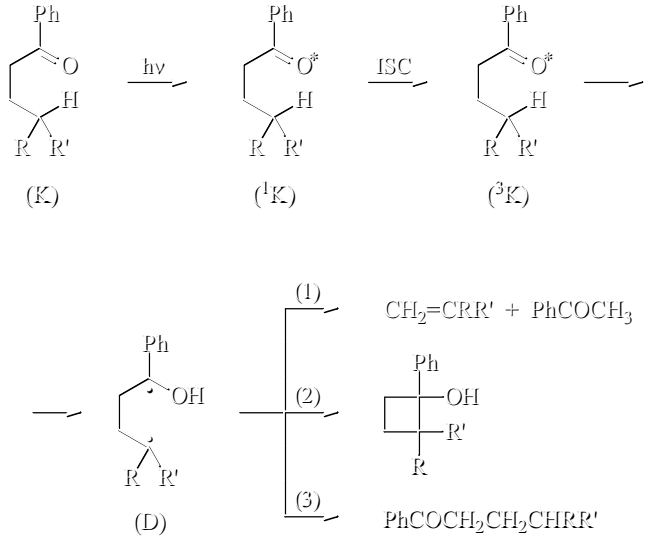
Analysis of stable products – example

Norrish type II photoreaction of valerophenone (0.1 mol/dm3)
in methanol
$\lambda_{irr} > 300$ nm

$$C_6H_5COCH_2CH_2CH_2CH_3 \xrightarrow{h\nu} C_6H_5COCH_3 + CH_2{=}CHCH_3 + \text{cyclobutanol derivative}$$



Norrish type II Photoreaction



$$A \xrightarrow{h\nu} A^* \longrightarrow I \longrightarrow B + C$$

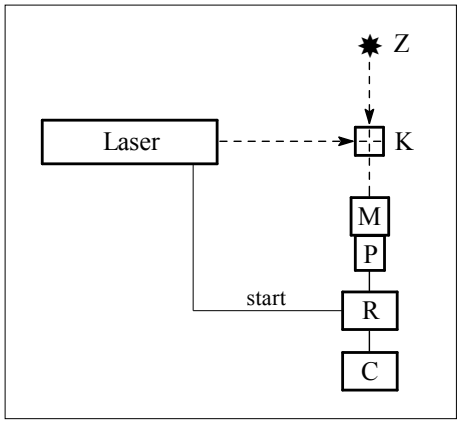
Identification of short-lived reactive intermediates

1. Spectroscopic methods - flash photolysis
   - UV-Vis absorption and emission
   - IR
   - NMR (CIDNP)
   - EPR

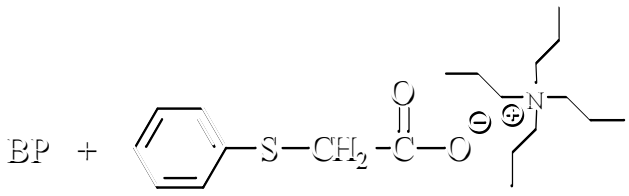
2. Chemical methods

3. Kinetic methods

ns laser flash photolysis



Benzophenone–(Phenylthio)acetic Tetrabutylammonium Salt



Sovent: CH_3CN

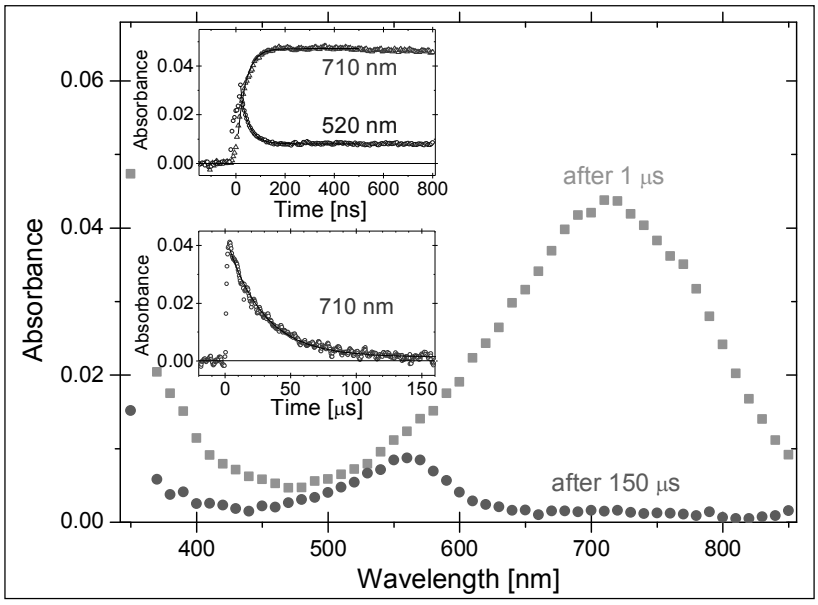
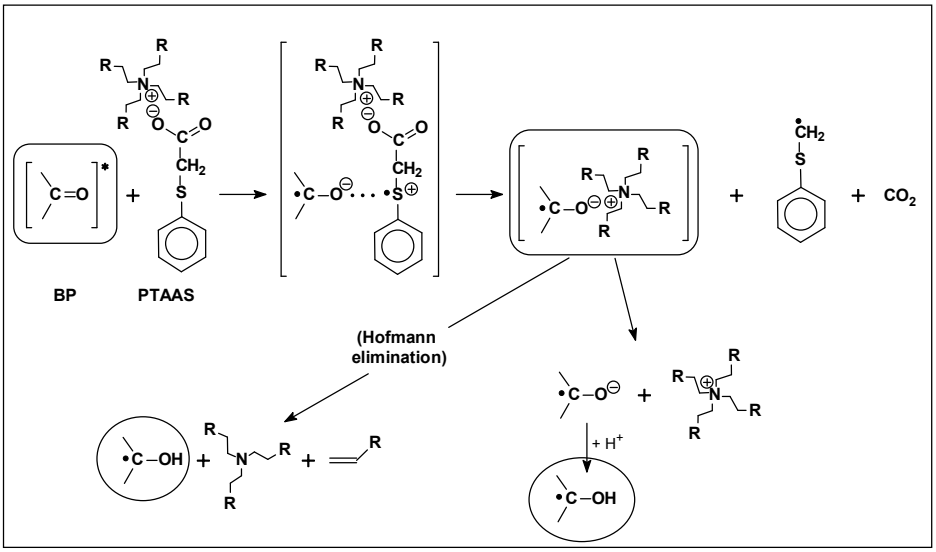
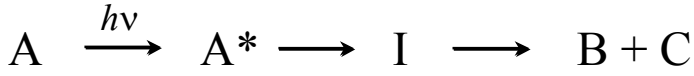


