

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

Bronislaw Marciniak

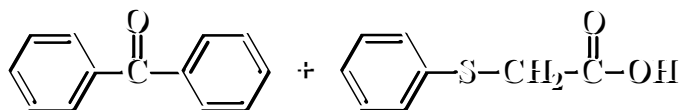
Faculty of Chemistry, Adam Mickiewicz University,
Poznan, Poland

2014/2015 - lecture 6

5. Examples illustrating the investigation
of photoreaction mechanisms:

- sensitized photooxidation of sulfur (II)-containing organic compounds
example III

System studied



Solvent: CH₃CN

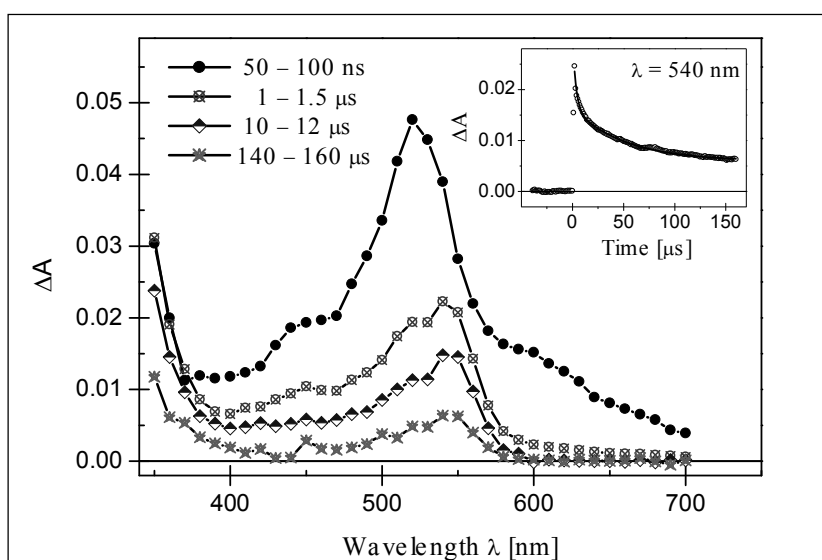


Fig. Transient absorption spectra following laser flash photolysis recorded at four different delays time benzophenone ($[BP] = 2 \times 10^{-3}$ M) and (phenylthio)acetic acid ($[C_6H_5-S-CH_2-COOH] = 2 \times 10^{-2}$ M) in Ar-saturated acetonitrile. Inset: kinetic trace at $\lambda = 540$ nm

