Photolysis of Butenedial and 4-Oxo-2-pentenal Under Atmospheric Conditions

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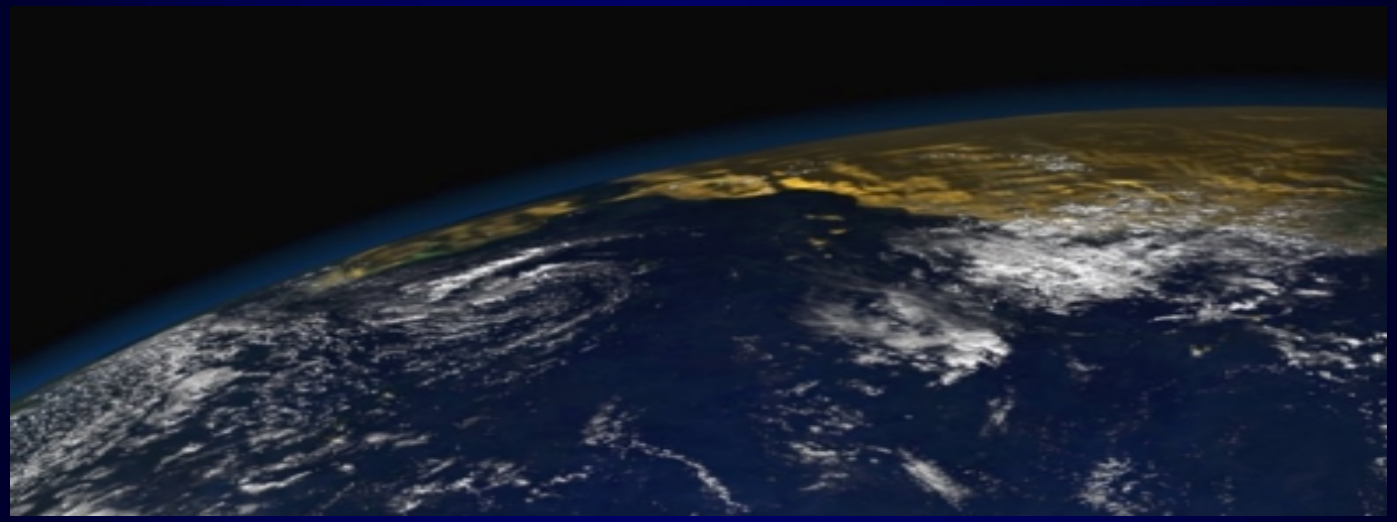
The Atmosphere



Photochemical reactor

Major reactive species

- Ozone (O_3)
- Hydroxyl Radical (OH)
- Sunlight ($\lambda > 290$ nm)

Hydroxyl Radical OH

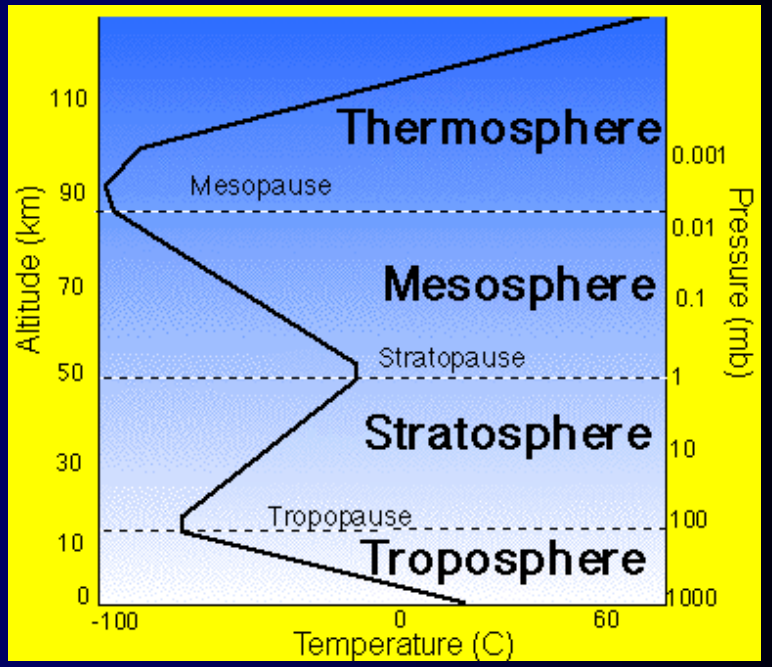
Formation of OH radicals

$$O_3 \xrightarrow{h\nu\ (\lambda<310\ nm)} O_2 + O(^1D)$$

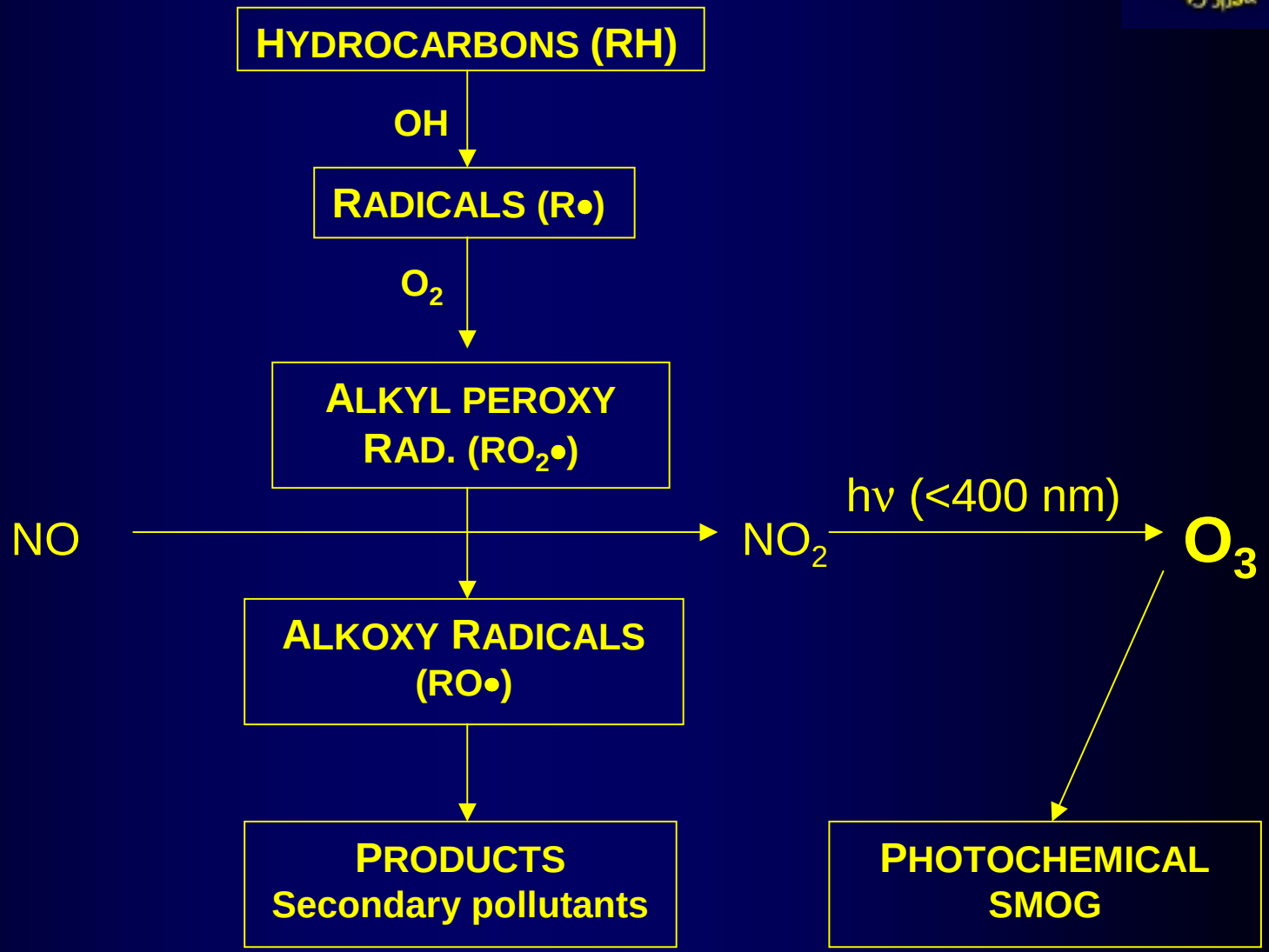
$$O(^1D) + H_2O \longrightarrow 2\ OH$$

- Reaction with hydroxyl radical (OH) is the major fate of most hydrocarbons in the troposphere

