Chemical kinetics in AOPs

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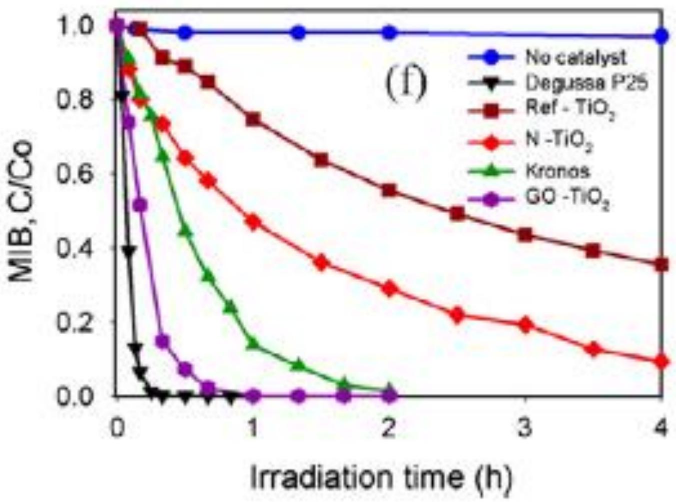
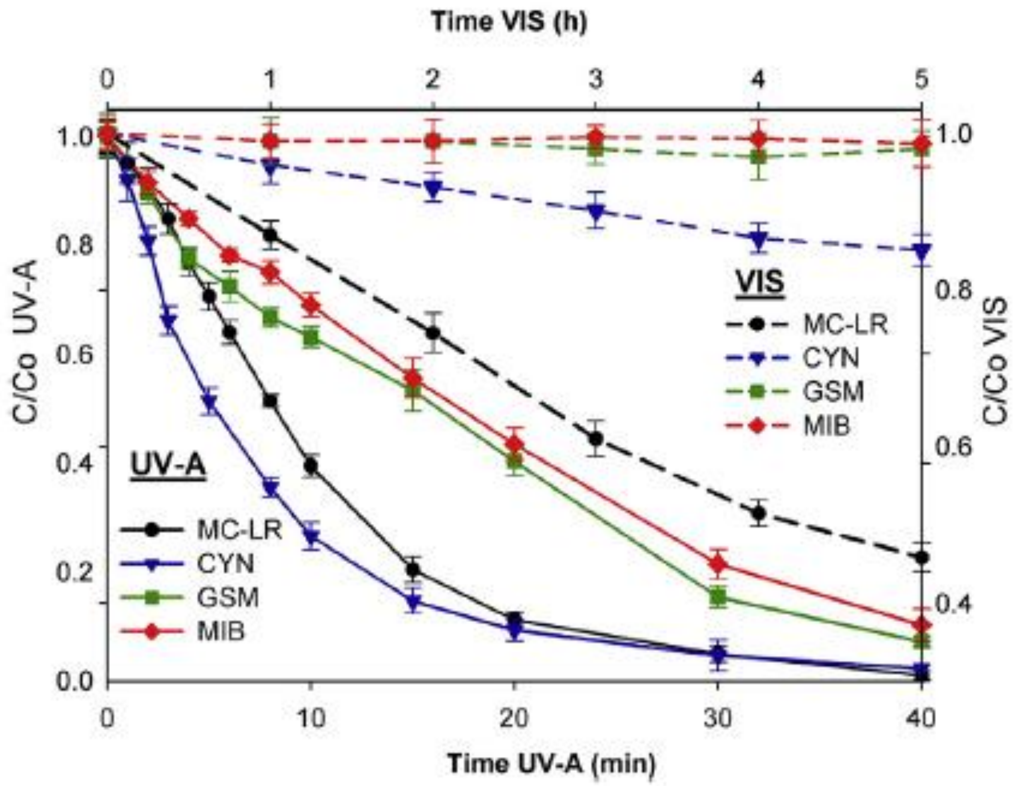


Why chemical kinetics ?

- Evaluate the effectiveness and efficiency of AOPs.
- Compare AOPs objectively.
- Have clues about the underlying mechanisms.
- Study the effects of various process parameters.
- Optimization studies.
- Prediction of the course of the process.



Source: Fotiou et al. Water Research 2016
https://doi.org/10.1016/j.watres.2015.12.006

From observed degradation to mechanisms…

Environmental Science & Technology Article

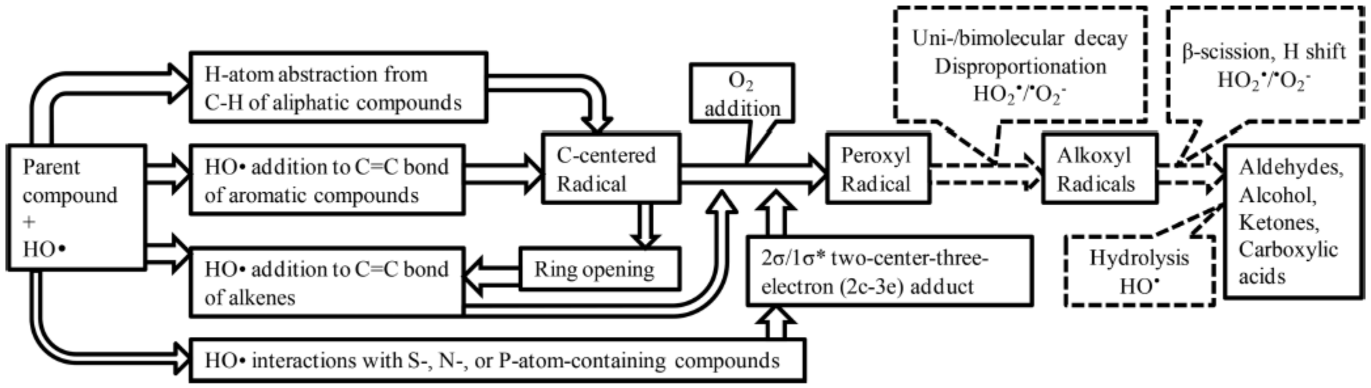


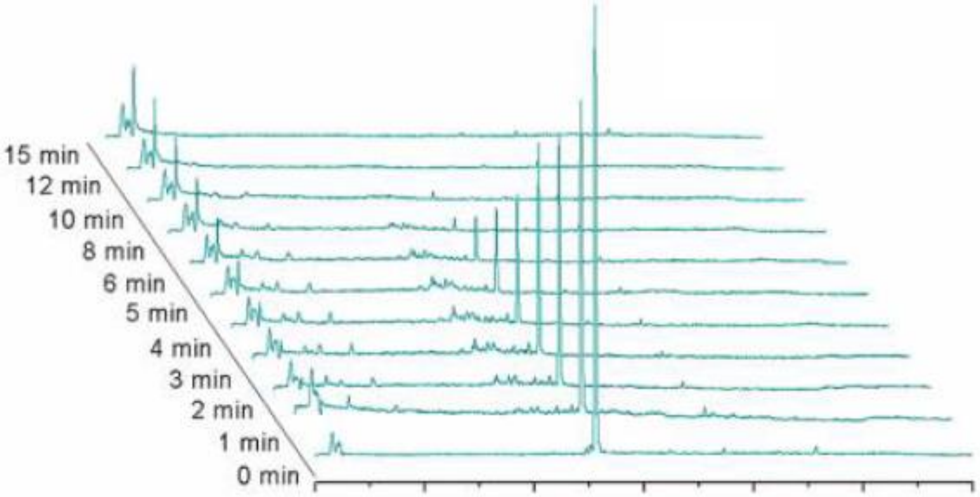
Figure 1. Known and unknown reaction pathways of organic compound degradation induced by hydroxyl radicals in aqueous phase AOPs.

