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Addition of Oxide Radical Ions (O^-) to Nitrite and Oxide Ions (O^{2-}) to Nitrogen Dioxide

Richard W. Fessenden and Dan Meisel*

Notre Dame Radiation Laboratory and
Department of Chemistry and Biochemistry
University of Notre Dame, Notre Dame, Indiana 46556

Donald M. Camaioni*

Pacific Northwest National Laboratory
Richland, Washington 99352

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The redox chemistry of nitrogen oxides is complex, involving both radicals and radical ions. Knowledge of their kinetics and reaction mechanisms is fundamental to understanding these reactions in general and especially those relevant to understanding of atmospheric NO_x chemistry. Renewed interest in radiolytically induced processes of these species results from their frequent presence in nuclear materials in various storage facilities. As part of a study to understand the radiation effects in nitrate and nitrite solutions, the nitrate dianion, NO_3^{2-}, in water has been reinvestigated recently.[1] The one-electron reduction potential of nitrate in water (eq 1) was determined and the mechanism of its decomposition in water elucidated (reaction 2).

$$NO_3^{\ -} + e^- \rightarrow NO_3^{\ 2-}\ (E° = -0.89\ \mathrm{V}) \tag{1}$$

$$NO_3^{\ 2-} + H_2O \Leftrightarrow 2OH^- + NO_2 \tag{2}$$

Many acids catalyze the decomposition reaction 3. Protonation

$$NO_3^{\ 2-} + HA \rightarrow OH^- + A^- + NO_2 \tag{3}$$

of the radical dianion may proceed via the acid form HNO_3^- but its formation was questioned in this study. Analysis of the kinetics of reaction 3 suggested that the proton transfer from the HA is concerted with scission of the O_2N-O^{2-} bond. Mezyk and Bartels proposed a similar mechanism based on analysis of the activation parameters of the reaction of the H atom with nitrate.[2] Accordingly, the reaction may be viewed as an O^{2-} transfer reaction to the acid (or water).

From the redox potential of eq 1 and of NO_2 ($E°(NO_2/NO_2^-) = 1.04$ V; all redox potentials are vs NHE)[3] and nitrate ($E°(NO_3^-/NO_2^-) = 0.01$ V) one calculates $K_2 \approx 1 \times 10^{-2}$ M for the equilibrium constant of reaction 2. Combined with the rate constant[1,4] $k_2 = 10^3\ \mathrm{M^{-1}\ s^{-1}}$, the rate constant of the back-reaction is $k_{-2} \approx 1 \times 10^5\ \mathrm{M^{-2}\ s^{-1}}$. Thus it is conceivable that at molar concentrations of OH^- the oxide ion, O^{2-}, may react with NO_2 to produce NO_3^{2-}. Such a finding is entirely novel; it predicts that conditions may be accessible for hydroxide to add to NO_2 thereby converting a strongly oxidizing species to a strongly reducing one.

Another novel route to the production of NO_3^{2-} may exist at highly basic solutions. The conjugated base of hydroxyl radicals, O^- ($pK_a = 11.9$), rarely adds to organic molecules but its addition to small inorganic molecules and ions is known (e.g., addition of O^- to oxygen, CN^-, SCN^-).[4c] Whereas the reaction of oxide radicals with nitrite ions has been studied before, it was suggested to proceed via electron transfer. The transfer of O^- from CO_3^- radicals to nitrite ions (and many other possible acceptors, including NO_2) was investigated earlier.[4b] However, this reaction is too slow to allow detection of the intermediate and NO_2 was suggested to be the product.

In this report we provide evidence that O^- at least partially adds to nitrite ions.

$$NO_2^{\ -} + O^- \rightarrow NO_3^{\ 2-} \tag{4}$$

We also find indications for the reaction of O^{2-} with NO_2, the reverse reaction −2. There are several reports in the literature that organic radicals undergo an analogous addition reaction with nitrite to yield nitroanions.[5] We estimate that reaction 4 is highly exoergic ($\Delta G° = -20$ kcal/mol).[6]

Pulse radiolysis was utilized to generate the radicals and time-resolved ESR to unequivocally identify them and study their kinetics.[7] Experiments were initially done to determine if the ESR lines of NO_2 and NO_3^{2-} could be seen in solution. The detection of NO_3^{2-} from the reaction of e_{aq}^- with nitrate was tried first. Lines attributable to NO_3^{2-} were found in neutral to basic (1 M OH^-) solutions of nitrate. The ESR parameters are $a = 43.4$ G and $g = 2.00458$ with a line width of 0.20 G. These parameters resemble those of NO_3^{2-} in solids, where there is some variability depending on the particular matrix.[8] These lines disappeared when N_2O was added (to convert e_{aq}^- to additional OH) so the identification is not in doubt. The oxidation of nitrite by OH in N_2O saturated solutions was then studied.[4c] No lines attributable to NO_2 were found in solutions containing 1−10 mM nitrite at near neutral pH. On this basis, the ESR line width of NO_2 in water must be larger than ~3 G.

