THE NOX SYSTEM INNUCLEAR WASTE

(see also:
"Interfacial Radiolysis Effects in Tank Waste Speciation")

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A. The NOx System in Nuclear Waste

i. Why and Which NOx is Important?

We have shown that, even at concentrations relevant to HLW, the yields of the primary reducing radicals of the NOx family are not altered significantly. Most primary radicals that result from the irradiation of water in highly concentrated waste simulants are rapidly converted to NO_2 radicals, and to a lesser degree to NO radicals. We determined quantitatively the rates of the major reactions involved in these conversions.

$e^-_{aq} + NO_3^- \longrightarrow \mathbf{NO_3^{2-}}$ $\quad k_1 = 9.7 \times 10^9\ M^{-1}\ s^{-1}$ (1)

$\mathbf{NO_3^{2-}} + H_2O \longrightarrow \mathbf{NO_2} + 2OH^-$ $\quad k_2 = 5.5 \times 10^4\ s^{-1}$ (1a)

$NO_2^- + OH \longrightarrow \mathbf{NO_2} + OH^-$ $\quad k_{11} = 6.0 \times 10^9\ M^{-1}\ s^{-1}$ (2)

$O^- + NO_2^- (+ H_2O) \longrightarrow \mathbf{NO_2} + 2OH^-$ $\quad k_{1a} = 3.1 \times 10^8\ M^{-1}\ s^{-1}$ (2a)

$H + NO_2^- \longrightarrow \mathbf{NO} + OH^-$ $\quad k_3 = 7.1 _ 10^8\ M^{-1}\ s^{-1}$ (3)

NO_2 and NO are mild oxidants. Two questions to address:

a. What do we know on $\mathbf{NO_3^{2-}}$?

b. How much $\mathbf{NO_2}$ / **NO**, and what are their reactivities?

Why NOx and Which?

- **Hydroxyl Radicals:**

$OH + NO_2^- \longrightarrow NO_2 + OH^-$ $k=1.0\times10^{10}\ M^{-1}\ s^{-1}$ (1)

The basic form, O^-:

$O^- + NO_2^- \ (+ H_2O) \longrightarrow NO_2 + 2OH^-$ $k=3.1\times 10^{8}\ M^{-1}\ s^{-1}$ (1a)

- **Hydrated Electrons:**

$e^-_{aq} + NO_3^- \longrightarrow NO_3^{2-}$ $k = 9.7\times10^{9}\ M^{-1}\ s^{-1}$

t ~ 20µs: $(+ H_2O) \longrightarrow NO_2 + 2OH^-$ (2)

- **Hydrogen Atoms:**

$H + NO_2^- \rightarrow NO + OH^-$ $k=7.1\times10^{8}\ M^{-1}\ s^{-1}$ (3)

ii. Reducing Radicals:

An important intermediate in the conversion of the intermediates from reducing, e^-_{aq} radicals, to the oxidizing NO_2, is the short-lived NO_3^{2-} radical obtained from the reaction of e^-_{aq} with nitrate (Reaction 1).

A. We determined the redox potential of the couple NO_3^-/NO_3^{2-} across the whole pH range. We also determined the redox potential for the analogous nitrite species i.e. of the couple NO_2^-/NO_2^{2-}.

B. We have shown that the protonated froms of NO_3^{2-} are too short-lived to observe.

Implications: Whereas H_2 generation from NO_3^{2-} is possible, it is very inefficient under tanks' conditions. On the other hand, electron transfer from NO_3^{2-} to nitrite is thermodynamically favorable, but kinetically the reaction is slow. Kinetic modeling of the tanks chemistry requires that this reaction,

$$NO_3^{2-} + NO_2^- \longrightarrow NO_3^- + NO_2^{2-},$$

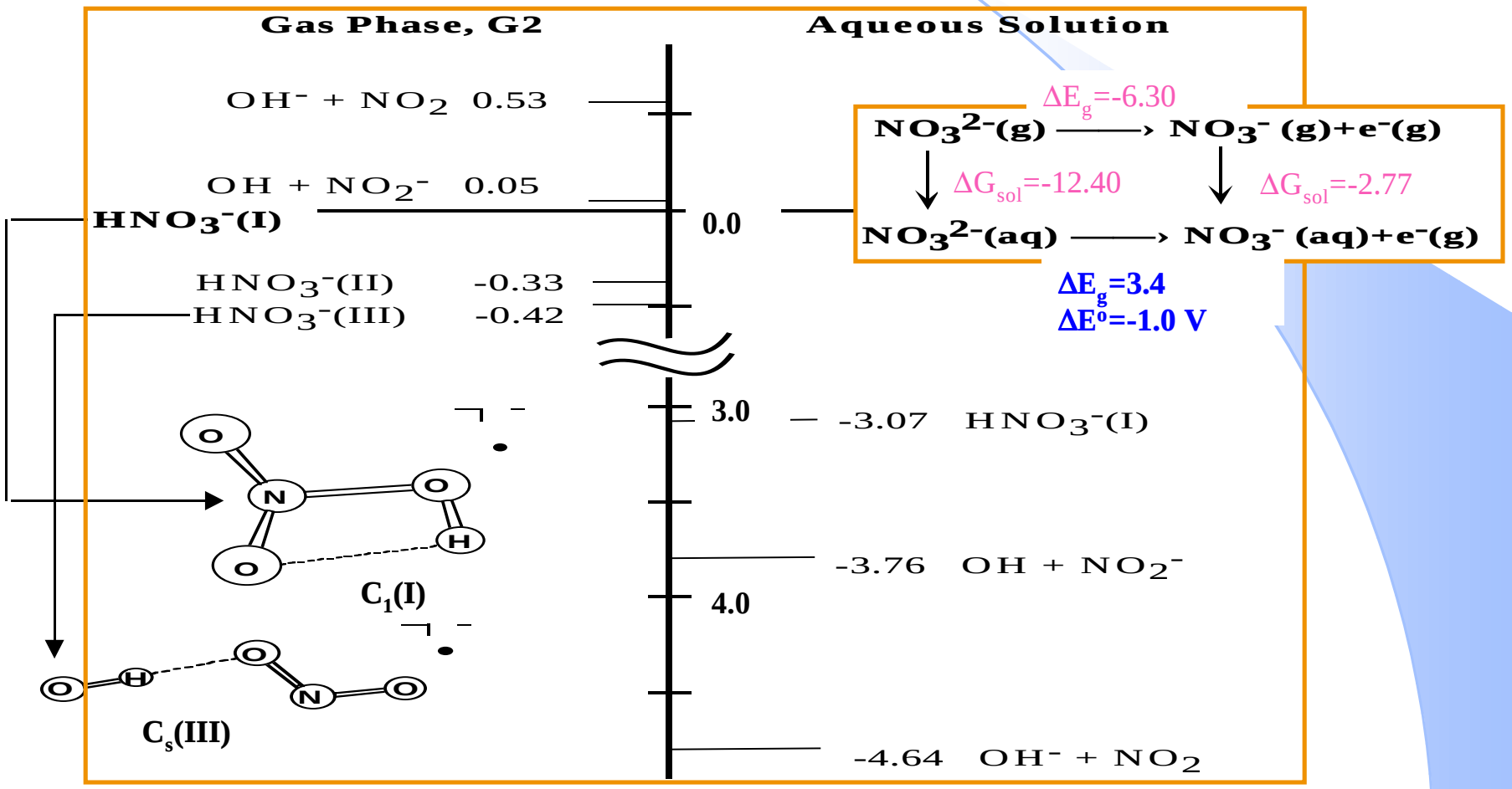
occurs in the tanks with an efficiency that is determined by the $[NO_2^-]$ at the specific tank. Thus, the chemistry in the tanks may be diverted from NO_2 to NO radicals at a [nitrite]-dependent efficiency via

$$NO_2^{2-} + H_2O \longrightarrow NO_2 + 2OH^-.$$

Whereas NO_2 provides facile pathways for organic degradation, NO provides pathways for N_2O generation. The NO_2 radical is important to the resolution of the organic tanks issue and NO, and subsequently N_2O, is an important component of the flammable gas issue.

NOx from Theoretical Estimates

Energies in eV



Redox Potential of NO_3^{2-}

From Theory: Eo=-1.04 to 1.10 V vs. NHE

$$NO_3^{2-}(g) \xrightarrow{\Delta G_{gas}} NO_3^{-}(g) + e^{-}(g)$$

$$\downarrow \Delta G_{solv}^{NO_3^{2-}} \qquad \downarrow \Delta G_{solv}^{NO_3^{-}}$$

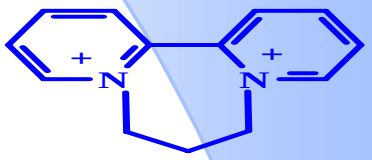
$$NO_3^{2-}(aq) \xrightarrow{\Delta G_{aq}^{NO_3^{-}/2-}} NO_3^{-}(aq) + e^{-}(g)$$

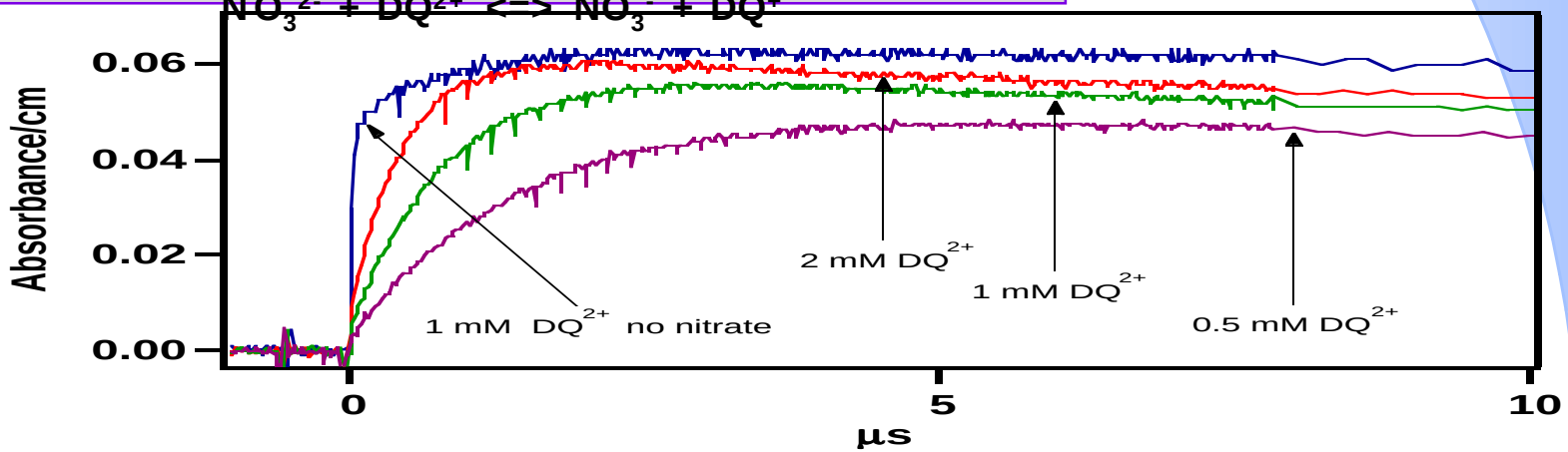
$$\Delta G_{aq}^{NO_3^{-}/2-} = \Delta G_{gas} + \Delta G_{solv}^{NO_3^{-}} - \Delta G_{solv}^{NO_3^{2-}}$$

