Unprecedented Homogeneous Reduction of Ionic Nitrogen Oxo Compounds to Ammonia by Organics in Sulfuric Acid

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Emissions from automobiles and gas- and oil-burning power plants constitute the main source of nitrogen oxides (NO_x) and hydrocarbons in the atmosphere.[1] The ideal approach to emission control would be to design a catalytic system for the reduction of NO_x that would (a) utilize the reducing species present in the exhaust, particularly unburned and partially oxidized hydrocarbons, and (b) operate under oxidizing conditions. Very recent work has demonstrated that it is indeed possible to reduce NO_x to N_2 by hydrocarbons in an oxygen atmosphere at temperatures ≥300 °C.[2,3] Both supported transition metals and the H-form zeolites were found to be effective. However, no mechanistic details are available. In order to arrive at a detailed fundamental understanding of the mechanism of NO_x reduction by hydrocarbons, it is desirable to have a well-defined *homogeneous* system that operates under relatively mild conditions and can be examined by standard solution-phase probes. As detailed below, we have discovered that, in sulfuric acid, ionic nitrogen oxo compounds can be reduced to ammonia in high yields by organics even in an oxidizing environment. In the case of NO_3^- and NO_2^+ ions (the former is converted to the latter in sulfuric acid: $NO_3^- + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_2O$), the overall reaction represents a remarkable $8e^-$ reduction. To our knowledge these reductions are without precedent.

We have found that, in 96% H_2SO_4 at around 170–190 °C, dihydrogen and a variety of organic substrates including alkanes were effective for the reduction of nitrogen oxo species (Table 1). In a typical reaction, 0.10–0.20 mmol of $NaNO_3$ was dissolved 0.5–1 mL of 96% H_2SO_4 in a glass vessel (use of 100% H_2SO_4 led to greatly diminished yields). For gaseous reductants, the vessel was placed in a Parr stainless steel bomb, pressurized with the gas, and heated. For liquid reductants, the liquid was added to the reaction mixture, and the vessel (usually a sealed NMR tube) was heated. Note that, in the latter cases, there was no possibility of any vapors or gases coming into contact with metal. In all cases, no attempt was made to exclude dioxygen from the reaction mixture. At the end of the reaction, a ^1H-NMR spectrum was run and the concentration of the NH_4^+ ion formed was measured by integration versus a capillary tube external standard consisting of DMSO dissolved in D_2O. Figure 1 shows the ^1H-NMR spectrum obtained when ethane was used as the reductant. The triplet at 5.57 ppm observed for the NH_4^+ ion resulted from ^{14}N–H coupling (J = 54.4 Hz). The lack of quadrupole broadening was due to the highly symmetrical T_d structure.[4] There was also no broadening as a result of exchange of H^+ between the NH_4^+ ion and the solvent. This was not unexpected since the NH_4^+ ion can only undergo H^+ exchange through a dissociative mechanism, a step which was expected to be extremely slow in a highly acidic medium. In order to confirm the formation of NH_4^+ ion, the reduction by ethanol was repeated using $Na^{15}NO_3$. As seen in Figure 2, the ^1H-NMR spectrum for the $^{15}NH_4^+$ ion was now a doublet due to ^{15}N–H coupling (J = 75.8 Hz). When the reduction of NO_3^- ion by ethanol was followed by ^{14}N-NMR spectroscopy, the only species observed were the

Table 1. Reduction of Ionic Nitrogen Oxo Species by Organics

nitrogen species used (NO_x, mmol)	reductant (gases, psi; liquids, mmol)	temp (°C)	time	yield (%) (NH_4^+/NO_x)
$N^VO_3^-$ ($NaNO_3$, 0.19)	H_2 (200)	170	18 h	20
$N^VO_3^-$ ($NaNO_3$, 0.15)	CH_4 (1000)	180	20 h	trace
$N^VO_3^-$ ($NaNO_3$, 0.15)	CH_4 (1000) +$HgSO_4$	180	20 h	~100
$N^VO_3^-$ ($NaNO_3$, 0.15)	C_2H_6 (500)	175	22 h	60
$N^VO_3^-$ ($NaNO_3$, 0.12)	C_2H_5OH (0.17)	180	15 min	~100
$N^VO_3^-$ ($NaNO_3$, 0.07)	n-C_3H_7OH (0.135)	180	15 min	70
$N^VO_3^-$ ($NaNO_3$, 0.07)	THF (0.12)	175	15 min	60
$N^VO_3^-$ ($NaNO_3$, 0.125)	CH_3CO_2H (0.35)	175	15 min	60
$N^VO_2^+$ (NO_2BF_4, 0.075)	C_2H_5OH (0.17)	175	15 min	80
$N^{III}O_2^-$ ($NaNO_2$, 0.18)	C_2H_5OH (0.17)	175	45 min	60
$N^{III}O^+$ ($NOBF_4$, 0.20)	C_2H_5OH (0.17)	185	30 min	~100