Next, experiments were done with solutions of nitrite saturated with N_2O but looking at the expected lines of NO_3^{2-}. Figure 1 shows the time dependence of the central ESR line of NO_3^{2-} for various concentrations of OH^-. Other than the two reactions described above, reactions −2 and 4, it is difficult to suggest any other pathway for the generation of NO_3^{2-} in this system. In solutions containing ≥ 0.1 M OH^-, formation of the radical dianion can be seen ($<5\ \mu$s after the pulse) and then it decays via an apparent first-order process ($\tau > 10\ \mu$s). At the higher base concentrations this decay leads to a nonzero pseudoequilibrium level that decays at a slower time scale. The maximum observed concentration increases with $[OH^-]$, but is less than the total initial yield of OH and e^-_{aq}. The rate of decay appears to decrease upon increasing $[OH^-]$. Furthermore, the rate of appearance of the radical is slower than the time resolution of the ESR spectrometer. The center-field ESR line was used in all kinetic analyses to minimize polarization effects. The observed kinetic features could not be fit with the known reactions for the system (Table 1), nor could it be fit even by allowing eq 2 to be reversible, regardless of the value selected for K_2. We suggest that reaction 4 at least partially generates NO_3^{2-}.

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[6] $E_4 = E°(O^-/OH^-) - E°(NO_3^-/NO_2^-) + E°(NO_3^-/NO_3^{2-}) = 1.77 - 0.01 - 0.89 = 0.87$ V.

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[8] See, for example: Rustgi, S. N.; Box, H. C. *J. Chem. Phys.* **1973**, *73*, 4763 ($a = 49.7$, $g = 2.0046$). Edo, B.; Iwasaki, M. *J. Phys. Chem.* **1982**, *86*, 2084 ($a = 43.0$, $g = 2.0040$).

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Table 1. Kinetic Model for Simulating the Pulse Radiolysis of Alkaline Nitrite Solutions

no.	reaction	forward (back) rate constants	refs
1	$e^-_{aq} + N_2O \rightarrow N_2 + O^-$	9.1×10^9 M^{-1} s^{-1}	(a) ref 4c
2	$e^-_{aq} + NO_2^-$ $(+ H_2O) \rightarrow NO + OH^-$	3.5×10^9 M^{-1} s^{-1}	ref 15a
3	$OH + NO_2^- \rightarrow NO_2 + OH^-$	1×10^{10} M^{-1} s^{-1}	ref 4c
4	$OH + OH^{--} \Leftrightarrow O^- + H_2O$	1.3×10^{10} M^{-1} s^{-1} (9.4×10^7 s^{-1})	ref 15b
5	$H + OH^- \rightarrow e^-_{aq} + H_2O$	2.0×10^7 M^{-1} s^{-1}	ref 15c
6	$O^- + NO_2^-$ $(+ H_2O) \rightarrow NO_2 + 2OH^-$	4.7×10^7 M^{-1} s^{-1} [a]	(b)
7	$O^- + NO_2^- \rightarrow NO_3^{2-}$	1.8×10^7 M^{-1} s^{-1}	(b)
8	$NO_3^{2-} + H_2O \Leftrightarrow NO_2 + 2OH^-$	1×10^3 M^{-1} s^{-1} (500 M^{-2} s^{-1})	(b) forward rate: refs 1, 4a
9	$2NO_2 \Leftrightarrow N_2O_4$	5×10^8 M^{-1} s^{-1} (6800 s^{-1} for hydrolysis)	ref 15d
10	N_2O_4 $(+ H_2O) \rightarrow NO_3^- + NO_2^- + 2H^+$	1000 s^{-1}	ref 15d
11	$NO + NO_2$ $(+ 2OH^-) \rightarrow 2NO_2^-$	1×10^9 M^{-1} s^{-1}	ref 4a and 15d

[a] N_2O concentrations were estimated to be 0.11, 0.16, 0.22, and 0.23 M for 2, 1, 0.3, and 0.1 M NaOH, respectively, using Henry's constant for water[16a] and the modified Sechenov equation[16b] to correct for effects of ionic strength. [b] Rate constants for reactions 6 and −8 of Table 1 were adjusted to give the best fit to the curves in Figure 1.