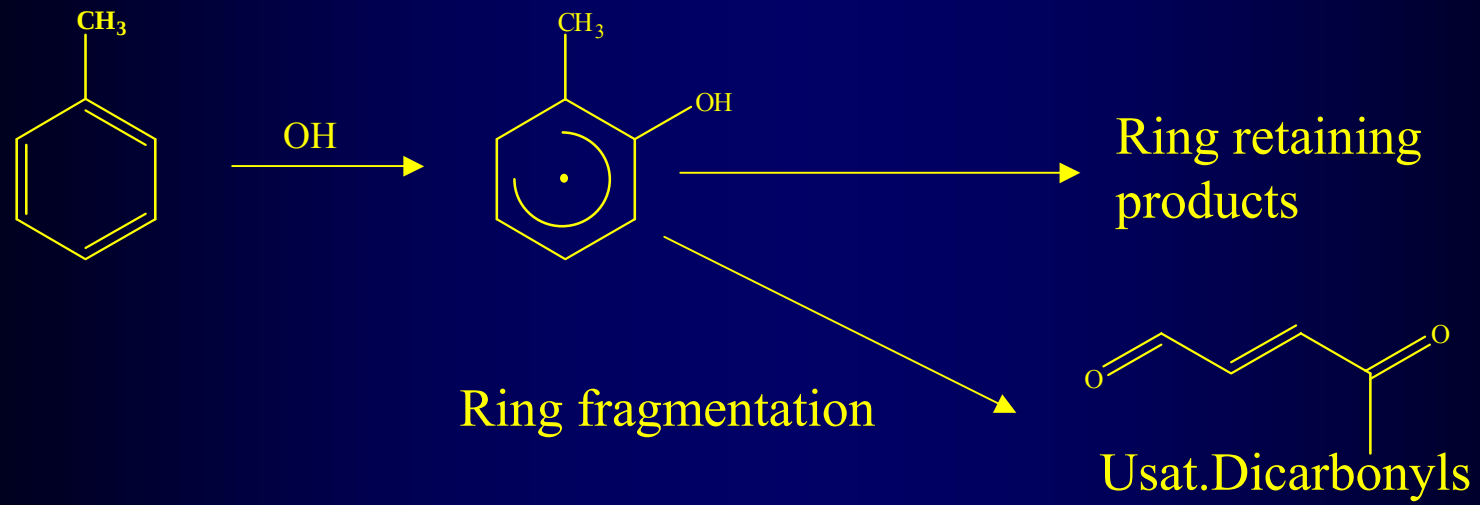
- Hydroxyl radical reaction can lead to the further formation of radicals (R•) and ultimately tropospheric ozone in polluted urban air



Why Radicals are Important



Atmospheric Oxidation of Aromatics



- Unsaturated dicarbonyls have been seen as products during the OH initiated atmospheric oxidation of aromatics
- Unsaturated dicarbonyls due to their structure would be expected to undergo photolysis

  → **Radical source** and effect the radical balance in the atmosphere

Atmospheric Fate of Butenedial and 4-oxo-2-pentenal

Reaction with :
- Hydroxyl radical (OH)
- Ozone (O_3)
- Photolysis (>290 nm)

Natural Atmospheric Life-time (τ_{OH})

$$\tau_{OH} = \frac{1}{k_{OH}[OH]}$$

Reactant	Butenedial	τ	4-Oxo-2-pentenal	τ
OH radical ($k_{OH}/10^{-12}$)	24.1±8[a]	7.1 hours	55.8±2.1[a]	3.1 h
Ozone (O_3) ($k_{O3}/10^{-18}$)	2[a]	8.3 days	4.8±0.8[b]	3.5 days
Photolysis (J)	?		?	

Daily [OH] = 1.6×10^6 molecules cm^{-3}
Daily [O_3] = 7.0×10^{11} molecules cm^{-3}

[a]Bierbach *et al.* 1994, EST 28, 715
[b]Liu *et al.* 1999, EST 33, 4212

Objectives of This Work

- Synthesis of butenedial and 4-oxo-2-pentenal at the University of Newcastle Upon Tyne
- Scale up preparations
- Determination of rate coefficient of photolysis for butenedial and 4-oxo-2-pentenal under natural light conditions
- Identification of products and yields
- Devise mechanistic data in order to assess extent of radical formation

Butenedial and 4-oxo-2-pentenal

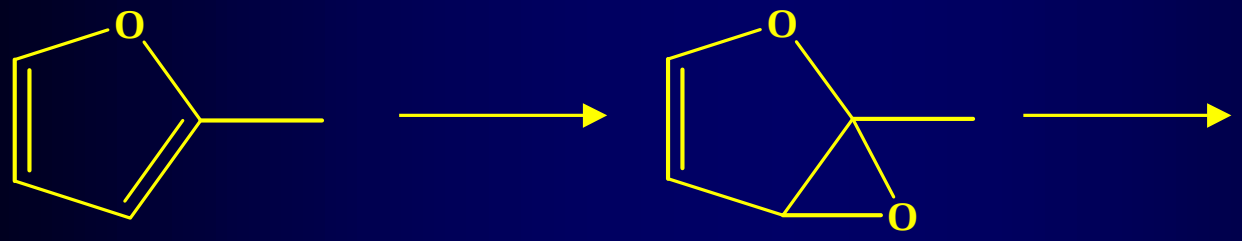
Unsaturated dicarbonyls

- Not stable
- Not commercially available
- Require reliable synthesis

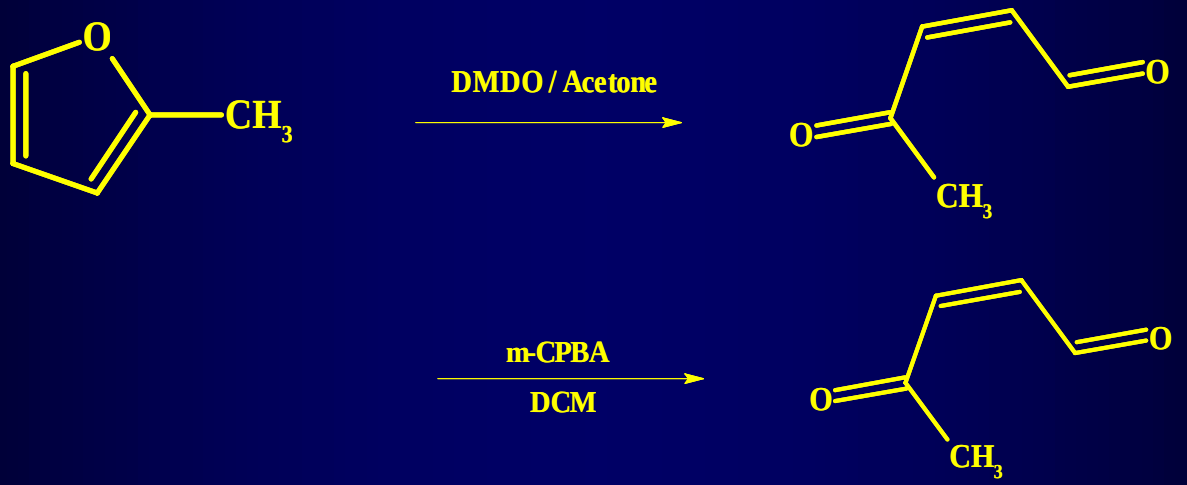
→ Collaboration with University of Newcastle Upon Tyne

Preparation of Unsaturated Dicarbonyls

The general procedure for the preparation, involves oxidative ring opening of substituted furan compounds.



