Chemical Mechanisms of Gas Formation in Hanford High-Level Wastes

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I. Introduction

As many as 28 of the 177 underground waste storage tanks at Hanford are known or suspected to evolve a mixture of potentially hazardous gases that includes H_2, N_2O, NH_3, and N_2.

The wastes in gas producing tanks contain large amounts of NO_3^-, NO_2^-, $Al(OH)_4^-$, OH^- and organics that orginally included metal chelating agents such as HEDTA, EDTA, and glycolate.

Studies on simulated wastes, first performed by Delegard (Rockwell-Hanford), indicated that $Al(OH)_4^-$, NO_x^-, and HEDTA or glycolate were necessary for gas production.

Subsequent work (GT) using N-15 labeled reagents indicated that all N_2O and N_2 and most of the NH_3 were derived from NO_2^-.

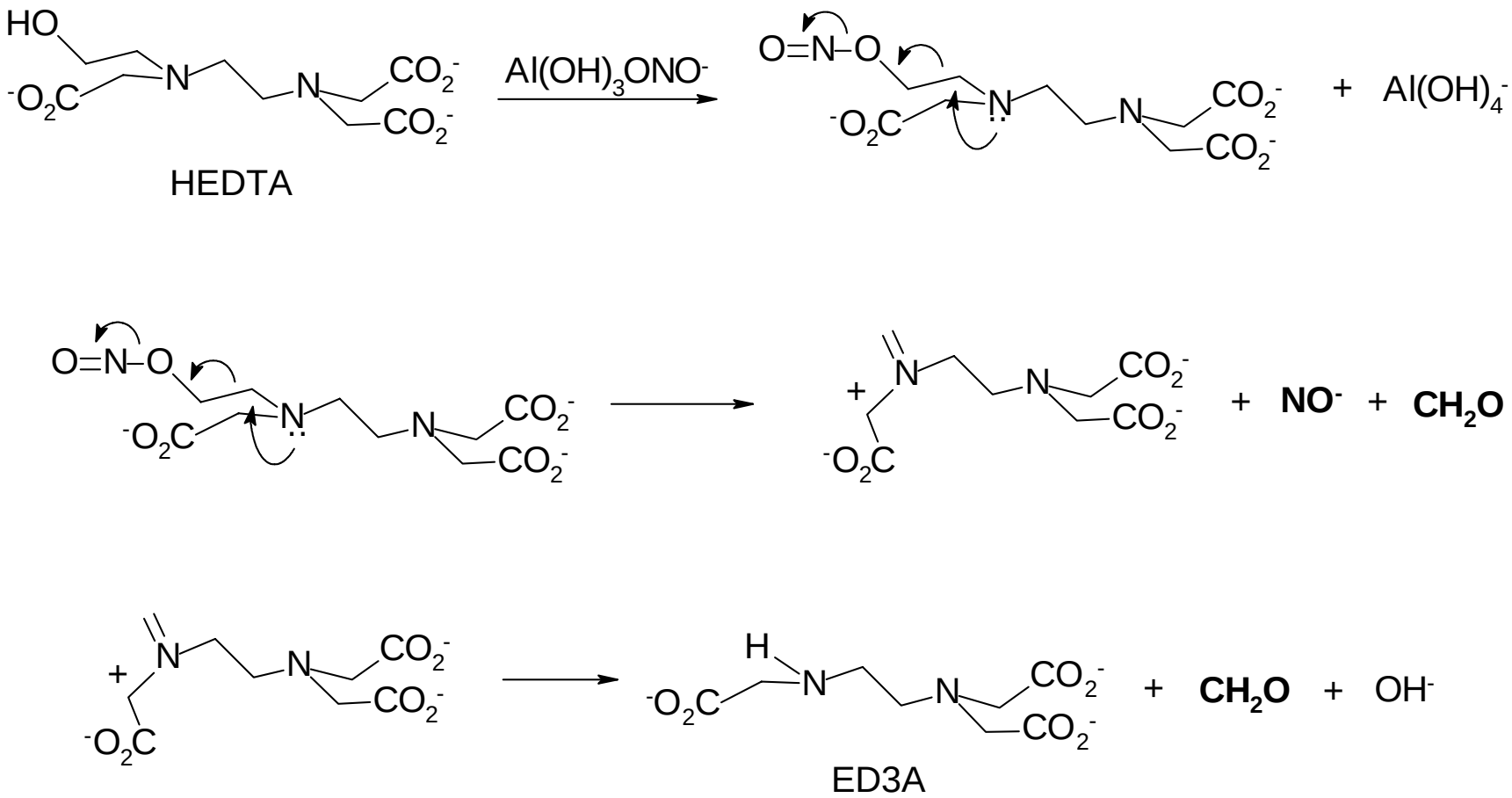
Studies on simulated wastes and other model systems suggest that HEDTA and glycolate undergo oxidative cleavage to give a mixture of C_1 and C_2 fragments, and in the case of HEDTA molecules such as ED3A and EDDA.

Formate, oxalate, ED3A and EDDA have been detected in actual wastes.

