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NITROUS ACID AS AN OXIDANT IN ACIDIC MEDIA.

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David S./Ross [redacted] Georgina P./Hum

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It has been found that benzyl and aliphatic alcohols are rapidly oxidized by nitrous acid to the corresponding carbonyl compound at 25°C in 50-70% sulfuric acid. The oxidations are very rapid, complete within minutes for most substrates; the process appears to be quantitative, at least in runs with alcohol concentrations in the 10^{-14} M range. For the benzyl alcohols, an electron withdrawing para-substituent, such as nitro, retards the rate, while an electron donating group, such as methyl, increases the

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rate. Thus, some cationic character must be present in the process. The rate increases with increasing acidity, peaking at 60% sulfuric acid, and declining thereafter. Surprisingly, ethers are oxidized as well, with the most unlikely case, the methyl ether of 2-phenyl-2-propanol, cleanly and rapidly yielding acetophenone. For primary and secondary alcohols and their ethers, the proposed mechanism for oxidation includes initial electrophilic attack by NO^+ on oxygen, followed by elimination of HNO. In these cases, the nitrous acid is regenerated, probably through HNO oxidation by dissolved oxygen. Thus, an equivalent of nitrous acid oxidizes more than one equivalent of alcohol. For the tertiary alcohol case, we suggest elimination of alkyl nitrite; however, the mechanistic details remain to be fully established.

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NITROUS ACID AS AN OXIDANT IN ACIDIC MEDIA*

Introduction

Oxidations in nitric acid systems have been studied for decades. The process is important commercially, and oxidative side reactions in aromatic nitrations are a result of the oxidative power of the system. The mechanism of the oxidations, however, remains unclear.

Reports are available on the nitric acid oxidation of methoxyethanol,[1] benzyl alcohols,[2] benzyl ethers,[3] benzaldehydes,[4] aromatic nitroso compounds,[5] and formic acid[6] at temperatures from 25°C to 90°C. It is overwhelmingly clear that nitrous acid, or some other lower oxide of nitrogen, promotes the oxidations. If steps are taken to eliminate the accumulation of the promoter, the reaction does not take place.

Several oxidants have been suggested as operative in the system, including NO^+, NO_2, and N_2O_4, but no single reactant has been identified. Of direct importance to the current work is the account of Ogata and Sawaki[3] who studied the oxidation of benzyl ethers at 90°C in acidic, aqueous dioxane. They found an increase in rate with acidity, and suggested protonated NO_2, HNO_2^+, as the oxidant for both benzyl ethers and alcohols.

SRI's work in these systems, performed under ARO Contract No. DAAG29-76-C-0040, was initiated by Myhre's observation[7] that benzyl alcohols were very rapidly oxidized to benzaldehyde in sulfuric acid solutions containing N(III), but no N(V). We confirmed Myhre's findings and extended the effort to include the study of other alcohols and some ethers. We found the oxidation to be rapid enough for study at 25°C, with most reactions complete within tens of minutes. The kinetic data obtained, our findings on the stoichiometry of the reaction, and the reaction mechanism are discussed below.

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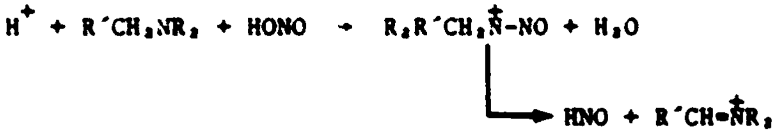
*A portion of the work described here was presented at the 175th National Meeting of the American Chemical Society, Anaheim, California, March 1978. A full manuscript is in preparation.

Background

Figure 1 shows the forms of the various oxyacids of nitrogen to be dealt with here as a function of acidity. N(V) is present as three forms over the range of sulfuric acid acidity: NO_2^+ down to about 90% acid, HNO_3 down to 40%-50%, and finally increasing amounts of NO_3^- at lower acidity.

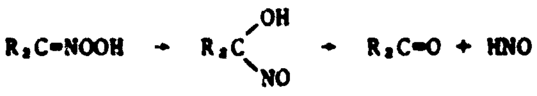
The N(III) family behaves similarly, except that the entire system is shifted to lower acidities. Thus NO^+ and HONO are the dominant forms of this oxidation state in the 100%-55% and 55%-0% acids, respectively. Nitrous acid is a relatively weak acid and is not converted to NO_2^- except in the pH range of acidity at the left-hand edge of Figure 1. Of importance to our later discussion is the overlap of forms in the 50%-60% acid range, where NO_3^-, HNO_3, NO^+, and HONO are all present in reasonable quantities.