Preparation of 4-oxo-2-pentenal



Atmospheric Photolysis

$$-\frac{dA}{dt} = \int_{\lambda} \Phi(\lambda)\sigma(\lambda)F(\lambda)\, d\lambda = J$$

J = photochemical rate constant (s^{-1})

Φ = quantum yield (molecules/photon)

F = photon flux (photons $cm^{-2}s^{-1}$)

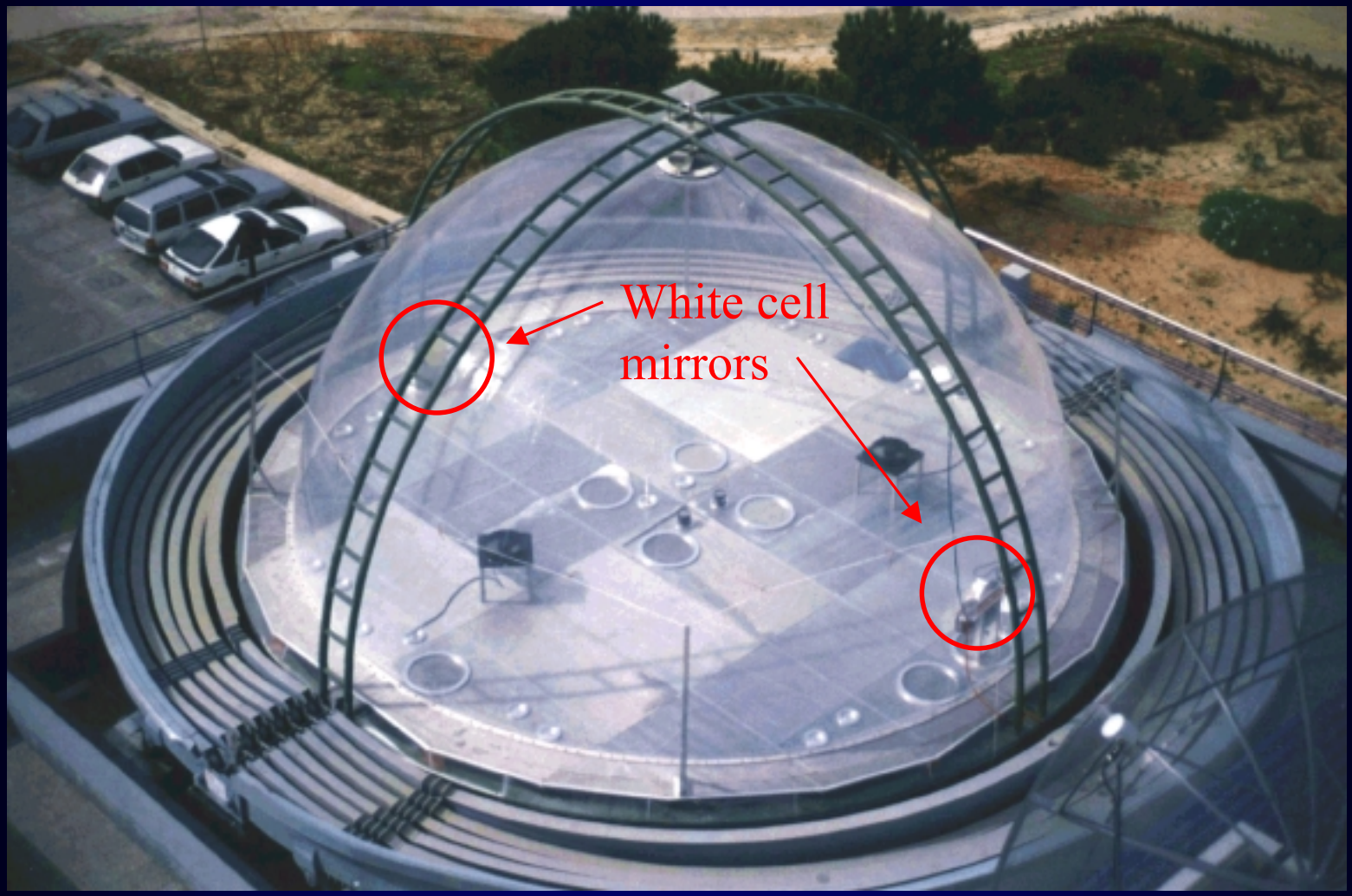
σ = absorption cross section (cm^2 $molecule^{-1}$)

Must measure J under natural light conditions

Valencia


Bay of Biscay
France
Spain
Portugal
Morocco
Atlanic Ocean
Balearic Sea
Gulf of Lion
Canary Islands
La Palma
Las Palmas
Gran Canaria
Farro
La Coruña
Castropol
Gijón
Oviedo
Santander
Bilbao
San Sebastián
Santiago
Lugo
Vitoria
Pamplona
Portbou
Vigo
Túy
Orense
León
Burgos
Logroño
Huesca
Girona
Palencia
Zamora
Valladolid
Soria
Zaragoza
Lleida
Barcelona
Salamanca
Segovia
Calatayud
Tarragona
Ávila
Madrid
Guadalajara
Teruel
Minorca
Cuenca
Castellón de la Plana
Inca
Artá
Toledo
Tarancón
Utiel
Palma
Majorca
Cáceres
Valencia
Lisbon
Badajoz
Albacete
Mérida
Ciudad Real
Alicante
Córdoba
Linares
Murcia
Jaén
Seville
Cartagena
Ayamonte
Huelva
Granada
Antequera
Almería
Jerez de la Frontera
Málaga
Cadiz
Algeciras
Gibraltar (U.K.)
Strait of Gibraltar
Ceuta (Sp.)
Melilla (Sp.)
Isla de Alborán (Spain)
Bay of Cádiz
Rio Miño
Rio Duero
Rio Tajo
Rio Guadiana
Rio Guadalquivir
Rio Ebro
Rio Pisuerga
Rio Jucar
Rio Genil
Rio Guadalmar