Experimental: E° from Equilibrium:

$$NO_3^{2-} + DQ^{2+} \leftrightarrow NO_3^{-} + DQ^{+}$$

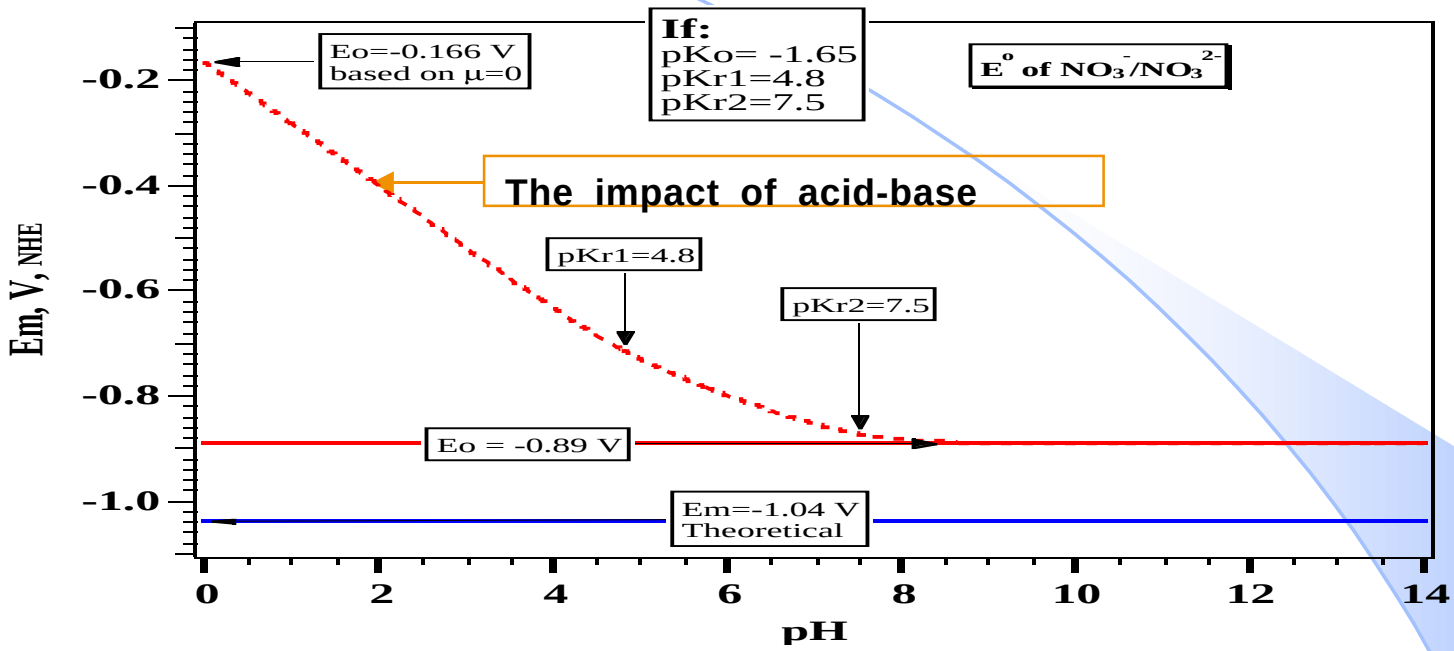
DQ^{2+}=

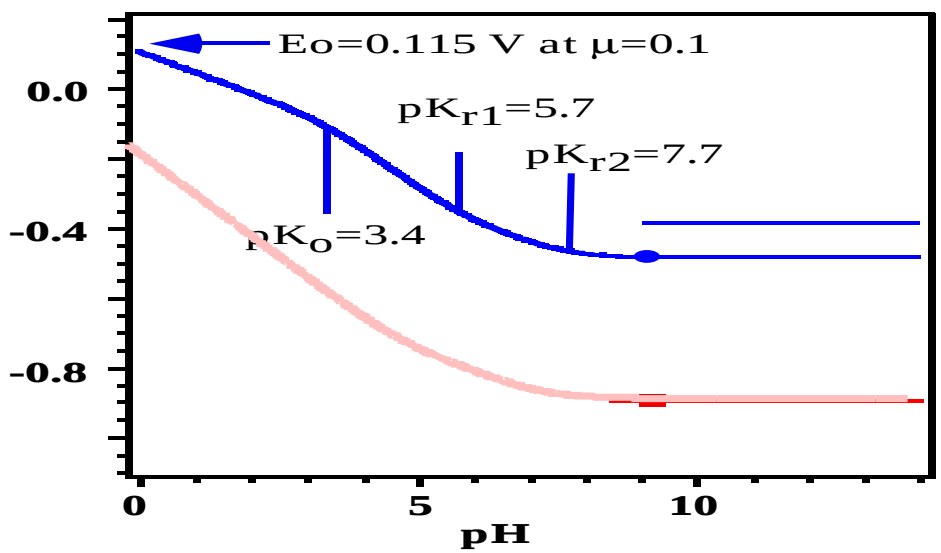




Redox Potnetials of NO_x^-/NO_x^{2-}

x=2 or 3

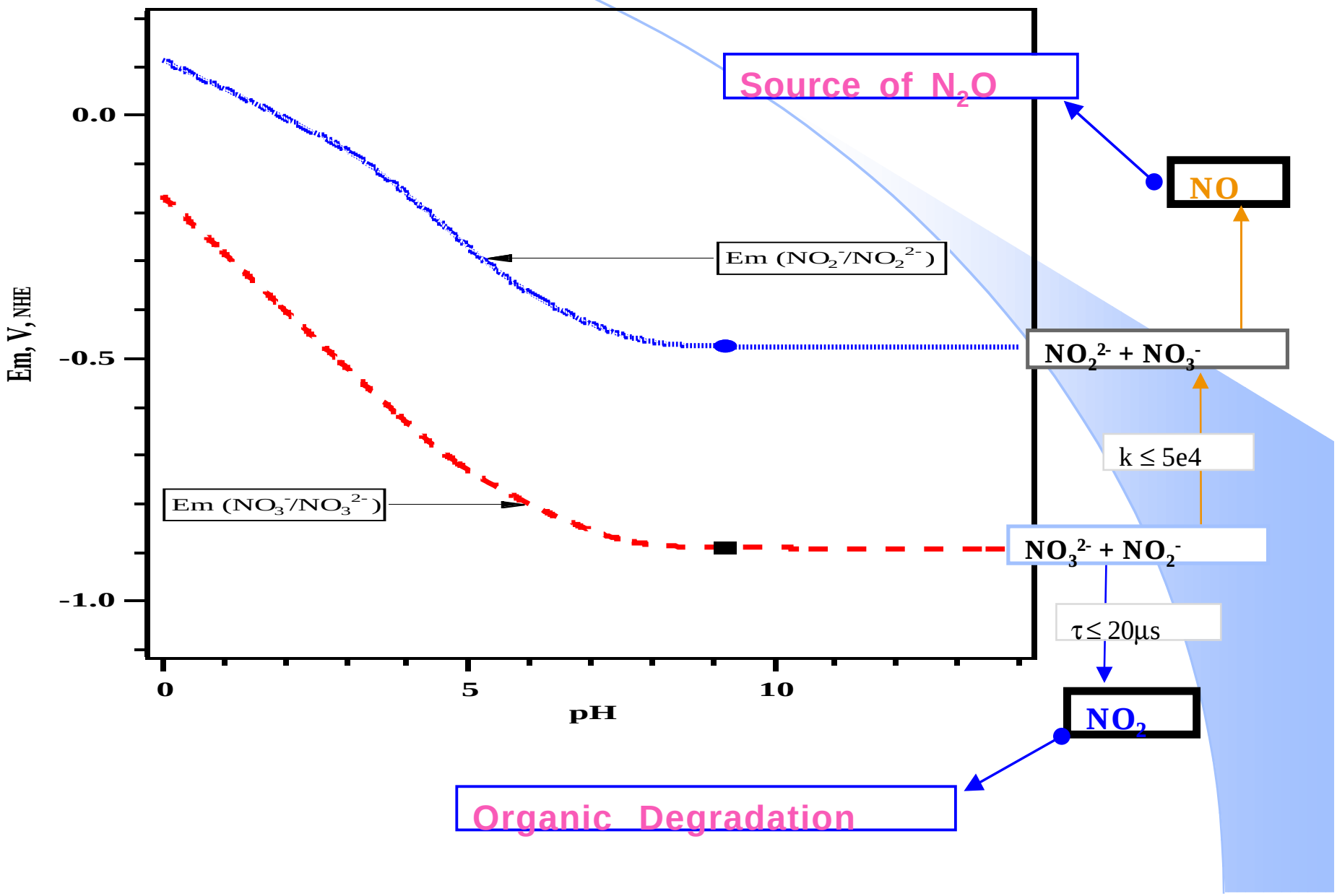




Repeat for
Redox Potential of NO_2^-/NO_2^{2-}

Theoretical: Em=-0.37 V
Em (NO_2/NO_2^{2-})= -0.47 V

Redox Potentials => NO or NO_2 Chemistry



iii. Oxidizing Radicals:

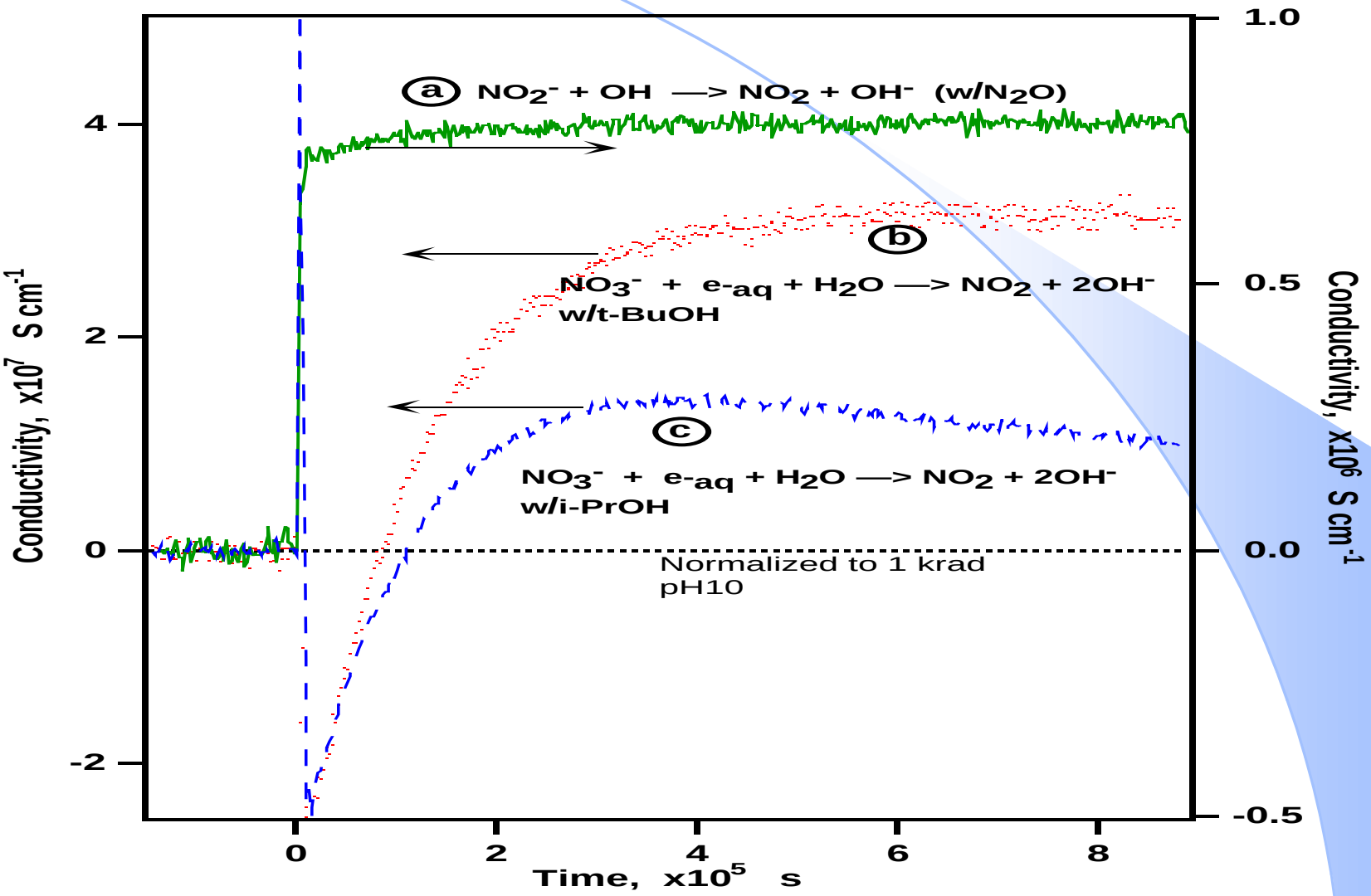
The NO_2 Reactions

The primary radical, which oxidatively degrades the organic molecules in the waste tanks, is suspected to be **NO_2**. To independently verify the identity of the major oxidizing radical, we compared radiolytic degradation results with results from degradation caused by genuine **NO_2** gas. We contacted aqueous alkaline solutions of organic species with gaseous **NO_2** (<50 ppm in N_2). Preliminary experiments have surveyed the reactions of NO_2 with nitrilotriacetate (NTA), iminodiacetate (IDA), glycine (Gly), and formate. All are chelators and their degradation products, abundant in the HLW. The results show that aminocarboxylates degrade via stepwise decarboxylation - dealkylation processes giving mainly formate and carbonate. The high preference for production of formate over oxalate suggests that the demethylation is initiated by decarboxylation: $R_2NCH_2CO_2^- + NO_2 \rightarrow R_2NCH_2 + CO_2 + NO_2^-$, followed by oxidative demethylation of the aminoalkyl radicals: $R_2NCH_2 + NO_2 + OH^- + H_2O \rightarrow R_2NH + NO_2^- + CH_2(OH)_2$. The hydrated formaldehyde is a known source for H_2 and formate in the waste tanks. Formate also degrades to carbonate when reacted with NO_2, but at a much slower rate than the aminocarboxylate compounds.

