Reactivity of Nitric Oxide with Simple Short-Lived Radicals in Aqueous Solutions

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Abstract: The kinetic parameters and spectral properties of the products of the reaction of nitric oxide (NO) with $(SCN)_2^-$, Br_2^-, CO_2^-, $CO_3^{-\bullet}$, and ethyl alcohol radicals were studied by the pulse radiolysis technique. The rate constants for the reaction of NO with these radicals are $k[NO + (SCN)_2^-] = (4.3 \pm 0.1) \times 10^9\ M^{-1}\ s^{-1}$, $k[NO + CO_2^-] = (2.9 \pm 0.5) \times 10^9\ M^{-1}\ s^{-1}$, $k[NO + CO_3^{-\bullet}] = (3.5 \pm 0.5) \times 10^9\ M^{-1}\ s^{-1}$, and $k[NO + \text{ethanol radicals}] = (3.0 \pm 1.0) \times 10^9\ M^{-1}\ s^{-1}$. $(SCN)_2^-$ radical forms an adduct that decomposes by first-order processes to yield ultimately NO_2^-. The $CO_3^{-\bullet}$ radical reacts with NO by O^- transfer with the direct formation of NO_2^-. The CO_2^- radical reacts with NO forming the $NOCO_2^-$ transient which reacts with excess NO yielding $N_2O_2^-$. The ethanol radical-NO adducts rearrange to yield ultimately oximes/hydroxamic acids. Preliminary studies of the reaction of NO with Br_2^- show that, while $NOBr_2^-$ is formed at a rate similar to that of $NO(SCN)_2^-$, $k(NO + Br_2^-) = (4.8 \pm 0.4) \times 10^9\ M^{-1}\ s^{-1}$), the corresponding NOBr transient decays by a very complex mechanism that is currently being studied in greater detail. Mechanisms by which the various NO−adducts decay are discussed.

Introduction

Until recent years, nitric oxide (NO) was just one of the nitrogen oxides known to be a toxic environment pollutant which destroys ozone, causes acid rain, and possibly has carcinogenic properties.[1−5] Although NO is a stable free radical, it reacts with molecular oxygen in aqueous solutions to yield NO_2^-:[6,7]

$$4NO + O_2 + 2H_2O \rightarrow 4NO_2^- + 4H^+ \qquad (1)$$

While NO is not very reactive toward most stable molecules, it reacts rapidly with other free radicals and transition metals forming preferentially adducts.[1,2,5,8−12] Nitric oxide can be oxidized to the nitrosonium cation (NO^+) or reduced to the nitroxyl anion (NO^-). These interrelated redox forms can undergo charge-transfer reactions with electron acceptors or donors, form nitroxyl complexes, or undergo oxidation/reduction reactions that lead to formation of other nitrogen oxides or their derivative oxy-acids.[2,5]

Discoveries during the last decade that nitric oxide has unusual chemical properties have had an enormous impact on the biomedical, atmospheric, and ecological sciences. Last year, NO was chosen by *Science* as the molecule of the year,[3] because of its role in such important processes as (1) vascular smooth muscle relaxation; (2) platelet deagregation, (3) neuronal communcation, (4) immunological activation and cytotoxic activity, and (5) its property as an endothelium derived relaxation factor (EDRF).[1−5] The enormous scope of the activity of NO is derived not only from its redox reactions and ability to form adducts, but also because of its mobility and diffusibility through biological membranes.

Despite the many recent discoveries involving NO, some of its basic chemistry is still not well understood. The chemistry of NO and NO^- and their reactions with other free radicals or stable molecules are conveniently studied by pulse radiolysis. NO^- can be generated by this technique in the presence of various reactants such as organic and inorganic compounds, metal complexes, metals in higher oxidation states, free radicals, etc. Earlier radiation studies of NO in aqueous solutions describe the formation and properties of $N_2O_2^-$ and $N_2O_3^-$:[12,13]

$$NO + NO^- \rightarrow N_2O_2^- \qquad (2)$$

$$N_2O_2^- + NO \rightarrow N_3O_3^- \qquad (3)$$

$$N_3O_3^- + H_2O \rightarrow N_2O + HNO_2 + OH^- \qquad (4)$$

More recently it has been demonstrated that O_2^- can be generated in the presence of NO and that the two radicals react with each other forming peroxynitrite:[8−10]

$$NO + O_2^- \rightarrow ONOO^- \qquad (5)$$

Because of the great interest in the chemistry of NO in the above-mentioned fields, where free radicals have been shown