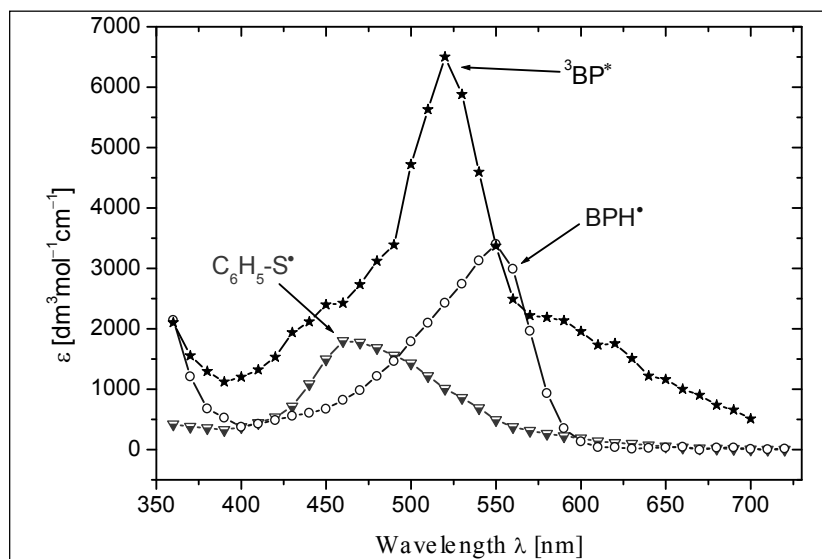


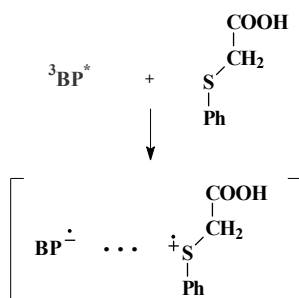
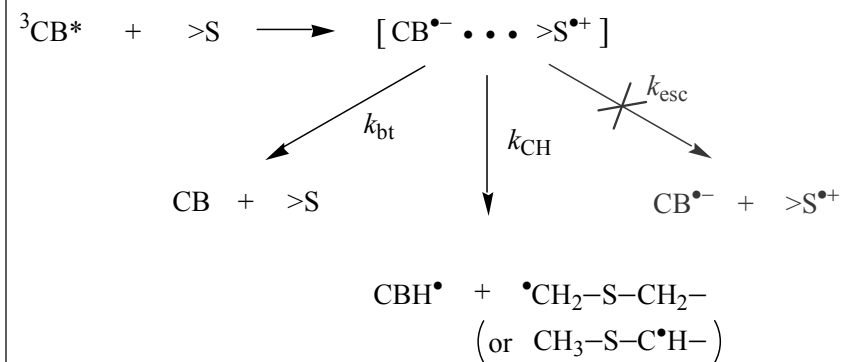
Fig. Reference spectra of intermediates (BPH•, ³BP*): (i) ketyl radical BPH• in acetonitrile, (ii) triplet state of benzophenone ³BP* in acetonitrile, and (iii) phenylthiyl radical C₆H₅-S• in water (from pulse radiolysis)

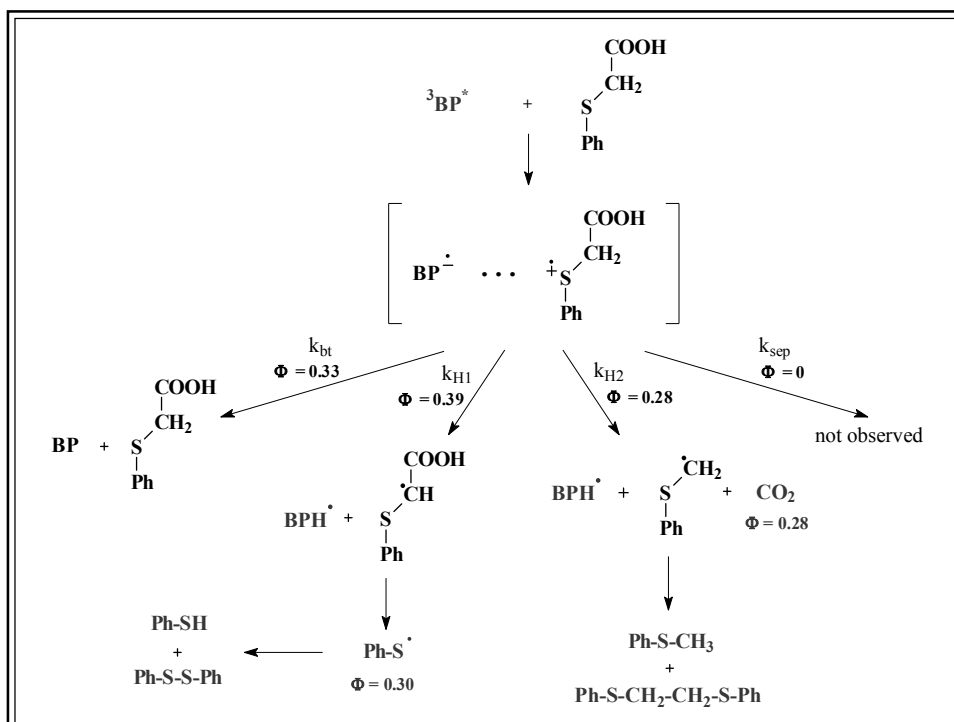
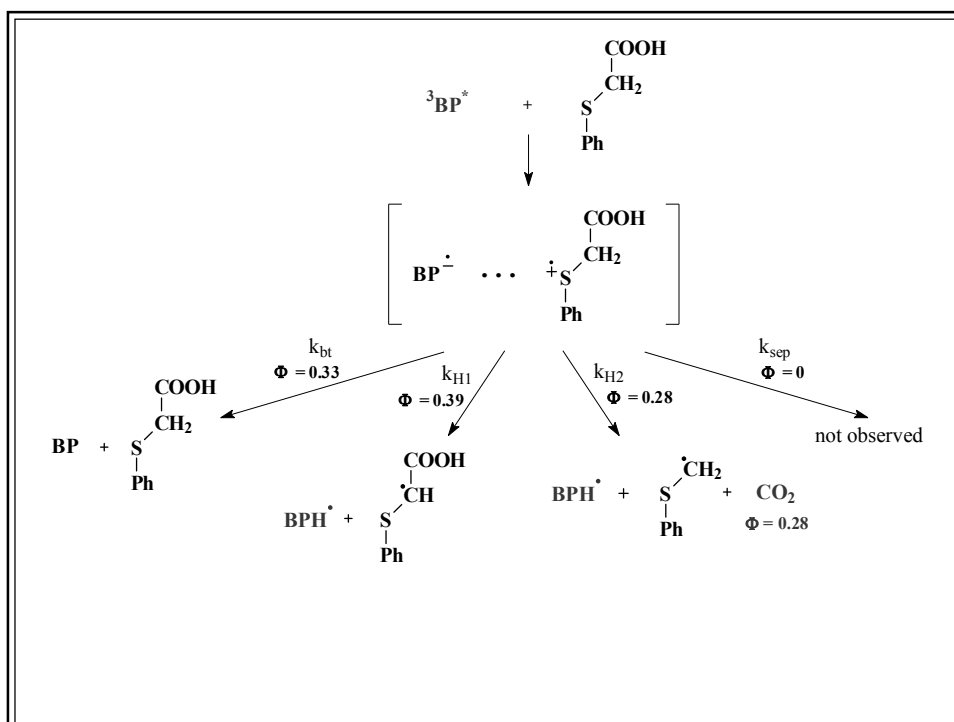
Table 1a. Quenching rate constants of benzophenone triplet state by (phenylthio)acetic acid (k_q) and quantum yields for formation of intermediates, disappearance of benzophenone (Φ_{BP}), and formation of CO₂ (Φ_{CO_2})

