Radiation Chemistry Research at Pune University

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INDIA


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(INDIA)
SRILANKA

Chemistry Department, University of Pune
55 years old

Human Resources

Teaching Staff	32
Non-teaching Staff	43
Research Students	60
M.Sc. Students	170
Ph. D. Studnets	50

Academic Details

M.Sc.

*Under Academic Flexibility

*Admission through Entrance Examination {DoC - NCL}

* Credit System

Branches

- Analytical
- Biochemistry
- Inorganic
- Organic
- Physical

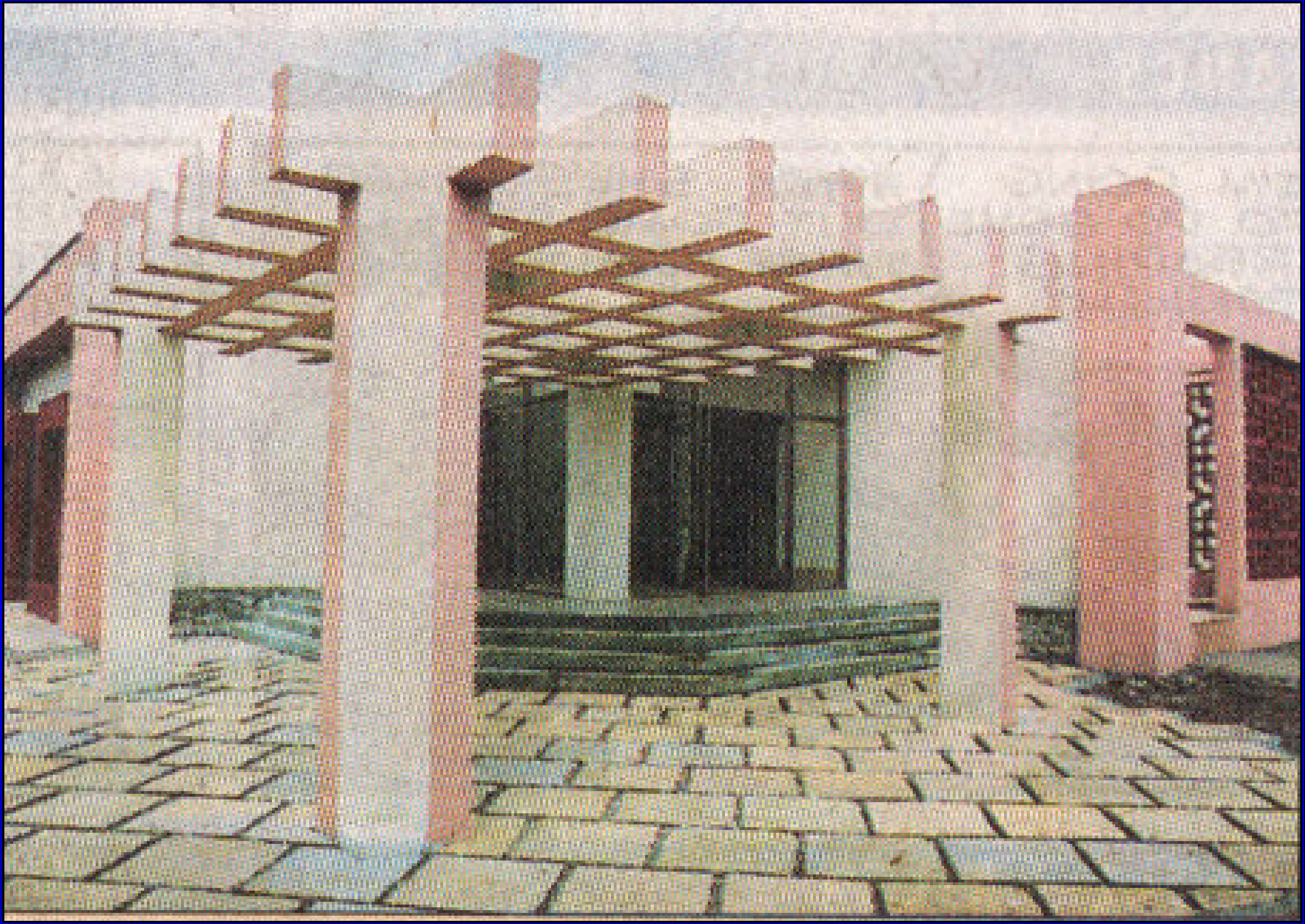
Areas of Research

- Structure - Reactivity Studies of Substituted Benzenes
- Free Radical Chemistry of Metal Complexes
- Redox Chemistry of Azo Dyes.
- Radiation Chemical Studies of Organic Sulphur Compounds