Mechanisms postulated on the basis of these and other studies are shown in the next four charts.

Proposed Mechanism for HETDA Degradation

$$Al(OH)_4^- + NO_2^- \rightleftharpoons \mathbf{Al(OH)_3ONO^-} + OH^-$$

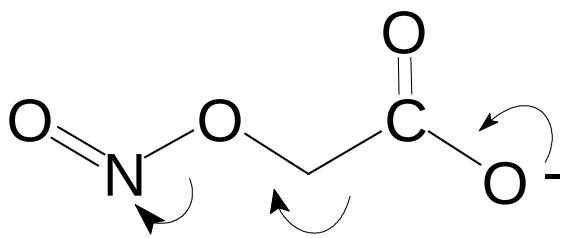


Decomposition of a Preformed Nitrite Ester

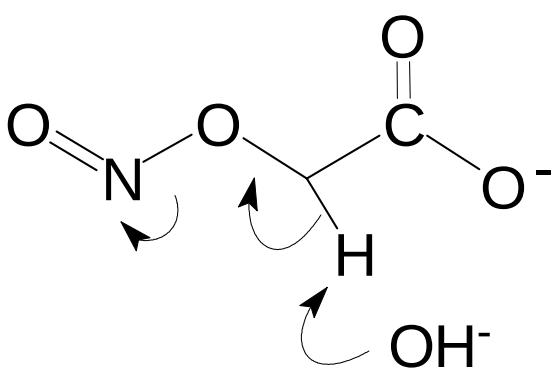
$$\text{t-BuONO} + HOCH_2CO_2CH_3 \longrightarrow \text{t-BuOH} + ONOCH_2CO_2CH_3$$

$$ONOCH_2CO_2CH_3 \xrightarrow[\Delta]{OH^-} ONOCH_2CO_2^- + CH_3OH$$

$$ONOCH_2CO_2CH_3 \xrightarrow[\Delta]{OH^-} H_2,\ N_2O,\ C_2O_4^{2-},\ HCO_2^-$$