The N(IV) and N(II) oxidation states of nitrogen have no common solution forms, and nitroxyl, HNO, is included in Figure 1 as the solution form of N(I), although little is known about its behavior in solution. It is formed in the reaction of tertiary amines with nitrous acid [8a]



$$H^+ + R'CH_2NR_2 + HONO \rightarrow R_2R'CH_2\overset{+}{N}\text{-}NO + H_2O$$
$$\rightarrow HNO + R'CH{=}\overset{+}{N}R_2$$

and in the Nef reaction[8b]



$$R_2C{=}NOOH \rightarrow R_2C\begin{matrix}OH\\NO\end{matrix} \rightarrow R_2C{=}O + HNO$$

It readily dehydrates to N_2O[8c]

$$2HNO \rightarrow H_2O + N_2O$$

Nitrosonium ion can be an oxidant in at least three ways. First, is the two-electron oxidation of tertiary amines just mentioned, in which NO^+ as an electrophile forms a cationic intermediate.

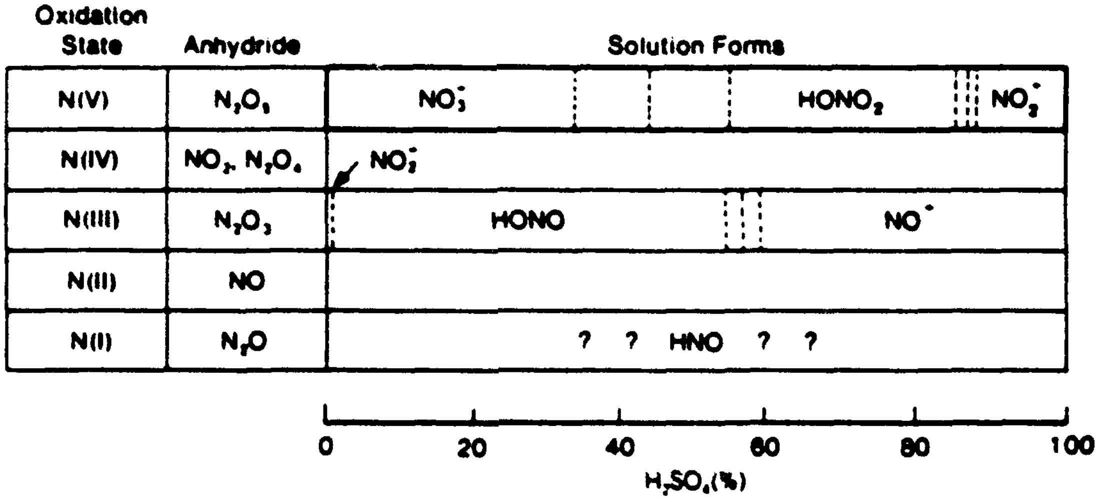


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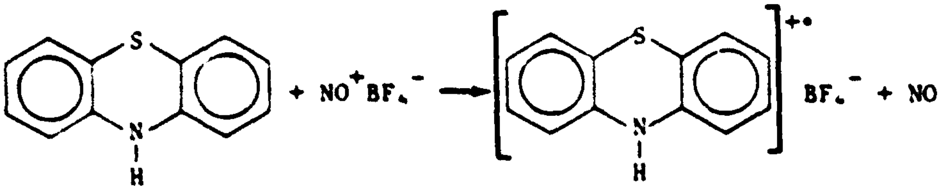
FIGURE 1 DISTRIBUTION OF THE POSITIVE OXIDATION STATES OF NITROGEN IN ACIDIC MEDIA

The dashed, vertical lines are for the 25, 50, and 75% points of conversion. The data for N(V) are from N. Deno, H. Peterson, and E. Sacher, J. Phys. Chem., 65, 199 (1961). The data for N(III) are from N. Bayliss et al., Aust. J. Chem., 16, 933 (1963).