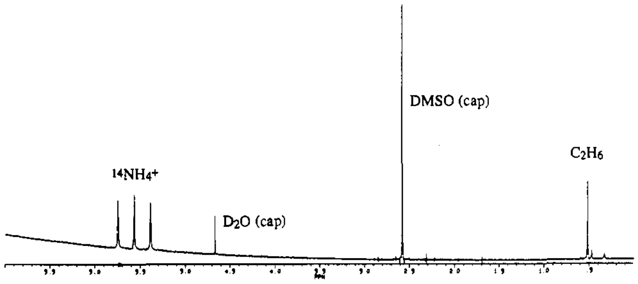

Figure 1. ^1H-NMR spectrum obtained after the following reaction conditions: C_2H_6 (500 psi), $NaNO_3$ (0.15 mmol), H_2SO_4 (1.0 mL), 175 °C, 22 h.

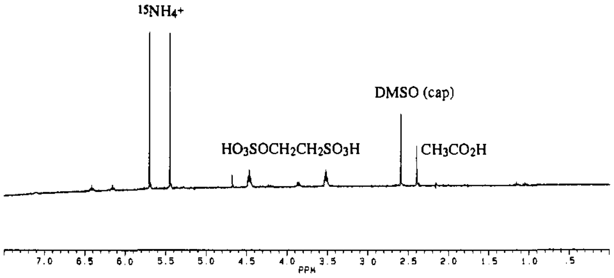

Figure 2. ^1H-NMR spectrum obtained after the following reaction conditions: C_2H_5OH (0.17 mmol), $Na^{15}NO_3$ (0.12 mmol), H_2SO_4 (0.5 mL), 170 °C, 30 min.

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NO_2^+ (formed in situ from NO_3^- and sulfuric acid) and NH_4^+ ions.

When the yield of NH_4^+ ion was less than quantitative, GC analysis indicated that NO and N_2O were the other major nitrogen-containing products. In all the reactions, little if any oxidized organic product was observed in the ^{1}H-NMR spectra. (For examples, see Figures 1 and 2. In Figure 2, $HO_3SCH_2CH_2OSO_3H$ was formed in a separate reaction between ethanol and sulfuric acid.[5]) The lack of soluble organic products was also verified by ^{13}C-NMR spectroscopy using $^{13}CH_3OH$ as the substrate. On the other hand, GC analysis of the reaction of $NaNO_3$ with ethanol indicated the formation of CO and CO_2 in approximately equal amounts. A separate experiment indicated that CO was not capable of reducing NO_3^- to the NH_4^+ ion.

Partially oxidized organics (alcohols, ethers, carboxylic acids) were more efficient reducing agents than the parent alkanes, which, in turn, were found to work better than aromatics (no more than a trace of NH_4^+ ion was observed with benzene, toluene, and pyridine). Among the alkanes examined, methane was the least reactive. However, when methane was employed as the reductant, the addition of $HgSO_4$, which is known to oxidize methane to the methanol derivative, CH_3OSO_3H,[5,6] led to a significantly enhanced yield of NH_4^+ ion. A control experiment showed that NH_4^+ ion was not formed when methane was left out of the reaction mixture. It is, indeed, quite remarkable that the $8e^-$ reduction of NO_3^- to the NH_4^+ ion occurred even in the presence of a strong oxidizing agent.