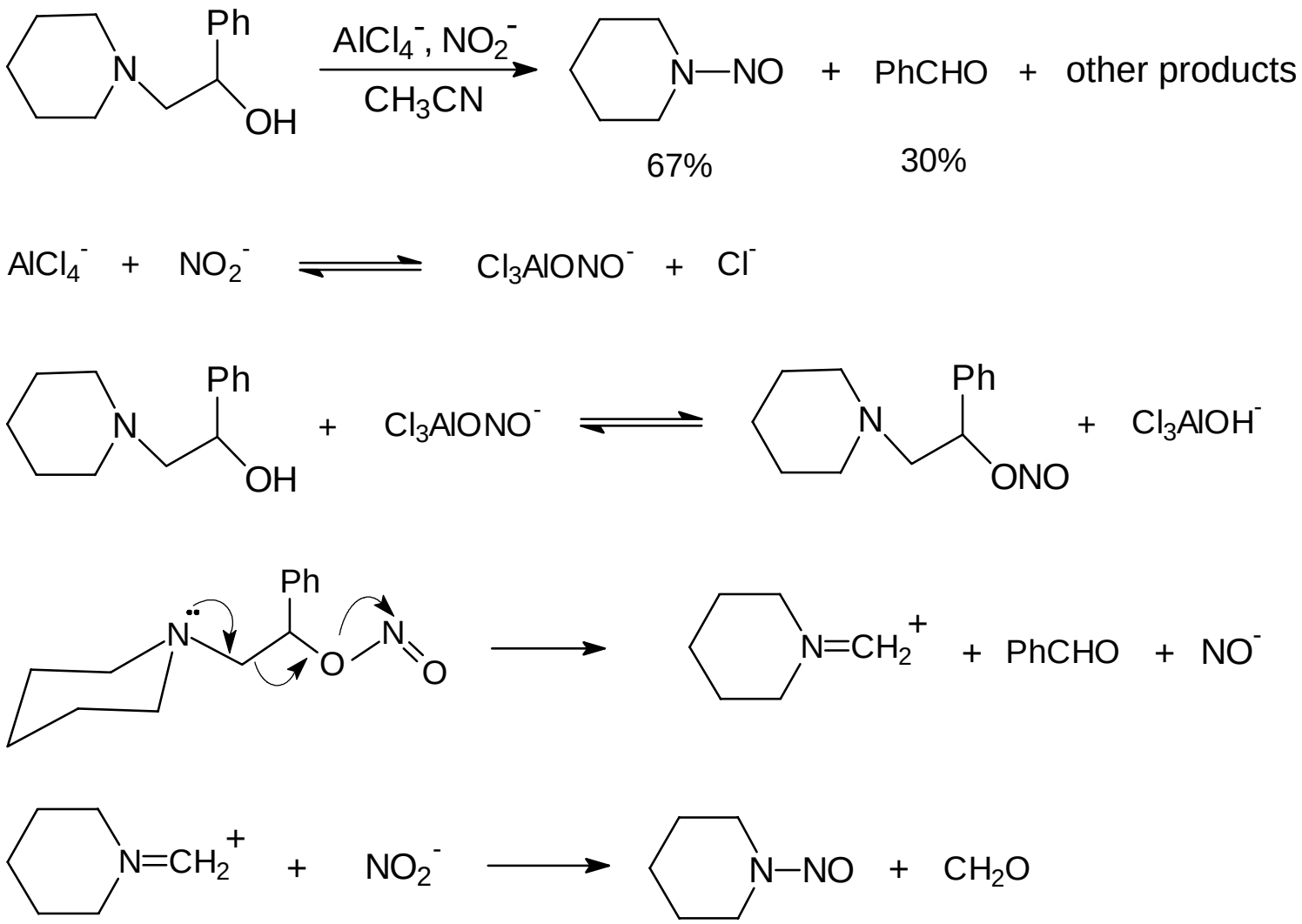


$$\longrightarrow NO^- + CH_2O + CO_2$$



$$\longrightarrow NO^- + HC(O)CO_2^- + H_2O$$

C-N Bond Cleavage in a Model System



Reactions Leading to Formation of Gases

$$CH_2O + H_2O \longrightarrow HOCH_2OH \xrightarrow{OH^-} HOCH_2O^- \xrightarrow{OH^-} {}^-OCH_2O^-$$

$${}^-OCH_2O^- \xrightarrow{H_2O} \mathbf{HCO_2^-} + \mathbf{H_2} + OH^-$$

Ashby, et al., 1993

$$CH_2O + NO^- \longrightarrow HC(O)NHO^- \xrightarrow{H_2O} \mathbf{HCO_2^-} + NH_2OH + OH^-$$

$$3\ NH_2OH \longrightarrow \mathbf{NH_3} + \mathbf{N_2} + H_2O$$

$$2\ NO^- \longrightarrow N_2O_2^{2-} \xrightarrow{H_2O} \mathbf{N_2O} + 2\ OH^-$$

II. Research Objectives

Studies of reactions in simulated wastes and on model systems strongly implicate an aluminum-nitrite as the species that activates NO_2^- for reaction with organics and NO^- as the species formed from the nitrited organic.

No aluminum-nitrite species has been reported in the literature. As indicated in the next chart, relatively little is known about NO^-, a highly reactive species.

Objective 1. To discover ways to generate NO^- under conditions where it can be studied by spectroscopic methods and/or reactions under controlled conditions.

Objective 2. To obtain evidence for the existence and reactivity of aluminum-nitrite compounds.