N(III) can also be a one-electron oxidant with substrates with sufficiently low oxidation potentials. Bandish and Shiner[9] have succeeded in isolating crystalline perchlorate and tetrafluroborate salts of heteroaromatic and aromatic radical cations.



In similar work in spectrophotometric studies, we have found that the addition of NO^+ to a fresh solution of anthracene in concentrated sulfuric acid yielded the radical cation immediately, in contrast to its known slow formation in the acid medium.[10]

Finally, N(III) can be a two-electron oxidant via hydride abstraction, as shown by Olah and Ho,[11a] where nitrosonium ion salts in methylene chloride rapidly oxidize benzyl alcohols to aldehydes or ketones. In a similar manner, cumene was oxidized to a variety of products by nitrosonium ion salts in nitromethane.[11b] In a preliminary effort, we observed that cumene, ethylbenzene, and toluene react with N(III) at 25°C in 60% sulfuric acid. Although we have characterized neither the reaction nor the products, we expect to study these systems in detail.

Results

Kinetics of the Oxidation. The reactions were performed in sulfuric acid and followed spectrophotometrically. The condition N(III) >> substrate was used in the initial work, and good first-order behavior was observed. Aqueous nitrous acid systems are themselves unstable;[12] however, our rates of oxidation were generally substantially greater than those for N(III) decomposition, and no correction was made. The oxidation rates were unaffected by the presence or absence of N(V).

Table 1 contains the data obtained for a series of benzyl compounds. The rates for the para-substituted benzyl alcohols fall in the order Me > H > Cl > NO_2, thus, there is a cationic character to the process.

Table 1

FIRST-ORDER RATE CONSTANTS FOR OXIDATION OF BENZYLIC SUBSTRATES AT 25°C IN 60.0% H_2SO_4[a]

Substrate	$k \times 10^3$ (sec^{-1})	Substrate	$k \times 10^3$ (sec^{-1})
(b)	0.25	$PhCH_2OCH_3$	2.86
p-$MePhCH_2OH$	22.5	$PhCH_2ONO$	12.6[c]
$PhCH_2OH$	8.70	$PhC(CH_3)_2OH$	(d)
p-$ClPhCH_2OH$	6.14	$PhC(CH_3)_2OCH$	(d)
p-O_2NPhCH_2OH	0.04[e]		

---

[a] The N(III) concentration in these runs was 3.4×10^{-4} M. The substrate concentrations were 3.5×10^{-3} M. The rates were determined by monitoring the formation of carbonyl product. The corresponding benzaldehyde was the product, except for cumyl alcohol and its ether, where acetophenone was the product. The final yield of carbonyl product by uv absorption was $>$ 90% in each case.

[b] With no substrate present, the N(III) decomposes slowly; see reference 12.

[c] The observed rate constant is a function of the starting nitrite ester concentration. The value here is for an ester concentration of 3.4×10^{-4} M, with no added N(III); see text.

[d] Oxidation complete within seconds--too rapid for measurement under our conditions.

[e] Estimated initial rate. In this case the N(III) decomposed more rapidly than the substrate was oxidized.

The fact that the benzyl ether oxidizes at a rate only slightly slower than that for the corresponding alcohol is surprising and of interest mechanistically, suggesting that formation of the nitrite ester is not significant to the process. (The ether was shown to be otherwise stable in the acid medium in the absence of N(III).)

Consistent with the alcohol oxidations, the nitrite ester is oxidized at a rate comparable to that for benzyl alcohol, with an observed rate constant dependent upon the starting ester concentration. Clearly, under these conditions the nitrite ester is rapidly hydrolyzed to the alcohol and N(III),[illegible] and subsequent oxidation then takes place at a rate consistent with the N(III) concentration.

Also shown in Table 1 are data for a tertiary alcohol and its methyl ether. Unexpectedly, both of these compounds were readily converted to acetophenone; the fate of the lost methyl groups in each case was not established. As far as we are aware, these facile reactions, particularly the ether oxidations, are more rapid than any reported oxidations of similar substrates, and we plan further investigation of these systems. (The usual finding that anisoles are partially converted in mineral acid nitration media to phenols[14a] could be explained by this chemistry.)

A kinetic study was made over a range of acidity for both benzyl and chlorobenzyl alcohols; the results are plotted in Figure 2. The rate of oxidation peaks at about 60% acid, falling steeply on either side of that value. Also shown in the figure are the profiles for the distribution of the two N(III) species over the acid range. The peak in oxidation rate falls where N(III) is distributed equally between HONO and NO^+, and initially it would seem that the oxidation is thus dependent on both species.