Kamath et al. ES&T 2018, https://doi.org/10.1021/acs.est.8b00582

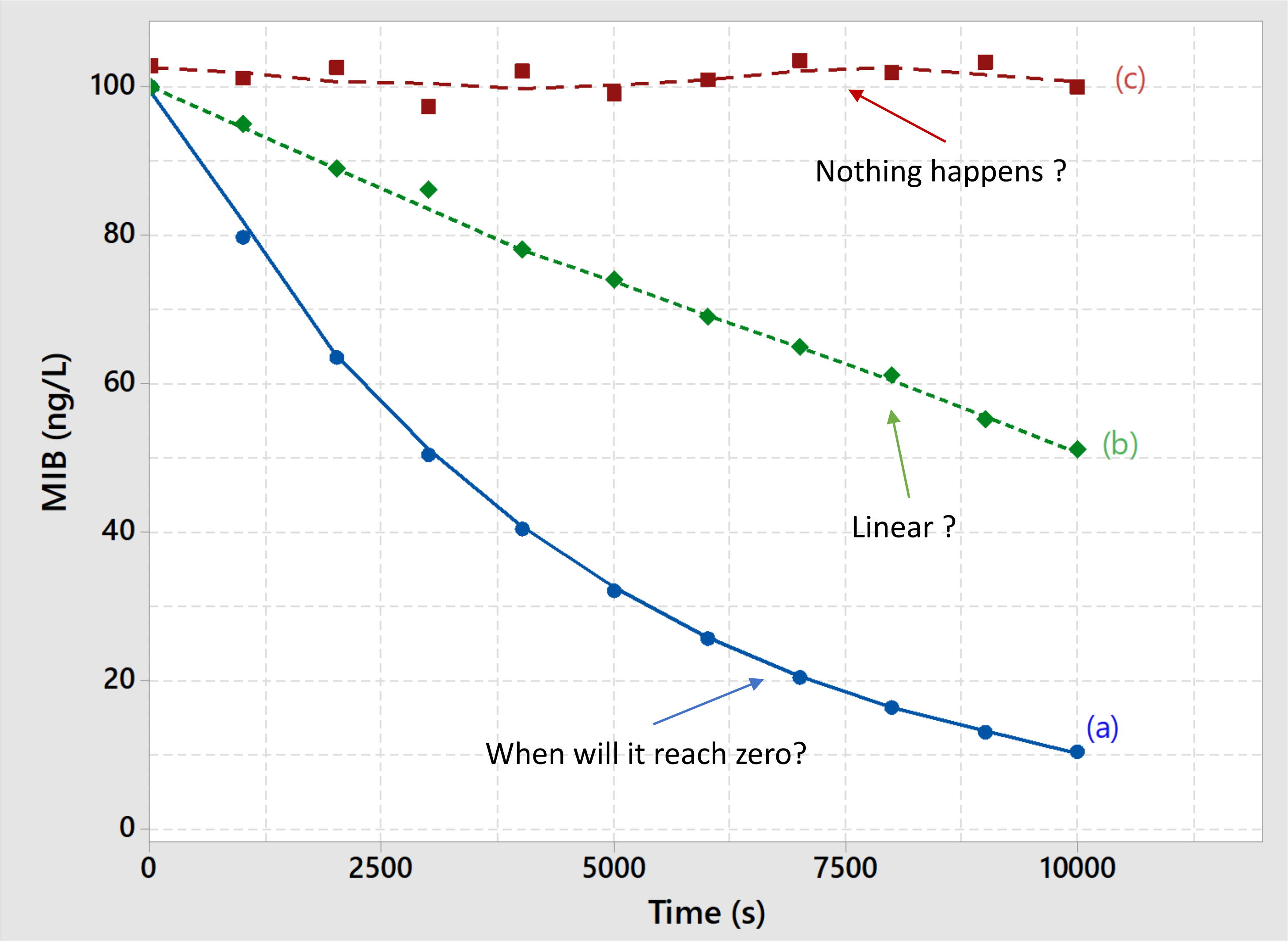
- Complex reactions in AOPs even with one starting compound and a single reactive species.
- Transformation products not completely detected - identified - quantified.
- Mass balances generally not achieved.
- Elusive mechanisms.

Monitoring of degradation processes

- Example: monitoring of degradation of a compound over time by various AOPs.
- Analysis e.g., by GC-MS, LC-MS, photometry.
- Plots of concentration over time.
- Initial observations?



Fotiou et al., Ind. Eng. Chem. Res. 2013, *https://doi.org/10.1021/ie400382r*



Plots (connecting line with smoothing) from simulated data

Example of "zero order" kinetics

$[MIB] = Concentration\ of\ MIB\ (e.g., in\ M)$

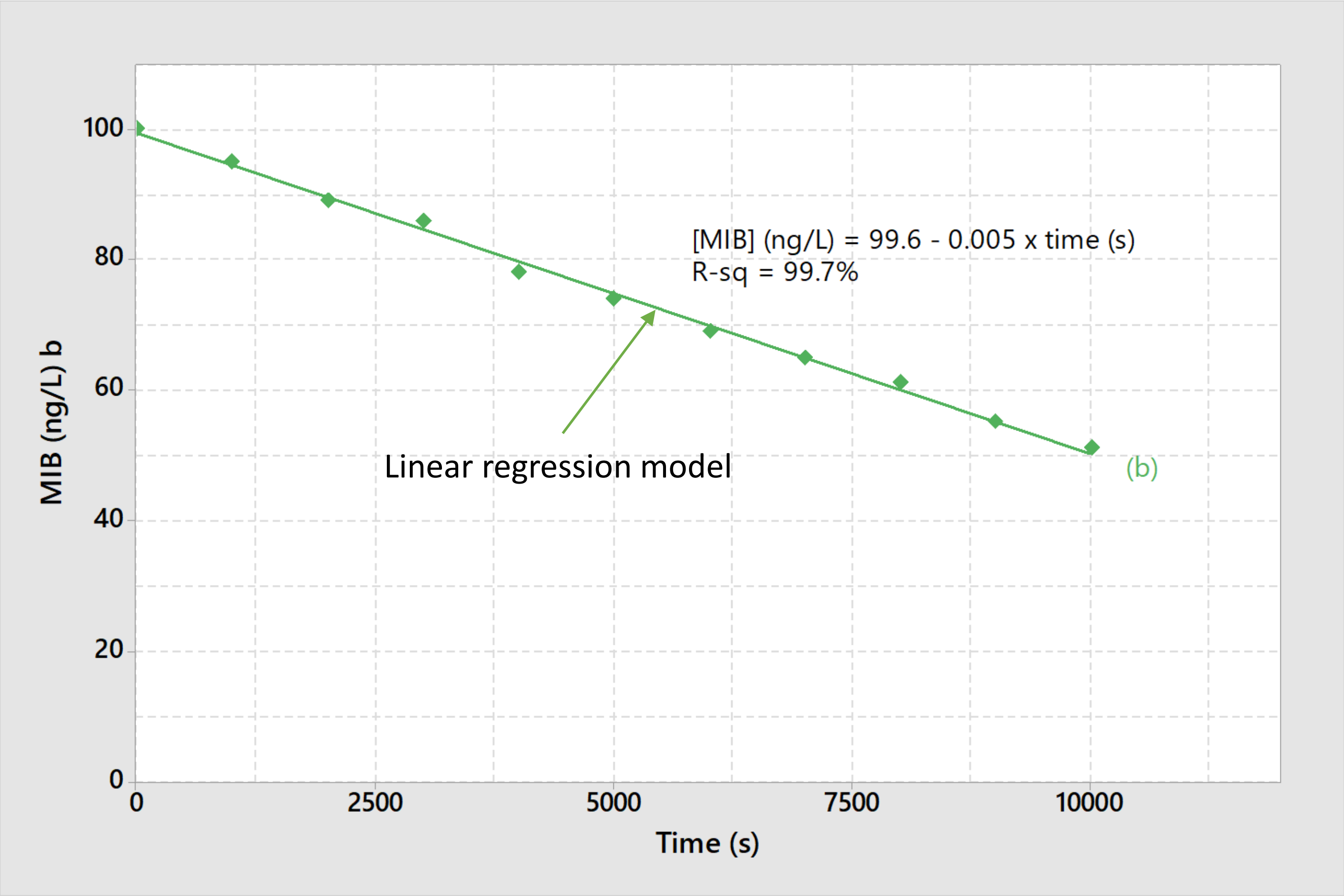
$\frac{d[MIB]}{dt} = rate\ of\ degradation\ of\ MIB\ (e.g., Ms^{-1})$