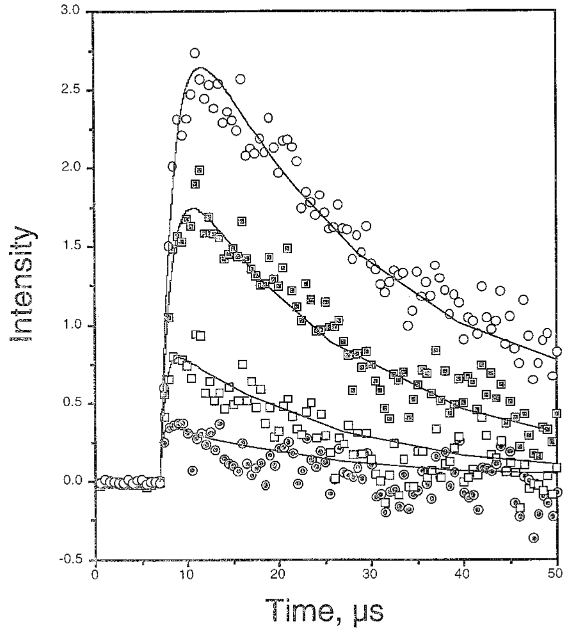

Figure 1. Effect of $[OH^-]$ on the time-dependent ESR signal for NO_3^{2-} (central line) following pulse radiolysis of 6 mM KNO_2 solutions saturated with N_2O: (⊙) 0.1, (□) 0.3, (⊡) 1.0, and (○) 2.0 M NaOH. Lines are calculated from simulations using the kinetic model in Table 1.

Simulations showed that such a reaction is consistent with the observed dependence of the yields and kinetics on $[OH^-]$.[9] An acceptable match to the data of Figure 1 is obtained on reacting O^- with NO_2^- to give NO_3^{2-} with a rate constant of 1.8×10^7 and to give NO_2 with rate constant of 4.7×10^7 M^{-1} s^{-1}, i.e., approximately 25% of the attack yields NO_3^{2-}. These values reproduce well the dependence of the maximum observed concentrations of NO_3^{2-} on $[OH^-]$. However, to obtain good fit to the decay of the dianion, it was necessary to include the reverse reaction in eq 2. Best fit is obtained with $k_{-2} = 500$ M^{-2} s^{-1}.

The production of NO_3^{2-} is not significant below 0.1 M OH^- even though the pK_a of OH radicals is 11.9. The reactivity of OH toward NO_2^- is much greater than that of O^- and it produces NO_2.[10] Therefore, attack on nitrite by OH is competitive with O^- attack at most base concentrations. The sum of rate constants for O^- attack on nitrite ions measured here is about 20% of the literature rate constant.[11] The discrepancy may result from changes in the activity of water at the high base concentrations. It is, however, clear that separating the kinetics of OH from O^- is difficult.[12]

We do not know the details of the faster component that leads "directly" to NO_2. Because nitrite ion is ambivalent, the possibility that the ET path might occur via attack at the O termini of nitrite was considered. This mode of attack might also produce an adduct, e.g., peroxynitrite dianion.[13] No resonances assignable to such an adduct were detected in the ESR spectra. To assess the potential for forming $ONOO^{2-}$ from addition of O^- to NO_2^-, the free energy of such a reaction was calculated using ab initio and self-consistent reaction field solvation methods.[14] The calculations show that NO_3^{2-} is more stable than $ONOO^{2-}$ by 34 kcal/mol. Interestingly, the free energy for reaction 2 was calculated to be 4 kcal/mol by the same methodology, some 25 kcal/mol more positive than the experimental value. Evidently, the parametrization of the solvation model is inaccurate for these dianions. Nonetheless, even if the energies of the dianions are scaled downward by 25 kcal/mol, the peroxynitrite dianion is too high in energy to be formed. Thus, $ONOO^{2-}$ is not a plausible intermediate.

Finally, we come back to reaction −2. Even though thermodynamically the reaction is feasible, experimental evidence is weak. Adjustments to several rate constants from their reported values could eliminate it from the scheme. For example, the simulated rate of decay is sensitive to the rates of radical termination, but except for reaction 11 in Table 1, the constants are not well established in strongly alkaline solutions. Nonetheless, because the simulations following the scheme in Table 1 do predict the observed second-order dependence on $[OH^-]$, we kept it in our computation. From the "fitted" rate constants for eq 2 we obtain $K_2 = 2$ M, which is reflected in a more negative redox potential than experimentally measured (−1.0 V rather than −0.89 V).

In conclusion, we provide experimental results showing that O^- radicals add, at least partially, to NO_2^-. Thus, a strongly oxidizing environment, dominated by OH/O^- radicals, is transiently transformed into a strongly reducing environment dominated by the NO_3^{2-} in the presence of high concentrations of base.

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(9) The IBM, Almaden Research Center, CA, "Chemical Kinetic Simulator 1.1" program (Hinsberg, W.; Houle, F.; Allen, F.) was used in the simulations.

(10) Previous work shows that $HONO_2^-$ is not a bound intermediate. Therefore, the reaction goes to NO_2 and OH^- instead of H^+ and NO_3^{2-}.

(11) Treinin, A.; Hayon, E. *J. Am. Chem. Soc*. **1970**, *92*, 5821. Buxton, G. V. *Trans. Faraday Soc*. **1969**, *65*, 2150.

(12) Even at 1 M OH^- ~48% of the attack on nitrite is by OH.

(13) S. Lymar, private communication.

(14) The electronic energies of the two ions in water were calculated with the Gaussian-98 program using the COSMO solvation model and B3LYP density function method. Both 6-31+G* and 6-311+G* basis sets were used and thermochemical corrections to Gibb's standard free energies were calculated and applied. Results for 6-311+G* and 6-31+G* were within 1 kcal/mol of each other.

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