Only preliminary kinetic studies have been done on tertiary alcohols, and it appears their rates continue to increase with acidity beyond the 60% point. The study will be continued.

The oxidation data for p-$ClPhCH_2OH$ are plotted in Figure 3, along with literature data on the nitrosation of phenol[15a] and the oxidation of nitrosophenol to nitrophenol.[15b] The nitrosation data were obtained

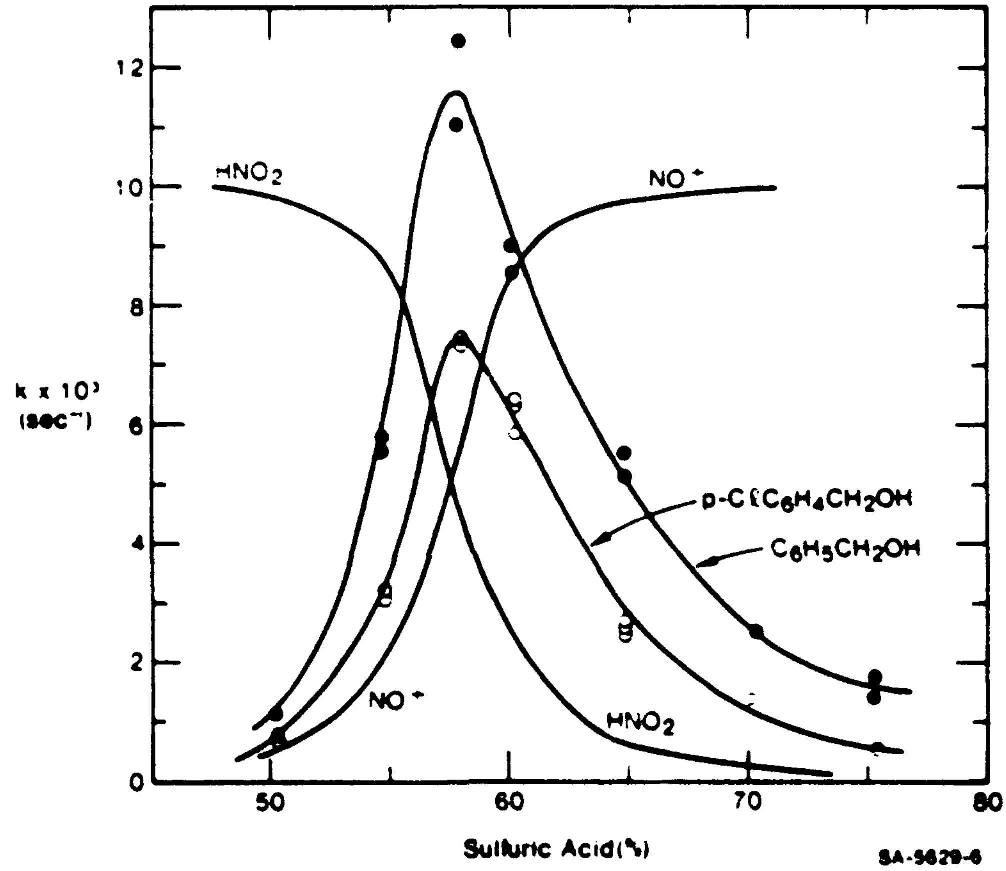


FIGURE 2 RATES OF OXIDATION OF PhCH$_2$OH and p-ClPhCH$_2$OH vs ACIDITY

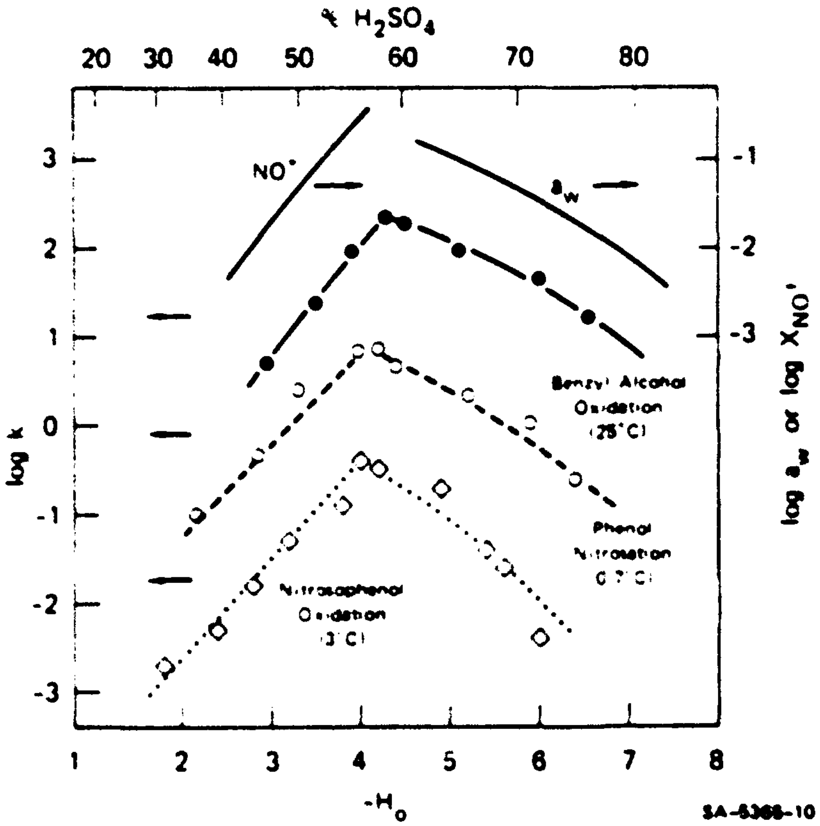


FIGURE 3 KINETIC DATA FOR ALCOHOL OXIDATION, PHENOL NITROSATION, AND NITROSOPHENOL OXIDATION

See text for details.

in perchloric acid, and the nitroso oxidations were run in sulfuric acid.[*] The Hammett acidity function is used as the abscissa because it conveniently represents the acidity region of interest and allows us to include the nitrosation data for the different acid medium.

When looked at in this way, all three processes display similar profiles. All three involve the chemistry of N(III), with nitroso oxidation requiring both N(III) and N(V) and the oxidation not proceeding unless both are present. The nitrosation and the nitrosophenol oxidation were run at similar temperatures, and the former is about 30-40 times faster than the latter. Our oxidation work with p-ClPhCH$_2$OH was at 25°C, and in a brief study of nitrosation of phenol at that temperature we found that the rates were almost identical. That similarity, however, appears to be coincidental, since as noted above for alcohols, the study established