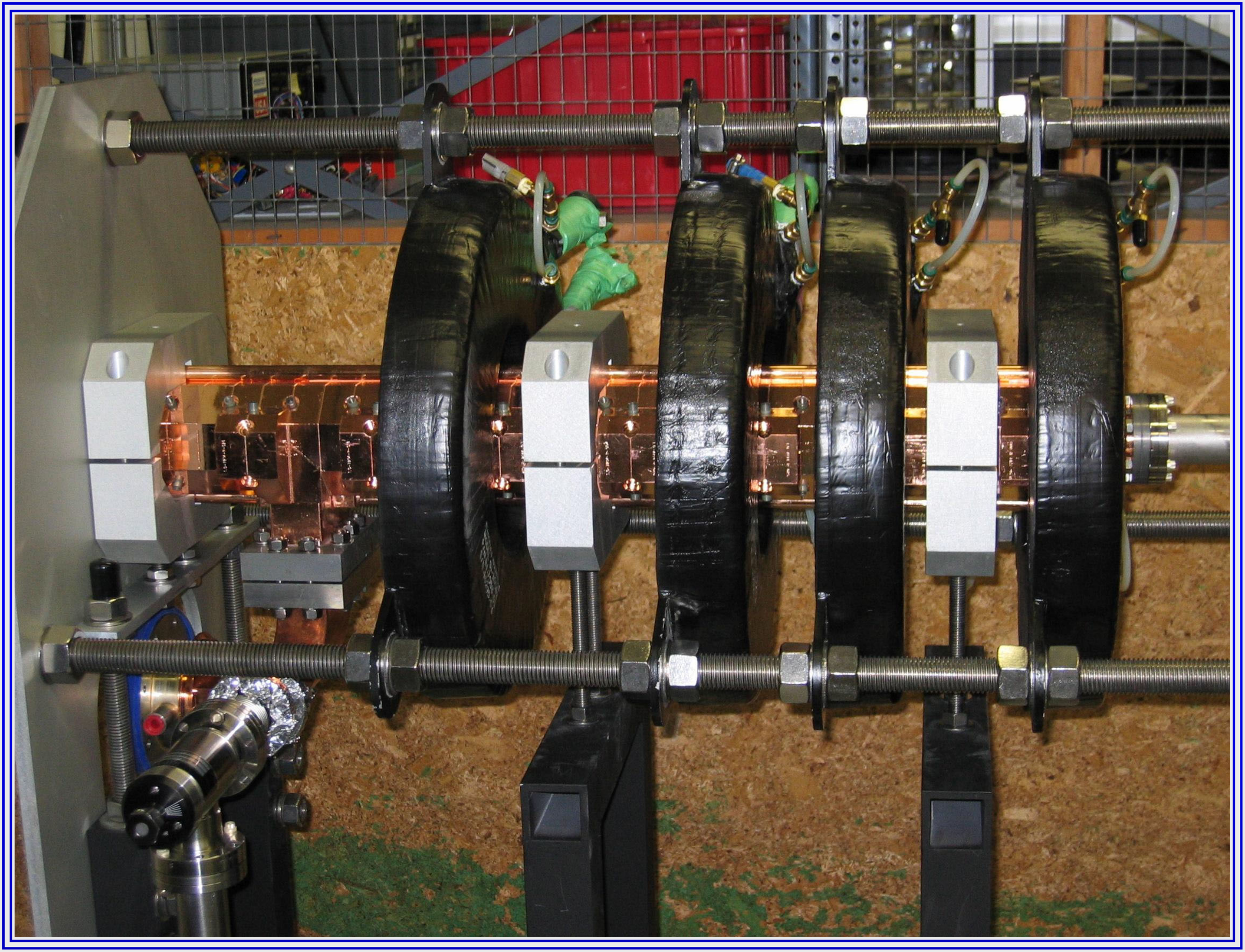
Specifications of the LINAC

Parameter	**Specification**
Electron beam energy	7 MeV
Peak beam current @ 10 ns	1 A
Peak beam current @ 3 µs	0.115 A
Beam diameter at exit window	2 mm
Jitter in pulse	± 200 ps
Pulse rate (Mains locked option)	50 to 200 pps in 12.5 pps steps
Radiation dose	0.1 to 100 krad / pulse
Dose due to dark current	< 1% of Beam current
Pulse to pulse reproducibility	± 1%
Energy spread	± 0.5 MeV
Exit window material	Titanium
Single shot and multiple shots	50 to 200 pps
Preset beam pulses	10 to 250 pulses in steps of 10 pulses
Pulse width - 10ns to 3µs	10, 20, 50, 100, 200, 400 ns & 3 µs

NCFRR: construction of the building completed in November 2003



LINAC



Experimental Methodology

Pulse Radiolysis

LINAC at BARC
Energy = 7 MeV
Pulse width = 50 ns
Dose / Pulse = 14 Gy
Conc. = 0.2 – 1 x 10^{-3} mol dm^{-3}

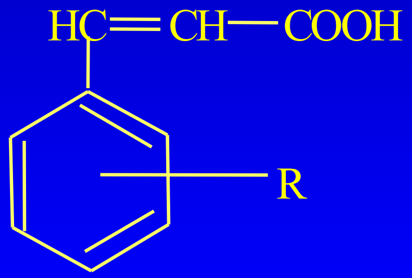
Steady State Radiolysis

^{60}Co γ source
HPLC
HPIC
UV – VIS.

Quantum Chemical Calculations

Ab initio molecular orbital and hybrid density functional theory **B3LYP** method with **6-31 G (d,p)** basis set were used.
Mullikien charge population on substituted and unsubstituted cinnamic acid was calculated.