Relative reactivities of NTA>IDA>Gly>formate were quantitatively determined by competition experiments in which each of the aminocarboxylates was oxidized in the presence of formate-^{13}C to obtain initial production rates of formate-^{12}C and carbonate-^{13}C. Similar reactivity patterns were obtained in both the radiolytic and NO_2 contact approaches.

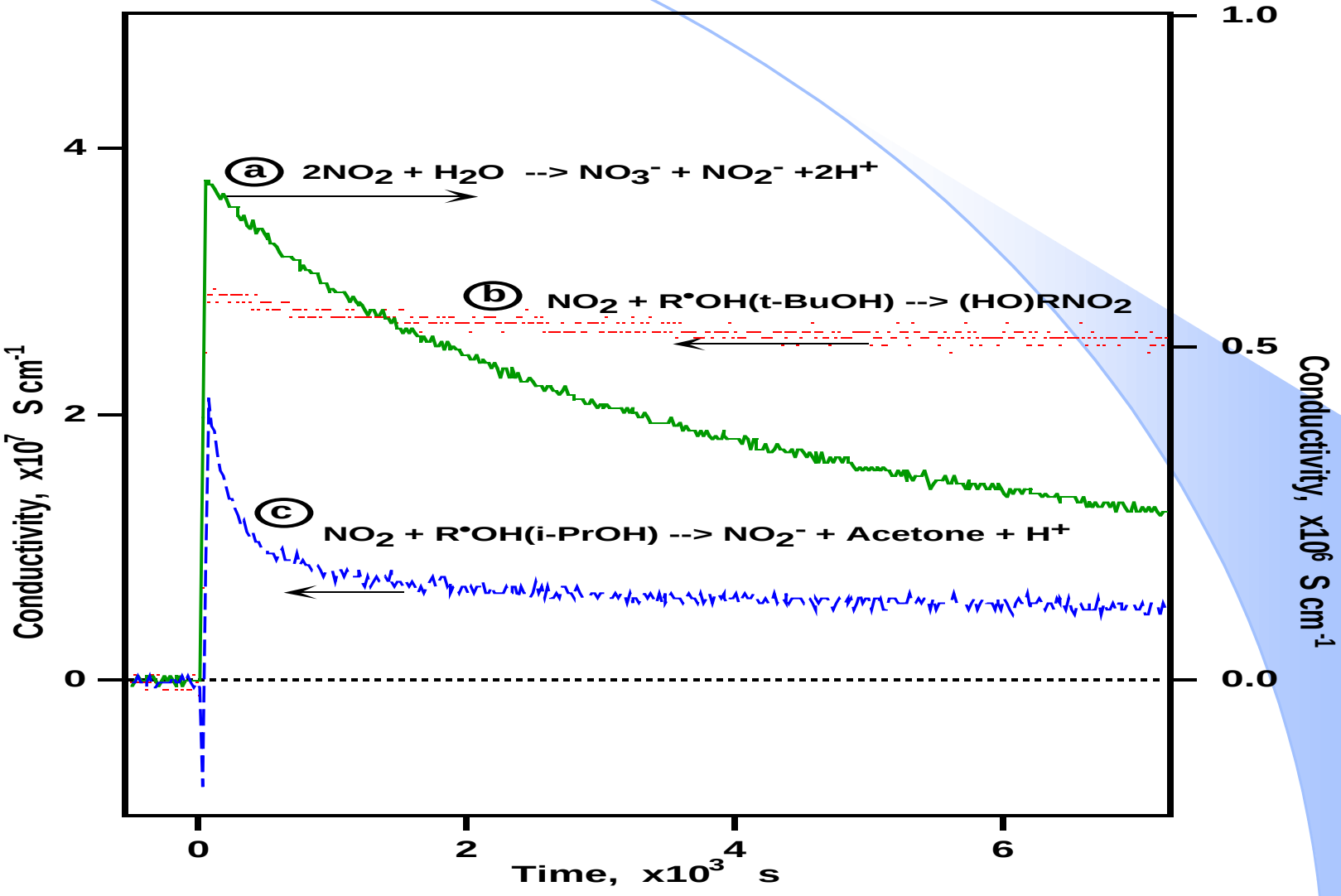
NO_2 Reactions from Conductivity

Generation of NO_2 (pH 10)



NO_2 Reactions from Conductivity

$R^{\bullet}OH + NO_2$ (pH 10)



Reactions of NO_2 with Hydroxyalkyl Radicals

Radical	Reaction	Conditions	Rate constant	Comment
$CH_2C(CH_3)_2OH$	$R + NO_2 \rightarrow RNO_2$ addition	0.5 mM $NaNO_3$, 0.1 M t-BuOH, Ar, pH 4 & 10 *conductivity*	$6 \times 10^9\ M^{-1}s^{-1}$	estimated c.a. 15.5 % in reaction NO_2+NO_2
$(CH_3)_2COH$	$R + NO_2 \rightarrow NO_2^- + Ac + H^+$ electron-transfer	0.5 mM $NaNO_3$, 0.1 M i-PrOH, Ar, pH 4.1 & 5.1 & 10 *conductivity*	$6.5 \times 10^9\ M^{-1}s^{-1}$	from kinetics c.a. 20% in addition reaction $CH_2CHOHCH_3$ (13.3%)
$CH_3(CH_2)_2CHOH$	$R + NO_2 \rightarrow NO_2^- + Ket. + H^+$ electron-transfer	0.5 mM $NaNO_3$, 0.1 M 1-BuOH, Ar, pH 4 & 10 *conductivity*	$5.4 \times 10^9\ M^{-1}s^{-1}$	from kinetics c.a. 60% in addition reaction $CH_3CH_2CHCH_2H$ (58.5%)
CH_2OH	$R + NO_2 \rightarrow NO_2^- + Ket. + H^+$ electron-transfer	0.5 mM $NaNO_3$, 0.1 M MeOH, Ar, pH 4 & 9 *conductivity*	$3 \times 10^9\ M^{-1}s^{-1}$ $1.2 \times 10^9\ M^{-1}s^{-1}$	from kinetics estimated c.a. 67% in reaction NO_2+NO_2
CH_3CHOH	$R + NO_2 \rightarrow NO_2^- + Ket. + H^+$ electron-transfer	0.5 mM $NaNO_3$, 0.1 M EtOH, Ar, pH 4 & 10 *conductivity*	$1.0 \times 10^{10}\ M^{-1}s^{-1}$	from kinetics

Reactions of NO_2^- with Reducing Radicals

Radical	Reaction	Conditions	Rate constant	Comment
$(CH_3)_2COH$	$R + NO_2^- \rightarrow$ NO + Ac + OH^- e-transfer	$NaNO_2$, i-PrOH, Acetone, Ar pH 4.7, 9 &10 *conductivity*	1.3×10^6 $M^{-1}s^{-1}$	from kinetics and yield
		i-PrOH, Acetone, BQ, $NaNO_2$, Ar *optical*	1.7×10^6 $M^{-1}s^{-1}$	competition with BQ
$(CH_3)_2COH$	$R + HNO_2 \rightarrow$ NO + Ac + H_2O e-transfer	$NaNO_2$, i-PrOH, Acetone, Ar pH 3 - 4 *conductivity*	1.5×10^8 $M^{-1}s^{-1}$	from kinetics
CH_3CHOH	$R + NO_2^- \rightarrow$ NO + Ket. + OH^- e-transfer	EtOH, BQ, pH 7, $NaNO_2$, N_20 *optical*	1.3×10^6 $M^{-1}s^{-1}$	competition with BQ
CH_3CHOH	$R + HNO_2 \rightarrow$ NO + Ket. + H_2O e-transfer	$NaNO_2$, EtOH, N_20 pH 3 - 4 *conductivity*	1.0×10^8 $M^{-1}s^{-1}$	from kinetics
CH_2OH	$R + NO_2^- \rightarrow$ NO + Ket. + OH^- e-transfer	$NaNO_2$, MeOH, N_20, pH 9 *conductivity*	$< 1 \times 10^5$ $M^{-1}s^{-1}$	estimated from yield
CH_2OH	$R + HNO_2 \rightarrow$ NO + Ket. + H_2O e-transfer	$NaNO_2$, MeOH, N_20, pH 3 *conductivity*	3.0×10^6 $M^{-1}s^{-1}$	from kinetics
CO_2^-	$R + NO_2^- \rightarrow NO_2^{2-} + CO_2$ electron-transfer	HCOONa, BQ, pH 7, $NaNO_2$, N_20 *optical*	4.3×10^6 $M^{-1}s^{-1}$	competition with BQ
NO_3^{2-}	$NO_3^{2-}+NO_2^- \rightarrow NO_2^{2-}+NO_3^-$ e-transfer	$NaNO_3$, BQ, pH 9, $NaNO_2$, Ar *optical*	$< 5 \times 10^4$ $M^{-1}s^{-1}$	estimated competition with BQ

iv. Organic Radicals Reactions w/ NO_2 and NO_2^-:

Using methodologies based on conductivity changes we recently measured rate constants of reactions of organic radicals of model HLW compounds with NO_2^- (nitrite) and with NO_2.

a. For NO_2 radicals, two possible pathways were identified:

1) Electron transfer to form nitrite and

2) Radical combination to form organic-nitro moieties.
This occurs via either via the O or the N atoms at nearly equal probabilities to yield RNO_2 or RONO.

b. For NO_2^-, electron transfer is a leading pathway and it becomes faster at lower pH's.

Implications: Pathways for organic + NO_2 are important in "Organic Aging" issues. Electron transfer generates an aldehyde from organic, ROH, radicals, which is a known potential H_2 source. Electron transfer to nitrite converts NO_2 to **NO**. The latter provides another route for production of N_2O.

V. Interfacial Radiolysis processes:

1. **Electrons generated in the solid:** We determined the effect of particulate material in the waste on radiolytic yields of electrons (and thus reducing, fuel generating, species). Yields of e^-_{aq}, at increasing concentrations of silica particles up to 50% weight, were measured. We find that if the particles are small enough (largest sizes measured were 22 nm in diameter) the concentration of reducing radicals in the water actually increases. This is an unexpected observation of exceptional importance and direct relevance to the tanks' chemistry, as well as to long term storage in waste forms other than glass (e.g. grout, saltstone, etc.). Long term storage in a matrix composed of small particles may defeat the purpose of the matrix. It may "channel" the radiation energy into the small quantities of water that are present in the matrix pores. This effect may lead to very efficient radiolysis of water, along with its adverse safety effects. In tanks, it may lead to preferential generation of gaseous products in the vicinity of solid particles. This, in turn, favors attachment of gas bubbles to the solid particles, thus contributing to the gas retention problem. It may also alter the chemistry that prevails in tanks with floating organic layers following tank-draining operations. As the aqueous phase is depleted, and the organic layer comes into contact with the solid-rich sludge phase, the enhanced deposition of energy in the vicinity of the particles may trigger enhanced organic radiolysis. On the other hand, this observation proves the feasibility of the concept of "radiocatalysis".