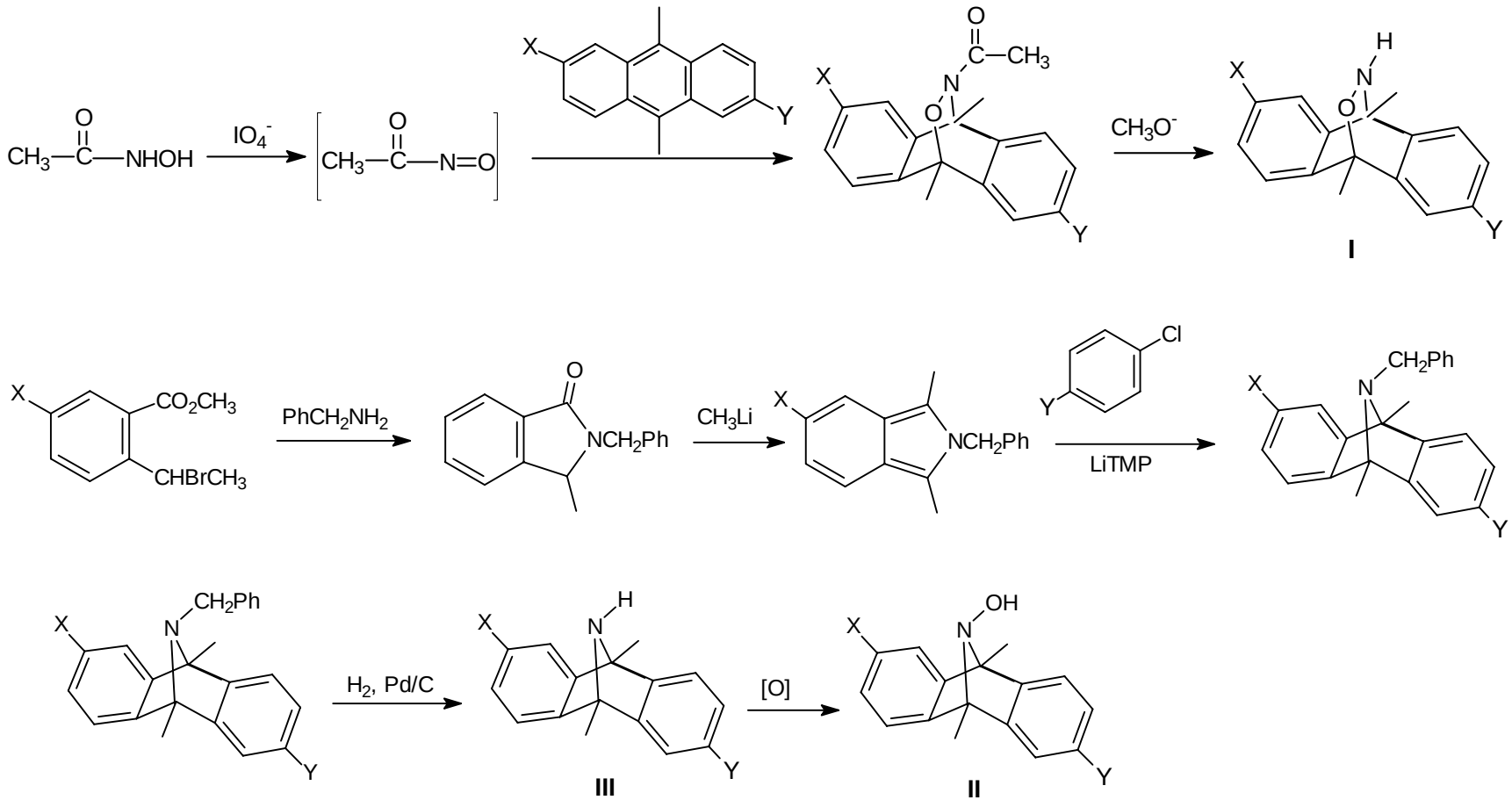
Known About NO^-

- Exists in triplet ($^3\Sigma^-$, gs) and singlet states ($^1\Delta$, 6050 cm^{-1})
- Has two conjugate acids, HNO and HON
- Reacts (singlet?) with aldehydes to give hydroxamic acids
- Dimerizes (singlet/triplet?) to $N_2O_2^{2-}$, precursor to N_2O
- Reacts with O_2 to give $ONOO^-$ (triplet reaction?)

Unknowns about NO^-

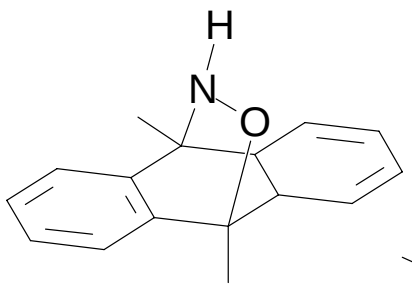
- Ground state in condensed phase (solvent dependent?)
- Can anion be generated in both electronic states in solution
- Lifetime of excited state in solution
- Mode of reaction with substrates as singlet or triplet
- Can anion be detected spectroscopically

Synthesis of Potential NO^- Precursors



I (X=Y=H) has been synthesized; synthesis of **II** (X=Y=H) is in progress.

Observations on Precursor I



very slow decomposition in $CHCl_3$

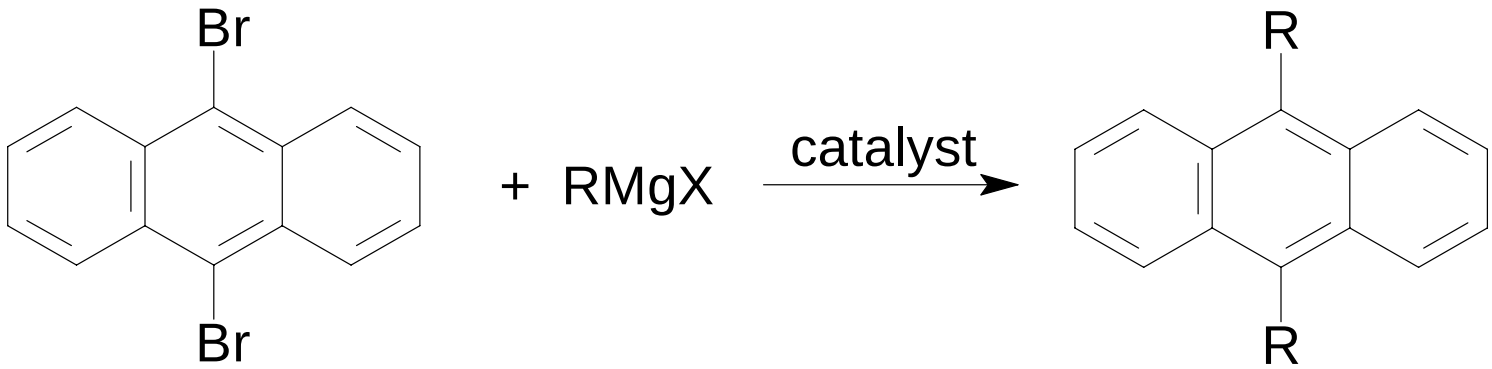
BuLi, THF → faster decomposition

hν → no apparent increase over thermal rate in $CHCl_3$

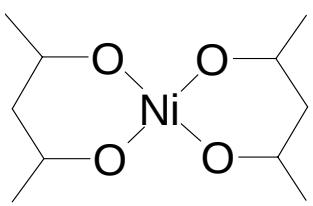
Solvent effects on stability of anion?