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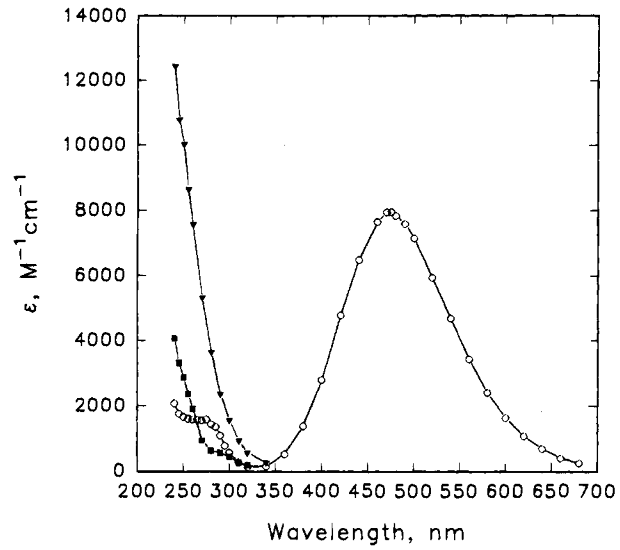

Figure 1. Spectra of $(SCN)_2^-$ (○), $NO(SCN)_2^-$ (▼), and NOSCN (■) in aqueous solutions at pH 6.8 and 24 °C.

to play vital roles, we decided to study some of its reactions with simple free radicals by the pulse radiolysis technique.

Materials and Methods

Materials. The following chemicals were used: KBr, Na_2CO_3, HCOONa, NaH_2PO_4, and Na_2HPO_4 (Baker Analyzed Reagents); KSCN (Matheson Coleman & Bell Manufacturing Chemists); nitric oxide (C.P.; Matheson Gas Products); nitrous oxide (99.999%) and argon (99.0%) (MG Industries).

All solutions were prepared by using water which after distillation had been passed through a Millipore ultrapurification system. The pH of the solutions was adjusted by addition of 25 mM phosphate. NO solutions were prepared by purging buffered solutions with argon to remove O_2, followed by bubbling for 20 min with NO. The NO gas was purified by passing it through a series of scrubbing bottles containing 1.0 M KOH, 0.50 M NaH_2PO_4/Na_2HPO_4 (pH 6.8), and Milli-Q water in this order. The NO saturated solutions (1.94 mM at 23 °C)[13] were stored in syringes and subsequently diluted with argon purged substrate solutions to the desired concentrations by the syringe technique. Preparation and pulse experiments were on the average completed within 45 min. New solutions were prepared for each series of pulse experiments. After use, the NO solutions were disposed of by mixing with oxygen containing $NaOH/Na_2CO_3$ solutions.

Methods. Pulse Radiolysis. Pulse radiolytic experiments were carried out using a 2-MeV Van de Graaff accelerator. Pulse lengths of 100−900 ns with doses ranging from 2.0 to 30 Gy were used. The thiocyanate dosimeter (0.01 M KSCN, 0.026 M N_2O, pH 5.5) served as a calibrant taking $G((SCN)_2^-) = 6.13$ and $\epsilon((SCN)_2^-)_{472nm} = 7950$ M^{-1} cm^{-1}. All pulse radiolysis studies were carried out in a cell with a 2.0-cm light path at 23 °C.

Since the experiments had to be carried out in a closed system in order not to loose some of the gases or have oxygen diffuse into the solutions (see reaction 1), a recently constructed air-tight premixing pulse radiolysis apparatus was used for these studies. The latter consists of three Hamilton Precision Liquid Dispenser (PDL II) units that are computer interfaced and operated by remote control. This setup is capable of mixing up to three solutions in a jet-mixer and pulse irradiating the mixture within 100 ms of mixing.

The experiments were run by mixing N_2O-saturated substrate solutions with water containing known concentrations of NO. The latter solutions were prepared by diluting NO-saturated water with argon saturated water, using the syringe technique. The concentrations of N_2O and NO were adjusted as required by a given experiment, taking into consideration their respective rates of reaction with e_{aq}^-. $G(OH)$ values were evaluated for specific experimental conditions using the Janata−Schuler equation.[14] All spectra and kinetic parameters were calculated on this basis. Typically, 3−15 μM of OH radicals were generated and no significant dose dependencies were found for this range.

Results and Discussion

Reaction of Nitric Oxide with $(SCN)_2^-$. It was established before commencement of the pulse radiolytic studies that the SCN^- and NO_2^- anions do not react with each other at pH 6.8 in 0.025 M phosphate buffer solutions. This was done by scanning the spectra (range 235−450 nm) of SCN^- (2.0 mM) and NO_2^- (2.5 mM) separately and in a mixture of both. The mixture was monitored (1 h) for absorbance changes at the peak of NO_2^- (350 nm). As no changes were observed, it was concluded that no reaction occurred.