Solvent	Laser flash photolysis					Steady-state photolysis	
	k_q [dm ³ mol ⁻¹ s ⁻¹]	Φ_{BPH^\bullet}	Φ_{BP^\bullet}	$\Phi_{C_6H_5-S^\bullet}$	$\Phi_{C_6H_5-S^\bullet-CH_2}$	Φ_{BP}	Φ_{CO_2}
CH ₃ CN	8.7×10^7	0.67	0	0.30	—	0.68	0.28
H ₂ O	1.9×10^9	< 0.10	0.97	0	~ 0.93	0.97	0.92
CH ₃ CN ^b	1.1×10^9	—	0.35	—	—	0.42	0.45

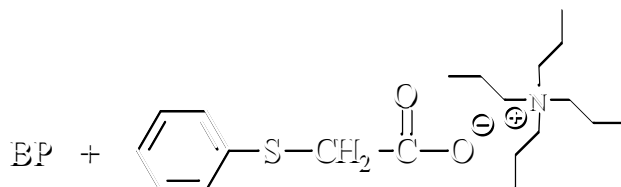
^b – results for tetrabutylammonium salt

Our Traditional Scheme





*Benzophenone–(Phenylthio)acetic
Tetrabutylammonium Salt*



Sovent: CH₃CN

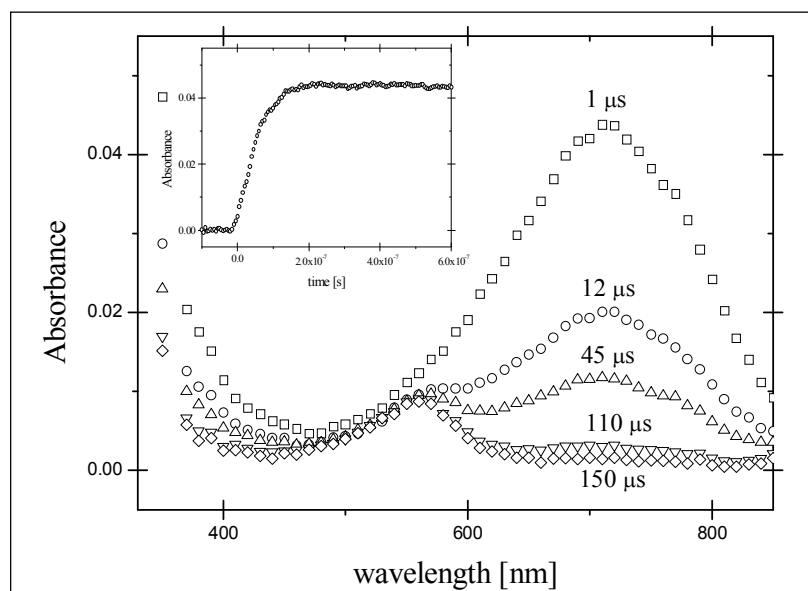


Fig. Transient absorption spectra of intermediates following the quenching of benzophenone triplet by Ph-S-CH₂-COO-N⁺(C₄H₉)₄ (0.01M).
Inset: kinetic trace at 710 nm.