European Photoreactor (EUPHORE)
CEAM Institute Valencia, Spain



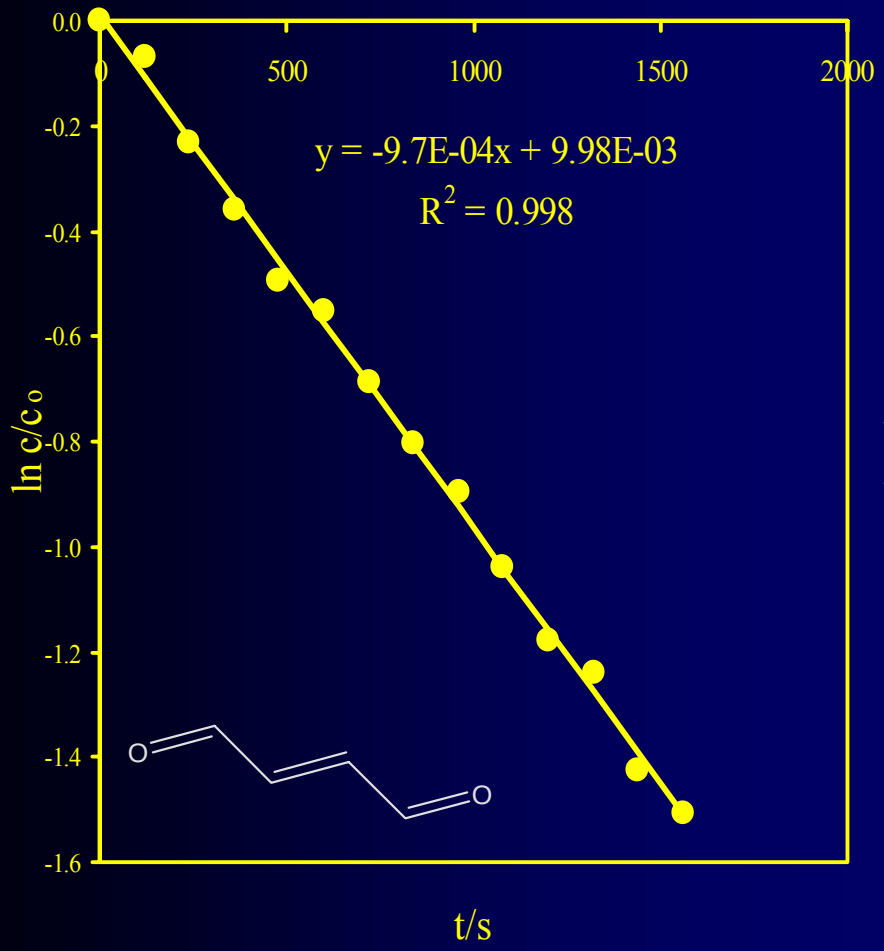
Experimental

Photolysis and product studies

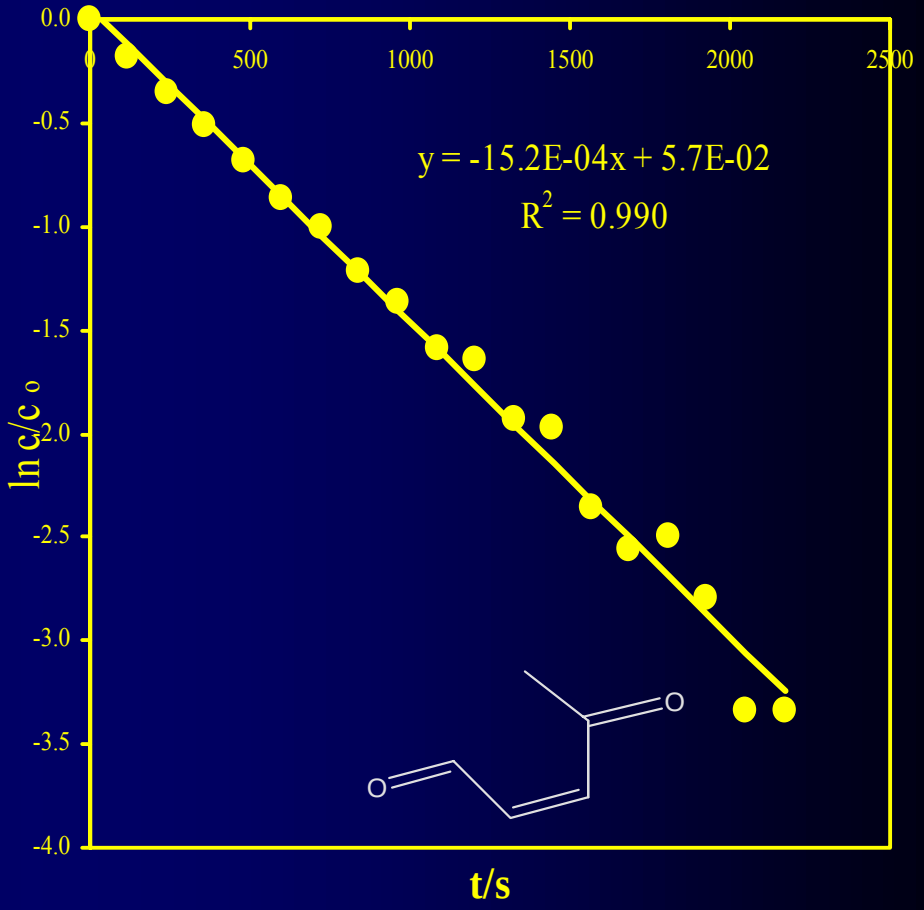
- Experiments in purified air
- Temperature range 297-303 K
- Light intensity and spectral distribution monitored with spectral radiant meter
- Photolysis rates J(NO_2) were calculated from these data.
- *In situ* long-path FTIR spectroscopy used to quantify reactant and products
- Concentrations determined by computer aided subtraction of calibrated reference spectra

First Order Photolysis Plots

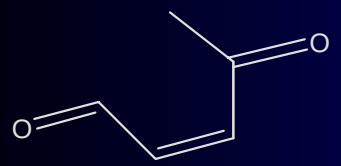
E-Butendial



Z-4-Oxo-2-pentenal



Photolysis Rates of E-Butenedial and Z-4-Oxo-2-pentenal

	$J_{(aldehyde)}$ $10^{-4}s^{-1}$	$J_{(NO2)}$ $10^{-3}s^{-1}$	$\frac{J_{(aldehydes)}}{J_{(NO2)}}$
	9.7±0.3	7.4±0.9	0.13±0.020
	15.9±0.75	8.0±0.4	0.20±0.017

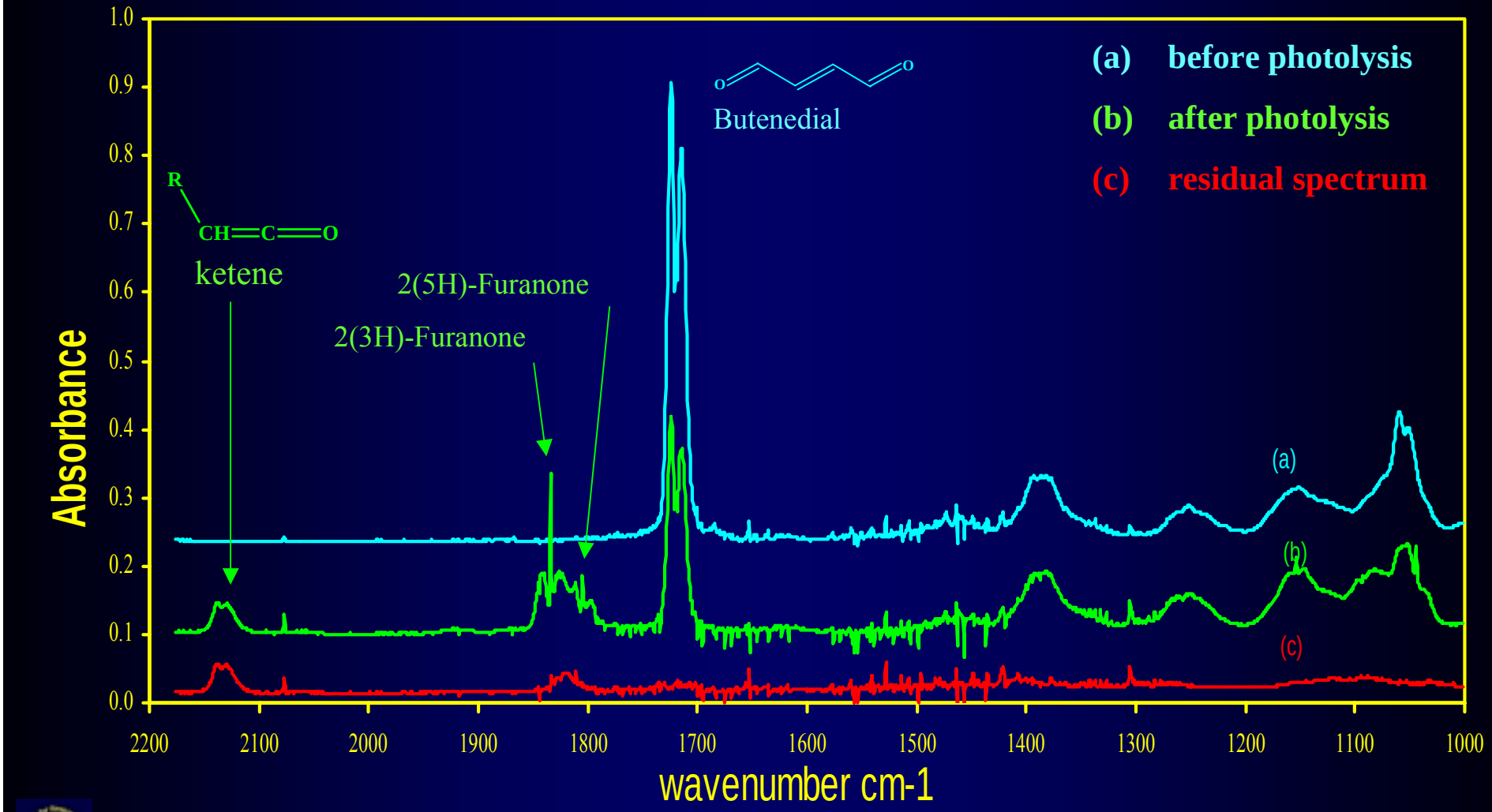
* quoted errors cover error limits of individual values, result averaged over two experiments