Redox Reactions of Cinnamic acid and its Derivatives

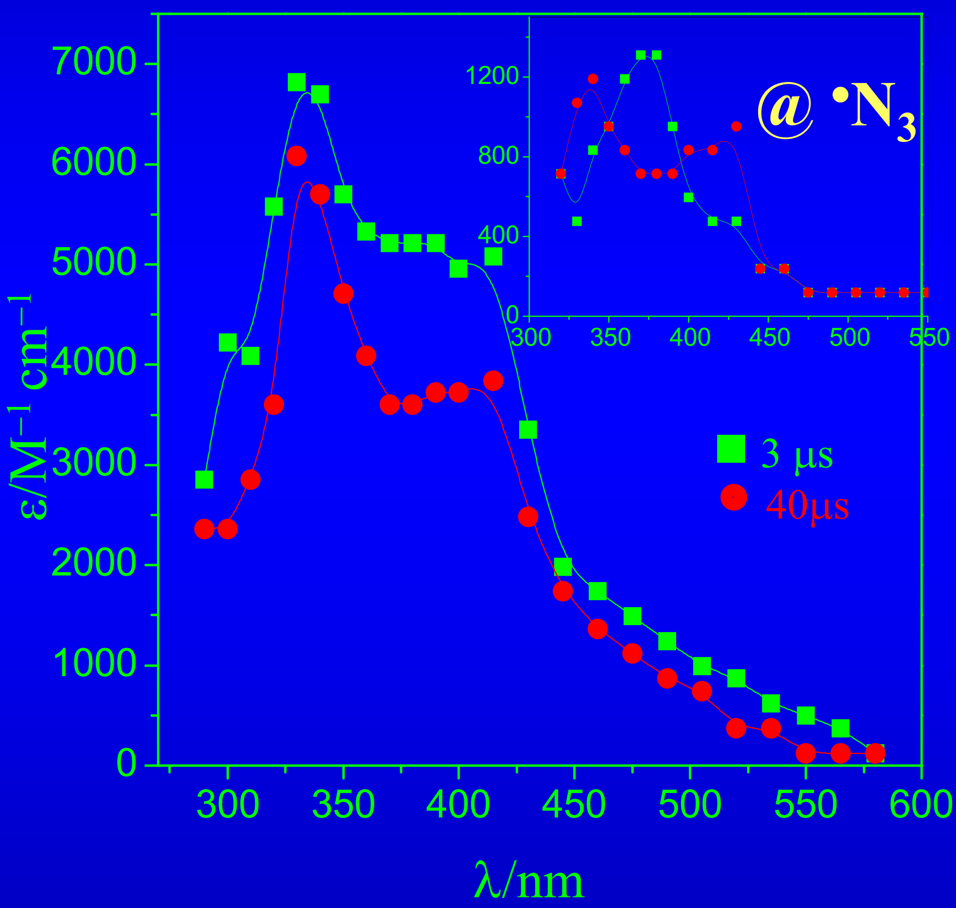


Hydroxycinnamic acids - widely distributed phenolic acids in plant tissue

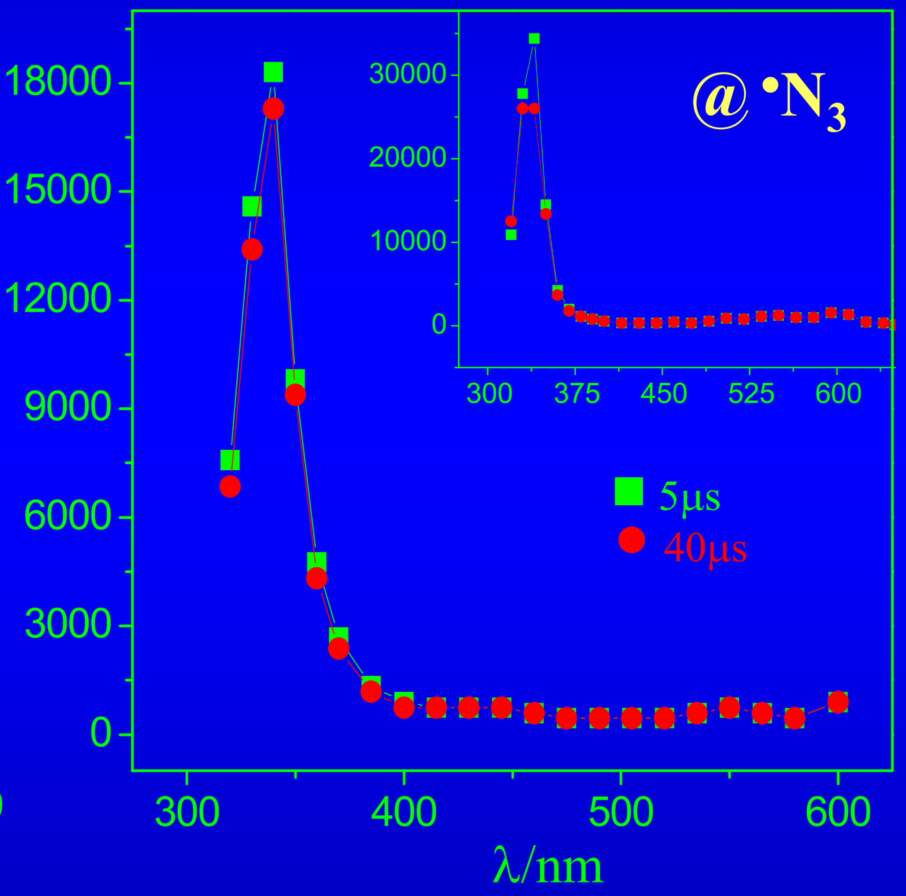
Cinnamic acid derivatives have been shown to be able to scavenge superoxide, peroxyl and hydroxyl radical.

The reaction of the •OH radical with cinnamic acid in aqueous solution proceeds *via* addition to both the ring and the olefinic group, the relative extent being 3:7 respectively (**Bobrowski *et al***).

Transient absorption spectra obtained in the reaction of $^{\bullet}$OH and $^{\bullet}N_3$ with hydroxycinnamic acids at pH 7



_m-_ hydroxycinnamic acid



_p-_ hydroxycinnamic acid

Table 1: Second order rate constant ($k/10^9\ M^{-1}\ s^{-1}$) and absorption maxima (λ_{max}/nm) measured in the reaction of $^{\bullet}OH$, $^{\bullet}N_3$ and e_{aq}^- with derivatives of cinnamic acid

Compounds	$^{\bullet}OH$				$^{\bullet}N_3$		e_{aq}^-	
	pH 3		pH 7		pH 7		pH 7	
	k	λ_{max}	k	λ_{max}	k	λ_{max}	k	λ_{max}
Cinnamic acid (CA)			8.1	310, 365		375 → 320	10.0	370
o- OH	1.6	360, 400	3.9	360	0.49	360	7.2	370
m-OH	4.2	330, 430	4.4	330, 390	(4.2)	370→ 340, 400	8.9	380
p-OH	3.4	350, 430	6.5	340	1.1	340	8.7	360
o -OCH_3	5.7	390, 450	1.6	410	0.06	320	8.8	370
m-OCH_3	5.7	350 ,430	4.5	330, 380	(4.7)	380	7.9	380
p-OCH_3	1.5	370, 415	3.2	350, 410	0.43	330	7.6	360
o-Cl	-	-	4.4	320	(4.7)	380→ 330	10	380
m-Cl	-	-	5.9	310, 370	(4.4)	380→ 330	11	380
p-Cl	-	-	3.4	360	(5.1)	380→ 320	11	380
o-NO_2	-	-	3.2	400	< 0.001	-	15.4	370
m-NO_2	-	-	3.0	310, 410	< 0.001	-	16.6	360
p-NO_2	-	-	2.8	370	3.7	365→ < 340	15.6	370

Table 2: The λ_{max} of the radical cation as predicted by the single electron excitation (CIS) calculations.

Compounds	Theoretical λ_{max} / nm	Experimental λ_{max} / nm
***o*-Hydroxycinnamic acid**	**222, 235, 241**	
***m*-Hydroxycinnamic acid**	**308, 328**	**370**
***p*-Hydroxycinnamic acid**	**290, 319**	
***o*-Methoxycinnamic acid**	**298, 321**	**320**
***m*-Methoxycinnamic acid**	**310, 332**	**380**
***p*-Methoxycinnamic acid**	**291, 318**	**330**
***o*-Chlorocinnamic acid**	**263, 324**	**320, 380**
***m*-Chlorocinnamic acid**	**265, 324**	**320, 380**
***p*-Chlorocinnamic acid**	**300, 339**	**320, 380**
***o*-Nitrocinnamic acid**		
***m*-Nitrocinnamic acid**	**333, 355, 361**	
***p*-Nitrocinnamic acid**	**339, 462**	**< 340**

Conclusions :

Cinnamic acid is ortho and para directing despite carboxylate group being an electron withdrawing.

The reaction of the $^{\bullet}$OH radical with cinnamic acid at pH 7 can proceeds *via* three ways i.e addition to the aromatic ring, addition to the aliphatic double bond and by electron transfer.

At acidic pH the reaction proceeds by two ways i.e addition to ring and addition to double bond .

Proc. Ind. Acad. Sci., 114 (6) 721-730 (2002)

Redox Chemistry of Ru(II) Complexes

- Ru(II) complexes have good charge transfer property.
- Pyridine based ligands form highly stable complexes and one electron oxidation and/or reduction does not cause considerable change in their geometry.
- Pulse Radiolysis + Chemical methods : effective technique in order to understand the redox chemistry of these complexes.