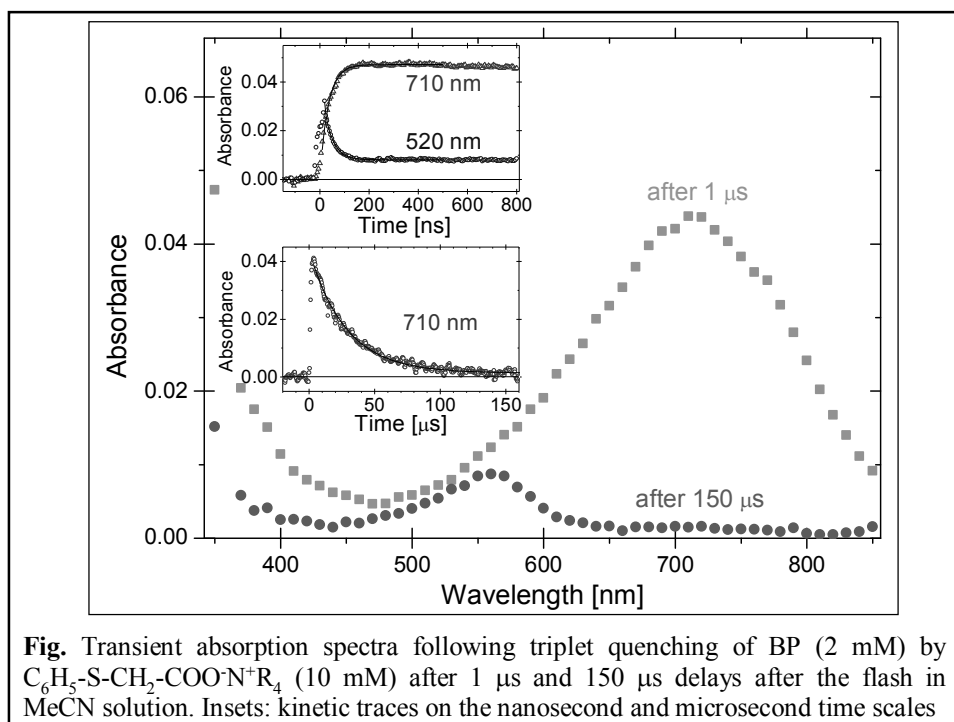
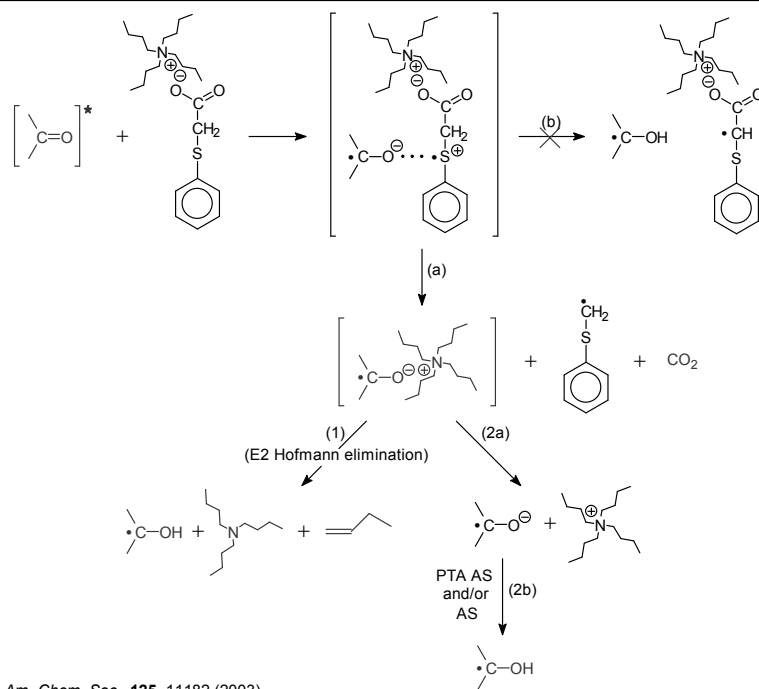
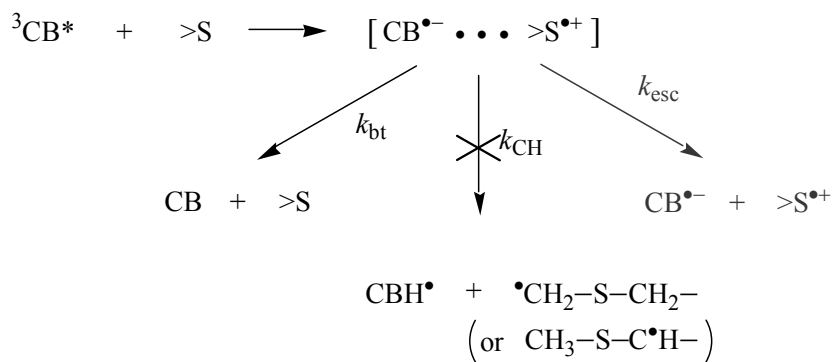