Product Studies

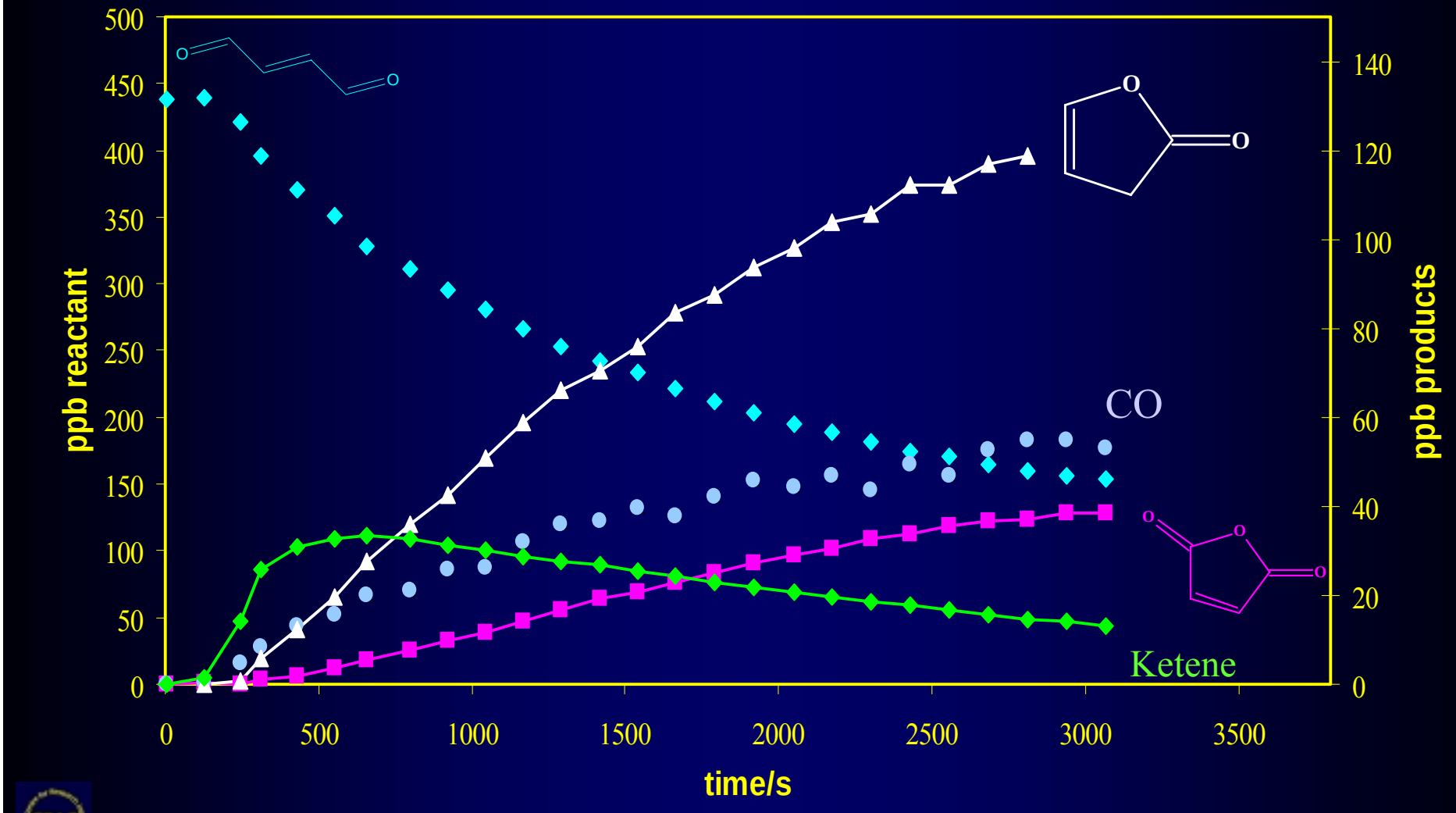
In situ FTIR allowed:

- Time resolved concentration-time profiles during the photolysis reaction
- Providing information about intermediate products and direct or delayed product formation
- Long path length (553.5 m) low detection limit

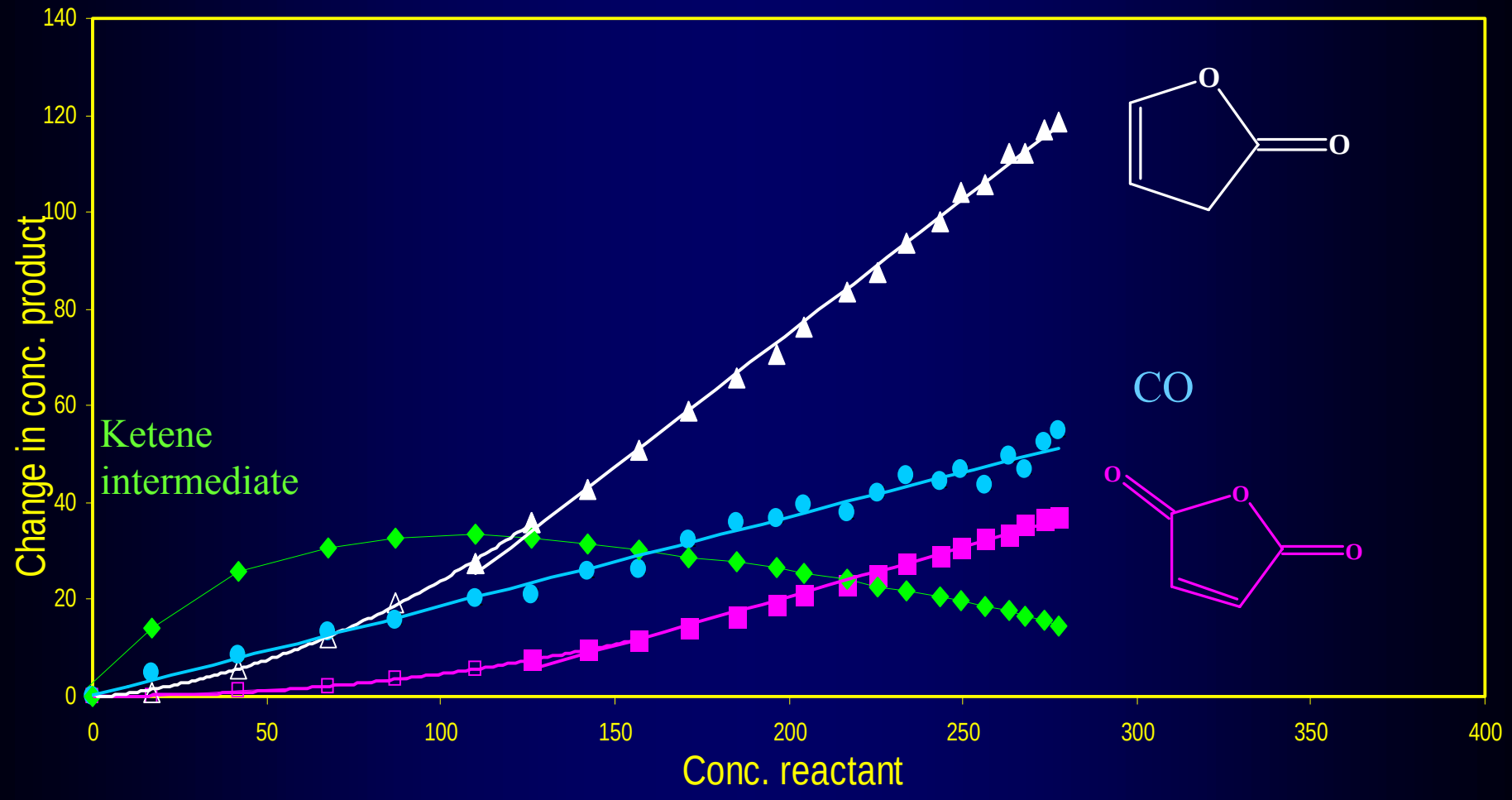
FTIR Spectra of E-Butenedial Reaction system