that the oxidation rate varied with substituent. In contrast to the observation of Granzow and Wilson,[15b] who found that the oxidation of p-nitrosophenol at 3°C was first-order in substrate, we found, in a brief study at 25°C, that the process is zero-order in nitrosophenol.

As shown in Figure 3, the rates all increase with increasing acidity up to about 60% sulfuric acid, and parallel the increase in NO$^+$ concentration. The rates then decline at greater acidities, following the decrease in the activity of water. Although the substrates are different (and thus for each case the specific chemistry of the rate controlling step is different),the N(III) chemistry must be the same for the three reactions. This point will be considered below in a formulation of the oxidation mechanism.

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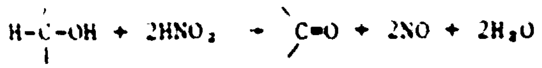
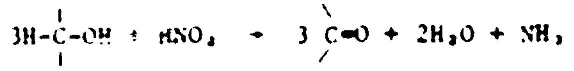
[*] We have taken some liberties in presenting these data. The nitrosation work included the kinetic study of anisole nitrosation. In that case, the kinetic profile was qualititatively similar to that shown for phenol in the figure, but was steeper on the low acid side and more shallow on the high acid side. Oxidation of the O-CH$_3$ group may have played a role in the difference in profiles. Similarly, for the nitrosophenol oxidation, a steeper curve can be drawn for the data on the high acid side, as the authors have done. To present our case, we suggest the data can be looked at as shown in Figure 3, but point out the difference in our approach.