Table 1b. Quenching rate constants of benzophenone triplet state by (phenylthio)acetic acid (k_q) and quantum yields for formation of intermediates, disappearance of benzophenone (Φ_{BP}), and formation of CO_2 (Φ_{CO_2})

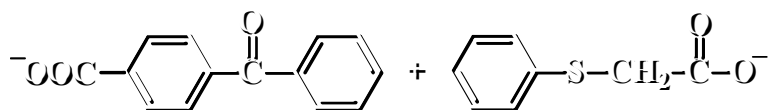
Solvent	Laser flash photolysis					Steady-state photolysis	
	k_q [$dm^3mol^{-1}s^{-1}$]	Φ_{BPH^*}	Φ_{BP^*}	$\Phi_{C_6H_5-S^*}$	$\Phi_{C_6H_5-S^*-CH_2}$	Φ_{BP}	Φ_{CO_2}
CH ₃ CN	8.7×10^7	0.67	0	0.30	—	0.68	0.28
H ₂ O	1.9×10^9	< 0.10	0.97	0	~ 0.93	0.97	0.92
CH ₃ CN ^b	1.1×10^9	—	0.35	—	—	0.42	0.45

^b – results for tetrabutylammonium salt

Our Traditional Scheme



System studied



Solvent: H₂O

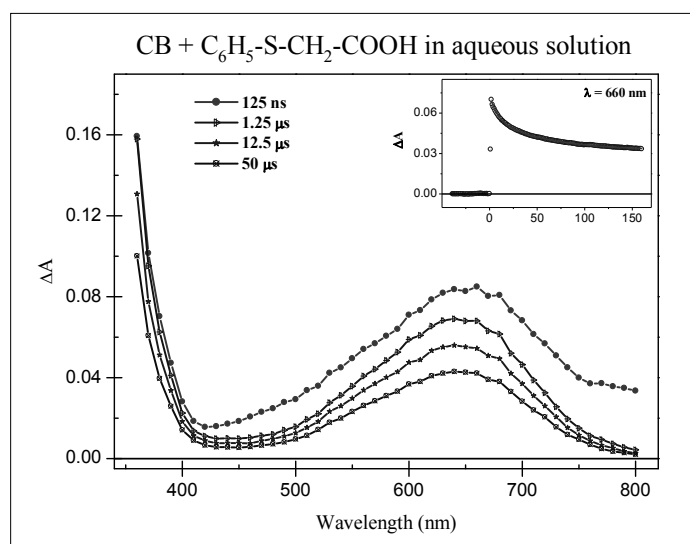


Fig. Transient absorption spectra following laser flash photolysis recorded at four different delay times. Benzophenone ([CB] = 2 mM) and (phenylthio)acetic acid ([C₆H₅-S-CH₂-COOH] = 20 mM) in Ar-saturated aqueous solutions pH = 7.5. Inset: kinetic trace at $\lambda = 660 \text{ nm}$