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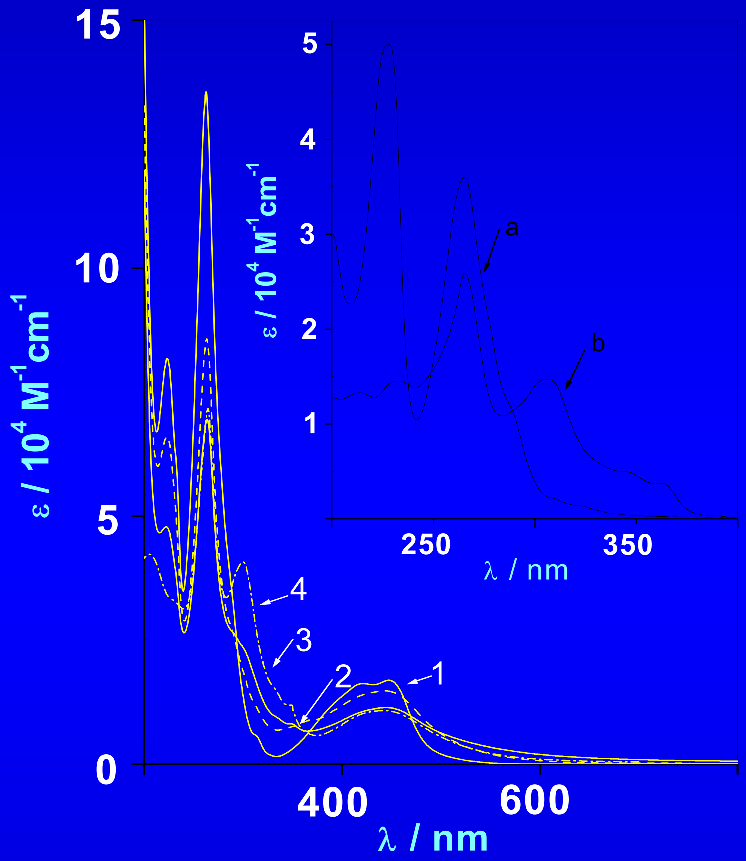
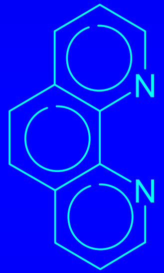
RUTHENIUM SYSTEM

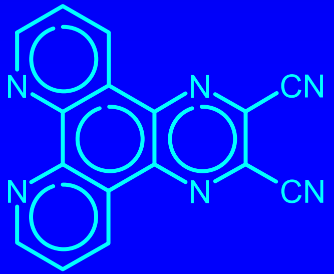


$[Ru(phen)_n(dicnq)_{3-n}]^{2+}$, n = 0, 1, 2, 3

phen = 1, 10-Phenanthroline
dincq = 6,7-Dicyanodipyrido[2,2-*d*:2’,3’–*f*]
quinoxaline



phen

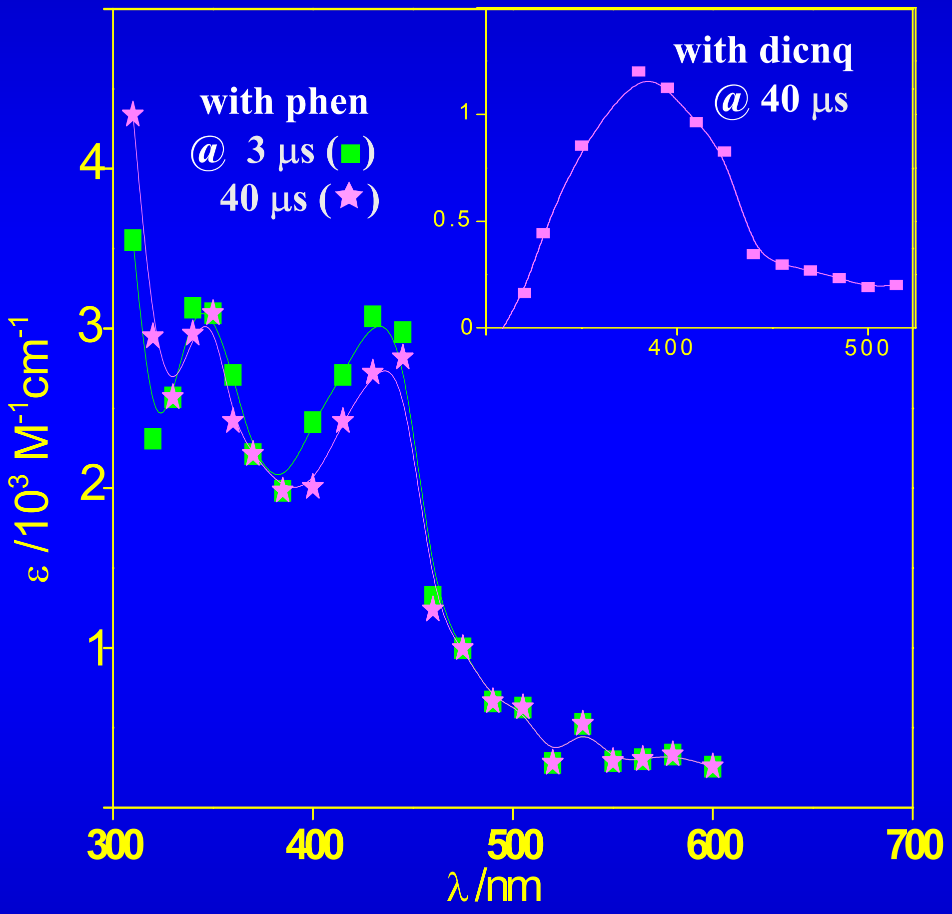


dincq

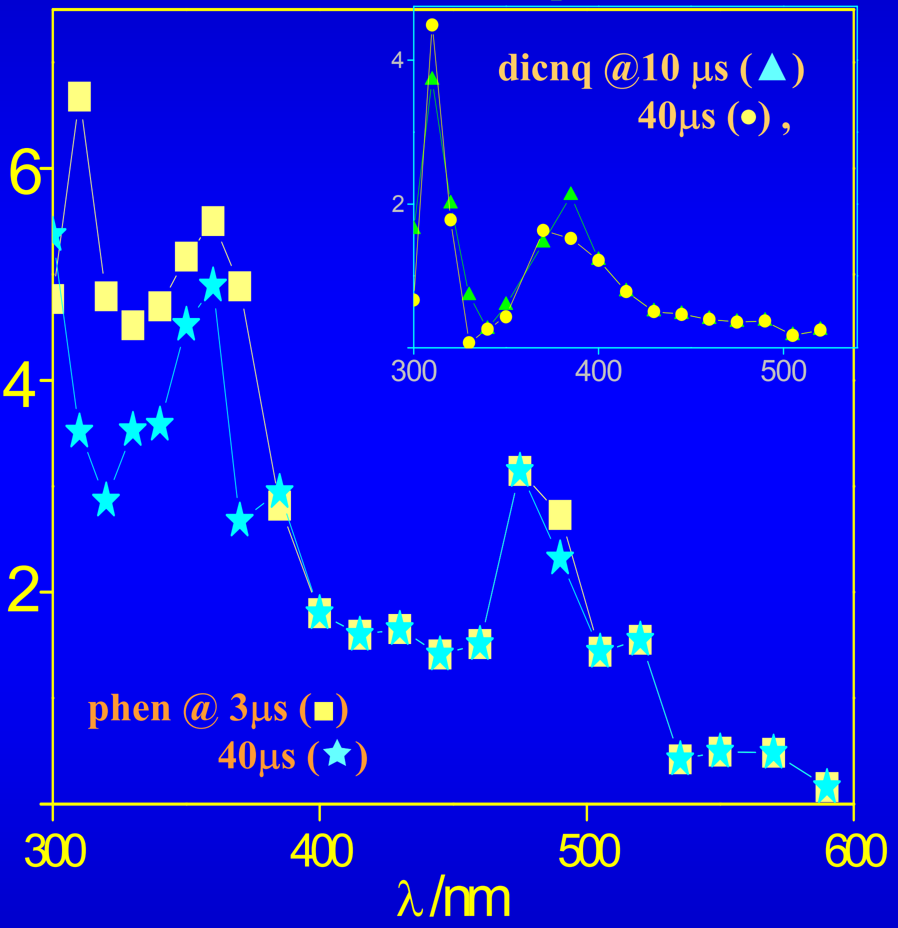
Absorption spectra of
1: $[Ru(phen)_3]^{2+}$ **2**: $[Ru(phen)_2(dicnq)]^{2+}$
3: $[Ru(phen)(dicnq)_2]^{2+}$ **4**: $[Ru(dicnq)_3]^{2+}$
Inset : **a** : phen **b** : dicnq