Fig. Transient absorption spectra following triplet quenching of BP (2 mM) by C_6H_5-S-CH_2-$COO^-N^+R_4$ (10 mM) after 1 μs and 150 μs delays after the flash in MeCN solution. Insets: kinetic traces on the nanosecond and microsecond time scales

Reaction scheme





Identification of short-lived reactive intermediates

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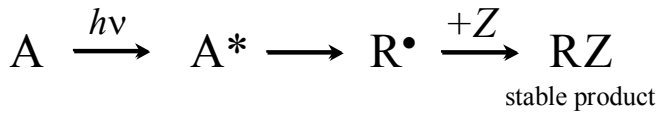
Identification of short-lived reactive intermediates

2. Chemical methods - chemical trapping



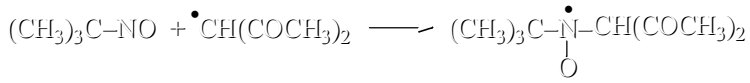
Scavenger (Z) of free radicals:
- does not absorb excitation light
- selectively react with R• with a large rate
- does not react with A, A* and RZ
- does not affect the mechanism of RZ formation
- form RZ easy to detect.

Typical scavengers: O_2, alkenes, RNO, I_2

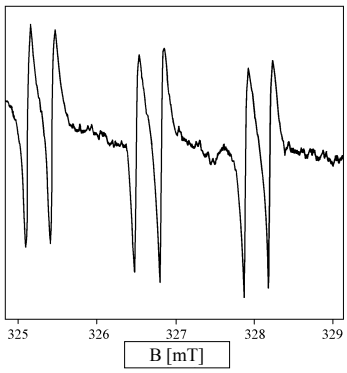
2. Chemical methods - example

Y.L. Chow, G. Buono-Core, *J. Am. Chem. Soc.* **108**, 1234, (1986)
„Role of the Acetylacetonyl Radical in the Sensitized Photoreduction of Bis(acetylacetonato)copper(II)"

Spin trapping of acetylacetonyl radicals (acac$^\bullet$):



EPR spectrum of the benzophenone-sensitized photoreduction of $Cu(acac)_2$, in the presence of 2-nitroso-2-methylpropane measured after two-minute irradiation of a methylene chloride solution of $Cu(acac)_2$ (1mM), 2-nitrozo-2-methylpropane (2 mM), and benzophenone (5 mM), hyperfine splitting constants:
a_N = 1.363 mT, a_H = 0.315 mT
and g = 2.0062.



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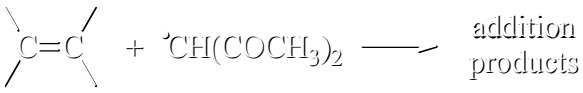
Trapping of acac$^\bullet$ with alkenes:

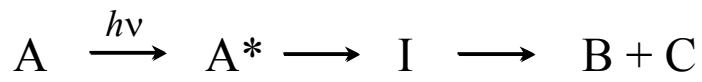


RZ product analysis: GCMS and NMR, IR

Conclusion: acac$^\bullet$ was proved to be the reactive intermediate in the sensitized photoreduction of $Cu(acac)_2$.

Different Actions of Scavengers

- Direct capture of free radicals.
- Repair of damage caused by radicals.
- This second mechanism is important for the repair of damage by free radicals in biological systems.