Spectral Resolutions

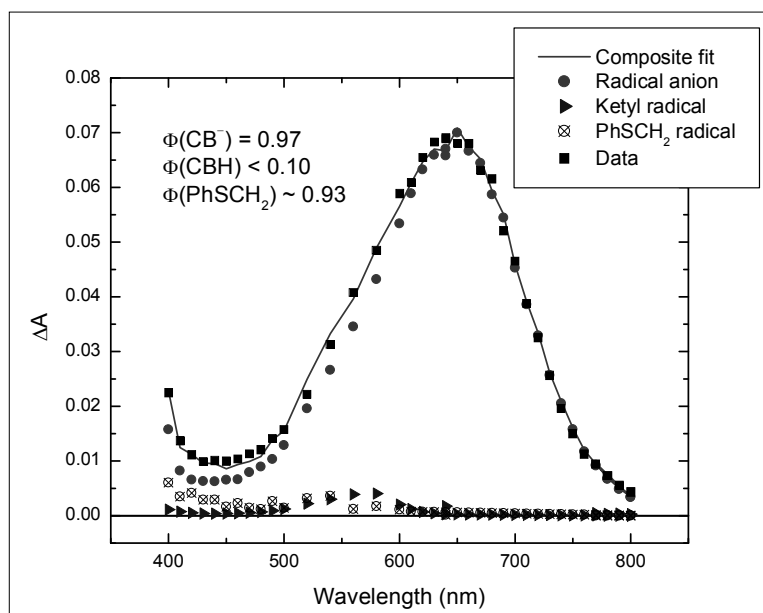


Table 1c. Quenching rate constants of benzophenone triplet state by (phenylthio)acetic acid (k_q) and quantum yields for formation of intermediates, disappearance of benzophenone (Φ_{BP}), and formation of CO_2 (Φ_{CO_2})

Solvent	Laser flash photolysis					Steady-state photolysis	
	k_q [$\text{dm}^3\text{mol}^{-1}\text{s}^{-1}$]	$\Phi_{\text{BPH}^{\bullet}}$	$\Phi_{\text{BP}^{\bullet}}$	$\Phi_{\text{C}_6\text{H}_5\text{-S}^{\bullet}}$	$\Phi_{\text{C}_6\text{H}_5\text{-S}^{\bullet}\text{-CH}_2}$	Φ_{BP}	Φ_{CO_2}
CH_3CN	8.7×10^7	0.67	0	0.30	—	0.68	0.28
H_2O	1.9×10^9	< 0.10	0.97	0	~ 0.93	0.97	0.92
$\text{CH}_3\text{CN}^{\text{b}}$	1.1×10^9	—	0.35	—	—	0.42	0.45

^b – results for tetrabutylammonium salt

Conclusions:

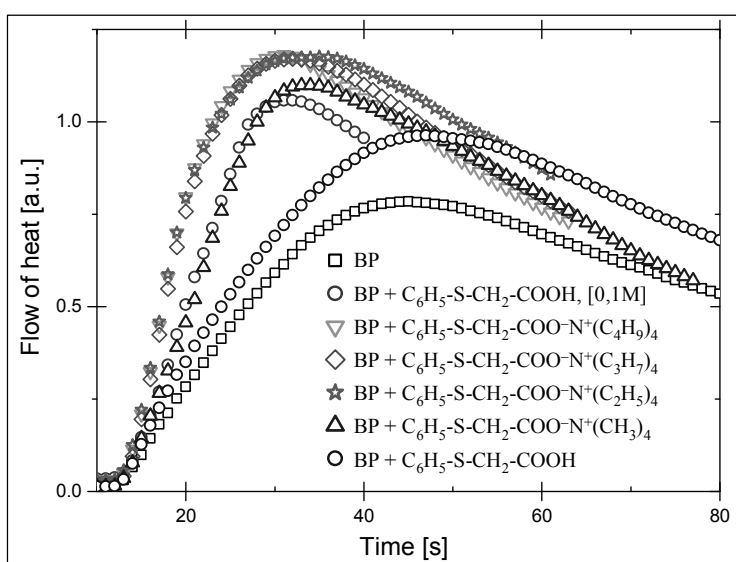
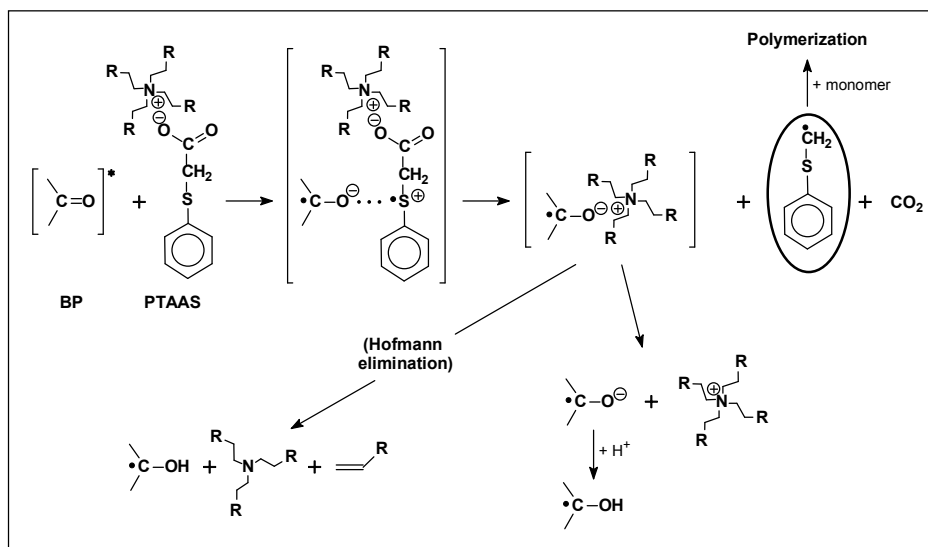
Photochemical pathways (primary and secondary reactions) for the sensitized oxidation of phenylthioacetic acid depend on