Time resolved absorption spectra of the ligands

Reactions with $^\bullet OH$

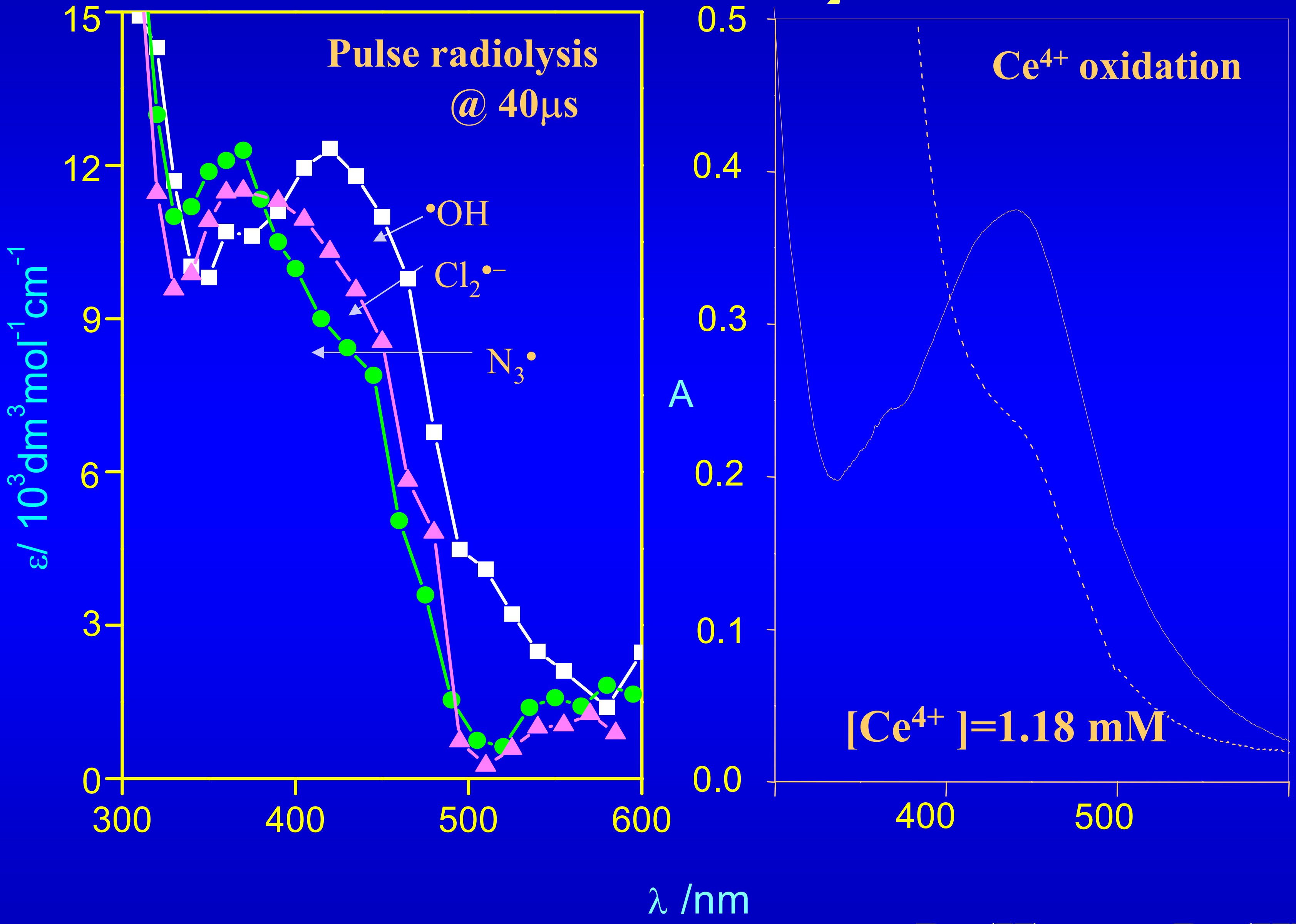


Reactions with e^-_{aq}



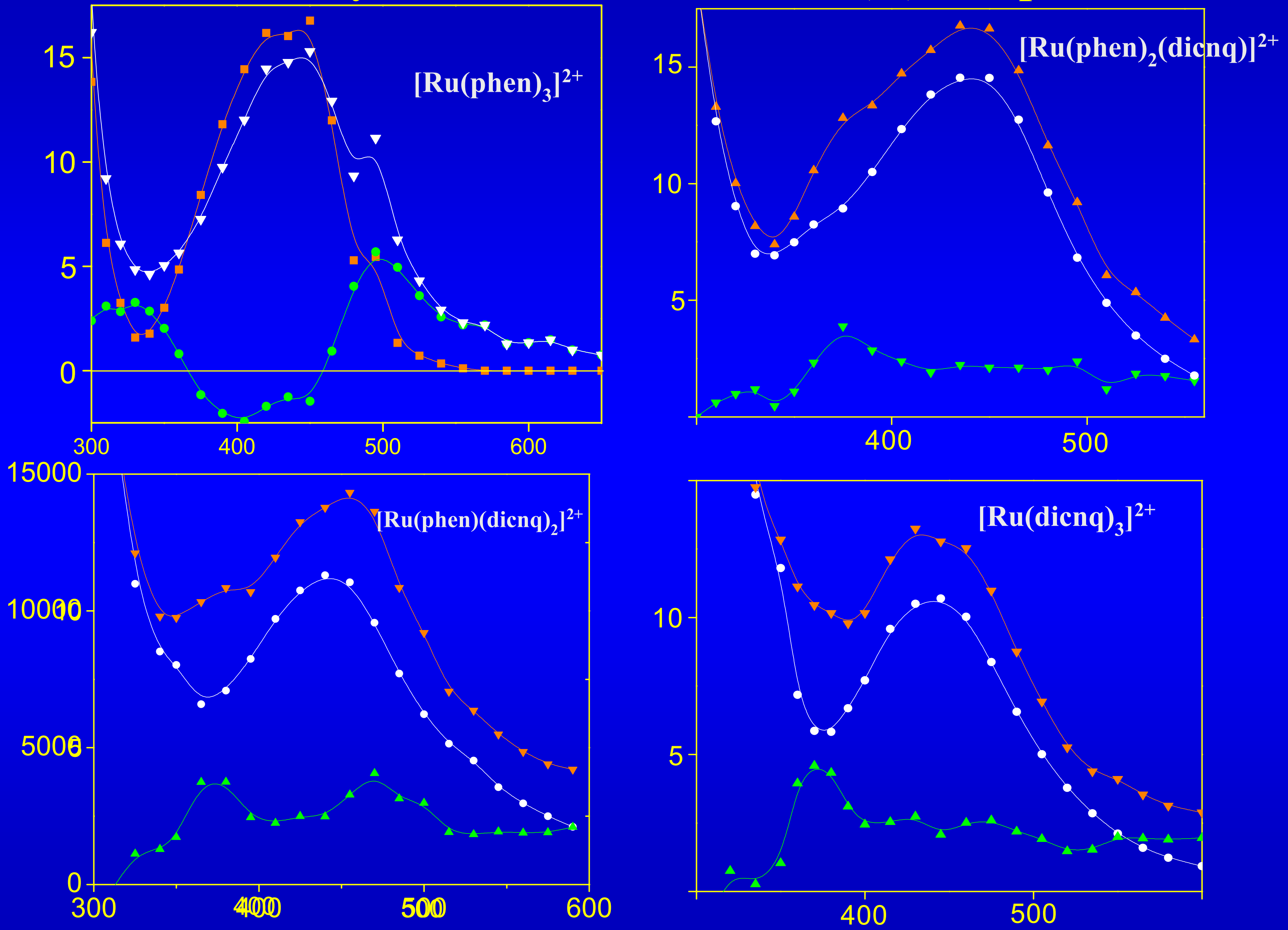
[phen] = 1 × 10 $^{-3}$ M , [dicnq] = 1 × 10 $^{-4}$ M dose/pulse ~ 7 Gy. at pH 7.