$k = rate\ constant\ (Ms^{-1})$

$$\frac{d[MIB]}{dt} = -k$$

$$[MIB] = [MIB]_0 - kt$$

$$t_{1/2} = \frac{[MIB]_0}{2k}$$



- Rate of degradation does not depend on MIB concentration.
- "Saturation" kinetics

Example of "first order" kinetics

$[MIB] = Concentration\ of\ MIB\ (e.g., in\ M)$

$\frac{d[MIB]}{dt} = rate\ of\ degradation\ of\ MIB\ (e.g., Ms^{-1})$

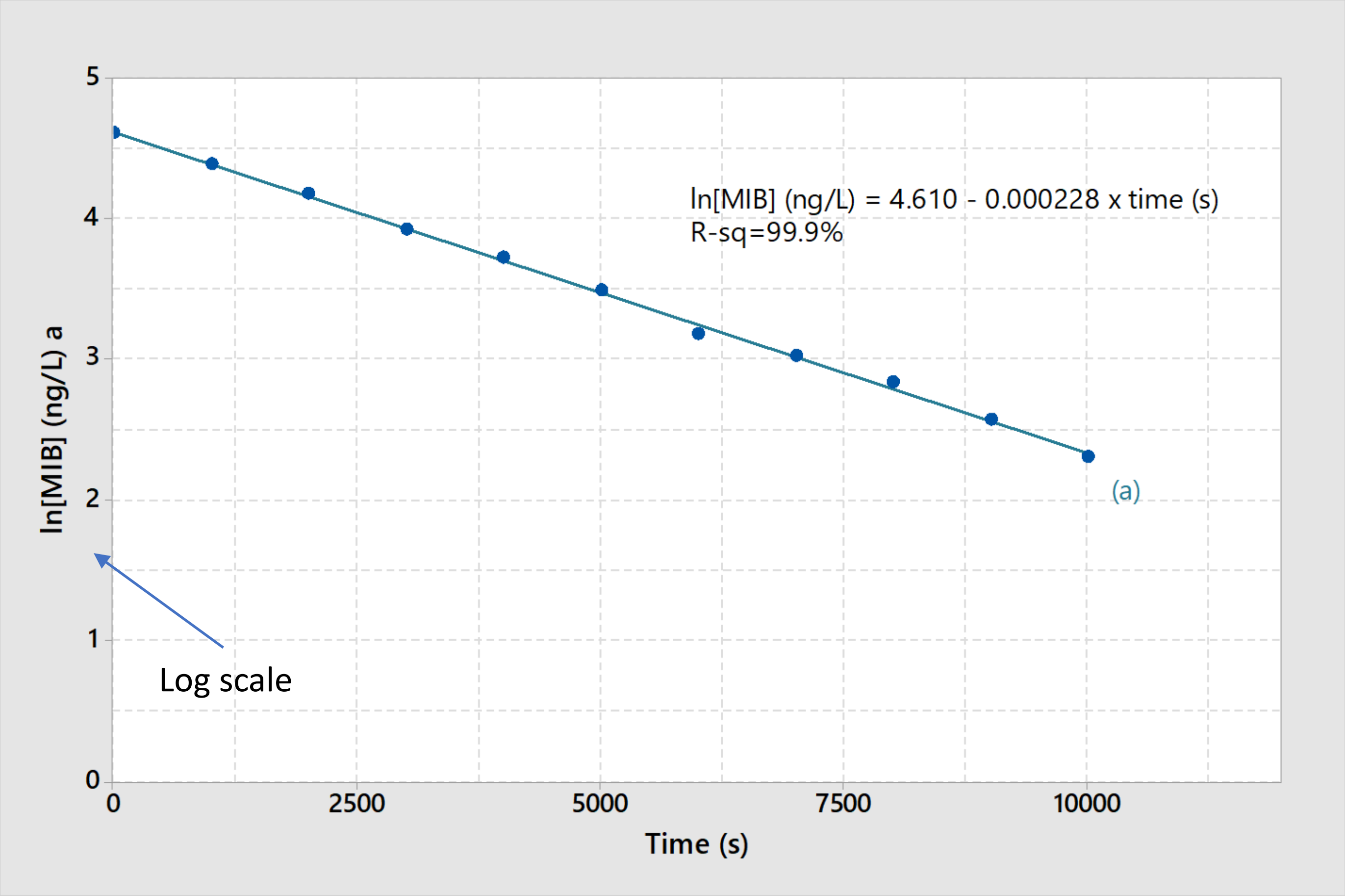
$k = rate\ constant\ (s^{-1})$

$$\frac{d[MIB]}{dt} = -k[MIB]$$

$$\ln[MIB] = \ln[MIB]_0 - kt$$

$$[MIB = [MIB]_0 e^{-kt}$$

$$t_{1/2} = \frac{\ln(2)}{k}$$



- Rate of degradation depends on MIB concentration.
- Common in AOPs

Example of “second order” kinetics

$[MIB] = Concentration\ of\ MIB\ (e.g., in\ M)$

$$\frac{\mathrm{d}[MIB]}{\mathrm{d}t} = rate\ of\ degradation\ of\ MIB\ (e.g., Ms^{-1})$$