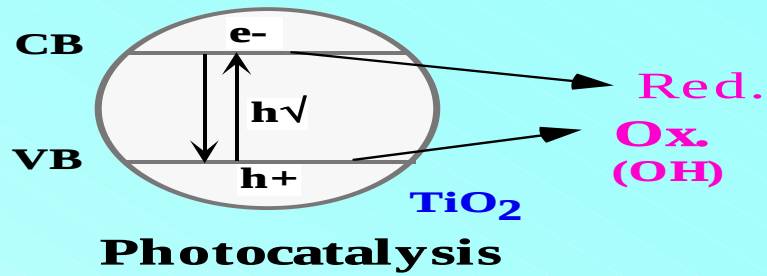
2. **Holes generated in the solid particles:** Contrary to electrons, we fail to observe the migration of holes out of the solid silica particles into the aqueous phase. Preliminary indications are that they cannot oxidize water to OH radicals but the reason is not clear at present. Current efforts are aimed at determining whether this is due to impurity or structural defects in the solid. Obviously, to obtain oxidative degradation of organics, silica is inappropriate. Other materials, probably TiO_2, are a better choice. Yet, there is no doubt that we achieve a high degree of charge separation at the solid/liquid interface.

from Grout to Radiocatalysis

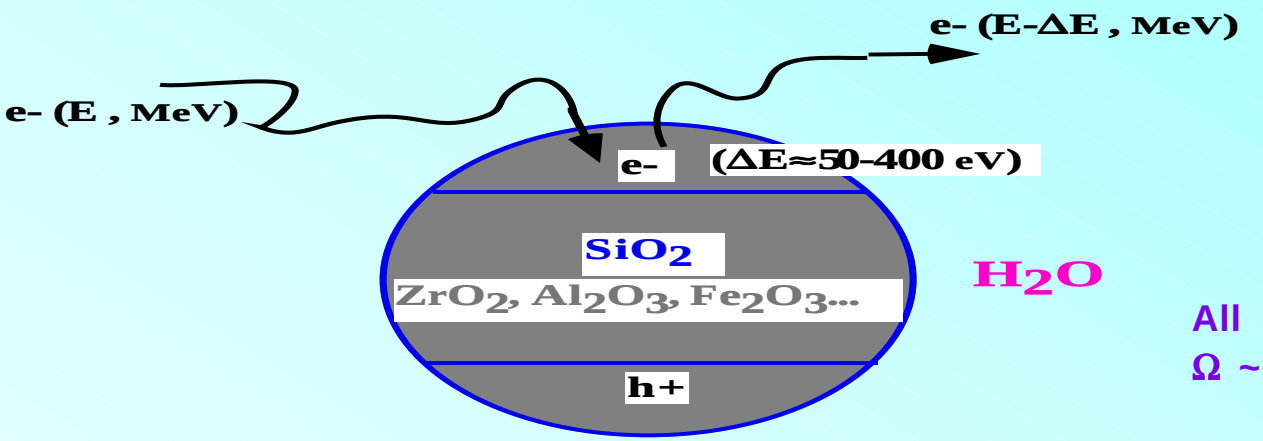
Interfacial Charge Transfer

Fate of secondary e-

Not range problem!