Reactions of $[Ru(phen)_2(dicnq)]^{2+}$



Ru(II) ⟶ Ru(III)

Reactions of hydrated electron with Ru(II) complexes



difference (👌) , corrected (▲) & parent spectrum (●) **pH 7 , dose/pulse ~ 7 Gy**

λ_{max} in nm k in 10^9 M^{-1} s^{-1}

Compound	•OH		O•–		SO•–	e^-_{aq}	
	λ_{max}	*k*	λ_{max}	*k*	λ_{max}	λ_{max}	*k*
phen	350 430	5.0	340 440	0.8	430	325 360 490	8.8
dicnq	380	(1.2)	380 450	(1.5)	380	310 380	(6.5)
$[Ru(phen)_3]^{2+}$	435 500	7.5	420	2.4	430	435 500	31.3
$[Ru(phen)_2(dicnq)]^{2+}$	425	8.2	420	(3.7)	Nd	440	25.7
$[Ru(phen)\,(dicnq)_2]^{2+}$	420	8.7	420	(2.4)	Nd	440	21.9
$[Ru(dicnq)_3]^{2+}$	380	11.8	400	1.0	Nd	440	16.0

Ru(II) Complexes

$$[\mathrm{Ru^{II}\,(phen)_n(dicnq)_{3-n}}]^{2+} \xrightarrow{{}^{\bullet}\mathrm{OH}} [\mathrm{Ru^{II}\,(phen)_{n-1}(phen\text{-}OH)(dicnq)_{3-n}}]^{2+}$$

n = 0, 1, 2, 3

$$[\mathrm{Ru^{II}\,(phen)_n(dicnq)_{3-n}}]^{2+} \xrightarrow{\mathrm{Cl_2^{\bullet-}}} [\mathrm{Ru^{III}\,(phen)_n(dicnq)_{3-n}}]^{3+}$$

n = 0, 1, 2, 3

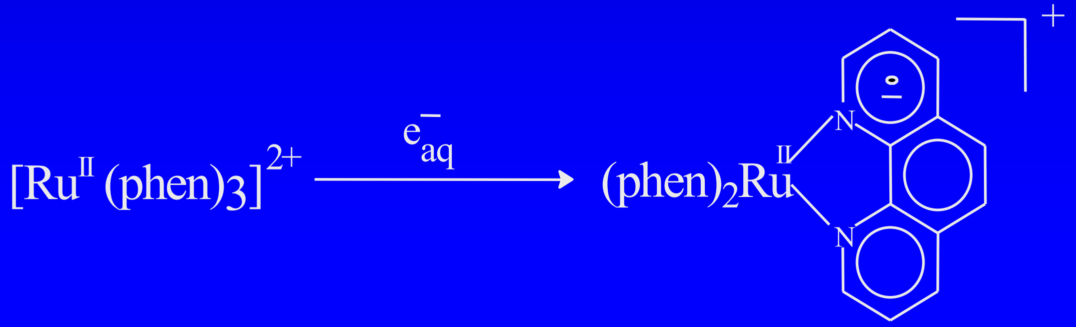
$$[\mathrm{Ru^{II}\,(phen)_3}]^{2+} \xrightarrow{\mathrm{SO_4^{\bullet-}}} [\mathrm{Ru^{III}\,(phen)_3}]^{3+} + \mathrm{SO_4^{2-}}$$

$$[\mathrm{Ru^{II}\,(phen)_2(dicnq)}]^{2+} \xrightarrow{\mathrm{N_3^{\bullet}}} [\mathrm{Ru^{III}\,(phen)_2(dicnq)}]^{3+} + \mathrm{N_3^{-}}$$

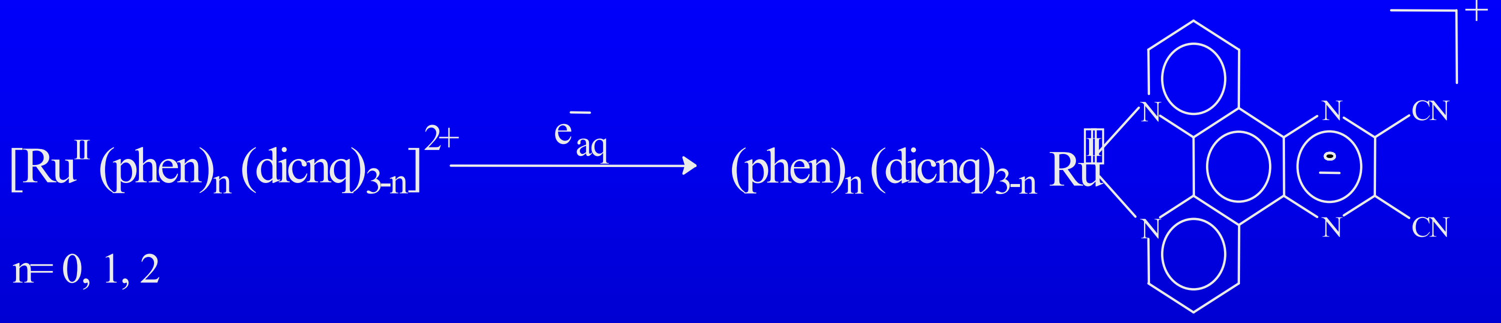
J. Photochem. Photobiol. A., Chem (in press).

