

# Reactivity of Peroxynitrite: Implications for Hanford Waste Management and Remediation

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Principal Investigators: [Sergei V. Lymar](#) and [James F. Wishart](#),  
Chemistry Department, Brookhaven National Laboratory,  
Upton, NY 11973-5000

Subcontractor: [James K. Hurst](#), Department of Chemistry,  
Washington State University, Pullman, WA, 99164-4360

This document contains a modified version of the poster presented at the EMSP National Workshop held in Atlanta, GA, April 24-27, 2000. Modifications have been made to protect unpublished data and their interpretation. Six slides concerning radiation effects on nitrates have been removed from the original poster. A PDF file containing complete version of the poster presentation can be obtained from the lead PI at [lymar@bnl.gov](mailto:lymar@bnl.gov)

# Background

## Hanford High Level Nuclear Waste

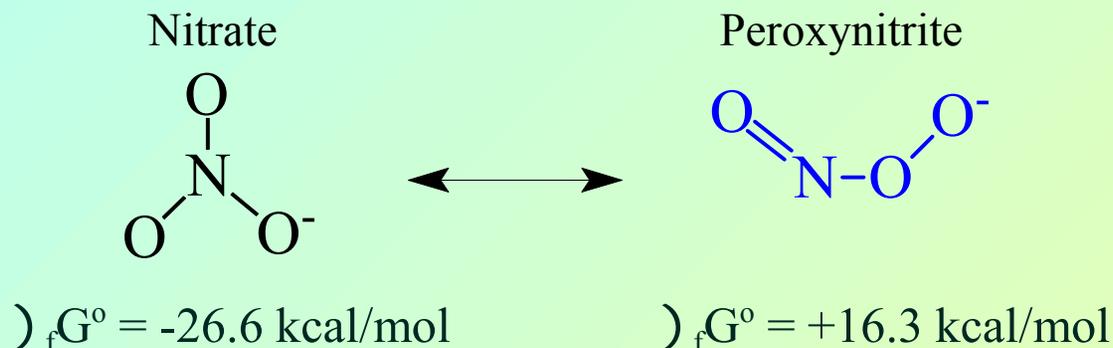
### Major Inorganic Components

Compound	Amount, % by weight			
	Liquid	Sludge	Salt cake	Slurry
H <sub>2</sub> O	40	34	11	56
<b>NaNO<sub>3</sub></b>	<b>21</b>	<b>25</b>	<b>82</b>	<b>15</b>
NaNO <sub>2</sub>	16	3.8	1.7	5.6
NaAlO <sub>2</sub>	13	1.2	1.4	6.0
Na <sub>2</sub> CO <sub>3</sub>	6.2	5.3	1.5	7.0
Na <sub>3</sub> PO <sub>4</sub>	2.3	16	1.6	0.8
NaOH	0.6	2.2	0.5	1.9



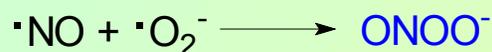
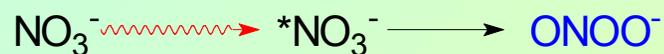
**P** Nitrate, precursor to peroxyxynitrite, is ubiquitous component in strongly alkaline Hanford wastes

# Peroxynitrite

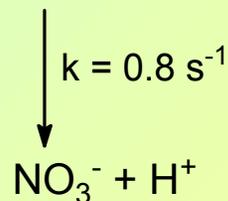
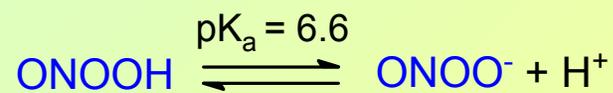


# Although  $\text{ONOO}^-$  is strong oxidant and nitrating agent, it is unreactive unless protonated or combined with Lewis acids such as  $\text{CO}_2$  or metal ions

# Formation pathways:



# Decomposition:



# Efficient, inexpensive synthesis (Baeyer-Villiger reaction):



# Project Scope

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This project provides information relevant to: (i) extent and nature of radiation-induced chemical modification of Hanford waste during storage and (ii) potential applications of peroxyxynitrite in remediation technologies. Within this context, the specific research objectives are:

- P** To determine the extent of radiation-induced peroxyxynitrite generation in nitrates
- P** Through mechanistic studies of peroxyxynitrite reactions to assess their contribution to the degradation of high level waste
- P** Determine the feasibility of using peroxyxynitrite for destruction of organic complexants and for removal of chromium for more efficient waste vitrification

# Progress Summary

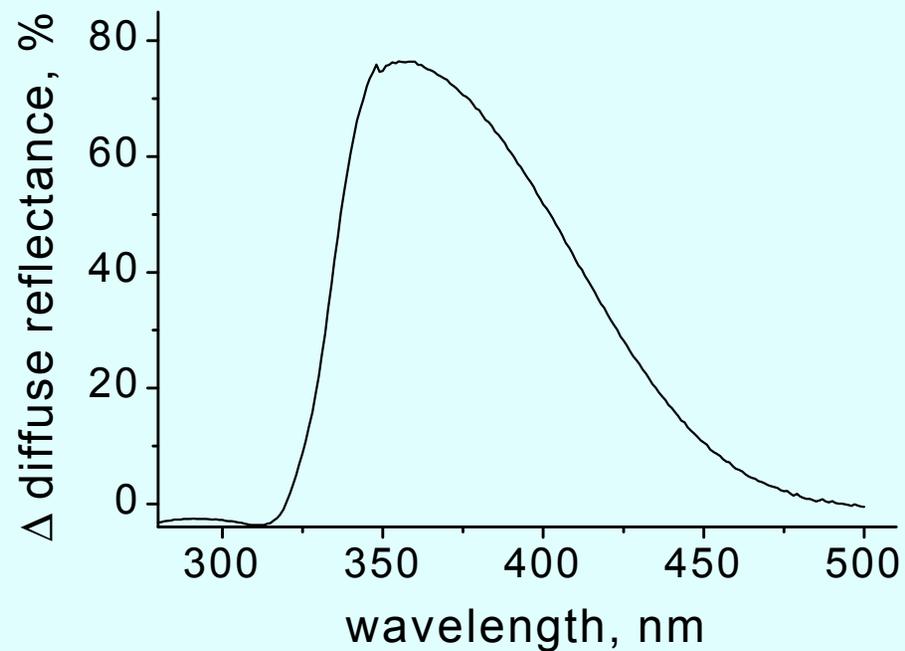
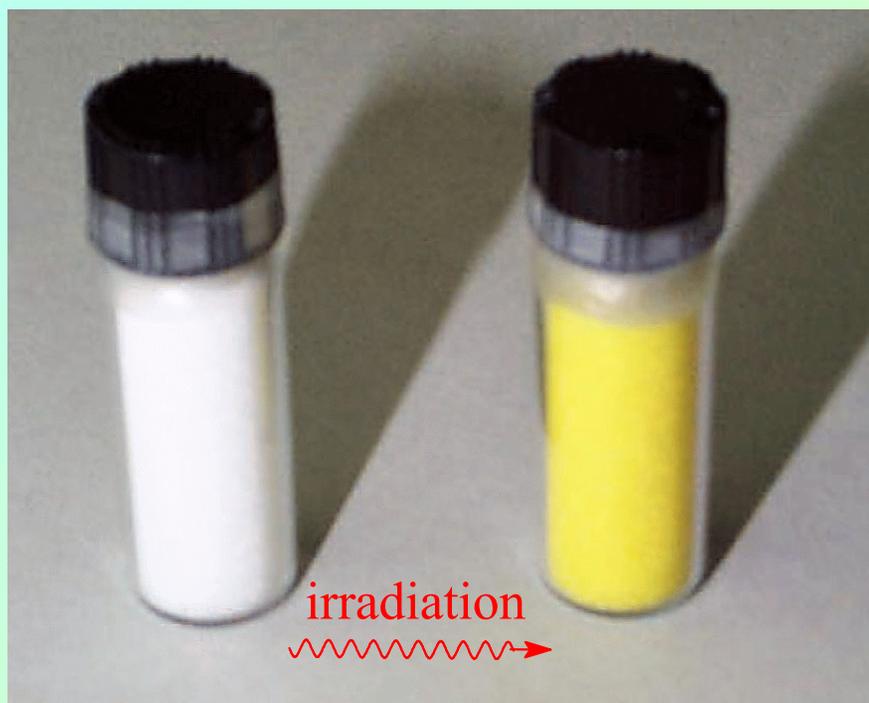
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The most significant results and implications of this project are:

- P** Establishing that peroxyxynitrite is a major oxidant produced by radiation in solid nitrates present in waste tanks. This can result in considerable accumulation of the chemical energy in solid waste
- P** Complete mechanistic description of the catalyzed peroxyxynitrite reactivity pathways. Radicals species produced by these reactions contribute to the waste chemical degradation
- P** Demonstration that peroxyxynitrite could find applications in the pretreatment of the Hanford waste for disposal. These include mineralization of organic complexants and oxidative dissolution of chromium

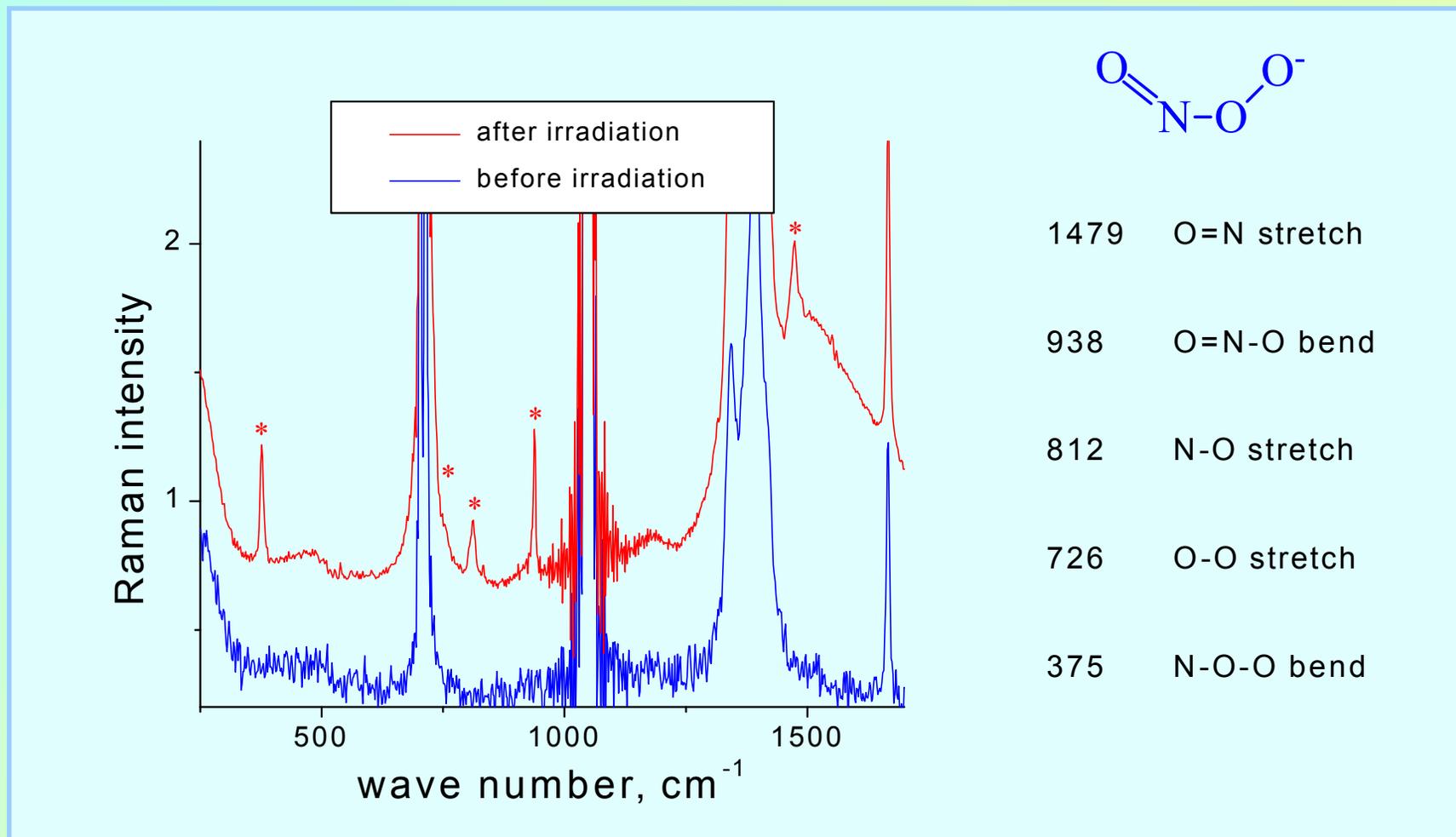
# Radiolytic Accumulation of Peroxynitrite