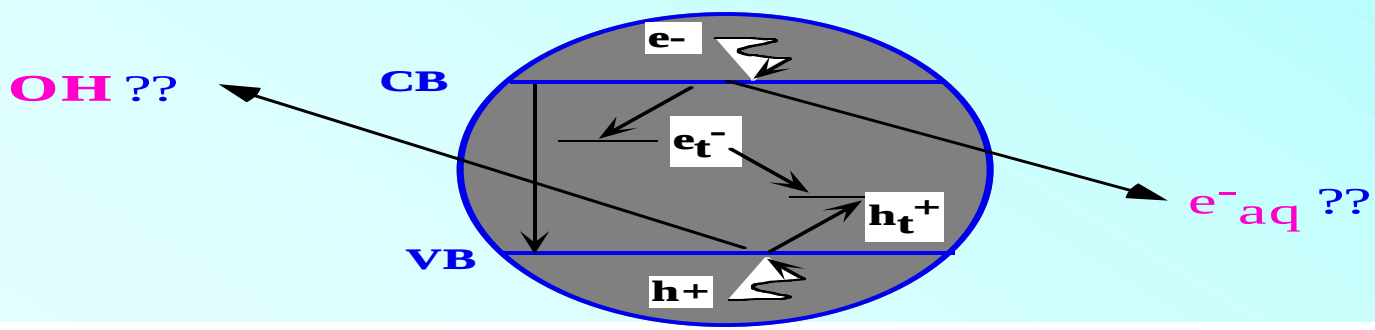


Photocatalysis

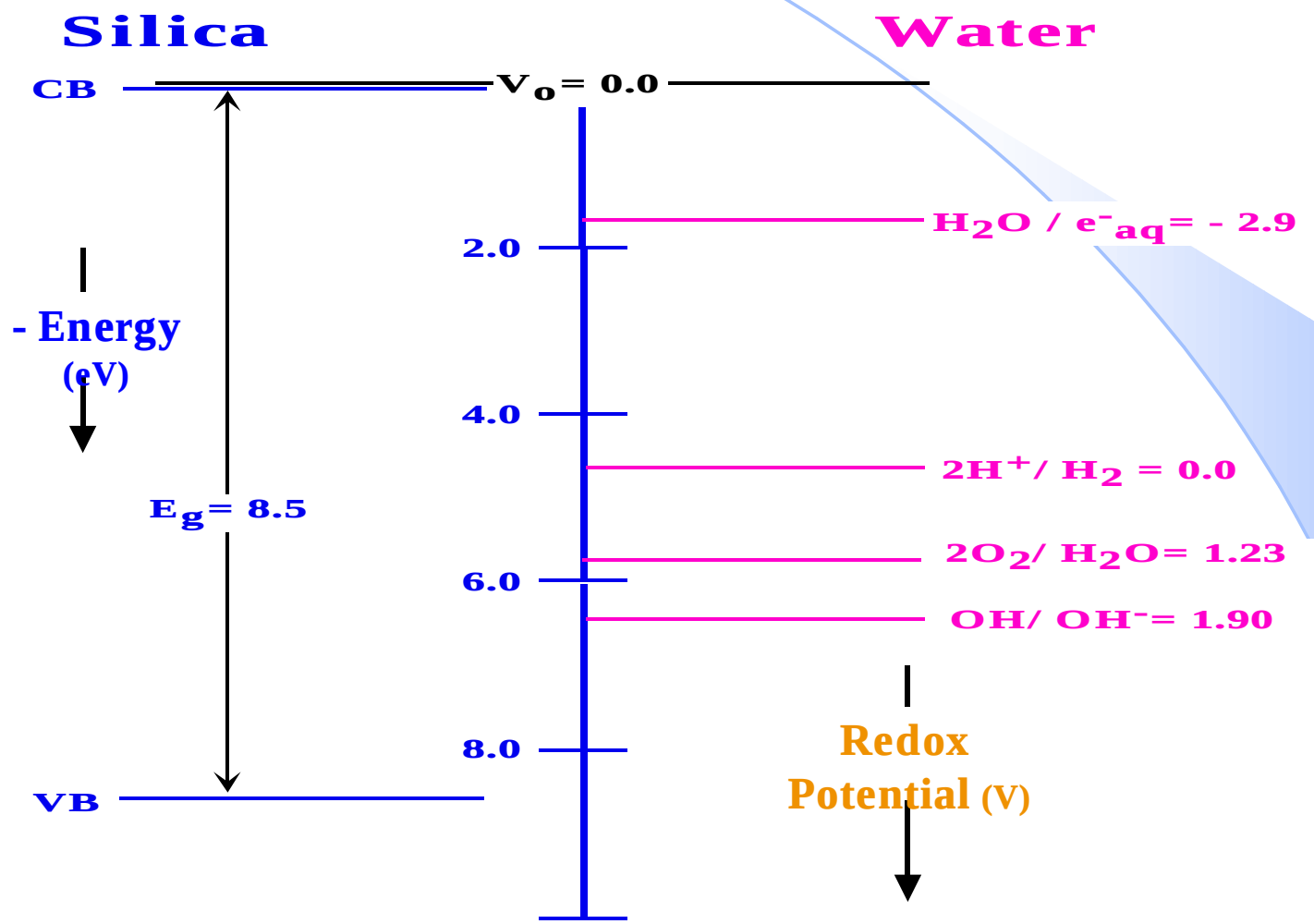


All at pH 10±0.2

Ω ~ -200 mV

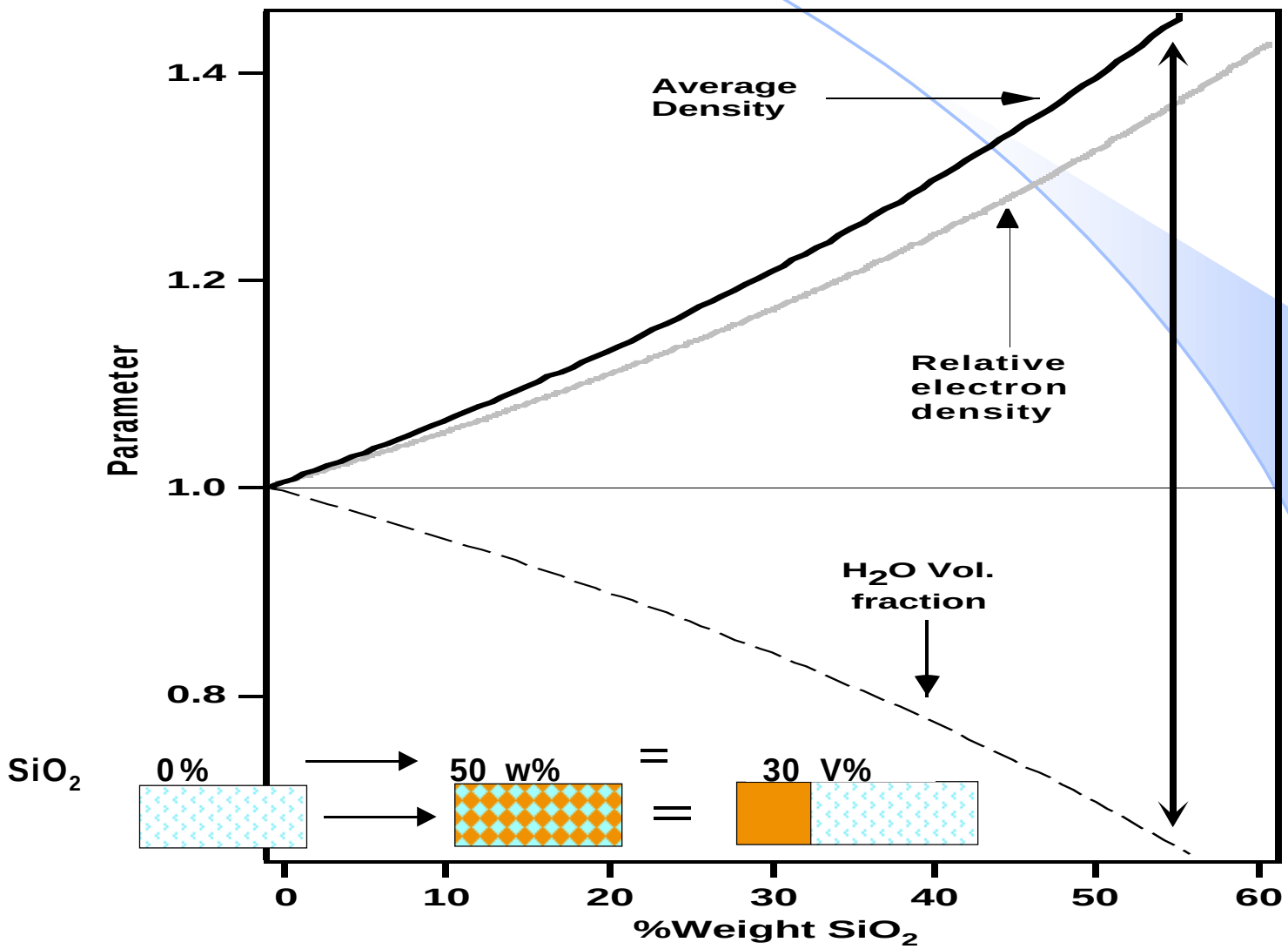


Energy Levels for SiO_2 & H_2O



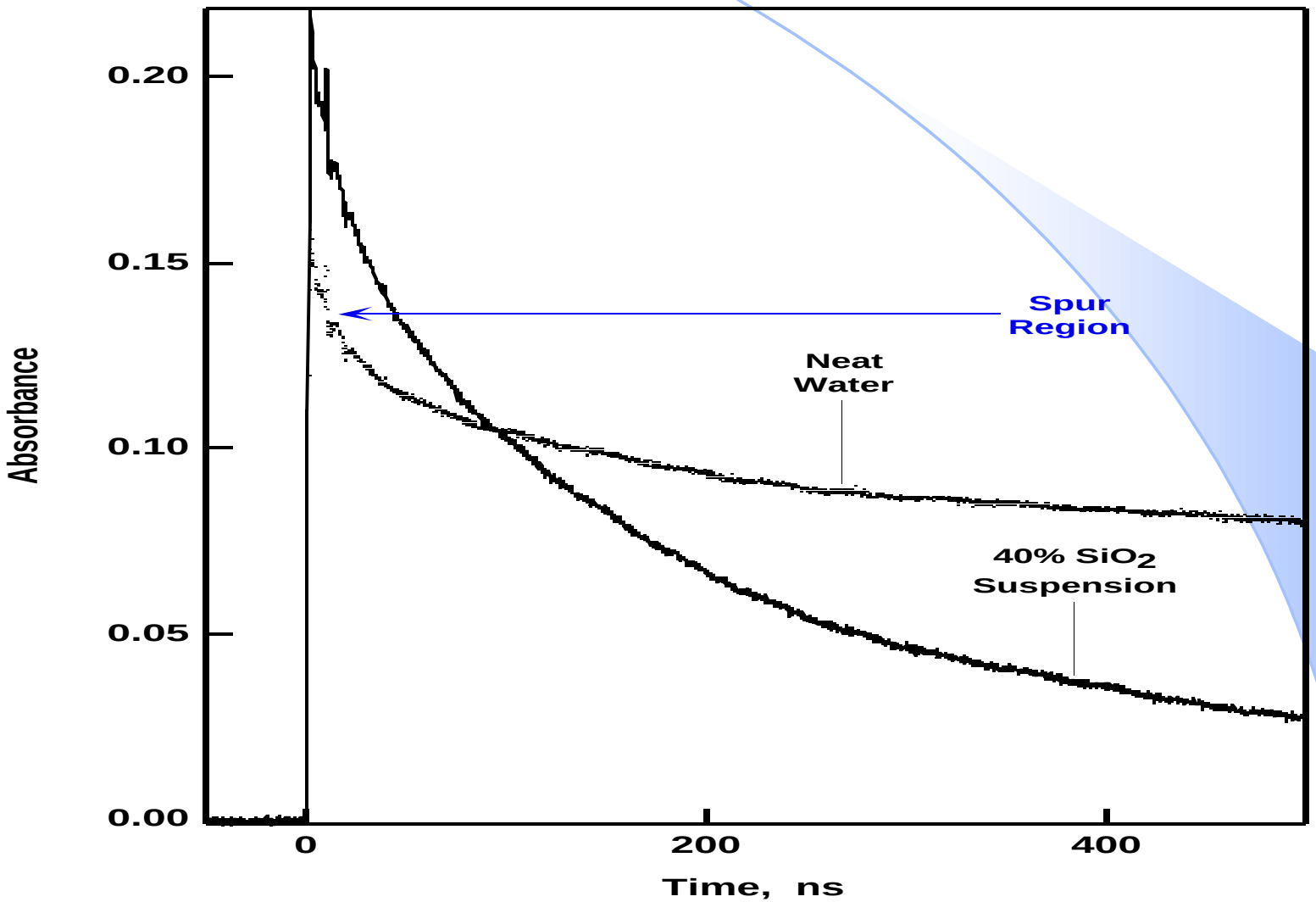
Yield of e^-_{aq} in SiO_2 Suspensions

Expectations

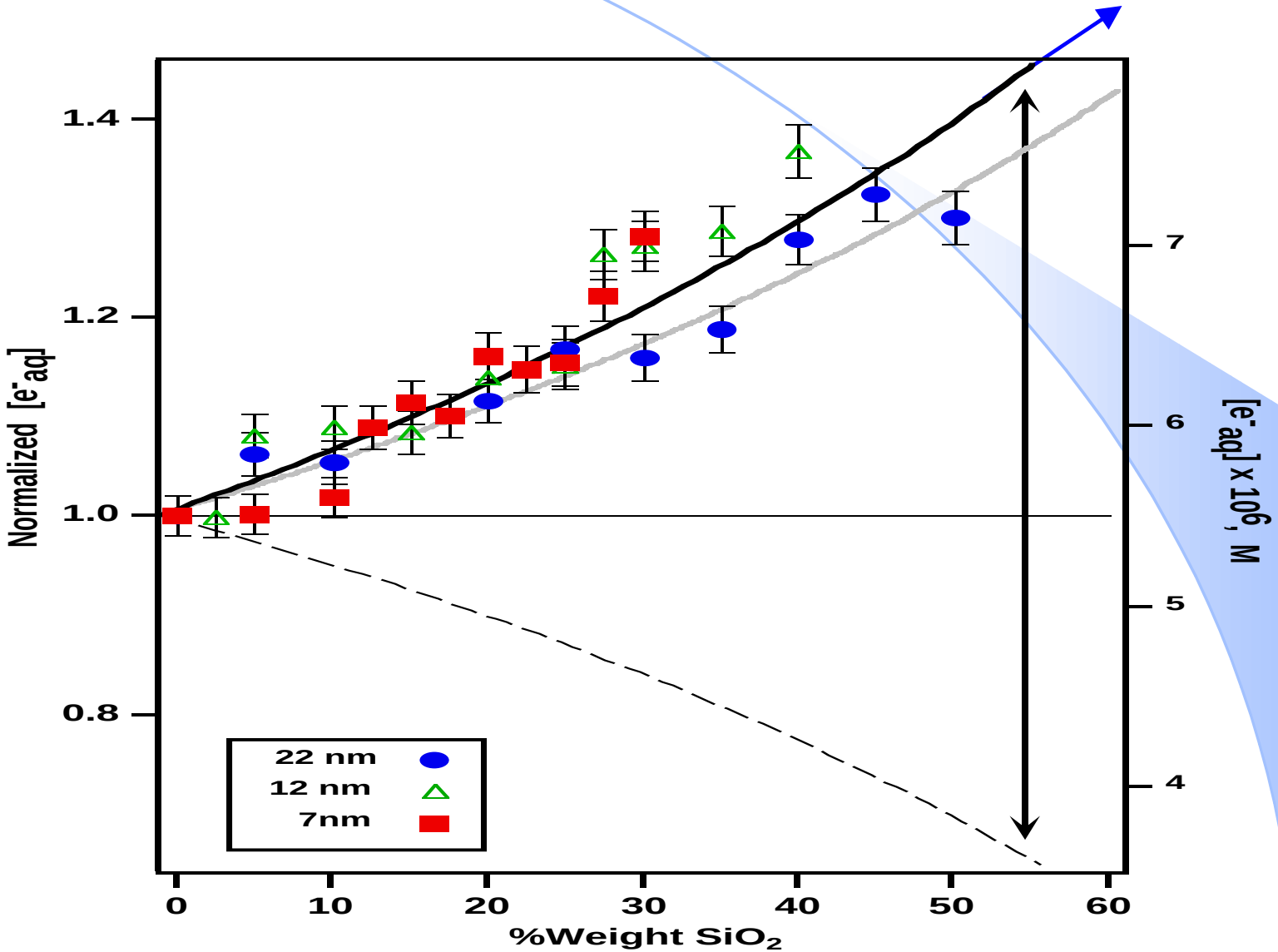


Yield of e_{aq}^- in the SiO_2 Suspensions

note: Less water more e^-_{aq} in water!