its ionization form (solvent used)

and the presence of *associated* counter cations (tetraalkylammonium salt)

*Application of Photooxidation
of Sulfur-Containing Organic
Compounds in Free Radical
Polymerization*

Reaction scheme



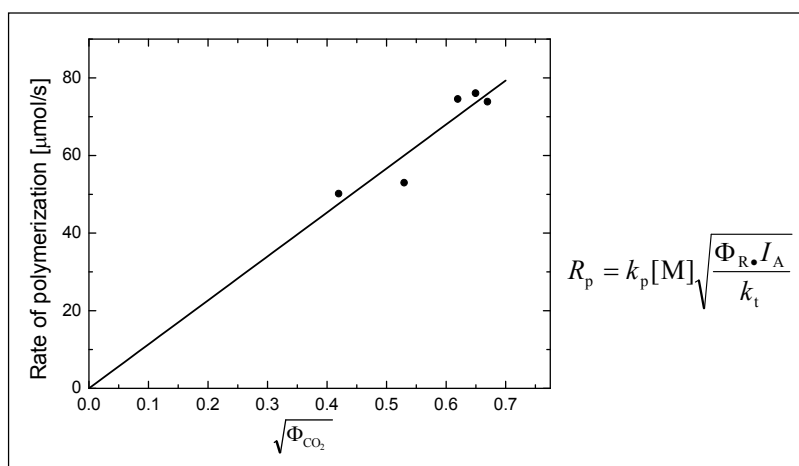
Photopolymerization kinetic traces

Polymerization rates (R_p), quantum yield of polymerization (Φ_p) and quantum yield of CO_2 (Φ_{CO_2})

Układy fotoinicjujące	R_p [$\mu\text{mol/s}$]	$\sqrt{\Phi_{\text{CO}_2}}$	Φ_p
BP	23,4	–	400
BP + <chem>c1ccc(cc1)S-CH2-COOH</chem>	52,9 ^a 28,4 ^b	0,53	910 ^a 480 ^b
BP + <chem>c1ccc(cc1)S-CH2-COO-.[N+](C)(C)(C)C</chem>	50,1	0,42	850
BP + <chem>c1ccc(cc1)S-CH2-COO-.[N+](CC)(CC)CC</chem>	76,0	0,65	1300
BP + <chem>c1ccc(cc1)S-CH2-COO-.[N+](CC)(CC)CC</chem>	74,5	0,62	1270
BP + <chem>c1ccc(cc1)S-CH2-COO-.[N+](CCCC)CC</chem>	73,8	0,67	1260

^a concentration of acid 0.1 mol/dm³

^b concentration of acid 0.01 mol/dm³



Plot of polymerization rate (R_p) vs. square root of the CO_2 quantum yield

Conclusions

- BP + C₆H₅-S-CH₂-COO-N⁺R₄ (R = n-butyl, n-propyl, and ethyl) were shown to be effective co-initiators of free-radical photopolymerizations.
- A linear correlation was found for the polymerization rates vs. the square root of the CO₂ quantum yields, and this indicates that the C₆H₅SCH₂• radicals are responsible for the initiation step of the polymerizations.
- Application of the laser flash photolysis and steady-state photochemical methods allowed led to description of the mechanism of free radical polymerization.