Photolytic stability of anion?

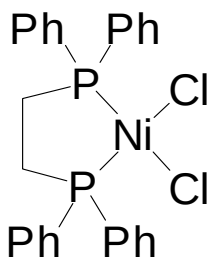
A New Synthesis of 9,10-Dialkylanthracenes



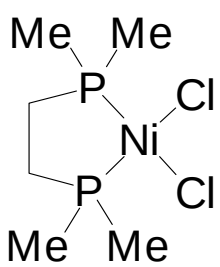
Catalysts



A



B



C

R	Catalyst (Yield, %)
Me	A (75), B(91)
Et	A(20, NMR), B(76)
Pr	B(71)
i-Pr	B(20, NMR), C(55)

Alternative syntheses using n-BuLi/RI gives significantly lower yields: Me (59), Et (33), Pr (51), i-Pr (0). Czarnik, *JOC*, **1988**.

Piloty's Acid and Analogs as NO^- Precursors

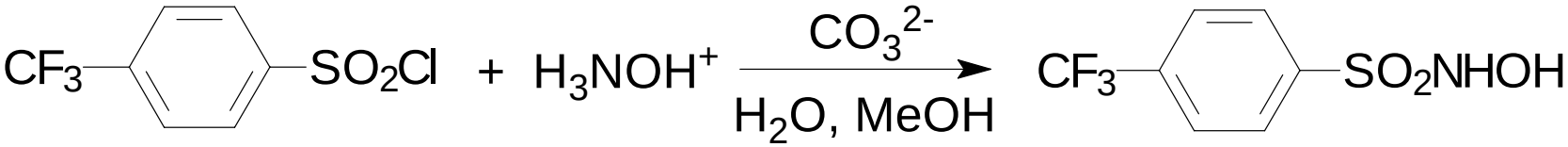
Piloty's acid reacts in aqueous base according to:

$$PhSO_2NHOH_{(aq)} \xrightarrow{OH^-} PhSO_2^-{}_{(aq)} + N_2O_{(g)}$$

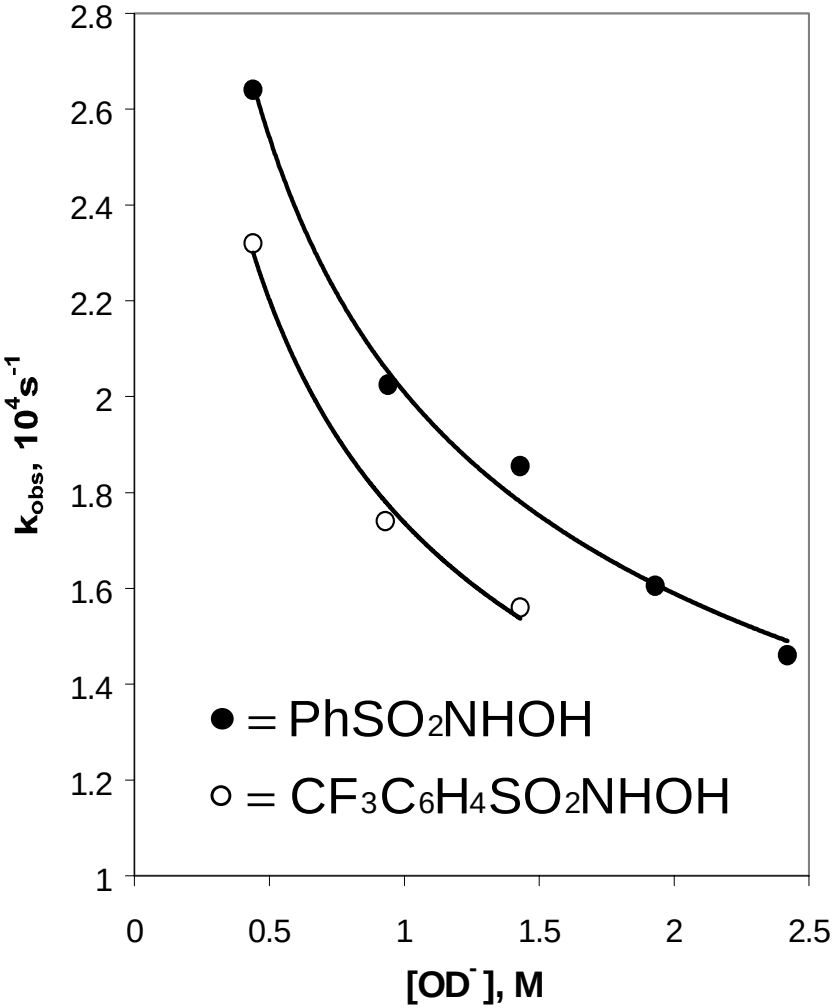
Reaction occurs via the conjugate base, PSO_2NHO^- and/or $PhSO_2NOH^-$, probably by elimination of HNO or NOH.