Radiation-induced coloration due to  $\text{ONOO}^-$   
in solid alkali nitrates

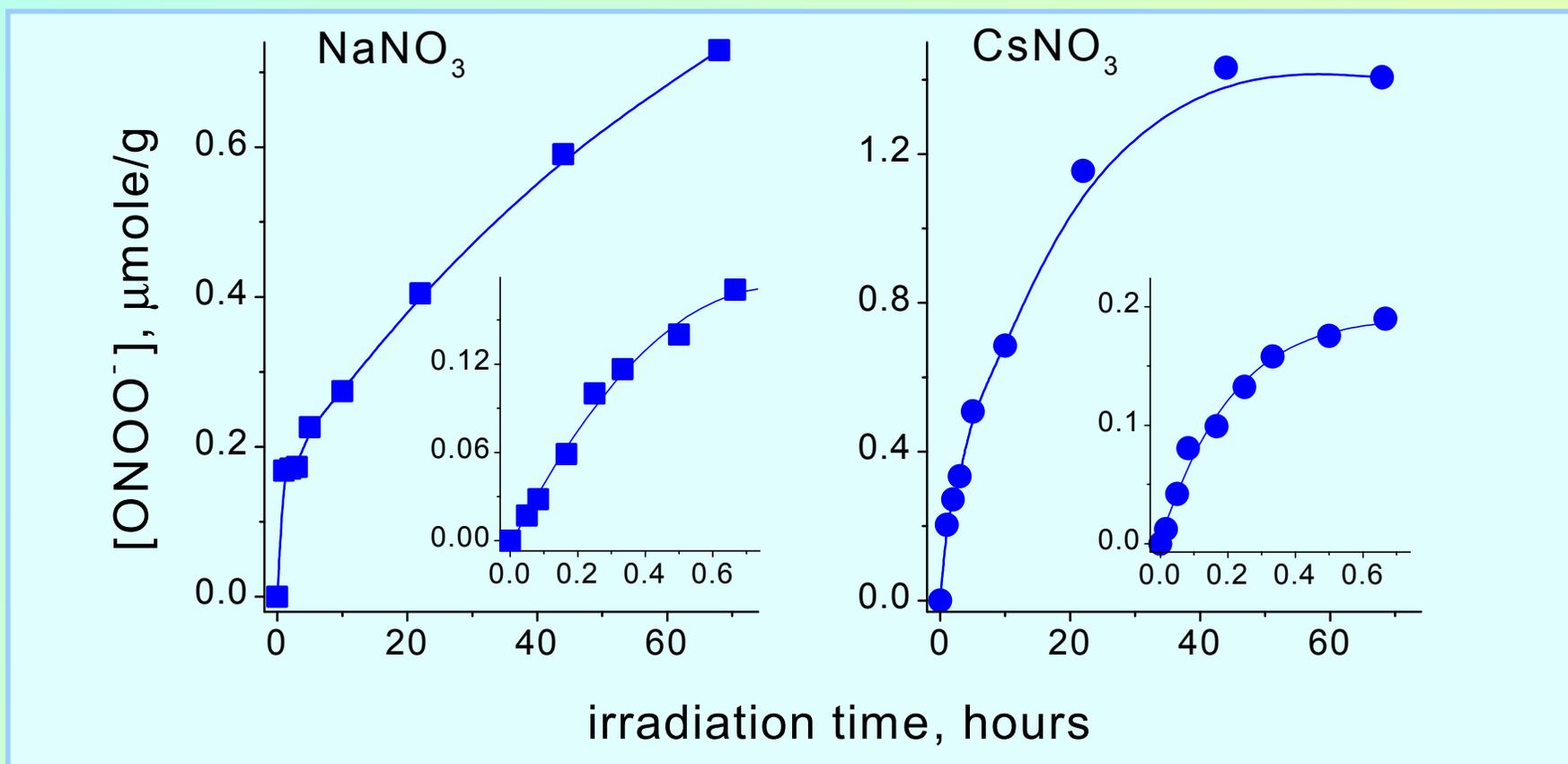


# Spectroscopic Detection of $\text{ONOO}^-$

## Raman spectral changes in irradiated $\text{CsNO}_3$

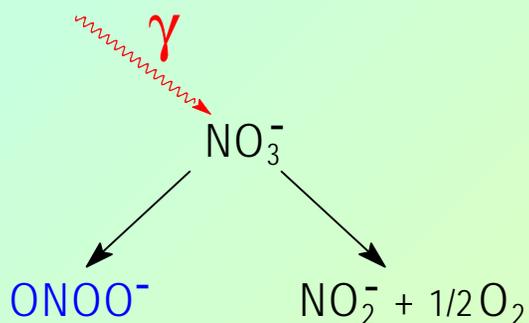


# Peroxynitrite Accumulation Kinetics



**P** Accumulation rapidly decelerates with absorbed radiation dose

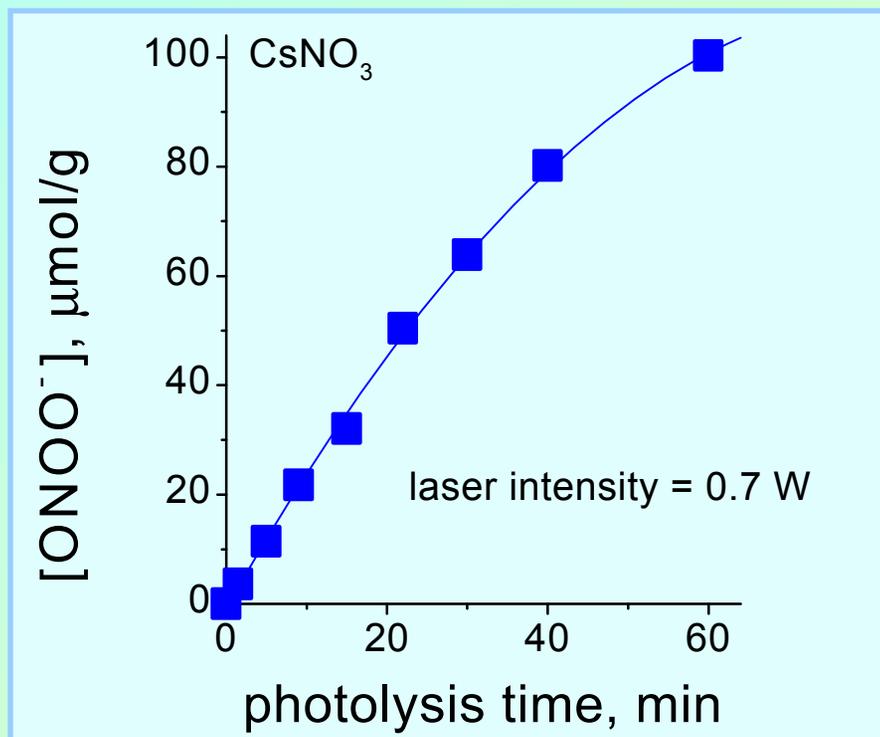
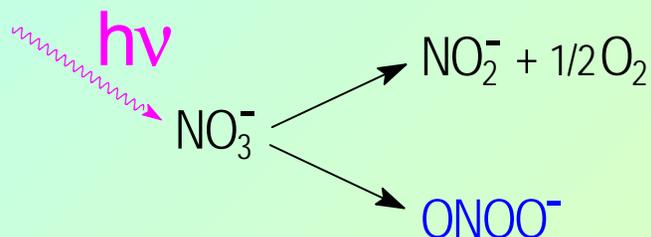
# Radiation Yields



Product radiation yields (molecules/100 eV)  
in solid alkali nitrates

Product Salt	ONOO <sup>-</sup>		NO <sub>2</sub> <sup>-</sup>
	Initial	Stationary	
NaNO <sub>3</sub>	0.60	0.01	0.17
KNO <sub>3</sub>	0.73	0.002	1.3
CsNO <sub>3</sub>	1.9	0.0	1.25