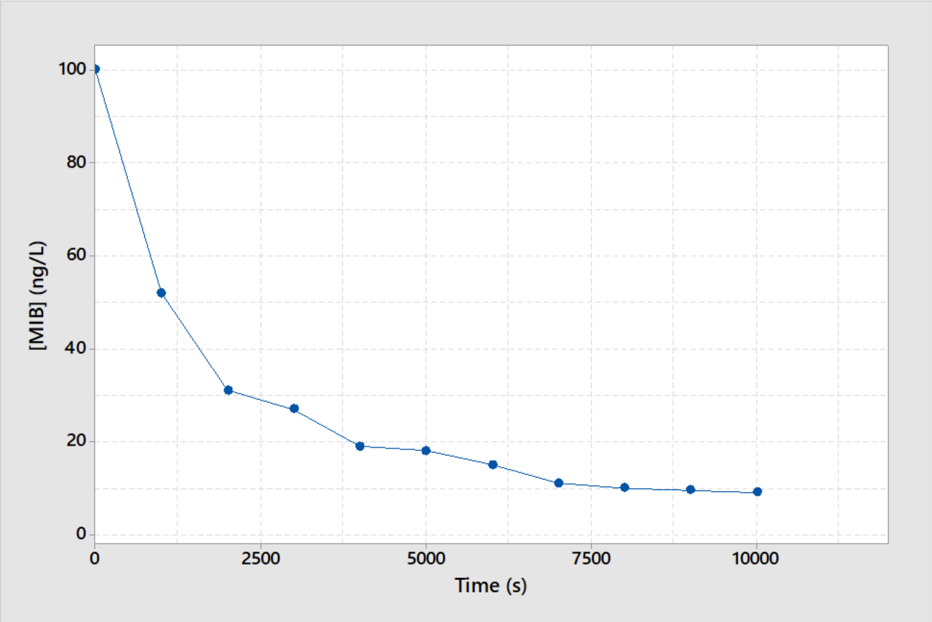
$k = rate\ constant\ (M^{-1}s^{-1})$

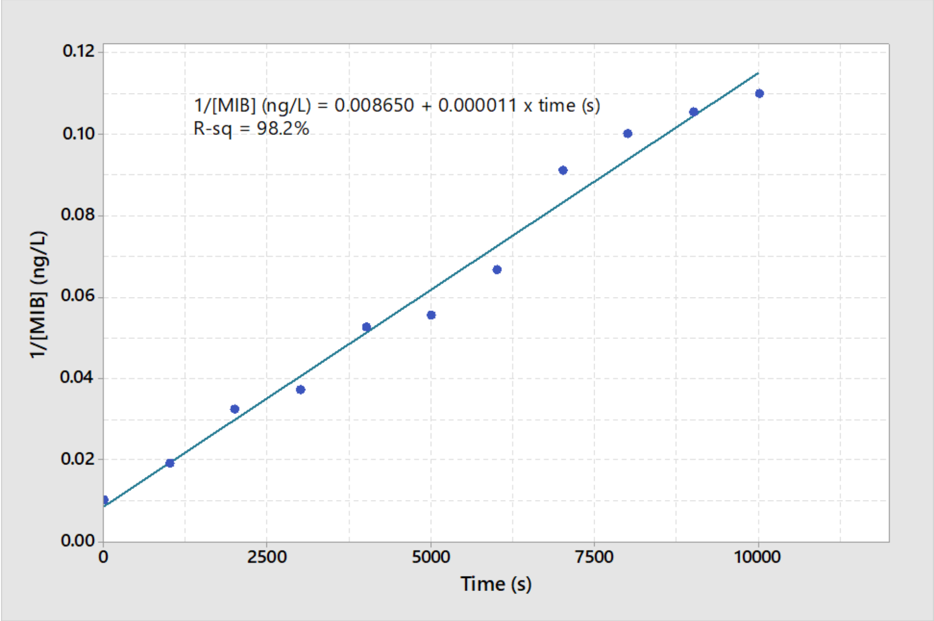
$$\frac{\mathrm{d}[MIB]}{\mathrm{d}t} = -k[MIB]^2$$

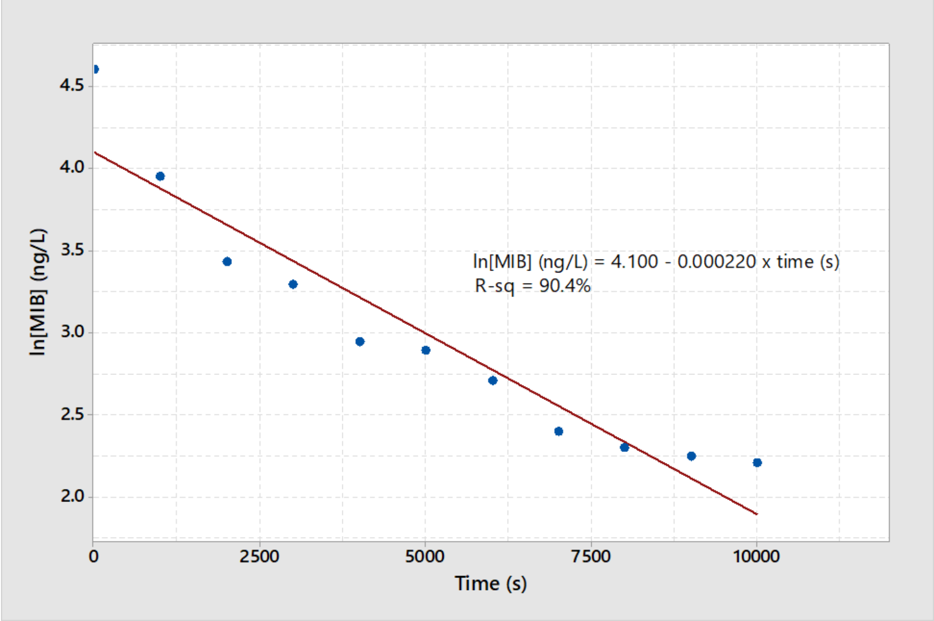
$$\frac{1}{[MIB]} = \frac{1}{[MIB]_0} + kt$$

$$t_{1/2} = \frac{1}{k[MIB]_0}$$

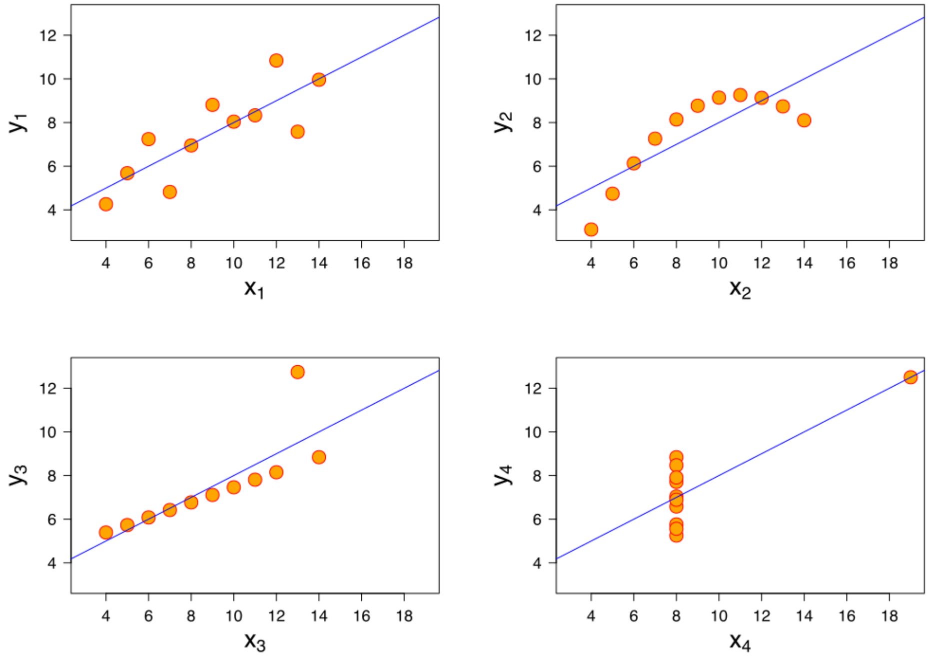
- Elementary bimolecular reactions







How to evaluate kinetic models?

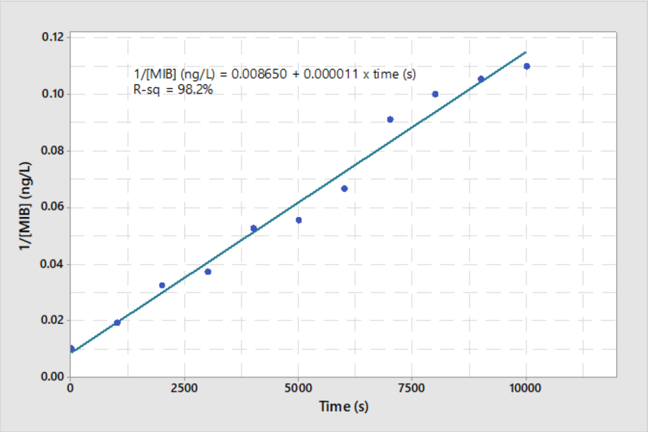


Anscombe's quartet: Correlation *(x,y)*=0.816,
Linear regression line y = 3.00 + 0.500 x,
R^2=0.67, **for all datasets.**

Anscombe (1973) DOI: 10.1080/00031305.1973.10478966

- R-sq vs adjusted R-sq (for more independent variables)
- Mean Square Error: $$MSE = \frac{1}{N}\sum_{i=1}^{N}(y_i - \hat{y}_i)^2$$
- Mean Absolute Error $$MAE = \frac{1}{N}\sum_{i=1}^{N}|y_i - \hat{y}_i|$$
- Distribution of residuals $(y_i - \hat{y}_i)$
- Outliers?