Stoichiometry of the Oxidation. The stoichiometry of the oxidation is surprising, being different for primary and secondary alcohols than it is for tertiary alcohols. Because the oxidation of a primary or secondary alcohol to the corresponding carbonyl compound is a two-electron process, oxidation by N(III) can take one of a number of possible routes, spanning values of an alcohol:N(III) ratio of 1:2 in which N(III) is reduced in one step to N(II)



$$\mathrm{H{-}C{-}OH + 2HNO_2 \rightarrow C{=}O + 2NO + 2H_2O}$$

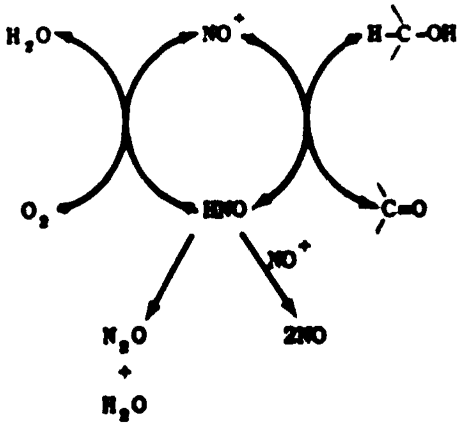
up to a 3:1 ratio, where six electrons are transferred and the nitrogen is reduced to ammonia, its lowest oxidation state



$$\mathrm{3H{-}C{-}OH + HNO_2 \rightarrow 3\,C{=}O + 2H_2O + NH_3}$$

We performed several experiments in which increasing quantities of benzyl alcohol were added to given quantities of N(III) in 60% sulfuric acid. Complete conversion to aldehyde was observed after one, two, and then three molar equivalents of alcohol were added. The addition of a fourth molar equivalent of alcohol to the mixture resulted in more aldehyde formation. With no further addition of alcohol, a 79% yield of aldehyde was realized, based on total starting alcohol. It is likely that yet more added alcohol would have been oxidized.

The conversion is not possible based on nitrogen as the ultimate electron sink, since as just discussed, a conversion of three equivalents of alcohol reduces the nitrogen to its lowest oxidation state. The following scheme is suggested for the oxidation, in which some other oxidant in the solution reoxidizes the reduced nitrogen back to N(III).



In this scheme we have settled on dissolved oxygen as the oxidant, although its action is currently unconfirmed, pending work in progress to establish its role. An obvious choice initially was sulfuric acid, possibly reduced in the process from S(VI) to S(IV). However, we have shown that under our conditions, the reverse process operates, S(IV) being oxidized to S(VI) by N(III).[16]

The proposal of a two-electron transfer in which nitroxyl is formed is based on results with isopropyl and t-butyl alcohols as substrates. As shown in Figure 4, a 0.5:1.0 mixture of t-butyl alcohol:N(III) in 60% sulfuric acid not surprisingly displays the loss of half an equivalent of N(III) after a few minutes, and during this period all the alcohol is consumed.

In a similar experiment with i-propyl alcohol, the N(III) seems to be consumed initially; however, after a brief period it appears that the N(III) is regenerated. It then disappears at the slow rate for nitrous acid decomposition in these systems, considerably more slowly than the alcohol is oxidized.

Discussion

The regeneration of N(III) appears to be possible only when a hydrogen is present on the oxygen-bearing carbon in the alcohol. Moreover, above 60% sulfuric acid the quantities of free water apparently become limiting, and for primary and secondary alcohols the oxidation rate declines accordingly.

The three reactions in Figure 3 must all follow the same general mechanistic scheme, namely,