# Photochemical Peroxynitrite Accumulation



Product quantum yields (%) at 248 nm in solid alkali nitrates

Product Salt	$\text{ONOO}^-$	$\text{NO}_2^-$	Ratio $\text{ONOO}^-/\text{NO}_2^-$
$\text{NH}_4\text{NO}_3$	0.03	0.2	0.16
$\text{NaNO}_3$	0.7	0.1	6.4
$\text{KNO}_3$	5.1	0.8	6.4
$\text{CsNO}_3$	11	1.1	10

- P UV photolysis affords doping nitrate salts with large amounts of  $\text{ONOO}^-$
- P electronically excited  $\text{NO}_3^-$  isomerizes to  $\text{ONOO}^-$

# Reactivity of Peroxynitrite in Solution

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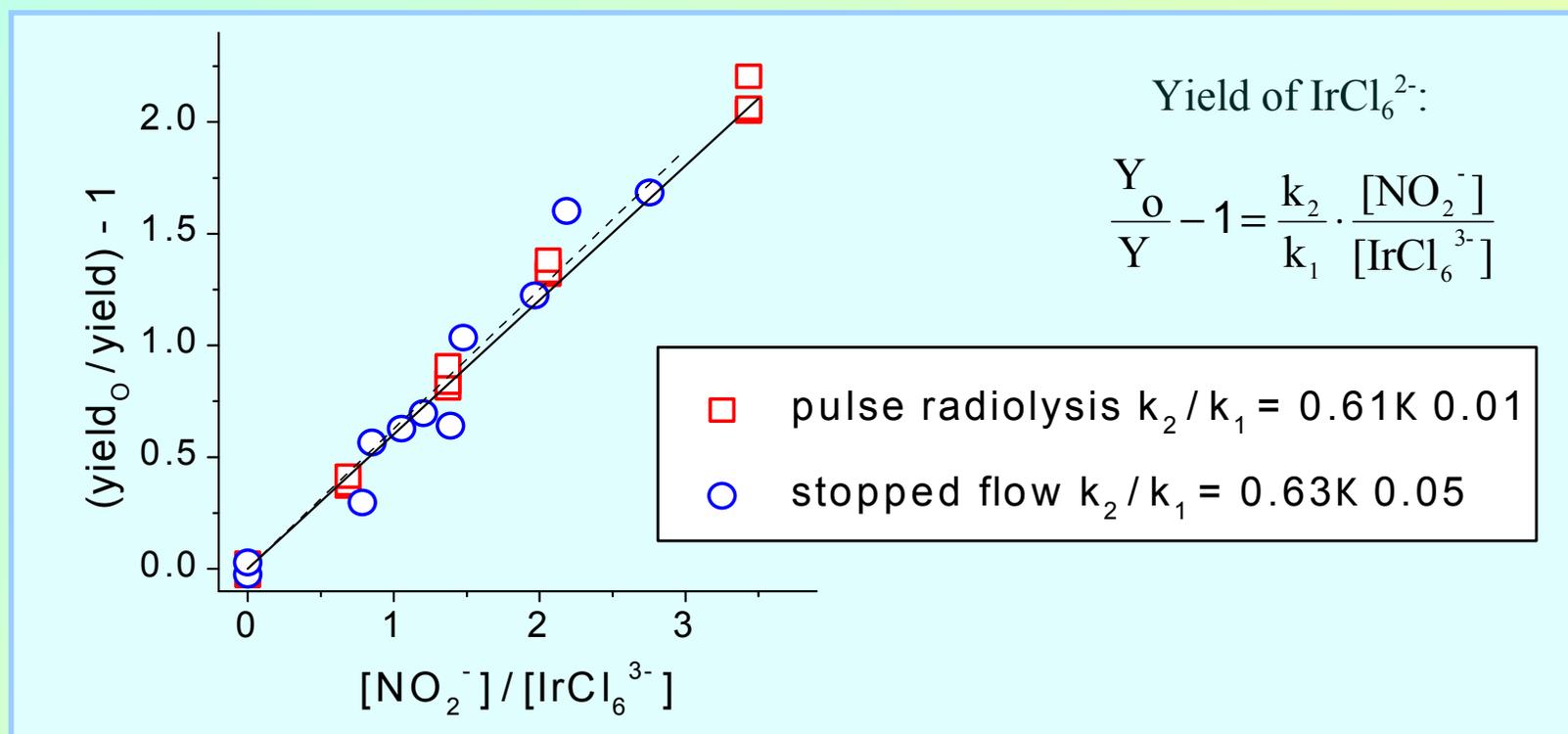
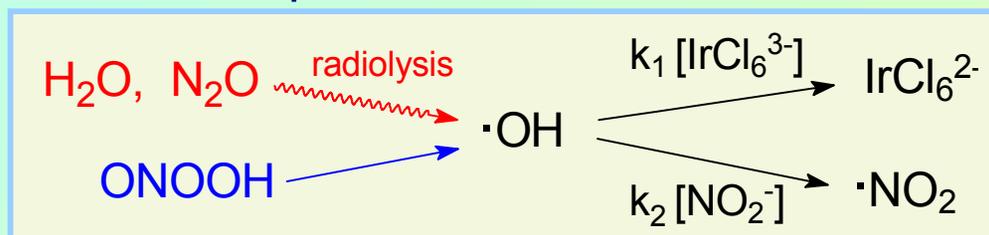
Proton- and Carbon Dioxide-Catalyzed Oxidations by  $\text{ONOO}^-$

- P**  $\text{H}^+$ -catalyzed oxidations proceed through equilibrium formation of conjugate peroxynitrous acid ( $\text{ONOOH}$ ); homolytic cleavage of O-O bond in  $\text{ONOOH}$  is the rate-determining step ( $k = 1.6 \text{ s}^{-1}$ )
- P**  $\text{CO}_2$ -catalyzed oxidations proceed through rate-determining formation of nitrosoperoxy carbonate ( $\text{ONOOCO}_2^-$ ) adduct;  
 $k(\text{CO}_2 + \text{ONOO}^-) = 3 \times 10^4 \text{ M}^{-1}\text{s}^{-1}$
- P** In both cases, limiting oxidation yields are below stoichiometric limits based upon consumption of  $\text{ONOO}^-$
- P** In both cases, strongly oxidizing radical species are produced as reactive intermediates