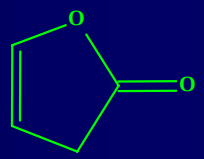
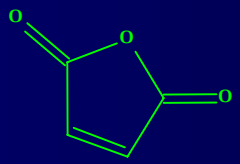
Concentration-Time Profile E-Butenedial Reaction System

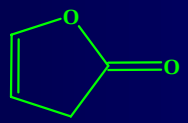
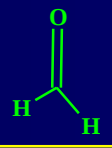
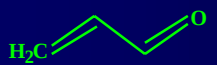
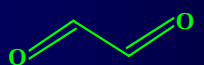
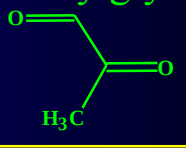


Product Yield Diagram E-Butenedial Reaction System

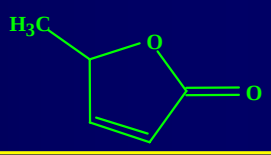
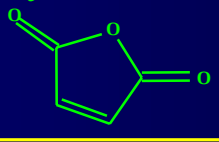


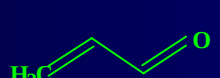
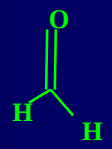
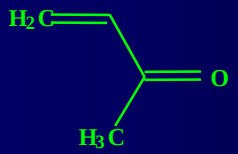
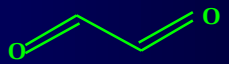
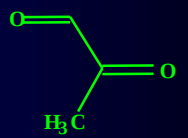
Product Yields of Butenedial Photolysis

Major products	2(3H)furanone 	Maleic anhydride 	CO
	delayed 55±2%	**delayed 20±1%**	**direct 18±3 %**

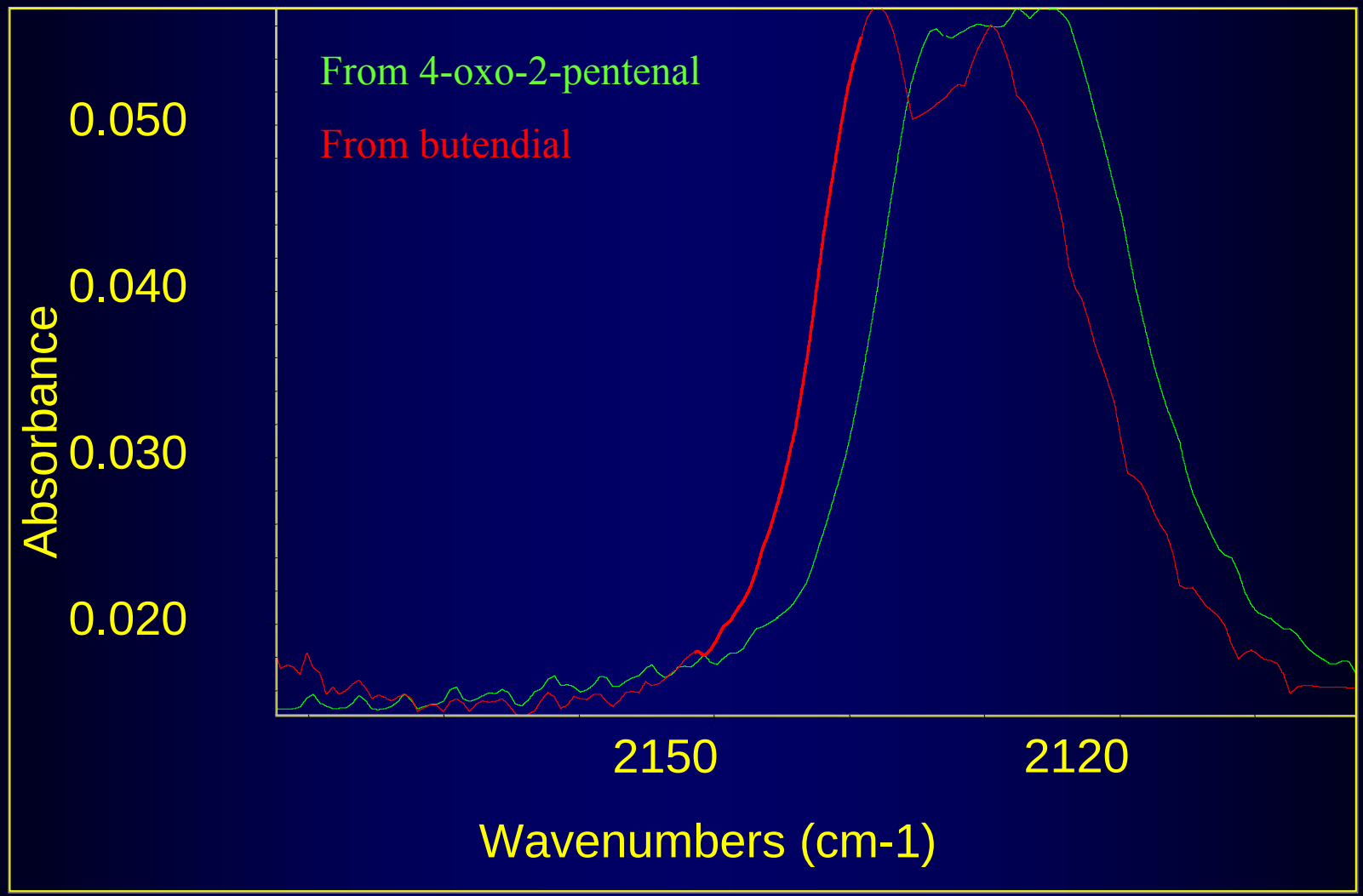
Minor products	2(5H)furanone 		Acrolein 	Glyoxal 	Methylglyoxal 
	max 3%	**max 2%**	**max 10%**	**max 2%**	**max 2%**