Identification of short-lived reactive intermediates

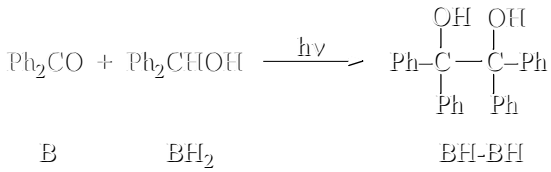
1. Spectroscopic methods - flash photolysis
   - UV-Vis absorption and emission
   - IR
   - NMR (CIDNP)
   - EPR

2. Chemical methods

3. Kinetic methods

3. Kinetic methods

Example (N.J. Turro, Modern Molecular Photochemistry, p. 261,
„Involvement of T_1 (n,π*) of benzophenone as the chemically reactive agent in the photoreduction of benzophenone by benzydrol"



B	→	B*	αI_a
B*	→	B	$k_d[B^*]$
B* + BH_2	→	BH	$k_r[B^*][BH_2]$
2BH	→	BH-BH	$k_p[BH]^2$
B* + Q	→	B + Q*	$k_q[B^*][Q]$

3. Kinetic methods

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„Involvement of T_1 (n,π*) of benzophenone as the chemically reactive agent in the photoreduction of benzophenone by benzydrol"

$$\frac{1}{\Phi_B} = \frac{1}{\alpha} + \frac{k_d}{\alpha k_r}\frac{1}{[BH_2]}$$

$$\frac{1}{\Phi_B} = \frac{1}{\alpha} + \frac{k_d}{\alpha k_r[BH_2]} + \frac{k_q[Q]}{\alpha k_r[BH_2]}$$

Experiments:

$k_d / k_r = 0.05$ M

$k_q / k_r = 500$

Taking $k_q = 1 \times 10^9$ $M^{-1}s^{-1}$

$k_d \sim 10^5$ s^{-1}

$\tau \sim 10$ μs

Conclusion:

T_1 (n,π*) of benzophenone is the reactive state.

$$A \xrightarrow{h\nu} A^* \longrightarrow I \longrightarrow B + C$$

Kinetic methods in the study of the mechanism of photochemical reactions

Procedure:

- assumption of the kinetic scheme
- appropriate equations should be derived, e.g. dependence of Φ_R vs. [A] or [Q]
- experiments, rate constants determnation and the interpretation of the results

Kinetic methods are so-called **indirect methods** and must confirmed by **direct methods**.

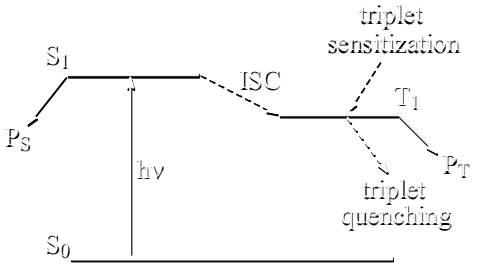
$$A \xrightarrow{h\nu} A^* \longrightarrow I \longrightarrow B + C$$

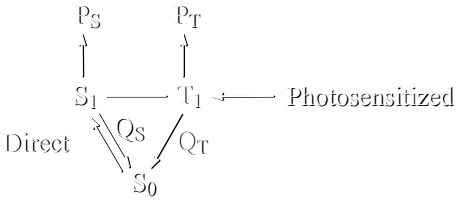
Determination of the reactive state in a photoreaction:

1. Direct methods (A, F, P, EPR)
2. Indirect methods (sensitization and quenching)

If the photoreaction is wavelenght- independent, the involvement of upper excited states can be neglected.

Question: S_1 or/and T_1





Experiment (result)	Reactive state (conclusion)
1. Only S_1 quenched, reaction inhibited	None
2. Only T_1 quenched, reaction inhibited	T_1
3. Only T_1 quenched, reaction uninhibited	S_1
4. Only T_1 sensitized, reaction does not occur	S_1
5. Only T_1 sensitized, reaction occurs	T_1 or $S_1 + T_1$

Experimental Methods for Detection of Intermediates and Excited States [Turro]

Reactive intermediate	Direct methods	Indirect methods
S_1	F, A	CIDNP, KINETICS, PRODUCTS
T_1	P, A, EPR	CIDNP, KINETICS, PRODUCTS
R_3C^+	A, F, P	MI, CHEM, PRODUCTS
R_3C^-	A, F, P	MI, CHEM, PRODUCTS
$R_3C^{\bullet}$	A, F, EPR	MI, CHEM, PRODUCTS
Biradical	A, F, P, EPR	CIDNP, MI, CHEM, PRODUCTS

Scheme of photochemical reaction

$$A \xrightarrow{h\nu} A^* \longrightarrow \underbrace{I}_{\textit{Intermediates}} \longrightarrow \underbrace{B + C}_{\textit{Stable products}}$$

- analysis of stable products
- identification of short-lived reactive intermediates
- identification of the excited states responsible for photochemical reactions