Research on Chemical Intermediates (In press)

Reactions with hydrated electron



$$[Ru^{II}(phen)_3]^{2+} \xrightarrow{e^-_{aq}} (phen)_2Ru^{II}$$



$$[Ru^{II}(phen)_n(dicnq)_{3-n}]^{2+} \xrightarrow{e^-_{aq}} (phen)_n(dicnq)_{3-n}\,Ru^{II}$$

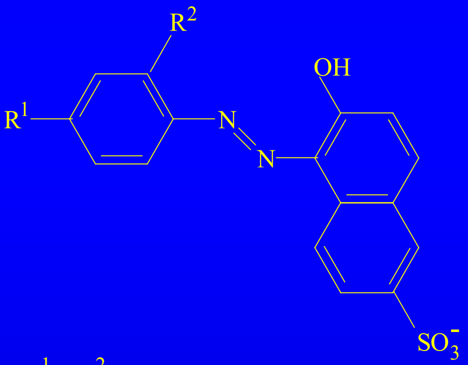
n= 0, 1, 2

Why Azo dyes?

- High stability towards light, aerobic biodegradation and common oxidant
- Environmental concerns-extremely difficult to remove.
- Reduction may lead to degraded products (aromatic amines), potential health hazard
- ~1 million tonnes of dye stuffs based on >10, 000 different structures

Oxidation of 1-arylazo-2-naphthol dyes by •OH & N_3•

Second-order rate constants ($k/10^{10}$ $M^{-1}s^{-1}$) for the reaction of •OH and N_3•

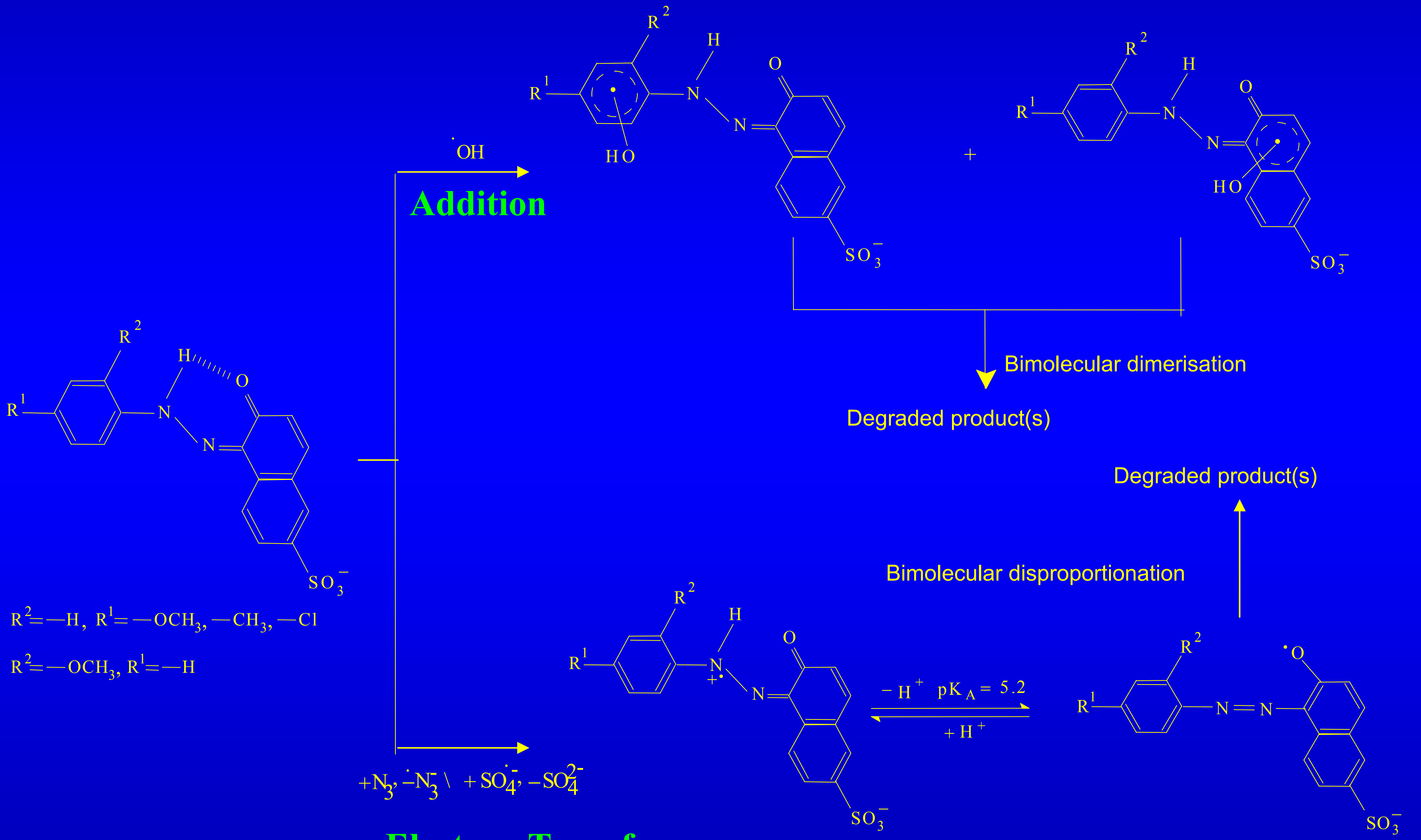


$R^1 = R^2 = —H, —OCH_3, —CH_3, —Cl$

1-arylazo-2-naphthol

Dyes	pK_a	pH	•OH k	N_3• k
Unsubstituted dye $R^1 = R^2 = H$	10.8	7.0 12.0	1.1	0.07 0.5
o-methoxy dye $R^1 = H; R^2 = OCH_3$	11.4	7.0	1.0	0.4
p-methoxy dye $R^1 = OCH_3; R^2 = H$	10.8	7.0	1.1	0.8
p-chloro dye $R^1 = Cl; R^2 = H$	10.5	7.0	1.0	0.05
p-methyl dye $R^1 = CH_3; R^2 = H$	10.9	7.0	1.2	0.2

Mechanism for the oxidation of 1-arylazo-2-naphthol by $^{\bullet}OH$ & $^{\bullet}N_3$



Addition

Bimolecular dimerisation

Degraded product(s)

Degraded product(s)