Product Yields of 4-Oxo-2-pentenal Photolysis

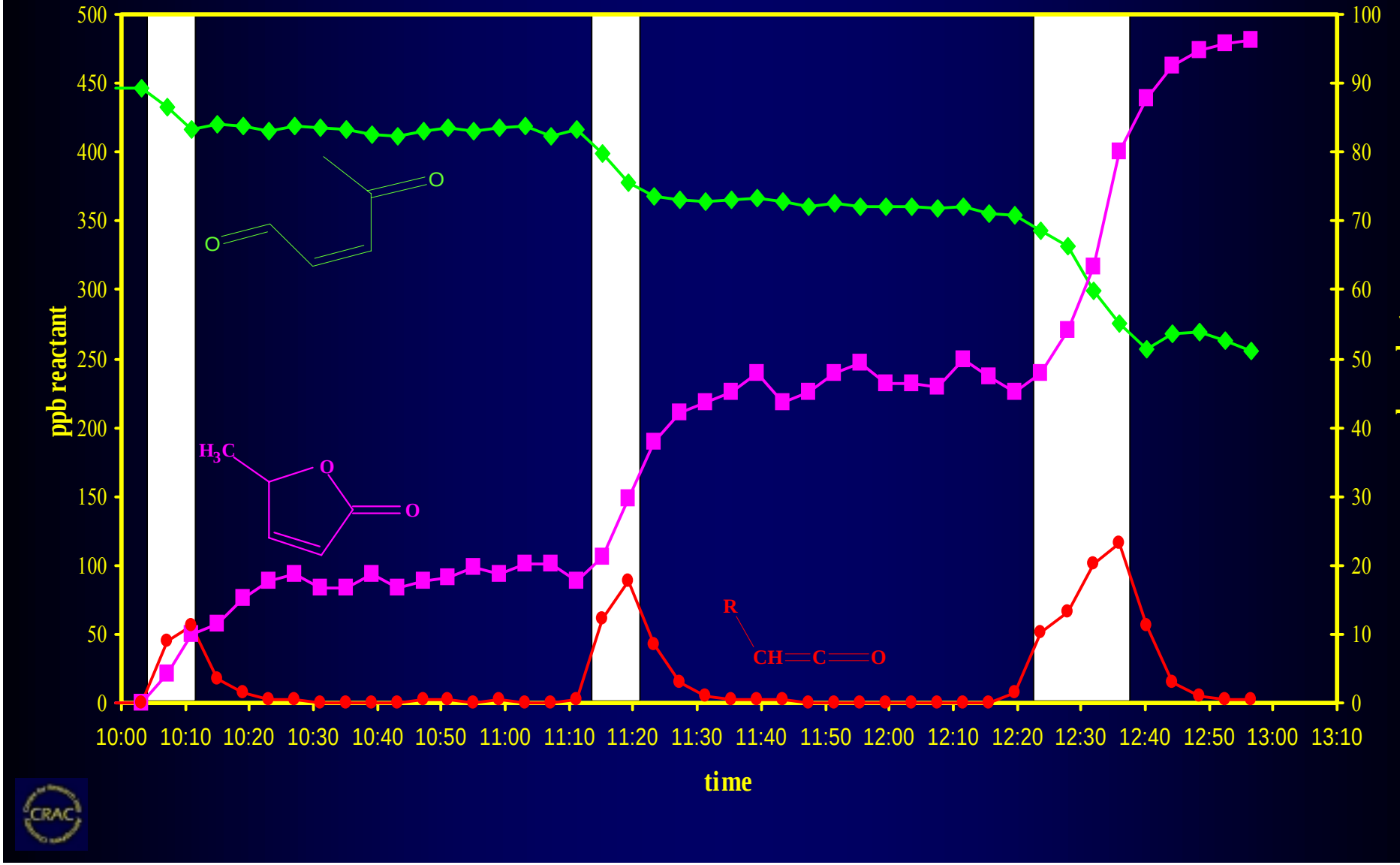
Major products	α- angelicalactone 	Maleic anhydride 	CO
	delayed 50±7%	**delayed 5.6±1.3%**	**direct 12±4%**

Minor products	Acrolein 	Formaldehyde 	MVK 	Glyoxal 	Methyl-glyoxal 
	max 8%	**max 1%**	**max 18%**	**max 1.5%**	**max 1.5%**

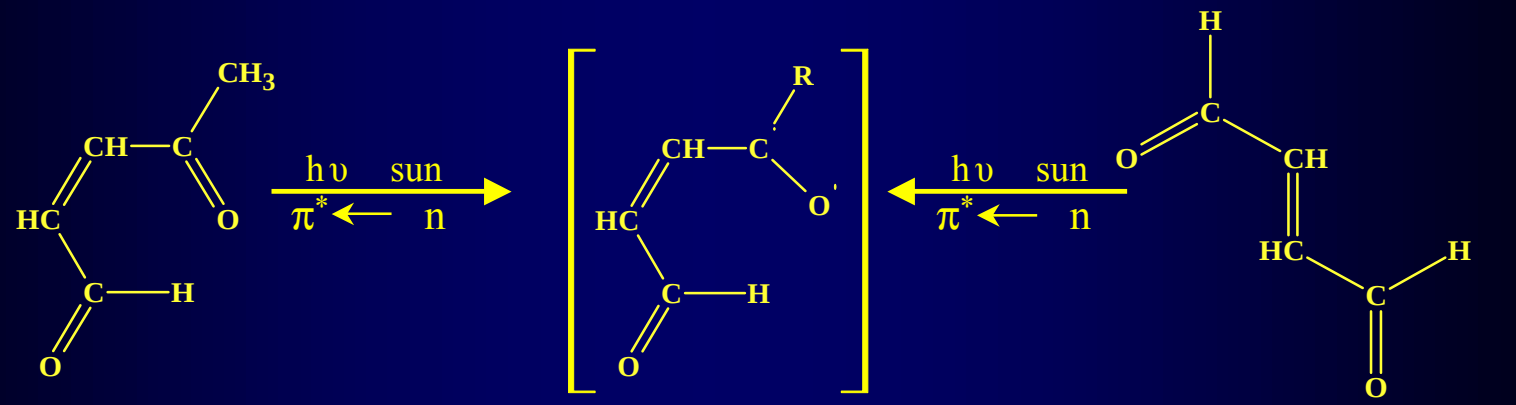
Ketene Intermediate

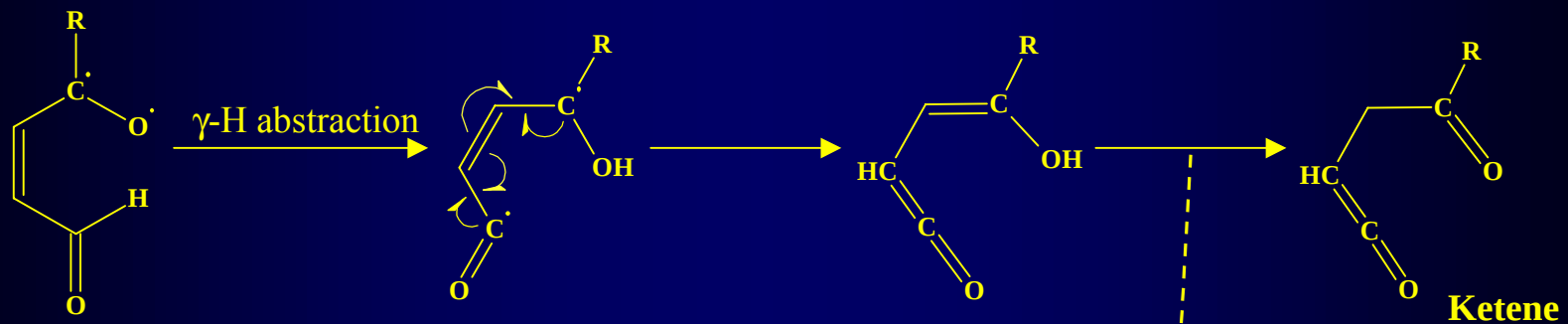


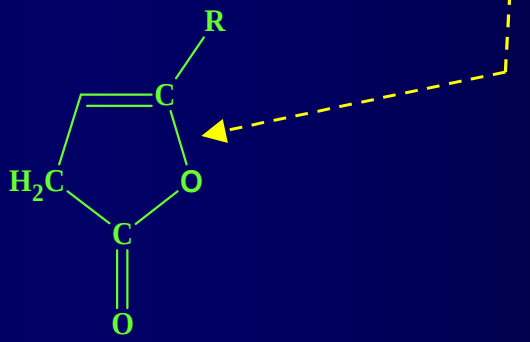
Characterisation of the Ketene Intermediate