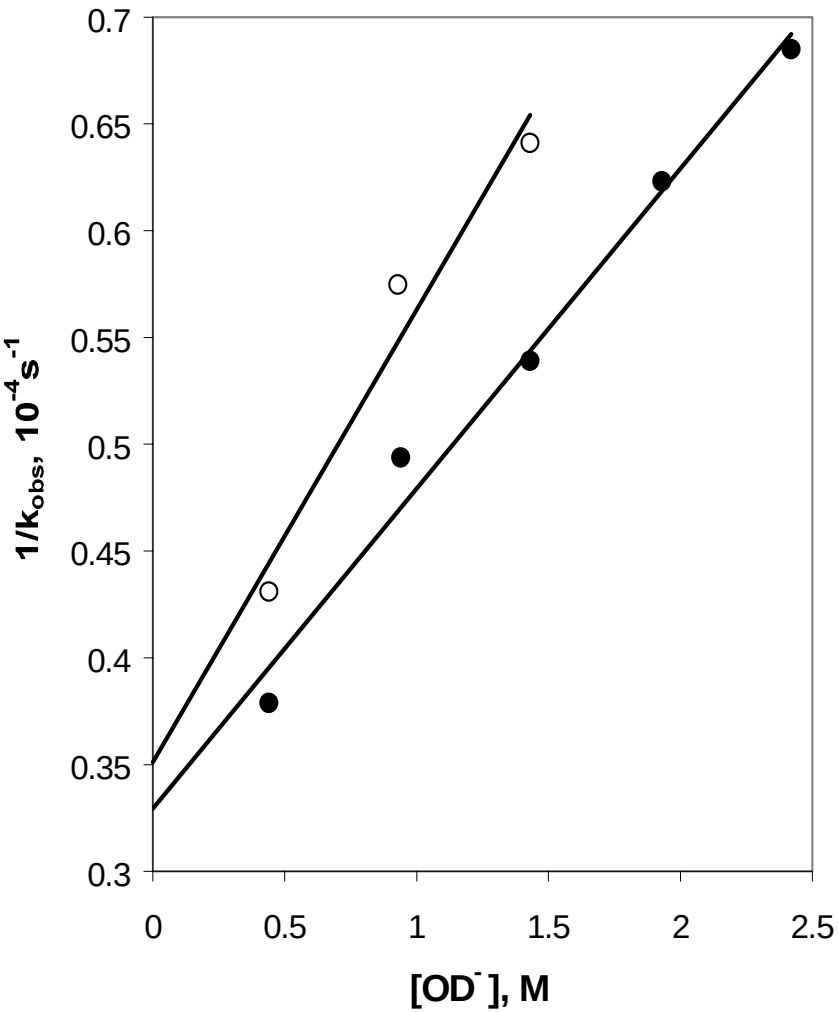
The pK_a of HNO is estimated as 4.7 so that HNO should be completely deprotonated (presumably rapidly); the pK_a of NOH is not known.

Will substitution of Piloty's acid by a *para*-CF_3 group stabilize the conjugate base and increase the rate of reaction?



Rate of Decomposition of X-$C_6H_4SO_2NHOH$ as Function of [OD^-], I = 2.5 M





Assuming that k is the first order rate constant for decomposition of the monoanion and K is the equilibrium constant for the reaction of the monoanion with OD^- then

$$\frac{1}{k_{obs}} = \frac{1}{k} + \frac{K}{k}[OD^-]$$

Compound	**k, $10^4 s^{-1}$**	**K, M^{-1}**
$PhSO_2NHOH$	3.04	0.45
$CF_3C_6H_4SO_2NHOH$	2.85	0.60

The CF_3 group does not increase the rate of decomposition of the monoanion, but does increase its acidity.

$Ni(CN)_4^{2-}$, suggested to be a NO^- trap, produces $[Ni(CN)_3NO]^-$ with both compounds, and has no effect on the rate of reaction of Piloty's acid (0.43 M $[OD^-]$ and 0.1 or 0.2 M $Ni(CN)_4^{2-}$).

Why Does Added $PhSO_2^-$ Decrease the Rate of Decomposition of $PhSO_2NHOH$?

No explanation has been given for the effect of added $PhSO_2^-$. A possible explanation is:

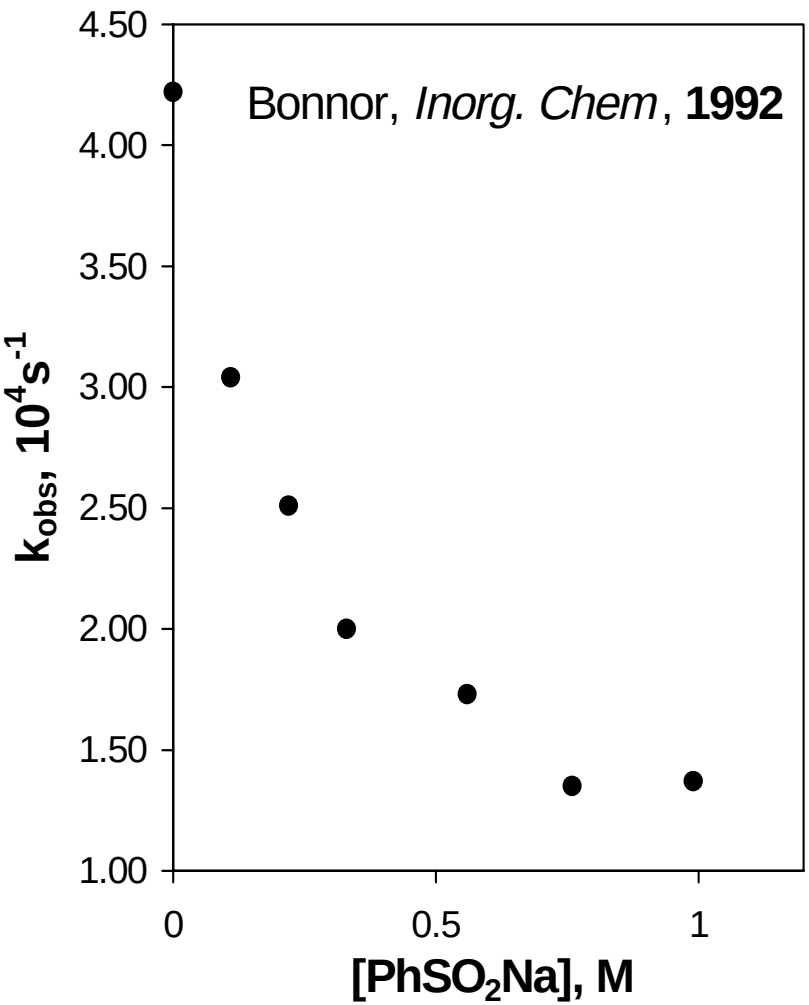
$$PhSO_2NHO^- \rightleftharpoons PhSO_2NOH^-$$

$$PhSO_2NHO^- \longrightarrow PhSO_2^- + HNO$$

$$PhSO_2NOH^- \rightleftharpoons PhSO_2^- + NOH$$

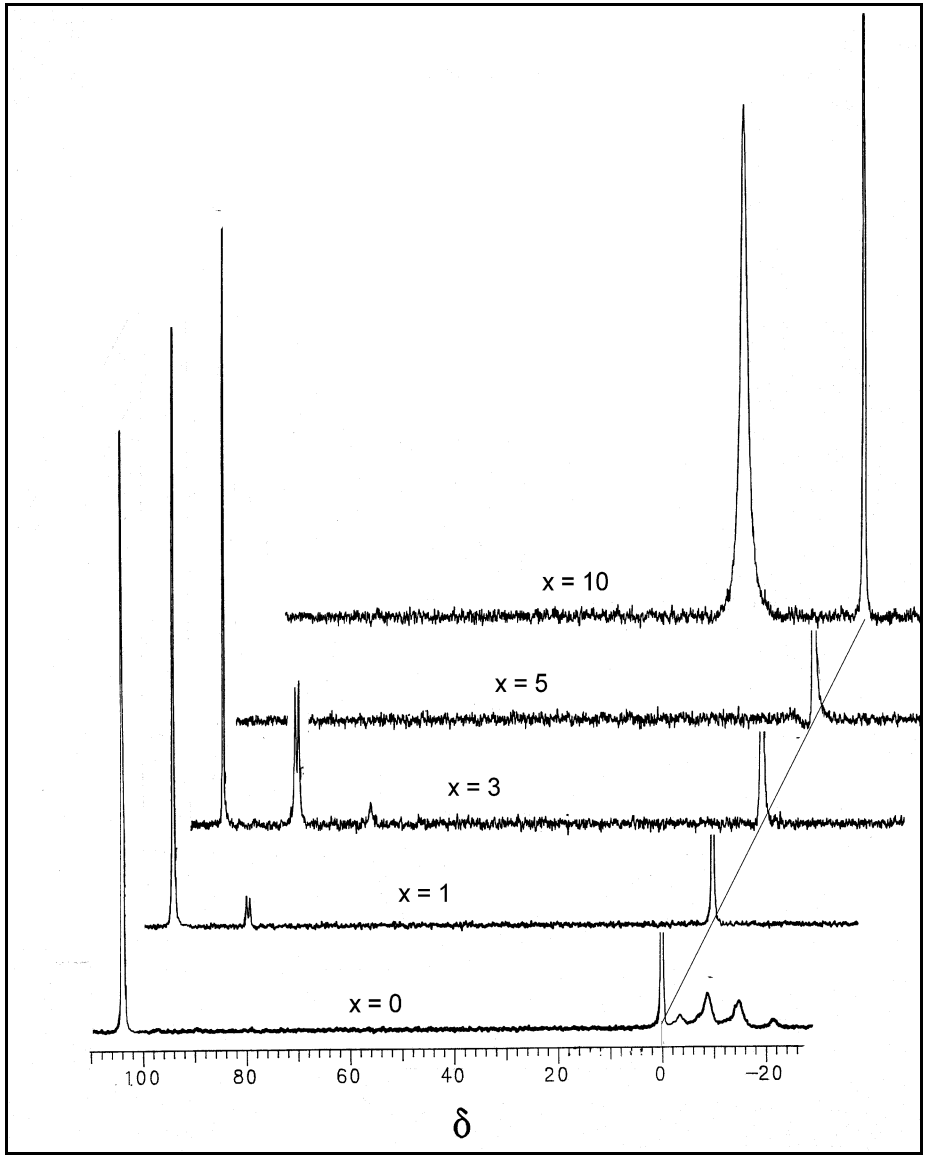
$$NOH/NHO + OH^- \longrightarrow NO^- + H_2O$$