Visual and statistical evaluation



R-sq=98.2%,

R-sq(adj) = 98.0%

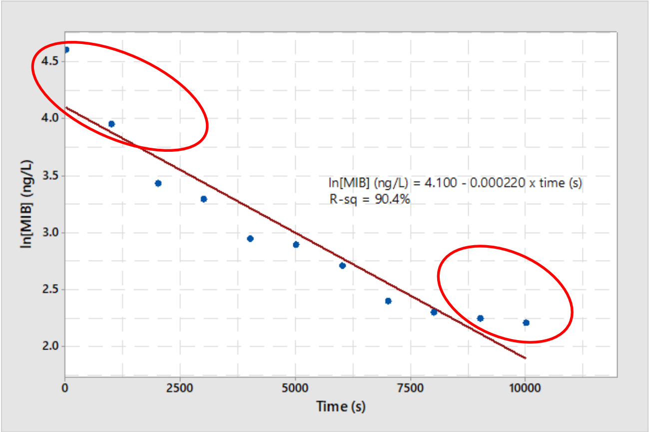
Residuals: no trends

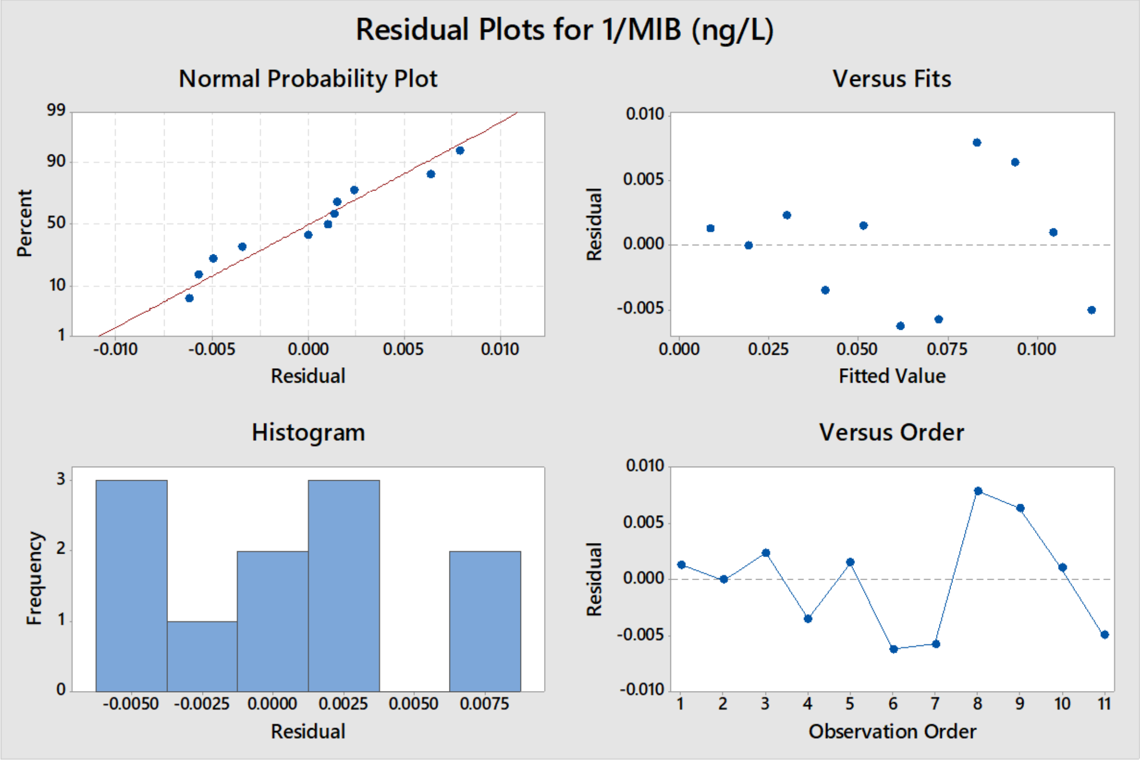
R-sq=90.4%,

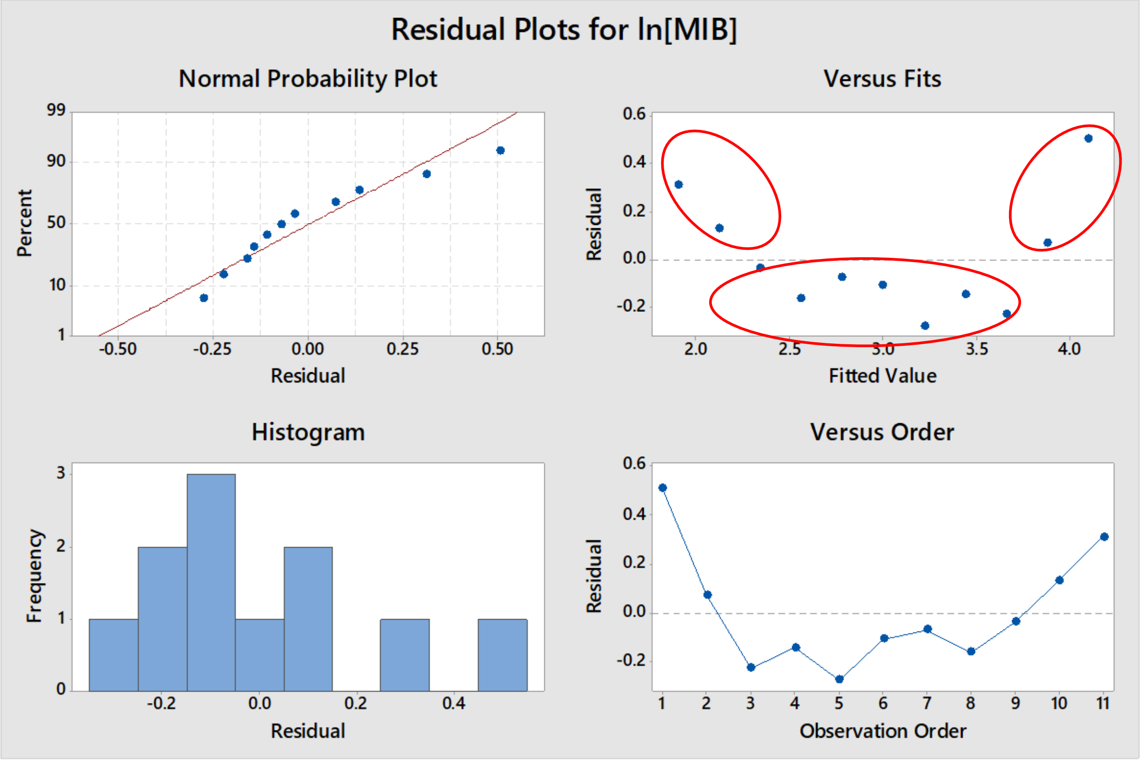
R-sq(adj) = 89.3%

Residuals: trends

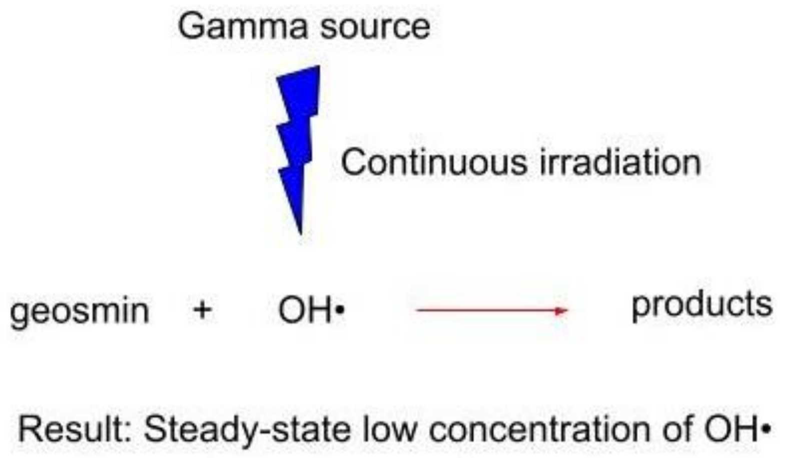
Caution with "outliers"