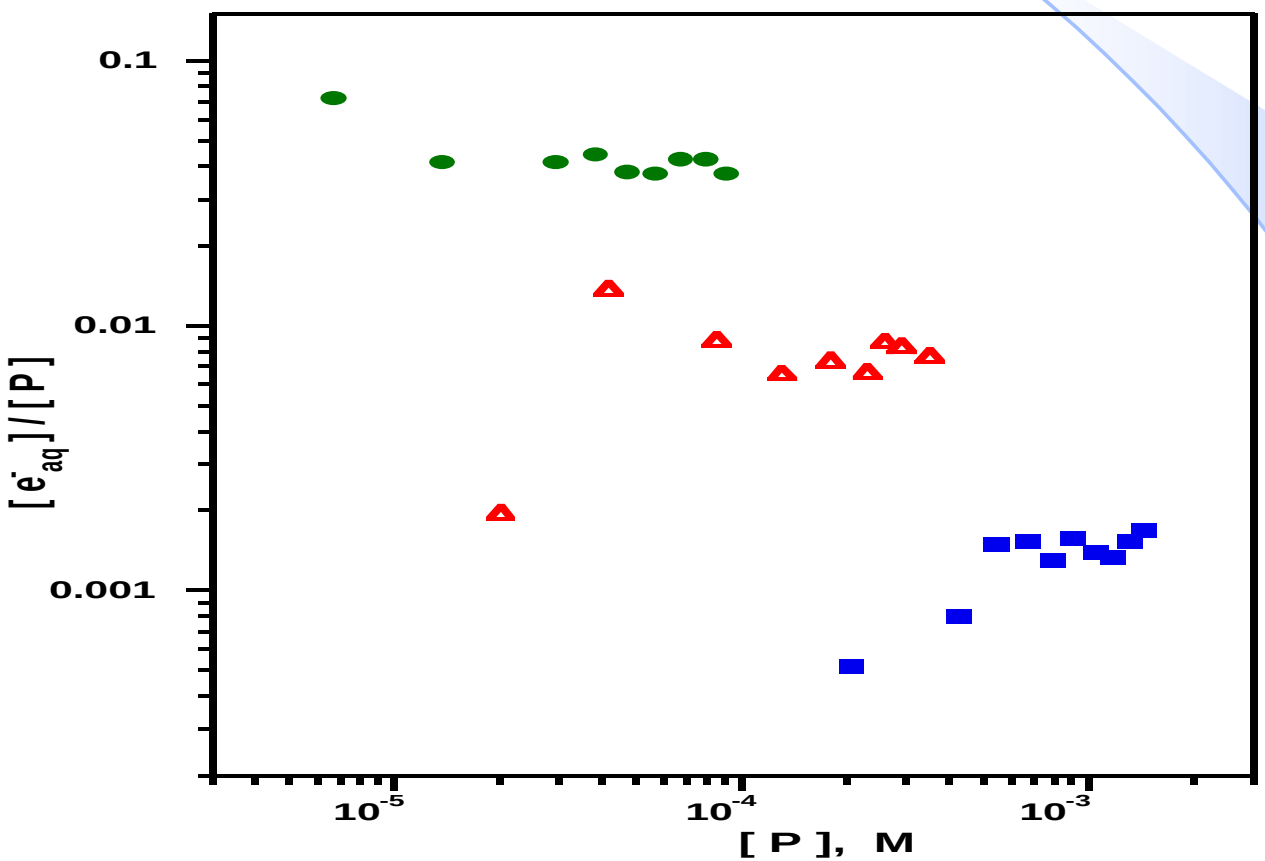


Yield of e^-_{aq} in SiO_2 Suspensions

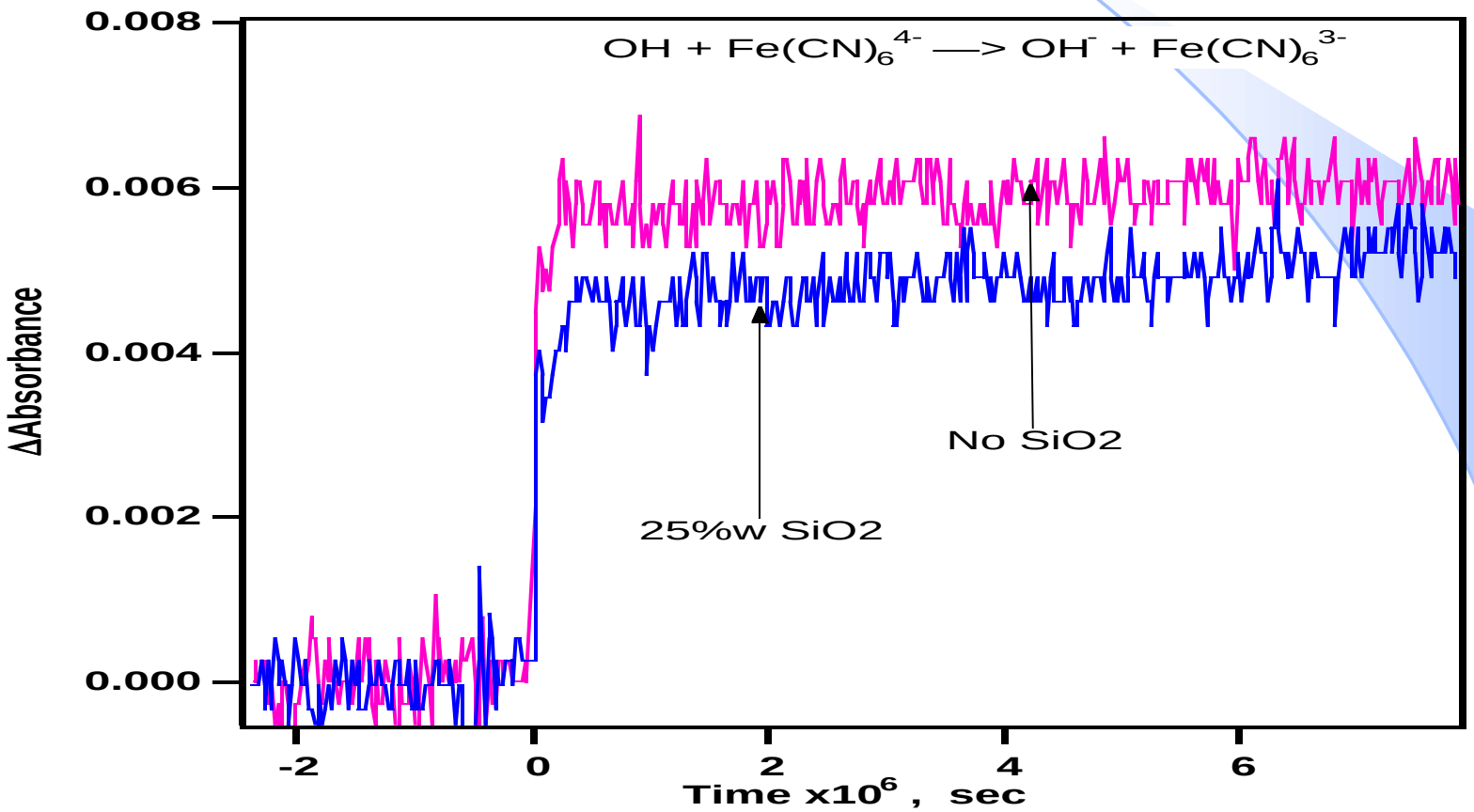


Yield of e^-_{aq} per SiO_2 Particle

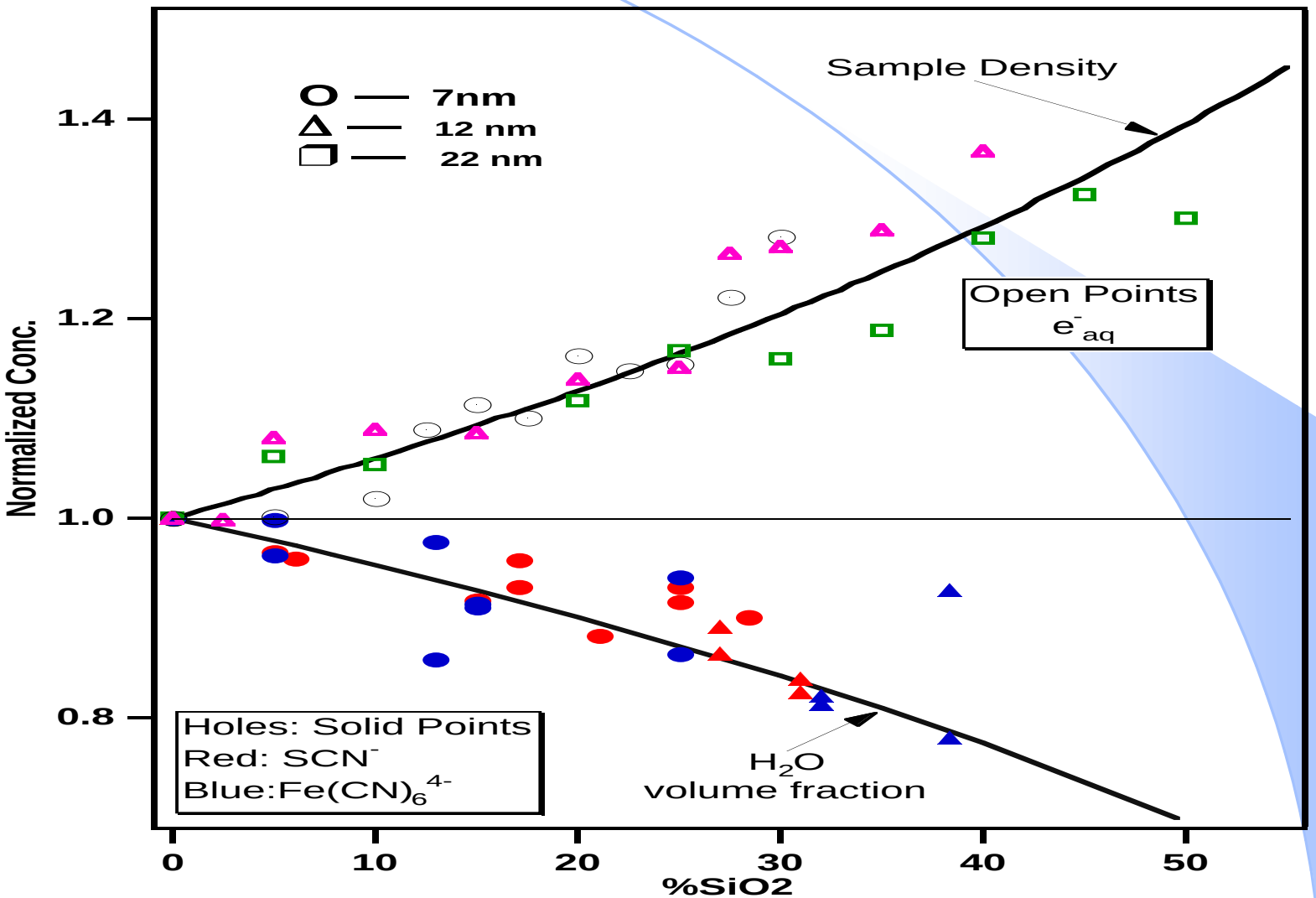
Note: e^-_{aq} per particle not per spur