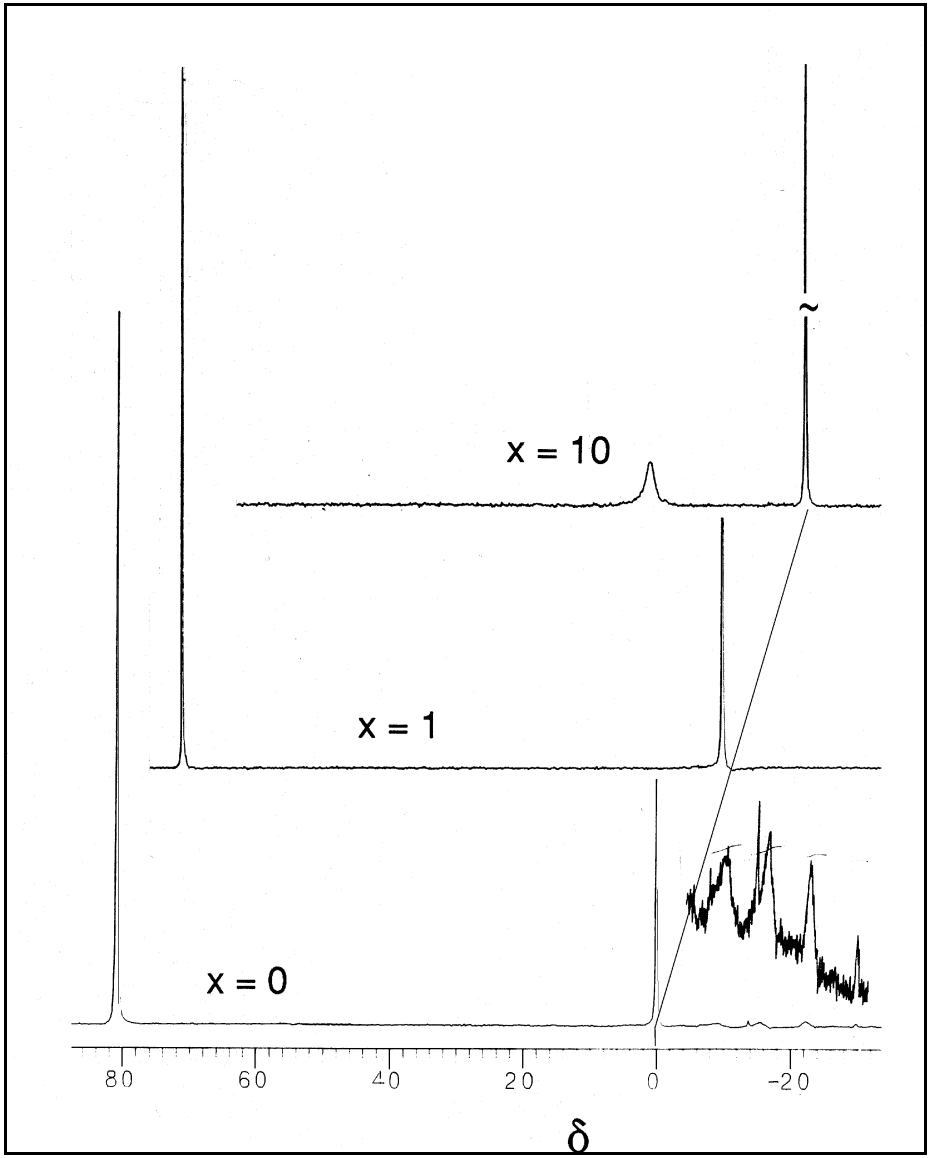
Based upon the expected electronic structures of HNO and HON the latter should be more electrophilic.



^{27}Al NMR Spectra of $AlCl_3$/[*n*-BU_4N]NO_2 in CH_3CN

- $[AlCl_3]_i$ = 0.12 M
- $Al(AN)_{6-x}Cl_x^{(3-x)+}$ $\delta < 0$
- $AlCl_4^-$, δ = 102
- Three new species; two probably include Cl^-, one possibly a dimer



^{27}Al NMR Spectra of $AlBr_3$/[*n*-BU_4N]NO_2 in CH_3CN

- $[AlBr_3]_i$ = 0.12 M
- $Al(AN)_{6-x}Br_x^{(3-x)+}$ $\delta < 0$
- $AlBr_4^-$, δ = 80.5
- Both $AlBr_3$ and $AlCl_3$ form a species with δ ~ 22 (6 coordinate?)