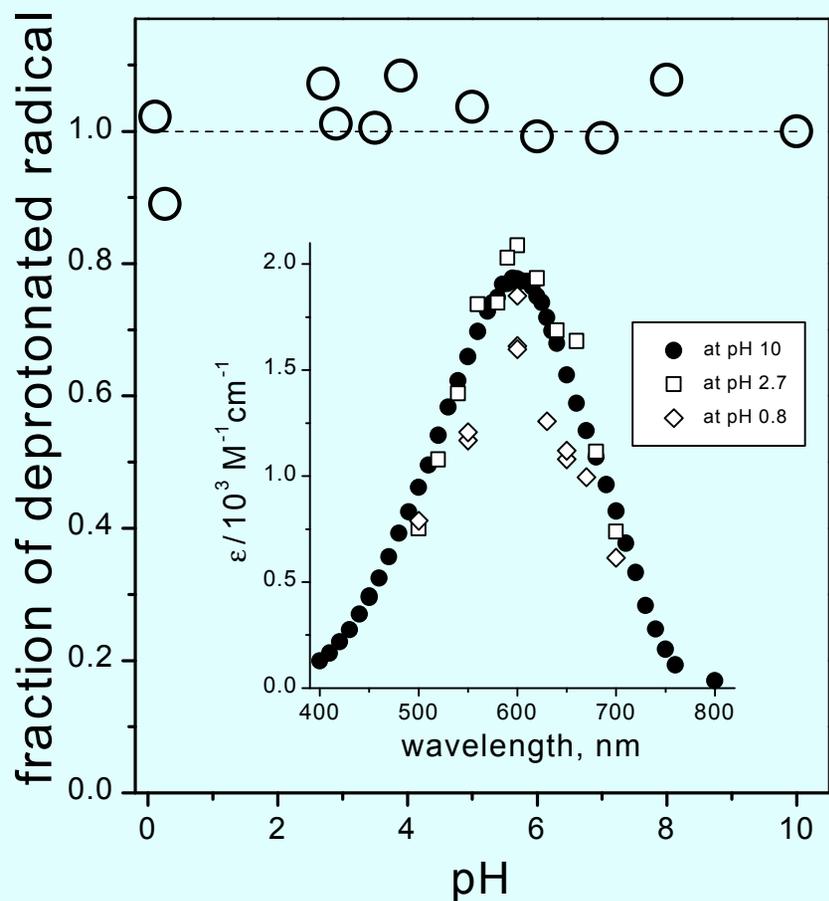
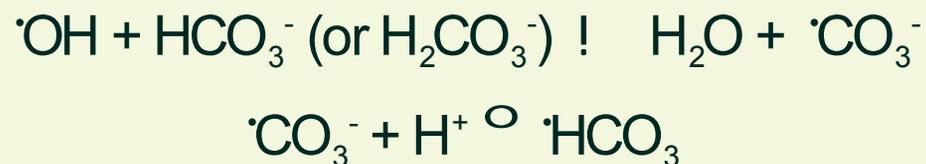
# Reactivity of ONOOH

Comparison with  $\cdot\text{OH}$  radical



**P** Reactivities of the oxidizing intermediate produced from ONOOH and the “authentic”  $\cdot\text{OH}$  radical are identical

# Acidity of Carbonate Radical



**P** Carbonate radical is a strong acid,  $\text{pK}_a(\cdot\text{HCO}_3) < 0$

**P** Rate constants tabulated for  $\cdot\text{CO}_3^-$  can be used over  $0 < \text{pH} < 14$  without change

# Oxidation of ONOO<sup>-</sup> by Inorganic Radicals

## Pulse radiolysis data

<b>•R/R- couple</b>	<b>E<sup>0</sup>(•R/R-) (V, NHE)</b>	<b>k(•R + ONOO<sup>-</sup>) M<sup>-1</sup>s<sup>-1</sup></b>
•OH/OH <sup>-</sup>	1.90	4.8 x 10 <sup>9</sup>
•CO <sub>3</sub> <sup>-</sup> /CO <sub>3</sub> <sup>2-</sup>	1.59	3.7 x 10 <sup>6</sup>
•N <sub>3</sub> /N <sub>3</sub> <sup>-</sup>	1.33	7.2 x 10 <sup>8</sup>
•NO <sub>2</sub> /NO <sub>2</sub> <sup>-</sup>	1.04	< 2 x 10 <sup>4</sup>
•ClO <sub>2</sub> /ClO <sub>2</sub> <sup>-</sup>	0.93	3.2 x 10 <sup>4</sup>

**P** Reaction pathways

electron transfer:



atom abstraction:



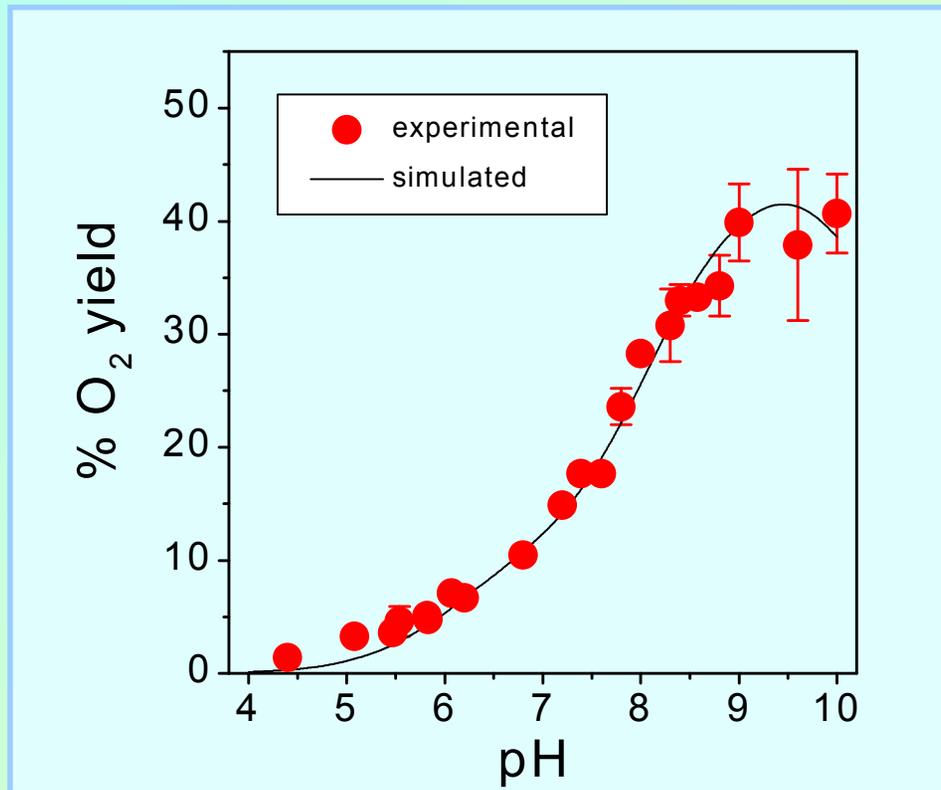
**P** Oxidation potential of ONOO<sup>-</sup> can be estimated as:

$$E^0(\bullet\text{ONOO}/\text{ONOO}^-) = 0.8 \text{ V}$$

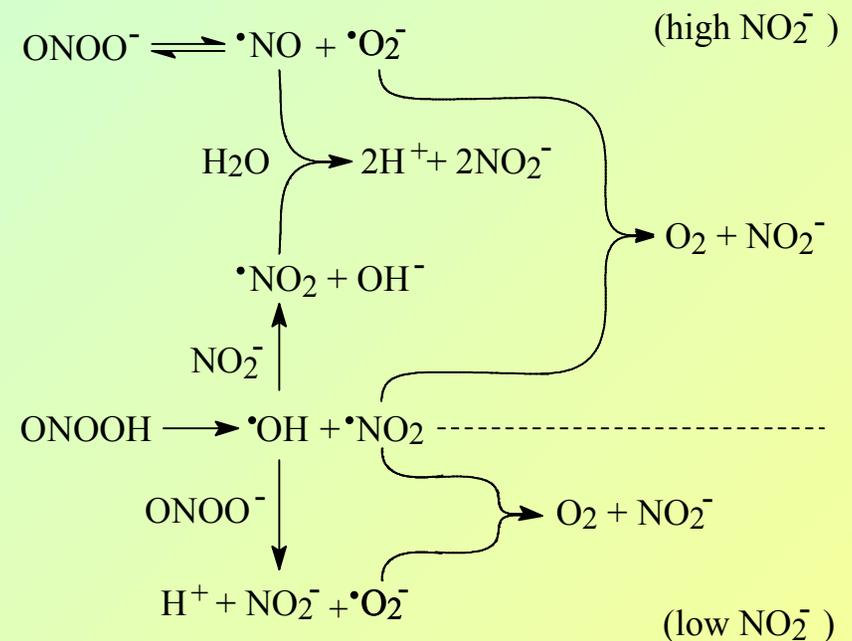
# Decomposition of Peroxynitrite in Solution



pH-dependent oxygen yield



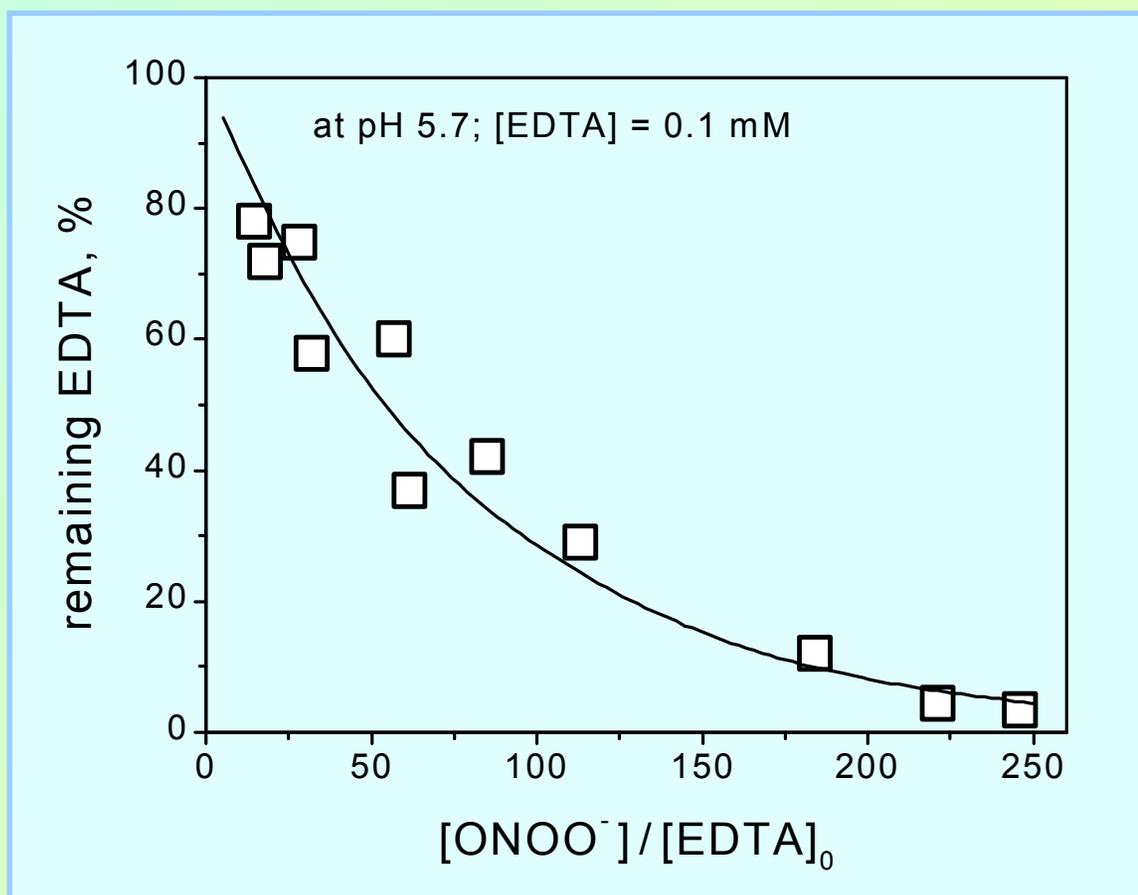
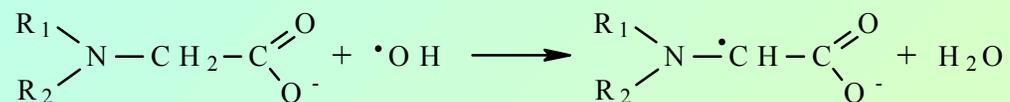
Simplified mechanism:



**P** NO<sub>2</sub><sup>-</sup> does not inhibit O<sub>2</sub> evolution, while organic ·OH scavengers do

**P** This inhibition is reversed above pH 8 by excess of NO<sub>2</sub><sup>-</sup>

# Oxidation of EDTA by Peroxynitrite



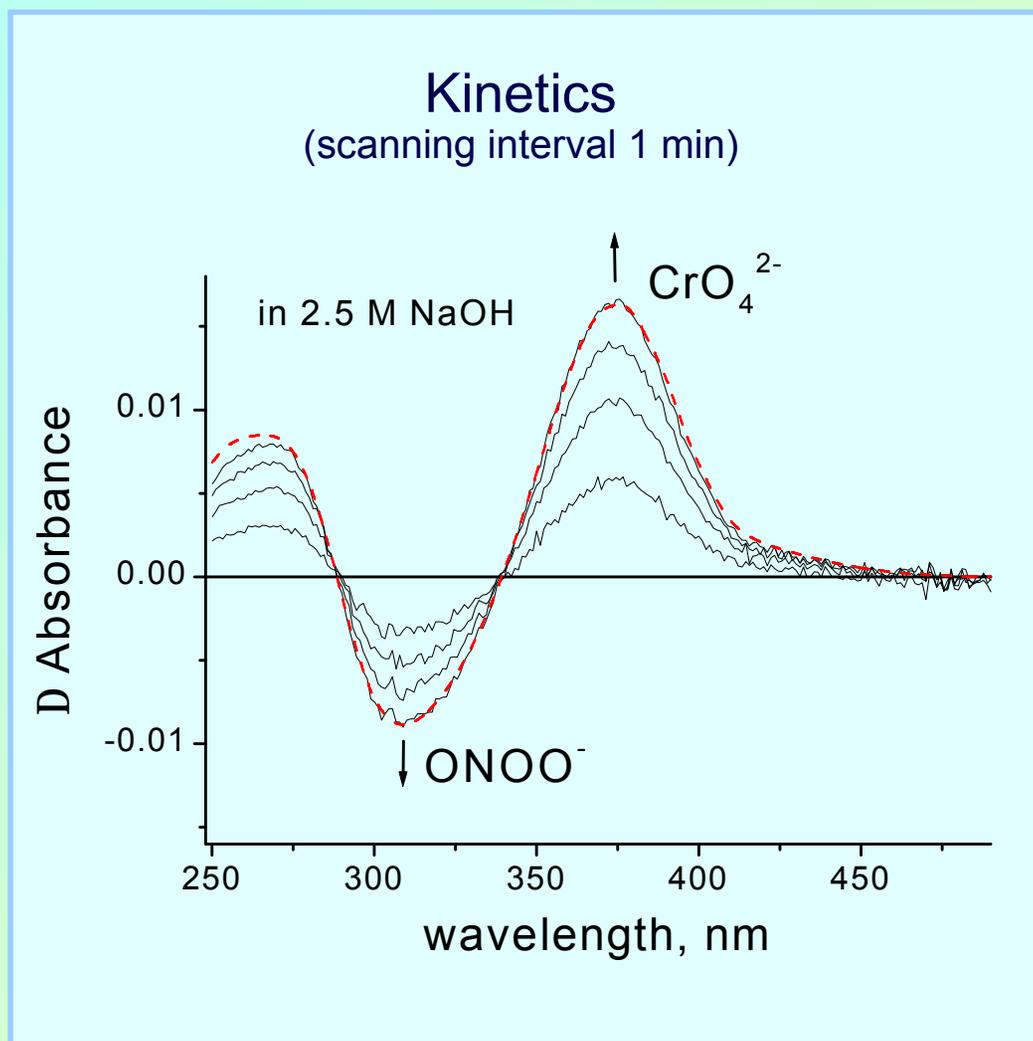
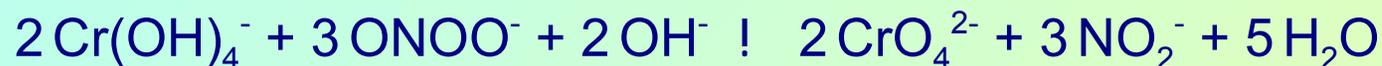
# Oxidative Dissolution of Chromium(III)

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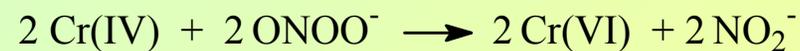
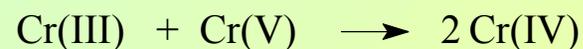
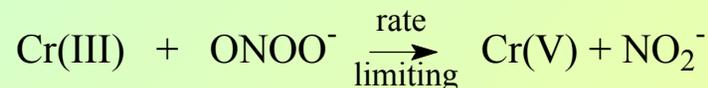
## Summary

- P** Oxidation cleanly produces Cr(VI) in the form of chromate,  $\text{CrO}_4^{2-}$
- P** Stoichiometric ratio  $\frac{[\text{ONOO}^-]}{[\text{Cr(III)}]}$  is 3/2, i.e., the oxidizing equivalents of  $\text{ONOO}^-$  are utilized completely
- P** The rate is first order in both  $[\text{ONOO}^-]$  and  $[\text{Cr(III)}]$ , suggesting that the rate-determining step is  $\text{S}_{\text{N}}2$  nucleophilic attack of  $\text{ONOO}^-$  on  $\text{Cr(OH)}_4^-$ . The rate constant for this step is  $6.5 \text{ M}^{-1}\text{s}^{-1}$
- P** Peroxynitrite is a better oxidant for Cr(III) than hydrogen peroxide; under identical conditions, the rate ratio is - 3
- P** The rate of oxidation decreases with the solution aging
- P** Addition of Mn(II) strongly promotes oxidation

# Oxidation of $\text{Cr}(\text{OH})_4^-$ by Peroxynitrite

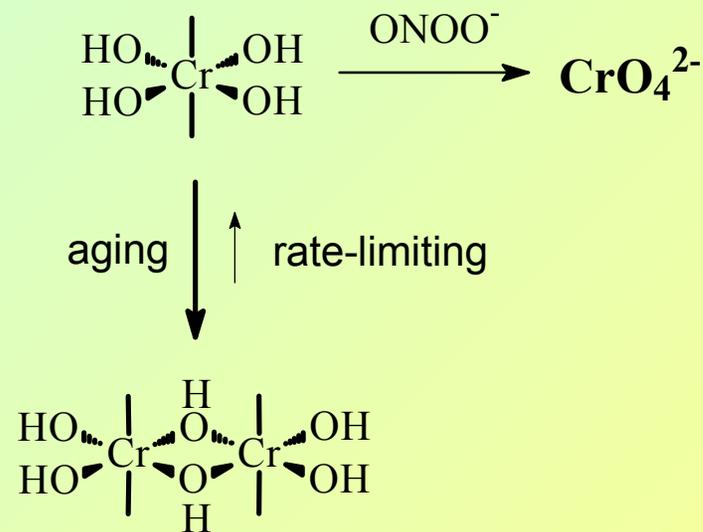
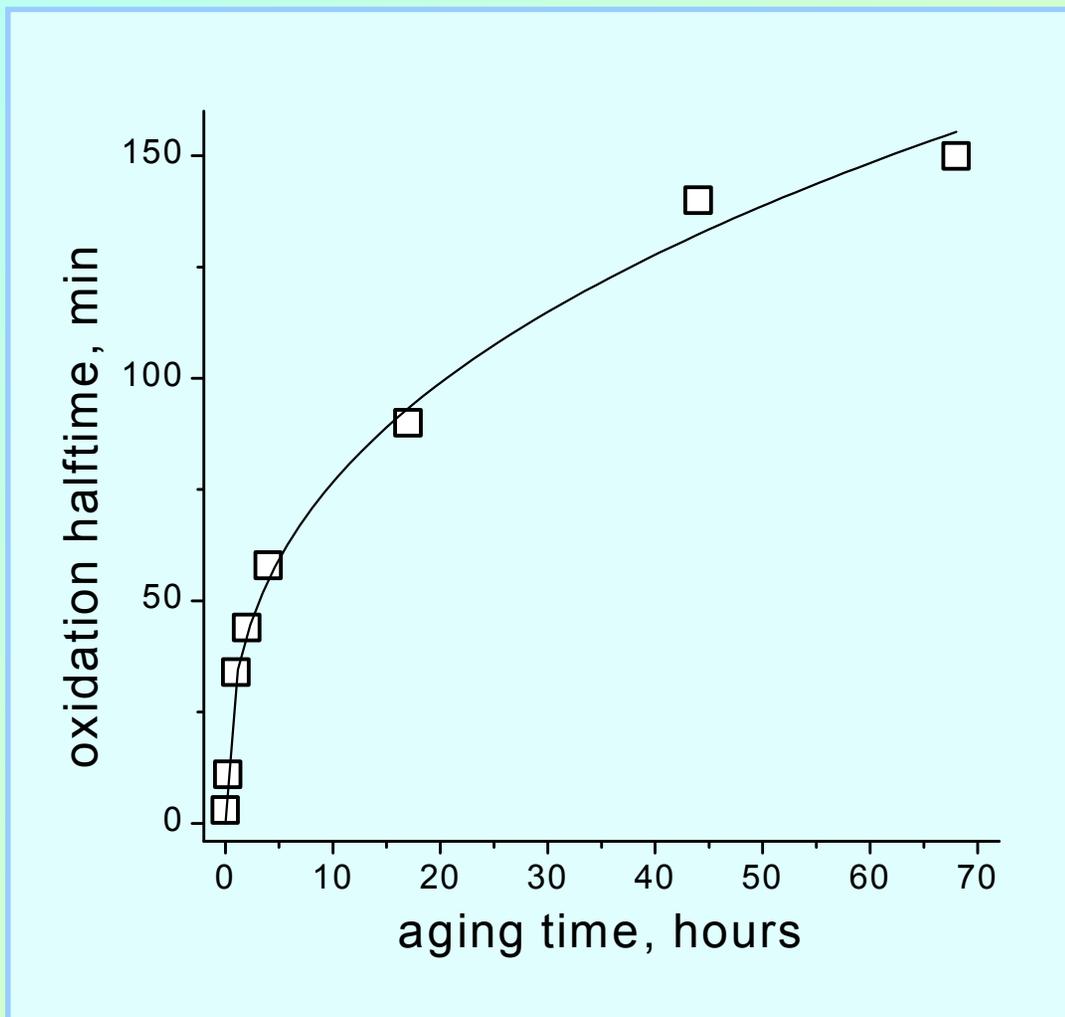