$$HNO_2 + H^+ \rightleftharpoons NO^+ + H_2O \qquad (1)$$

$$S + NO^+ \rightleftharpoons SNO^+ \qquad (2)$$

$$SNO^+ + H_2O \rightarrow \text{prod} \quad \text{(slow)} \qquad (3)$$

for which the observed second-order rate constants are

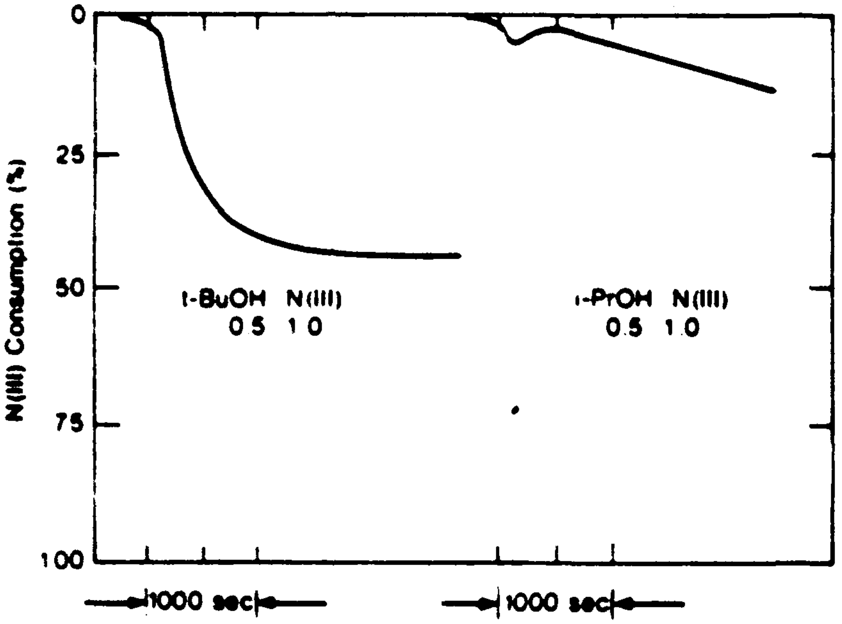


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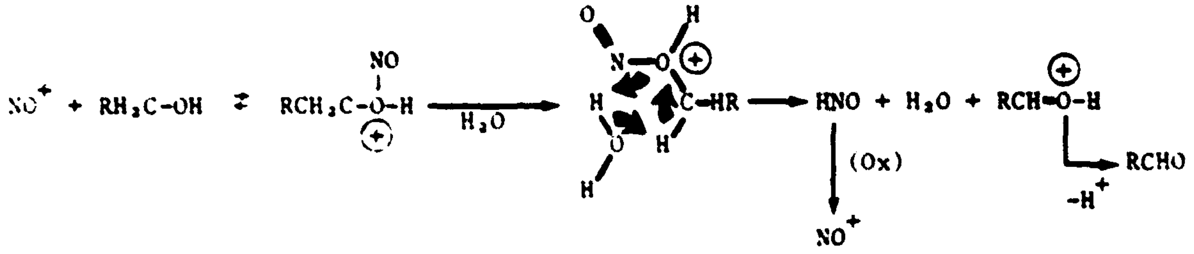
FIGURE 4 CONSUMPTION OF N(III) IN THE OXIDATION OF *t*-BuOH AND *i*-PrOH by N(III) IN 80% H_2SO_4

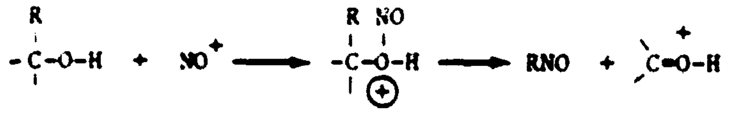
__low acid side__ $[N(III) = HNO_2]$ __high acid side__ $[N(III) = NO^+]$

$$k_{obs} = k(NO^+) \qquad k_{obs} = k_3K_2(H_2O)$$

Specifically for the oxidation of primary and secondary alcohols, we suggest a water-assisted elimination of HNO, which is then oxidized, presumably by oxygen:



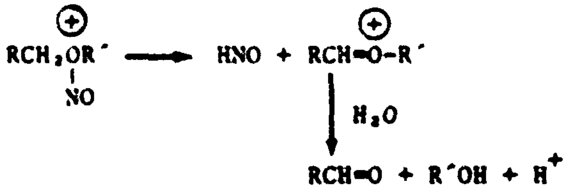
In contrast, tertiary alcohols cannot undergo such an elimination, and perhaps are converted through elimination of an alkyl nitroso compound



$$-\overset{R}{\underset{|}{C}}-O-H + NO^+ \longrightarrow -\overset{R}{\underset{|}{C}}-\underset{\oplus}{\overset{NO}{O}}-H \longrightarrow RNO + \rangle C=\overset{+}{O}-H$$

although this suggestion must be confirmed in future work.

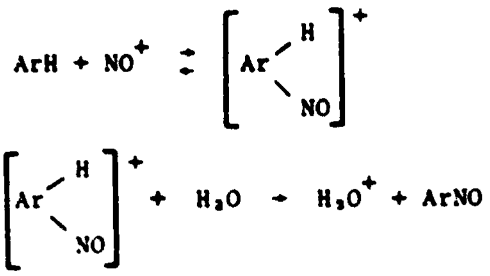
These reactions are written for alcohols, but can apply as well to the corresponding ether.