Steady state approximation



MIB + OH• ⟶ Products

This elementary reaction kinetics is expressed as:

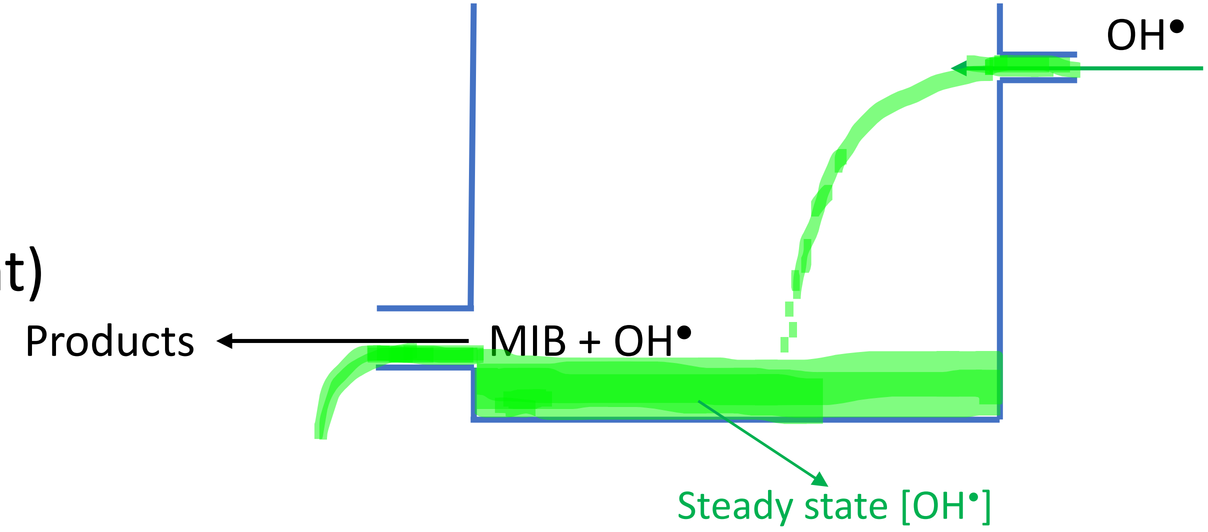
$$\frac{d[MIB]}{dt} = k[MIB][OH\,\bullet]$$

Under steady state conditions, [OH·]=constant

$$\frac{d[MIB]}{dt} = k'[MIB]$$ (1st order)

$k' = k[OH\,\bullet]$ (apparent or observed rate constant)

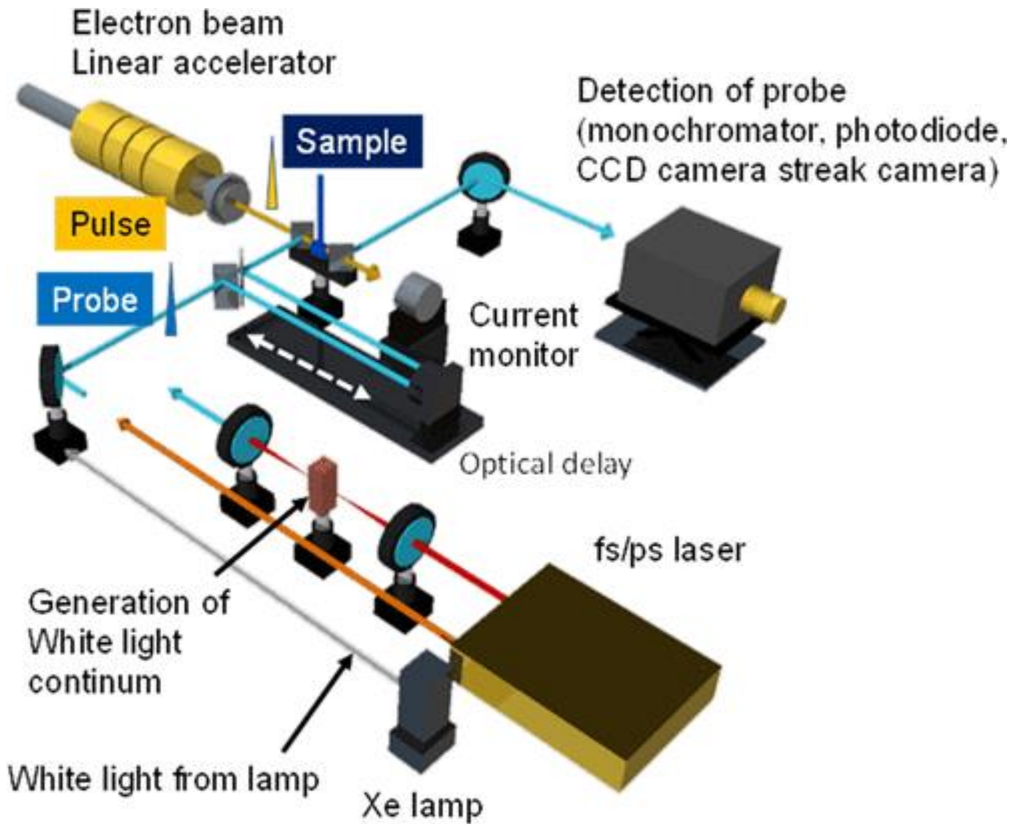
Also called "pseudo-first order" kinetics.



Determination of rate constants of radical reactions

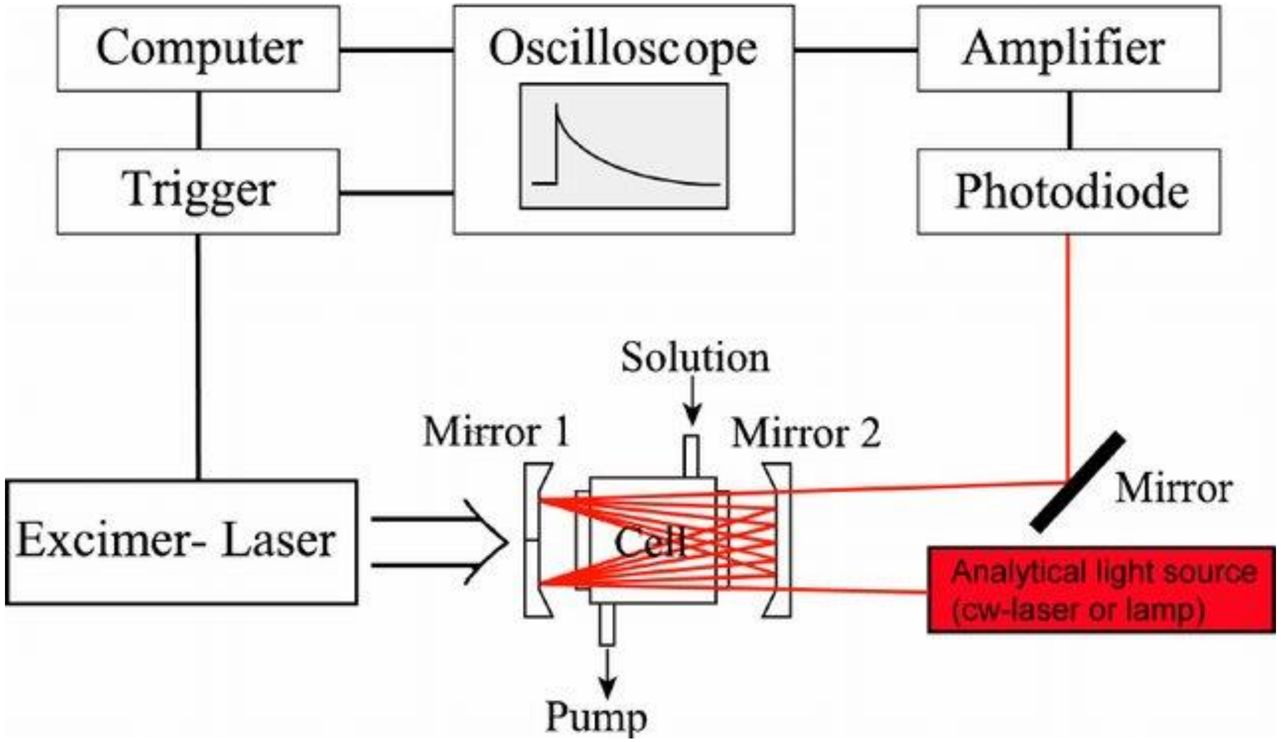
(reference methods - down to femtosecond timescale)