Yield of Holes (OH) in SiO_2 Suspensions



Relative Conc. of e^-_{aq} & OH in Heavily Loaded SiO_2 Suspensions

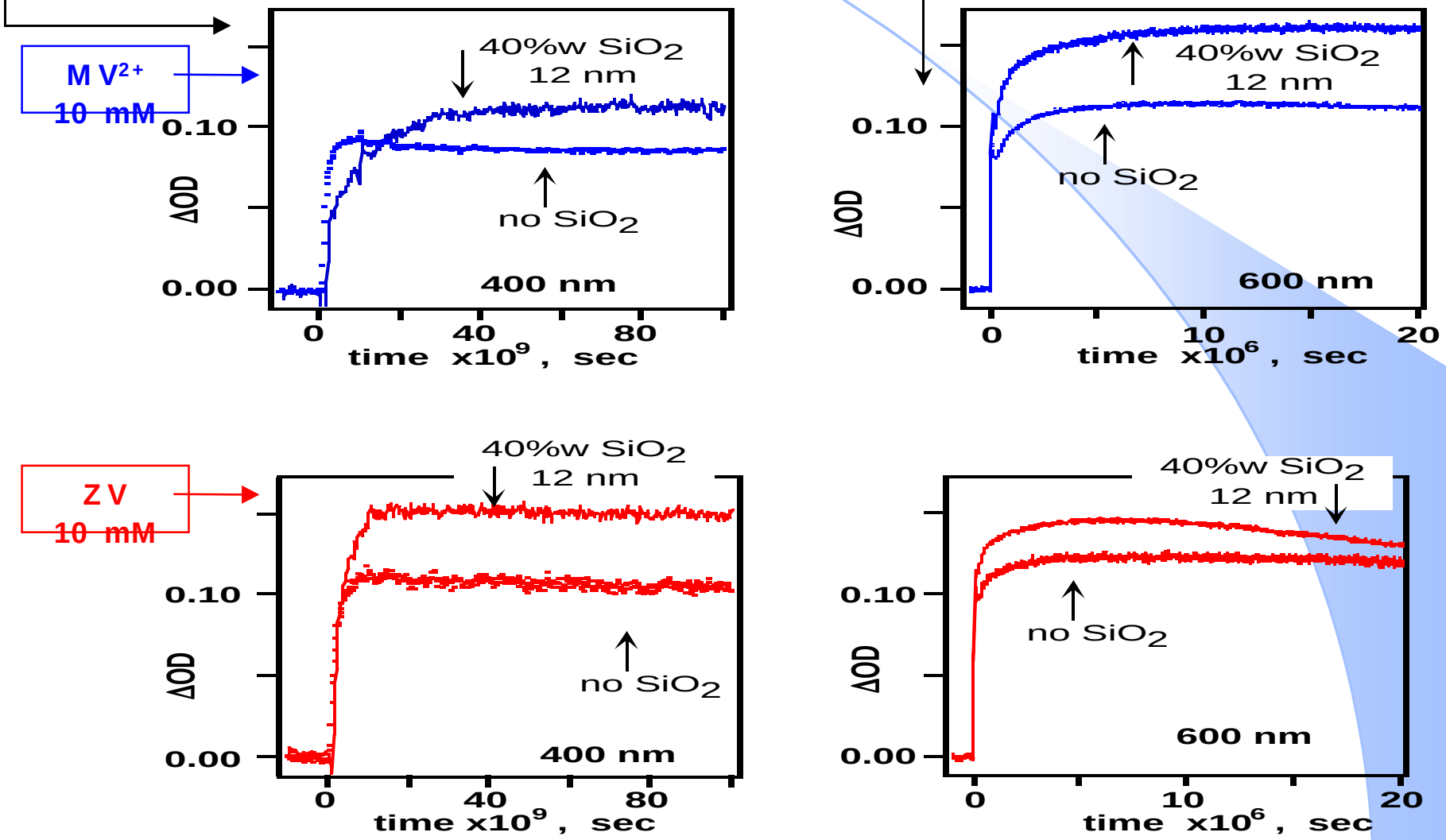


Implications

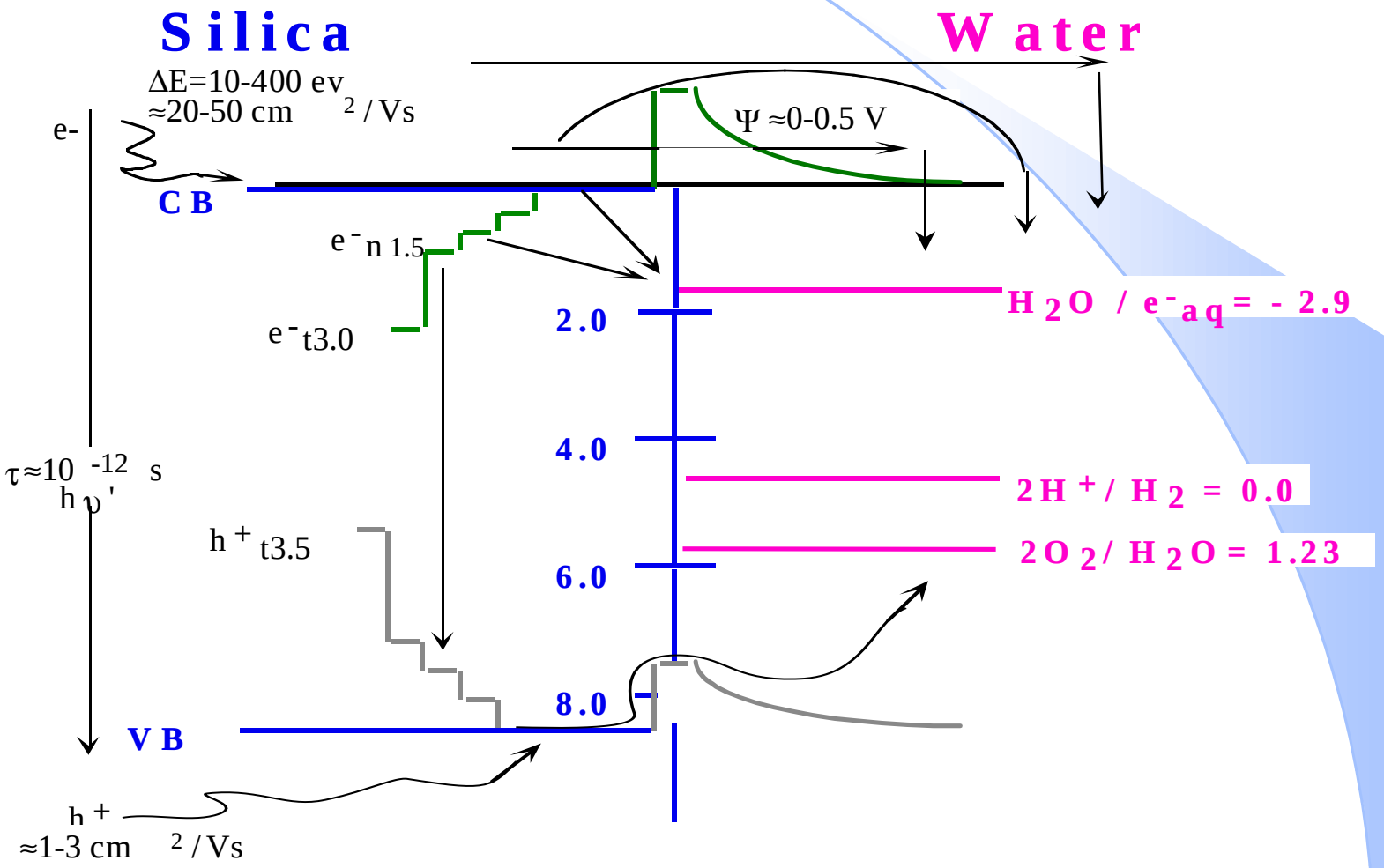
- Charge channeling into water
- Charge separation across interfaces

- **Implications to nuc. storage** (not in nanoparticle networks, grout etc.)
- **Radiocatalysis will work** (if Ox. - not SiO_2)
- **Retention consequences**
- **Tank draining & organic layers**

1. e^- Capture on the Way Back (not on way out)
2. H Atom Where from?



Interfacial Energetics & Dynamics



Conclusions

- **Yield of e^-_{aq} increases**

  (remains constant but energy comes from the solid)

- **Yield of h^+ (OH) drops**

  (less in the water but the sum remains constant)

The Dilemma:

- **Why follow absorption curve?**

  (generates spur? Where are the hole & H atoms?)

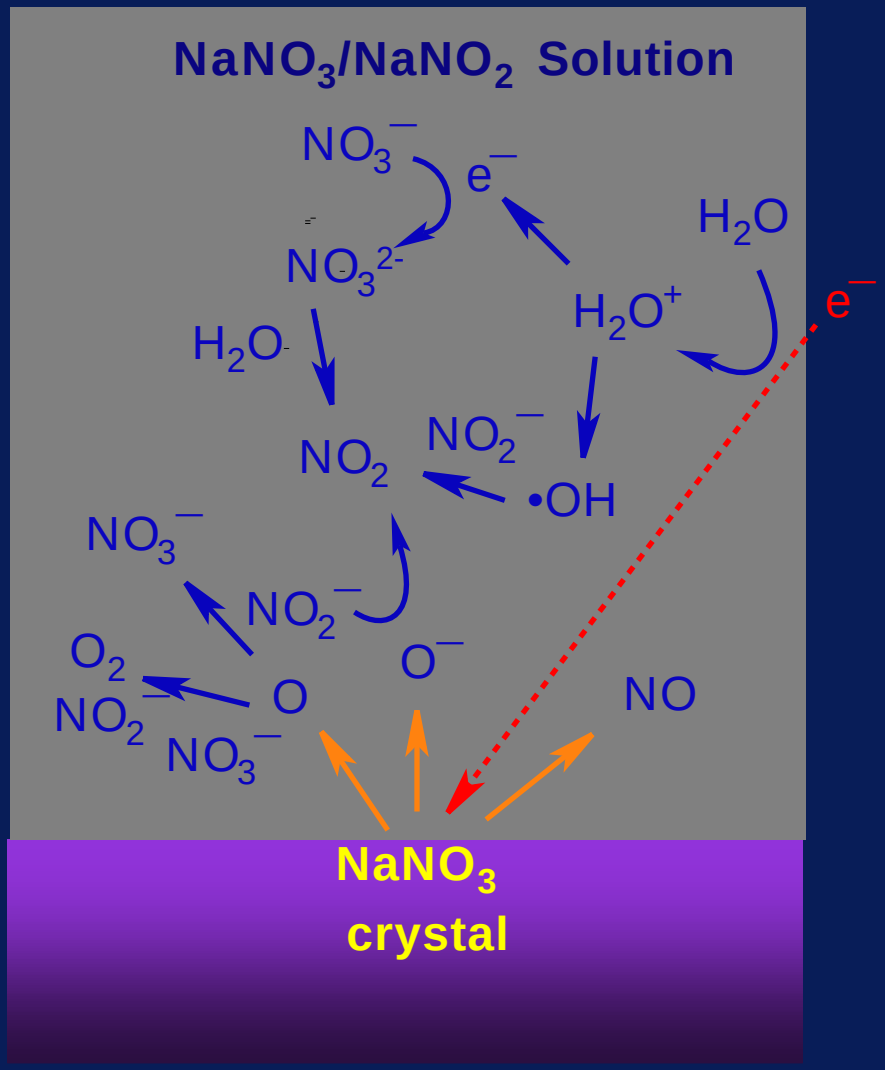
Next Question:

- Charge separation across the interface:

  For how long? how much? up to what %w?

Radiation-Induced Reactions at $NaNO_3$ Crystal/Solution Interfaces

Radiolysis of $NaNO_3$ crystals in aqueous solution is expected to produce NO_x radicals and nitrite ions. These oxidizing species degrade organic complexants and initiate gas generation reactions. Thus, a portion of our effort examines their reactions with organic complexants to develop models for organic degradation and gas generation in tank wastes.



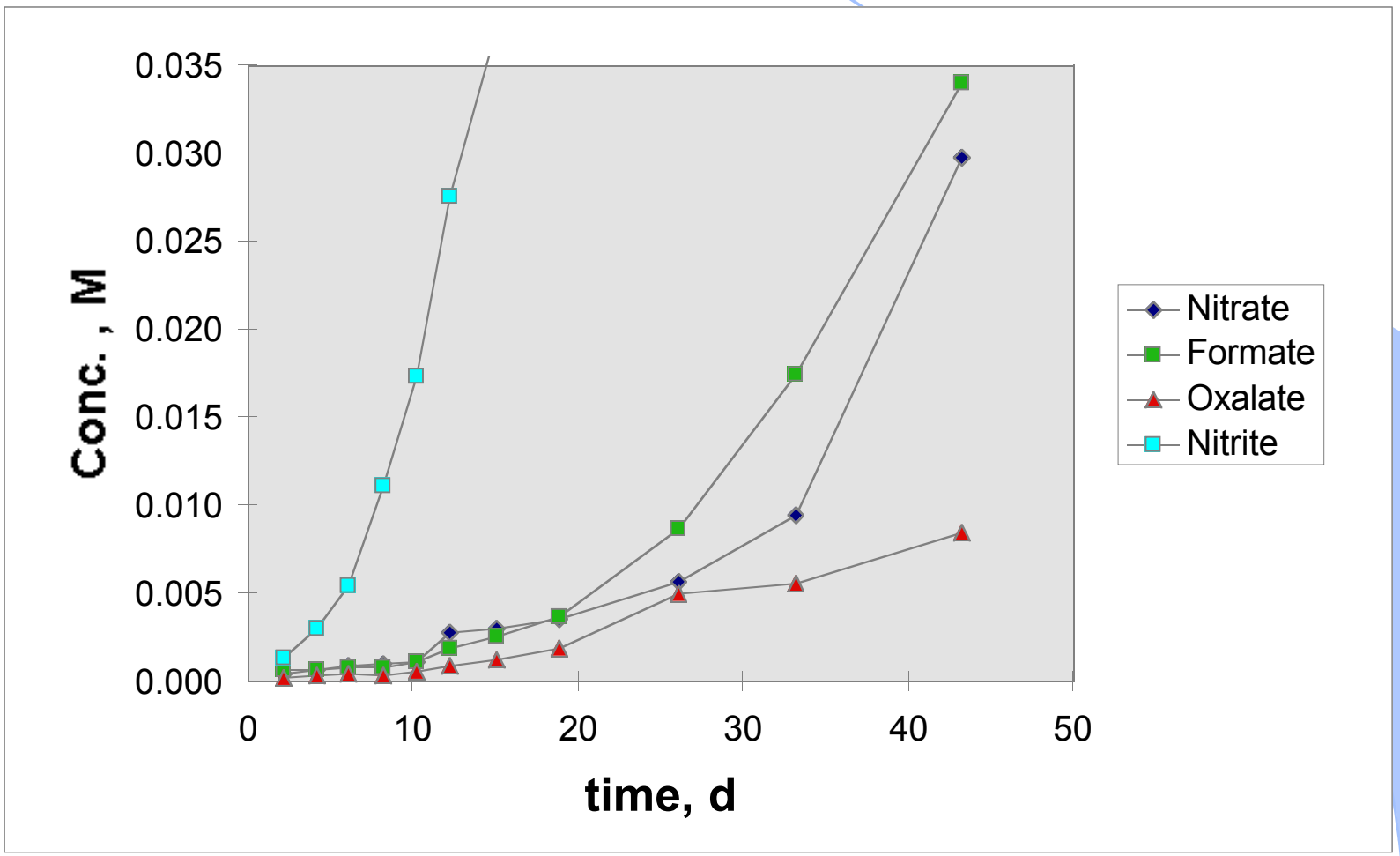
Reactions of NO_2 with Organic Complexants

γ-irradiation vs NO_2 gas

- An N_2 gas stream containing 10 ppm NO_2 is bubbled through an alkaline aqueous solution of the complexant.
- A second approach uses a γ source to irradiate alkaline $NaNO_3$, $NaNO_2$ solutions containing the complexant.
- The solutions are analyzed by ion chromatography and nuclear magnetic resonance spectroscopy.