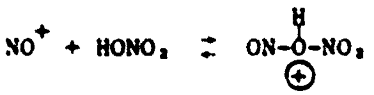
$$RCH_2\underset{NO}{\overset{\oplus}{O}}R' \longrightarrow HNO + RCH=\overset{\oplus}{O}-R' \xrightarrow{H_2O} RCH=O + R'OH + H^+$$

Although we currently have no evidence for the fate of the O-alkyl group, we presume that it is converted to its alcohol. We plan experiments with THF to establish the full route of ether oxidation.

Consistent with the general mechanism, equations (1)-(3), and in contrast to nitration, phenol nitrosation displays a primary kinetic isotope effect,[17] and the process is (ArH = phenol):



Nitrosophenol oxidation must also proceed through the same general mechanism. However, since both N(III) and N(V) must be present and since we find that the reaction is zero-order in nitrosophenol, S in the mechanism must be nitric acid. Thus we can surmise



$$\mathrm{NO^+ + HONO_2 \rightleftarrows ON{-}\underset{\oplus}{\overset{H}{O}}{-}NO_2}$$

$$\mathrm{HN_2O_4^+ + H_2O \rightarrow H_3O^+ + O{=}N{-}O{-}NO_2} \quad \text{(slow)}$$

As shown, the reaction between nitrosonium ion and molecular nitric acid yields the protonated form of O-bridged nitrogen tetroxide, which can then yield ONONO$_2$ in reaction with water in the slow step. The O-bridged material can fall apart to 2NO$_2$, which then rapidly oxidizes the nitrosophenol:

$$\mathrm{ONO{-}NO_2 \rightarrow 2NO_2}$$

$$\mathrm{NO_2 + ONPhOH \rightarrow O_2NPhOH + NO}$$

On the other hand, ONONO$_2$ can also easily yield NO$_3$, which is then the oxidant:

$$\mathrm{ON{-}ONO_2 \rightarrow NO_3 + NO}$$

$$\mathrm{NO_3 + ONPhOH \rightarrow O_2NPhOH + NO_2}$$

Experiments were also performed to establish some further chemistry of HNO. The work was done with i-propyl alcohol as the substrate in which, in contrast to the work described above, the alcohol was in large excess relative to the N(III) present. In these cases only the N(III) was monitored, and it was seen that (1) an induction period was always observed prior to the consumption of N(III); (2) the onset of the consumption of N(III) was a function of the starting quantities of N(III) and alcohol, but the ultimate rate of consumption was independent of the starting quantities; (3) when N(III) was added to a completed reaction solution (i.e., one with all the alcohol consumed), the added N(III) disappeared at a rapid rate identical to that ultimately achieved after the initial additions; and (4) a completed reaction receiving N(V) rapidly produced more N(III).

It is not fully clear what is happening here. The startling finding, however, that more N(III) could be produced with N(V) addition suggests that HNO is accumulating in the system, perhaps as a stable protonated species, H_2NO^+. Consistent with these observations it can be suggested that the apparent induction period represents the consumption of the oxygen (or other active oxidant) in solution while the alcohol is being oxidized. Then after the HNO oxidant is consumed, the alcohol continues to be oxidized

$$\mathrm{N(III)} + \mathrm{Alc} \rightarrow \mathrm{HNO} + \rangle\mathrm{C{=}O} \qquad (4)$$

with the only route now removing HNO being

$$\mathrm{NO^+} + \mathrm{HNO} \rightarrow \mathrm{H^+} + 2\mathrm{NO} \qquad (5)$$

Apparently while alcohol remains, equation (5) cannot compete with equation (4), and the HNO accumulates. When the system no longer contains alcohol, any added N(III) is consumed via equation (5), and when N(V) is added, it is consumed to form more N(III) via

$$2\mathrm{H^+} + \mathrm{HNO} + \mathrm{HNO_3} \rightarrow 2\mathrm{NO^+} + 2\mathrm{H_2O} \qquad (6)$$

We expect to continue this work and develop a full understanding of the chemistry of HNO.

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