## Proposed mechanism



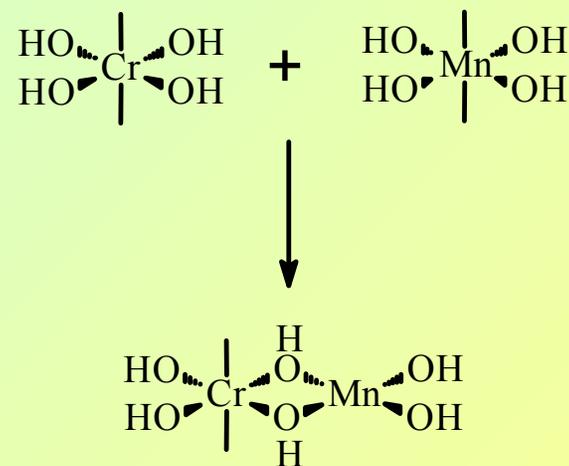
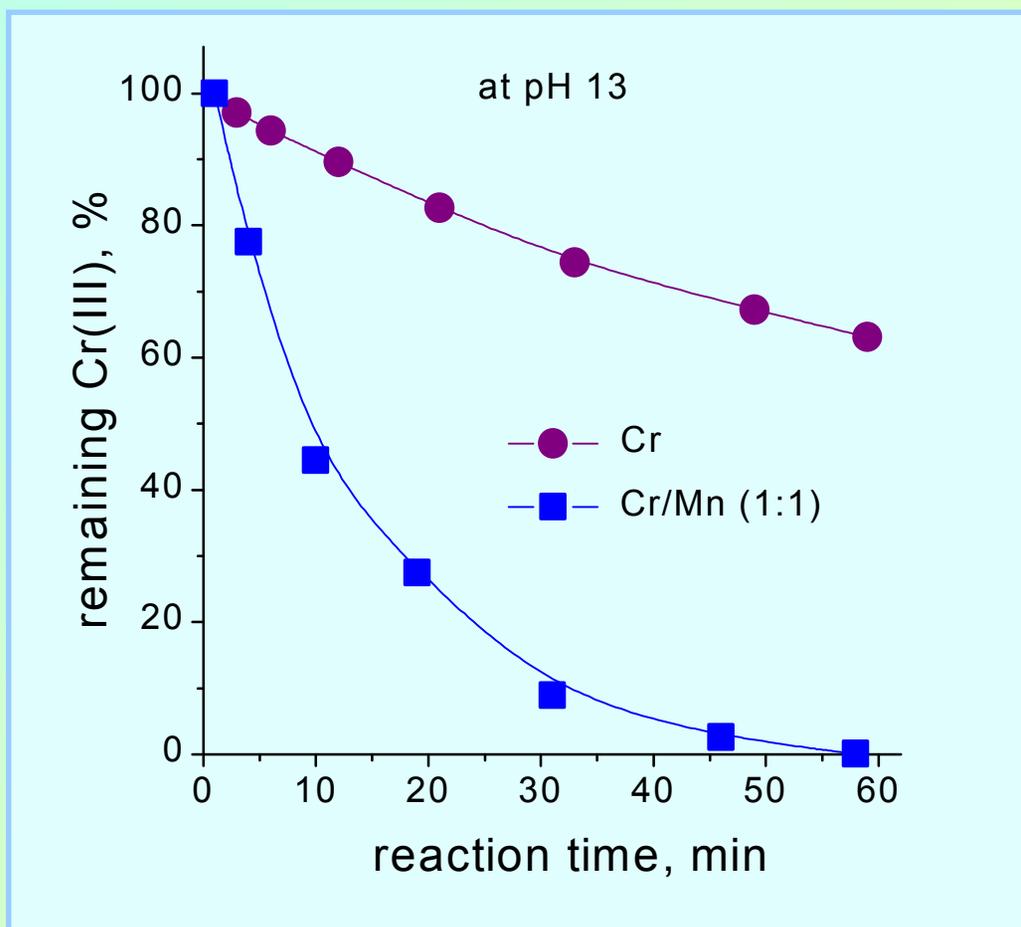
# Effect of Aging on Cr(III) Oxidation

Cr(III) aged in alkali prior to  $\text{ONOO}^-$  addition



# Catalytic Effect of Mn(II) on Cr(III) Oxidation

- P Mn accelerates oxidation of Cr
- P Oxidation proceeds to completion
- P Amounts of Cr and Mn found in Hanford tanks are nearly equal



# Acknowledgments and References

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The PIs are indebted to the following researchers for their contributions to this project

O. V. Gerasimov, E. N. Yurchenko, H. A. Schwarz, Brookhaven National Laboratory  
S. Goldstein and G. Czapski, The Hebrew University of Jerusalem  
J. W. Coddington, Washington State University

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