Pulse radiolysis



Kobayashi, Chem. Rev. 2019, 119, 6, 4413–4462

Flash photolysis



Hoffmann et al. 2014

Databases with bimolecular rate constants of radical reactions

Kinetics Database

Kinetics Database Resources

Simple Reaction Search

Search Reaction Database

Search Bibliographic Database

Set Unit Preferences

Contact Us to Submit an Article

Citation

Help

Other Databases

NIST Standard Reference Data Program

NIST Chemistry Web Book

NDRL-NIST Solution Kinetics Database

NIST Computational Chemistry Comparison and Benchmark Database

The NIST Reference on Constants, Units, and Uncertainty

NIST Chemical Kinetics Database

Standard Reference Database 17, Version 7.1 (Web Version), Release 1.6.8
Data Version 2022

A compilation of kinetics data on gas-phase reactions

Reaction Database Quick Search Form

Enter the reactant(s) and/or product(s) in the fields below. Fields may be left blank.

OH + phenol → + Submit Clear

If you would like more search options, try...
advanced reaction search form
bibliographic search form

Welcome
About the database.

Getting Started
A quick introduction to the database.

https://kinetics.nist.gov/kinetics/

Reaction Database Search Form

Fill in one or more of the text fields below. Searchable fields and logical operators may be changed via the pull-down menus. Additional help is available.

	Reactant	is	OH
and	Reactant	is	phenol
and	Product	is	
and	Product	is	
and	Squib	contains	

Submit Search Clear Form

Find only decomposition reactions

Restrict search to results of type any

Critical Review of rate constants for reactions of hydrated electrons, hydrogen atoms and hydroxyl radicals ($\cdot OH/\cdot O^-$) in Aqueous Solution

Cite as: Journal of Physical and Chemical Reference Data **17**, 513 (1988); https://doi.org/10.1063/1.555805
Submitted: 23 June 1987 • Published Online: 15 October 2009

George V. Buxton, Clive L. Greenstock, W. Phillips Helman, et al.

Reactivity of HO_2/O^-_2 Radicals in Aqueous Solution

Cite as: Journal of Physical and Chemical Reference Data **14**, 1041 (1985); https://doi.org/10.1063/1.555739
Published Online: 15 October 2009

Benon H. J. Bielski, Diane E. Cabelli, Ravindra L. Arudi, and Alberta B. Ross

Search Results

Click on a link in the table below to see detail on the selected reaction.

Records	Reaction
5 records matched	Phenol + $\cdot OH \rightarrow C_6H_5O + H_2O$
3 records matched	Phenol + $\cdot OH \rightarrow$ Adduct
11 records matched	Phenol + $\cdot OH \rightarrow$ Products
2 records matched	Phenol + $\cdot OH \rightarrow$ cyc-C(OH)CHCHCHCHCH(OH)
2 records matched	Phenol + $\cdot OH \rightarrow$ cyc-C(OH)CHCHCHCH(OH)CH
2 records matched	Phenol + $\cdot OH \rightarrow$ cyc-C(OH)CHCHCH(OH)CHCH
1 record matched	Phenol + $\cdot OH \rightarrow$ cyc-C(OH)2CHCHCHCHCH

Search returned 26 records.

Competition kinetics

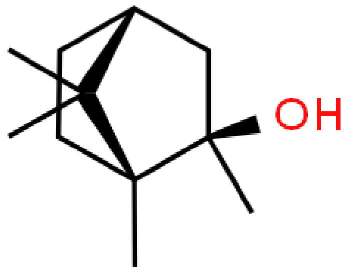
Can we determine 2nd-order rate constants of elementary bimolecular radical reactions from steady state experiments?

Example: Competition of $OH^{\bullet}$ for MIB and *p*CBA :

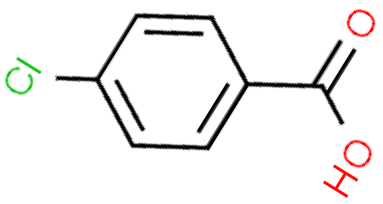
MIB + $OH^{\bullet}$ ⟶ Products   ***k_1= ?***

*p*CBA + $OH^{\bullet}$ ⟶ Products   **k_2= 5 x 10^9 M^{-1} s^{-1}**

(Buxton et al., 1988)



MIB



4-chlorobenzoic acid (competitor)

$$\frac{d[MIB]}{dt} = k_1\,[OH]^{\bullet}[MIB] = k_{1obs}[MIB]$$

$$\frac{d[pCBA]}{dt} = k_2\,[OH]^{\bullet}[pCBA] = k_{2obs}[pCBA]$$

- k_{1obs} & k_{2obs} are determined from a steady state experiment.
- Steady state [$OH^{\bullet}$] is determined from k_{2obs} (k_2 is known).
- **$k_1 = k_{1obs}$/[$OH^{\bullet}$]**

Huber et al. Environ. Sci. Technol. 2003, 37, 1016-1024 https://doi.org/10.1021/es025896h

He et al. Water Research 74, 2015, 227-238 https://doi.org/10.1016/j.watres.2015.02.011

Heterogeneous systems (e.g., TiO_2 photocatalysis)

- Most common degradation kinetic model: (pseudo) first order.
- Adsorption on the surface of the catalyst.
- Langmuir-Hinshelwood model:

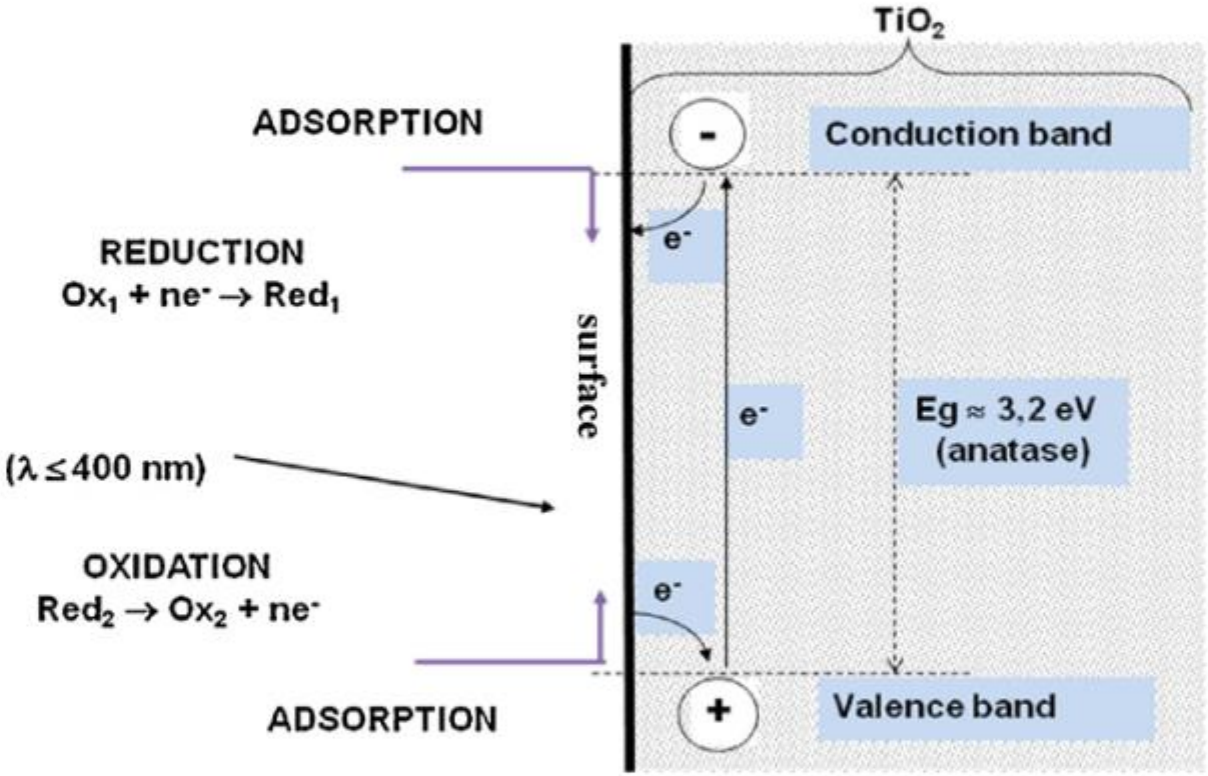
$$\frac{d[MIB]}{dt} = -k\theta = \frac{kK[MIB]}{1 + K[MIB]}$$