Bimolecular disproportionation

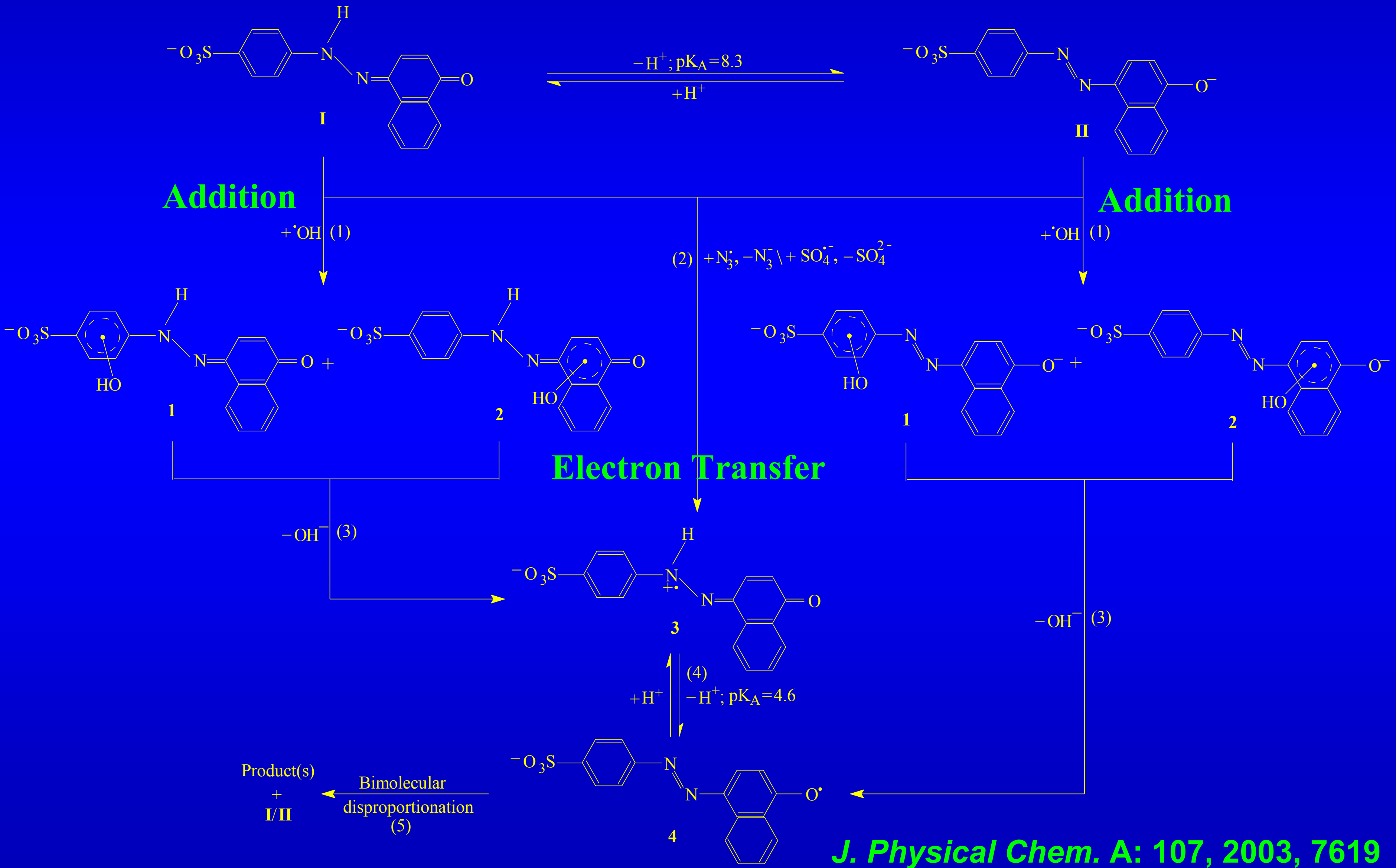
$R^2 = -H$, $R^1 = -OCH_3$, $-CH_3$, $-Cl$

$R^2 = -OCH_3$, $R^1 = -H$

Electron Transfer

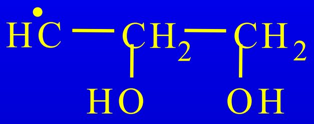
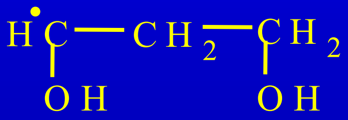
J. Physical Chem. A: 106, 2002, 2915

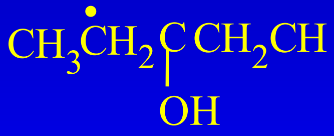
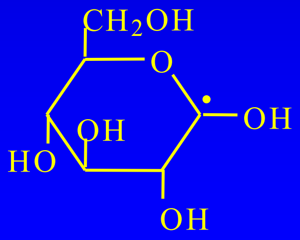
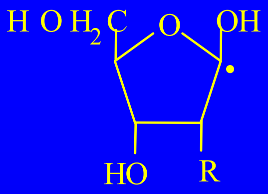
Mechanism for the oxidation of Orange I by $^{\bullet}OH$ & $N_3^{\bullet}$



J. Physical Chem. A: 107, 2003, 7619

Table : Rate constants (k /10^9 $M^{-1}s^{-1}$) for the reaction of various radicals with Orange II at pH 7

Reacting Species	***k***
$^{\bullet}CH_2OH$	1.1
$^{\bullet}CH_2CH_3OH$	2.3
$^{\bullet}C(CH_3)_2OH$	2.7
$^{\bullet}CH_2(CH_3)_2OH$	<0.01
$HO\overset{\bullet}{C}H-CH_2OH$	0.15
 $H\overset{\bullet}{C}-\underset{HO}{CH_2}-\underset{OH}{CH_2}$	0.62
 $H\overset{\bullet}{\underset{OH}{C}}-CH_2-\underset{OH}{CH_2}$	1.5

Reacting Species	*k*
 $CH_3\overset{\bullet}{C}H_2\underset{\substack{\mid\\ OH}}{C}CH_2CH$	2.0
	<0.01
 R = H	0.9
R = OH	<0.01
$CO_2^{\bullet-}$	1.7
$O_2^{\bullet-}$	<0.01
$HO_2^{\bullet}$	<0.01
$N_3^{\bullet}$	0.1

Conclusions

1. $^{\bullet}OH$ reaction - independent of substituents and dye forms.
2. $^{\bullet}OH$ adducts (1-arylazo-2-naphthol and 2-arylazo 1-naphthol), decay bimolecularly by dimmerisation (Stoichiometry = 1$^{\bullet}OH$: 1 dye).
3. $^{\bullet}OH$ adducts (orange I and O-methylated orange I) undergoes H_2O elimination (acid-base catalysed)to give one-electron oxidised radical.

4. $N_3^{\bullet}$ reaction – dependent on substituents ($\rho^+ = -2.0$) and dye forms.

5. Electron transfer reaction - one-electron oxidised radical - decay bimolecularly by disproportionation. (Stoichiometry = 2 $N_3^{\bullet}$: 1 dye), highly reducing in nature
6. e_{aq}^- and $^{\bullet}COH(CH_3)_2$ - the electron adducts protonates to hydrazyl radical,
7. bimolecularly disproportionate (Stoichiometry = 2:1).

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