We do not understand the mechanistic steps involved in the reduction of the nitrogen oxo compounds; however, the following observations are relevant. The hydrogen atoms of the NH_4^+ ion were derived from sulfuric acid either directly or through a subsequent high-temperature exchange process. Thus the yield of NH_4^+ ion did not diminish when THF-d_8 was used in place of THF. Acetonitrile formed the NH_4^+ ion when heated alone in sulfuric acid. However, this was not particularly surprising since a series of solvolysis steps would account for the product. More curious was the behavior of nitro compounds. In principle, the alkyl group in nitromethane or nitroethane would be capable of reducing the nitro group to NH_4^+ ion. However, when these compounds were heated alone in sulfuric acid at 170 °C, a new product was formed in high yields whose ^{1}H-NMR spectrum (broad singlet at 8.2 ppm[4]) was identical to that of hydroxylamine, NH_2OH, dissolved in sulfuric acid (presumably, NH_3OH^+ or a derivative thereof). In the case of nitroethane, a high yield of acetic acid was also observed. Heating a solution of NH_2OH in sulfuric acid with ethanol did not result in the conversion of NH_2OH to the NH_4^+ ion. Clearly, the NH_2OH ion was resistant to further reduction under the reaction conditions and cannot, therefore, be an intermediate in the reduction to the NH_4^+ ion. Even more curious was the observation that when an approximately 1:1 mixture of $C_2H_5{}^{14}NO_2$ and $Na^{15}NO_3$ was heated in sulfuric acid at 170 °C, the *only* observable nitrogen-containing product in the ^{1}H-NMR spectrum was the $^{15}NH_4^+$ ion, together with a small amount of the $^{14}NH_4^+$ ion (Figure 3)! Evidently, the following set of reactions had occurred. As noted above, $C_2H_5{}^{14}NO_2$ was initially converted to $^{14}NH_3OH^+$ and acetic acid. The formed $^{14}NH_3OH^+$ was oxidized by part of the $^{15}NO_3^-$ to N_2O, which was not detectable by ^{1}H-NMR spectroscopy. The balance of the $^{15}NO_3^-$ was reduced to $^{15}NH_4^+$ ion by the acetic acid present. Assuming the overall stoichiometry

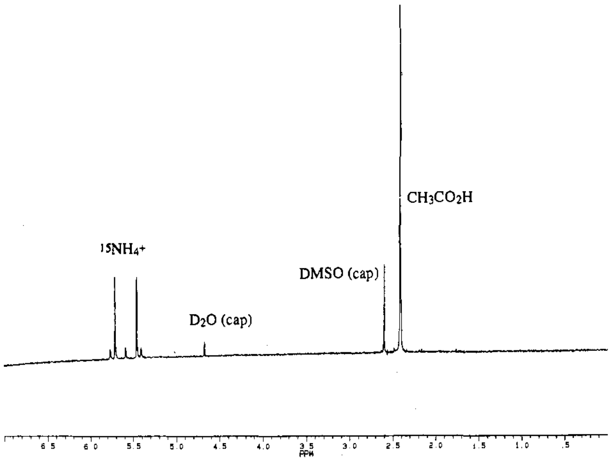

Figure 3. ^{1}H-NMR spectrum obtained after the following reaction conditions: $C_2H_5NO_2$ (0.14 mmol), $Na^{15}NO_3$ (0.15 mmol), H_2SO_4 (0.5 mL), 170 °C, 25 min.

$$2NO_3^- + 4NH_2OH + 2H^+ \rightarrow 3N_2O + 7H_2O$$

and a quantitative reduction of the ***remaining*** $^{15}NO_3^-$, a 50% yield of $^{15}NH_4^+$ ion was expected, and the observed yield was 53%. In further support of the above scenario, independent experiments showed that (a) at 175 °C, the addition of NO_3^- ion to NH_2OH dissolved in sulfuric acid resulted in the disappearance of the latter nitrogen species and the formation of N_2O (detected by GC analysis), and (b) at 180 °C, the reduction of NO_3^- ion by added acetic acid in sulfuric acid proceeded in high yields.

In conclusion, we have discovered the unprecedented reduction of ionic nitrogen oxo species to ammonia by organics in an oxidizing environment. The reactions occur in solution under relatively mild conditions. The scope and the mechanism of the reduction are currently under study.

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