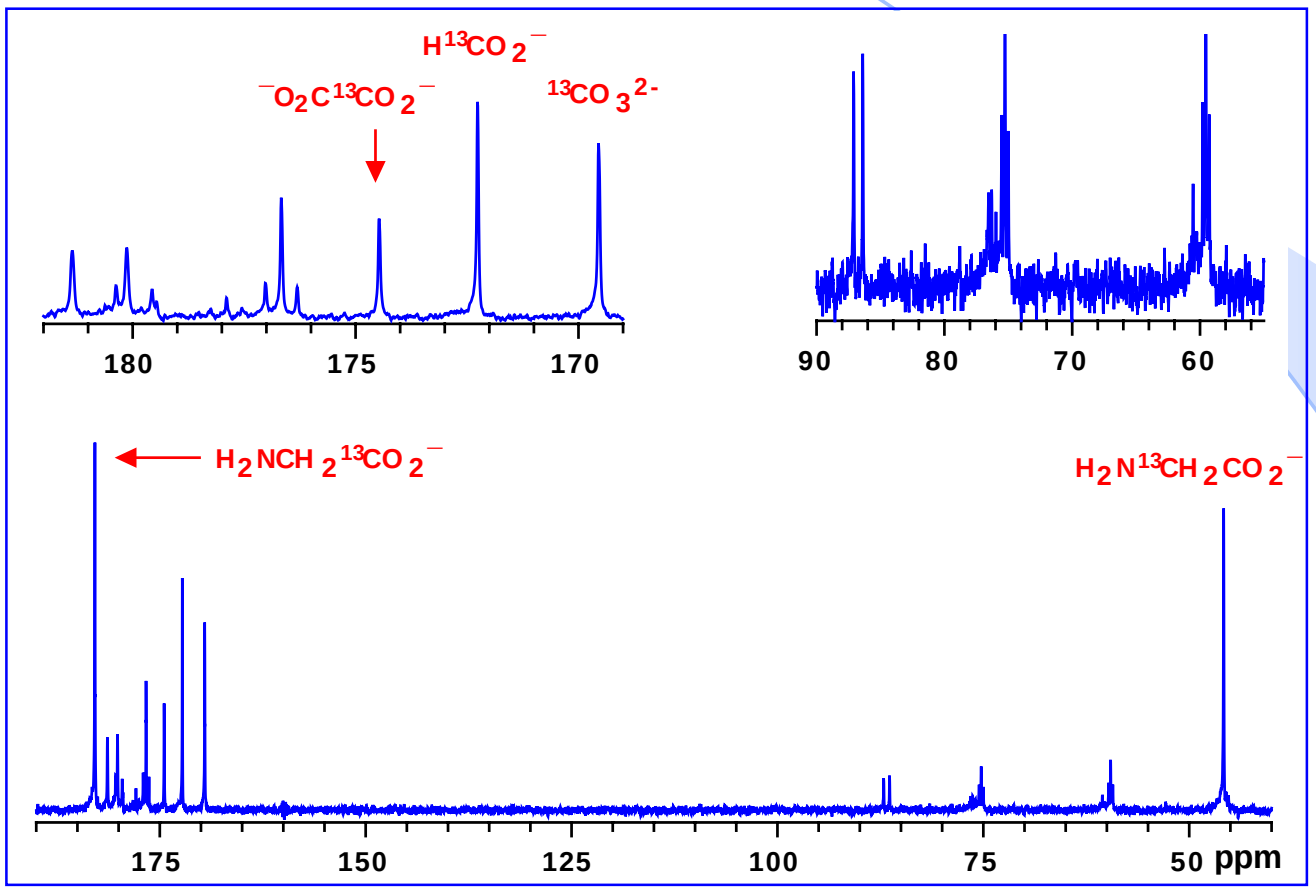
Products vs Time of Contact with NO_2 Gas

0.1 M Glycine in 1 M NaOH



Products of Reactions of Glycine with NO_2

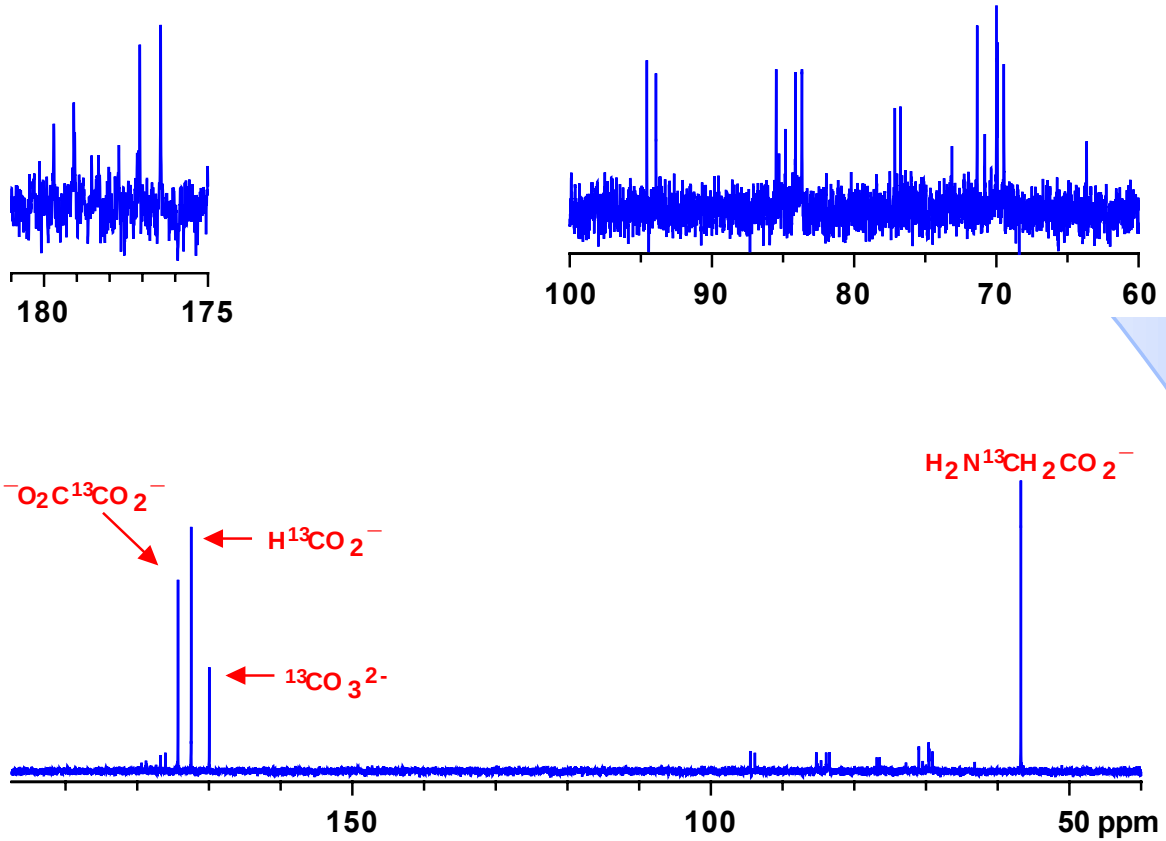
^{13}C NMR Spectra:
43 Days Contact with NO_2 Gas (10 ppm in N_2) at RT



Initial Solution:
Equal Conc. of 1- and 2-Labeled Glycines (0.1 M) in 1 M NaOH

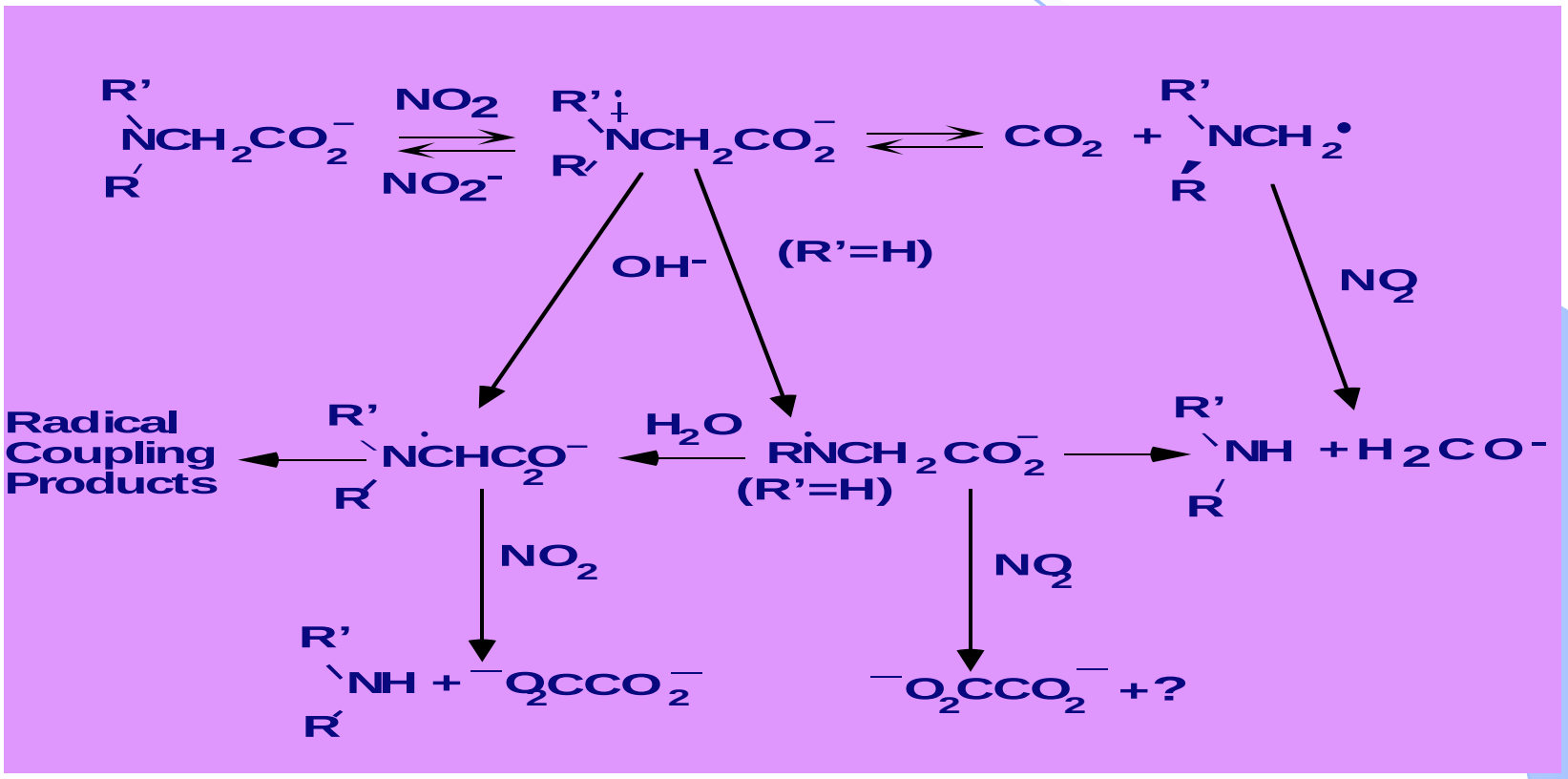
γ Irradiation of Glycine in Alkaline $NaNO_3$ Solution

^{13}C NMR Spectra after 29 MRad Dose at 25 °C



Initial Solution:
0.08 M 2-^{13}C-Glycine in 2 M $NaNO_3$, 2 M NaOH

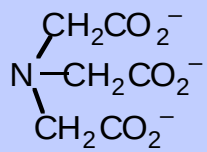
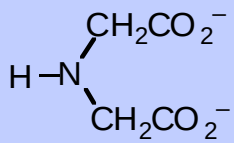
Mechanism for Oxidation of Complexants by NO_2 in Alkaline Solutions



Comparison of Complexant Reactivities in NO_2 Contact and γ Irradiation

$$R_2NCH_2CO_2^- \longrightarrow HCO_2^- + CO_3^{2-} + R_2NH$$

$$H^{13}CO_2^- \longrightarrow {}^{13}CO_2^{2-}$$

Complexant	k_{rel} (a) NO_2	k_{rel} (b) γ radiolysis
	19	10
	11	12
$H_2NCH_2CO_2^-$	4.5	7
$H^{13}CO_2^-$	1	1

a) From initial yields of $H^{12}CO_2^-$ relative to $^{13}CO_3^{2-}$ formed after contacting with NO_2

b) From decrease in complexant conc. relative to yield of $^{13}CO_3^{2-}$ after irradiation

Present Addresses

after Sep. 1st, 1998

Dan Meisel	Rad Lab, Notre Dame
Tim Schatz	Rad Lab, Notre Dame
Arnim Henglein	Rad Lab, Notre Dame
Andy Cook	Brookhaven National Lab