θ = fraction of surface coverage by MIB
K = Langmuir adsorption constant

When [MIB] is low (<<1), it simplifies to:

$$\ln[MIB] = ln[MIB]_0 - kKt \quad \text{(first order)}$$

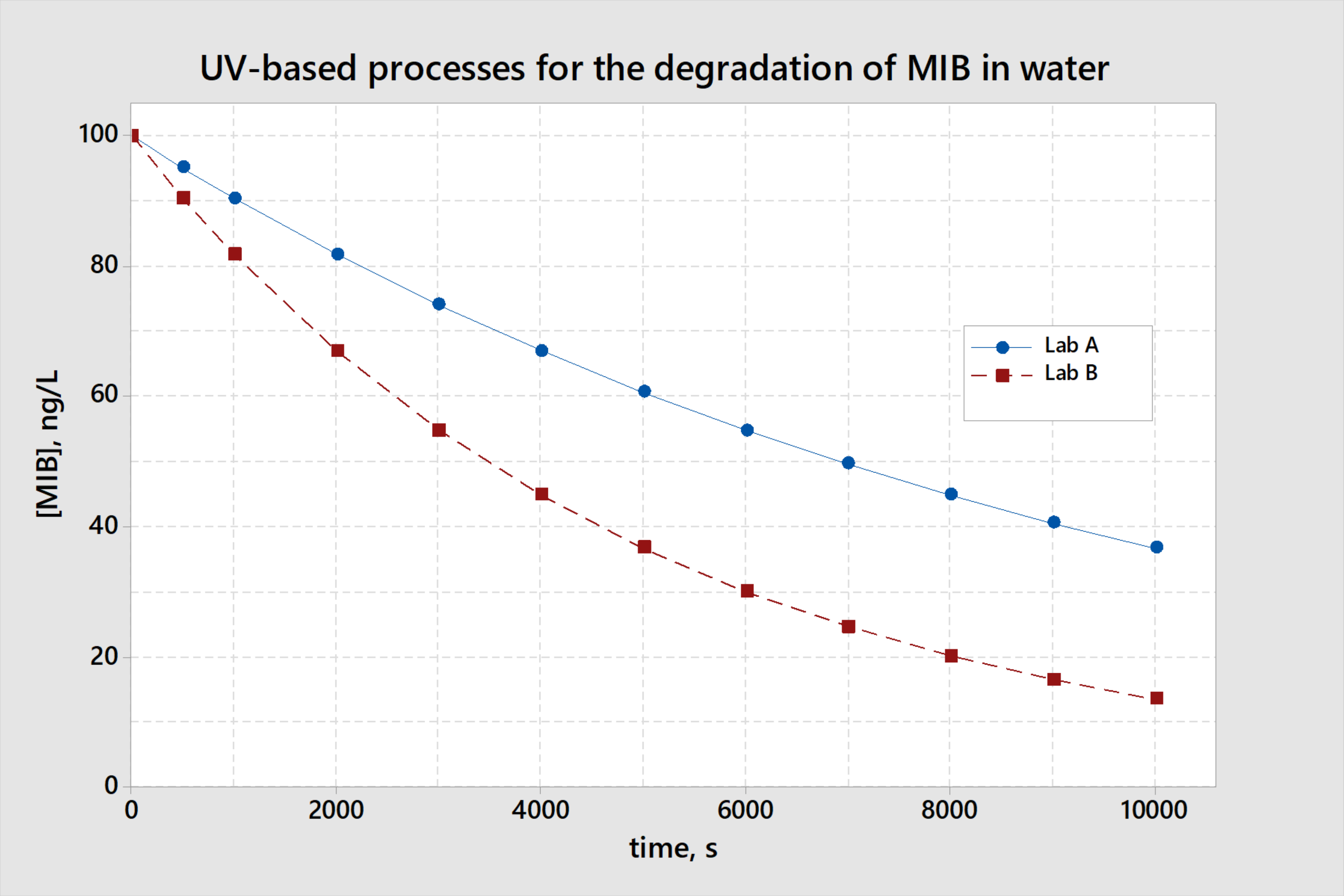
$K_{obs} = kK$



Herrmann 2010, Photochem. Photobiol. A.
https://doi.org/10.1016/j.jphotochem.2010.05.015

Zhang & Sillanpää, Chapter 5 in "Advanced Water Treatment – AOPs, Elsevier, 2020.

Which process is more efficient?



Electrical Energy per Order, E_{EO}

E_{EO} is the **electrical energy** necessary to reduce the concentration of a contaminant **by one order of magnitude** (90 % reduction) in a unit volume of water.

How it works:

$$MIB + OH^{\bullet} \longrightarrow \text{Products}$$

$$\frac{d[MIB]}{dt} = k[OH^{\bullet}][MIB] = k_{obs}[MIB] \quad \textit{(steady state approx. for OH}^{\bullet}\textit{)}$$

- From measurements of [MIB] vs time, ***k_{obs}* is determined** *(pseudo-first order kinetics).*
- From the integrated equation of 1st order $[MIB] = [MIB]_0\, e^{-k_{obs}t}$ the **time needed for 1 order of magnitude** reduction of [MIB] is calculated.
- Time is directly converted to **Energy** (known power consumption of the photoreactor).
- ***E_{EO}*** *is a* ***better metric*** *of* process efficiency but has limitations (dependency on concentration of reagents, photoreactor configuration, compound under study etc).

Bolton et al. *Pure Appl. Chem.*, Vol. 73, No. 4, pp. 627–637, 2001 https://doi.org/10.1351/pac200173040627
Bolton et al. Photochem. & Photobiol., 2015, 91: 1252–1262 https://doi.org/10.1111/php.12512
Keen et al. Pure Appl. Chem. 2018; 90(9): 1487–1499 https://doi.org/10.1515/pac-2017-0603

Take-home messages

- Reactions in AOPs are complex, as reactive radicals react in various ways and sites, leading to many transient or stable transformation products.
- Degradation of compounds often follow a 1st-order kinetic law, but zero-order or 2nd-order can be observed, depending on the conditions.
- Steady state conditions are often established in continuous UV or gamma-irradiation AOPs.
- In heterogeneous systems, adsorption plays a key role.
- The “reference” techniques to determine elementary bimolecular rate constants are pulse radiolysis and flash photolysis.
- Competition kinetics can help in determining bimolecular rate constants.
- Efficiency of AOPs is better evaluated by E_{EO}, but still depends on reactor configuration and other parameters.