Possible Mechanism
Formation of Ring Closure Products

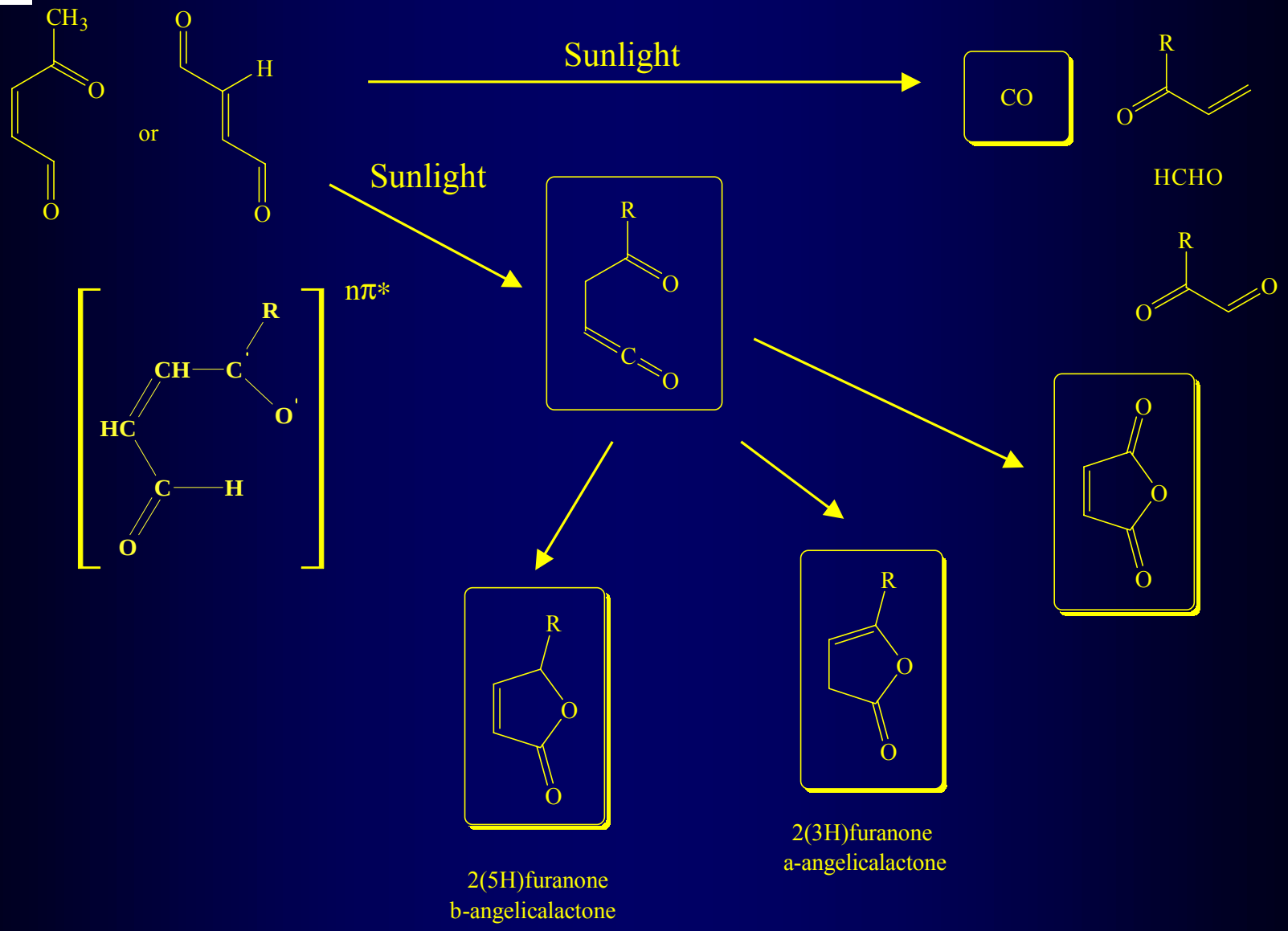






α-Angelicalactone (R = CH_3)
2(3H)Furanone (R = H)

Summary


CH3
O
O
or
O
H
O
Sunlight
CO
R
O
HCHO
Sunlight
nπ*
R
CH
C
O
HC
C
H
O
R
O
C
O
R
O
O
O
O
R
O
O
R
O
O
2(5H)furanone
b-angelicalactone
2(3H)furanone
a-angelicalactone

Summary

Reactant	Butenedial	τ	4-Oxo-2-pentenal	τ
OH radical ($k_{OH}/10^{-12}$)	24.1±8[a]	7.1 hours	55.8±2.1	3.1 h
Ozone (O_3) ($k_{O3}/10^{-18}$)	2[a]	8.3 days	4.8±0.8	3.5 days
Photolysis ($J/10^{-4}s^{-1}$)	9.7±0.3	17.2 min	15.9±0.75	10.5 min

- No high concentrations expected in ambient air
- Unsaturated dicarbonyl → Ketene Intermediate → products
- Photolysis leads mainly to ring closure products
- Little or no formation of radicals

Acknowledgements

Prof. Bernard Golding

Alistair Henderson

Klaus Wirtz (EUPHORE)

John Wenger

Lars Thüner

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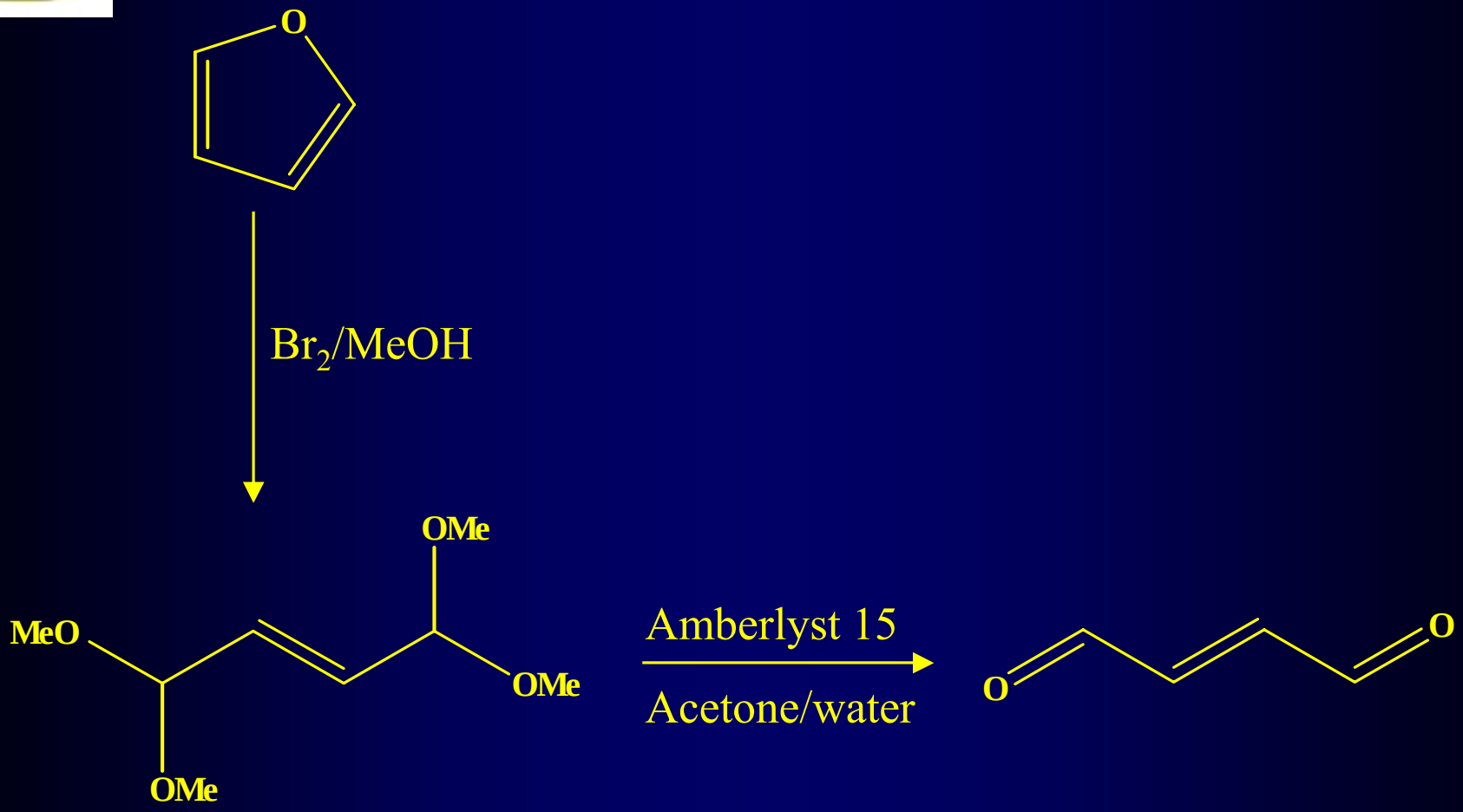
Preparation of Butenedial



Unsaturated Dicarbonyls

Parent Aromatic	Unsaturated Dicarbonyl
	Butenedial 4-oxo-2-pentenal 2-methyl-butenedial 2-methyl-4-oxo-pentenal Hexene-2,5-dione 3-methyl-hexene-2,5-dione

Ketene Formation and Decay