The study of the reaction of NO with $(SCN)_2^-$ was carried out by pulse irradiating premixed solutions containing 0.013 M N_2O, variable amounts of KSCN (10−100 mM), and NO (0.05 to 1.0 mM). Under these conditions all e_{aq}^- are converted to OH radicals which react with SCN^- to yield ultimately $(SCN)_2^-$:

$$N_2O + e_{aq}^- + H_2O \rightarrow OH + OH^- + N_2 \qquad (6)$$

$$OH + 2SCN^- \rightarrow (SCN)_2^- + OH^- \qquad (7)$$

In the absence of NO the observed spectrum of the $(SCN)_2^-$ radical shown in Figure 1 has a maximum at 472 nm ($\epsilon = 7950$ M^{-1} cm^{-1}) and a plateau region between 270 and 250 nm ($\epsilon = 1600 \pm 100$ M^{-1} cm^{-1}). The spectrum was corrected below 270 nm, where SCN^- begins to absorb, and the reported $\epsilon((SCN)_2^-) = (\epsilon_{obs} - 2\epsilon_{SCN^-})$. The $(SCN)_2^-$ radical decays by second-order kinetics, $2k = (2.6 \pm 0.3) \times 10^9$ M^{-1} s^{-1}, and the observed rate constant and spectrum in the 350−650 nm range are in good agreement with earlier reports.[15]

In the presence of NO the decays of $(SCN)_2^-$ becomes first order and is proportional to [NO]. The formation of a transient adduct $NO(SCN)_2^-$ (eq 8) was followed both at 260 nm where the adduct absorbs and at 472 nm where disappearance of $(SCN)_2^-$ was monitored. The results obtained at the two different wavelengths are within experimental error similar. At pH 6.8 the measured rate constant for reaction 8 is $k_8 = (4.3 \pm 0.2) \times 10^9$ M^{-1} s^{-1}:

$$NO + (SCN)_2^- \rightarrow NO(SCN)_2^- \qquad (8)$$

The spectrum of $NO(SCN)_2^-$ shows a continuous increase in absorbance in the lower UV range with an $\epsilon(NO(SCN)_2^-)_{260nm} = (7570 \pm 200)$ M^{-1} cm^{-1} (Figure 1). The absorption of $NO(SCN)_2^-$ above 350 nm is negligible. The adduct $NO(SCN)_2^-$ decays by a first-order process at a rate $k_9 = (2.1 \pm 0.1) \times 10^4$ s^{-1} that is independent of pH in the range 5.9 to 7.9; $[NO]_0 = 50-100$ μM and $[KSCN]_0 = 0.01$ to 0.1 M:

$$NO(SCN)_2^- \rightarrow NOSCN + SCN^- \qquad (9)$$

The product of reaction 9 shows similar spectral characteristics to those of $NO(SCN)_2^-$, but of lower molar absorbance. We attribute this absorbance to NOSCN with $\epsilon(NOSCN)_{260nm} = (1900 \pm 200)$ M^{-1} cm^{-1}. The corrected molar absorptivities, $\epsilon(NOSCN) = (\epsilon_{obs} - \epsilon_{SCN^-})$, are given in Figure 1. The spectrum of NOSCN shows characteristics similar to those of NOX (X = Cl, Br, I) in the gas phase.[16]

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Table 1. k_9 as a Function of pH

pH	[NO], μM	k_9, s^{-1}
5.9	100	730.0 ± 40.0
6.8	50	466.0 ± 40.0
6.8	100	450.0 ± 26.0
7.9	100	126.0 ± 10.0
11.5	100	1.3 ± 0.2

The transient NOSCN decays further by an acid-dependent first-order process (eq 10, 11) independent of $[NO]_0$ (Table 1) and of $[SCN^-]_0$ in the range between 0.1 and 0.01 M (data not shown). The rate of hydrolysis, which is roughly of a 0.5 fractional order in $[H^+]$, is consistent with the following mechanism:

$$NOSCN + H_2O \rightleftarrows (HO\text{-}NOSCN)^- + H^+ \qquad (10, -10)$$

$$(HO\text{-}NOSCN)^- + H^+ \rightarrow HNO_2 + SCN^- \qquad (11)$$

for which the values are $k_{11} \approx 800\ s^{-1}$ and $k_{-10}/k_{11} \approx 10^7$. The endproduct, which was identified as NO_2^-, was determined in an independent study using a ^{60}Co γ-ray source.

Preliminary studies of the reaction of NO with Br_2^- show that a $(NOBr_2^-)$ transient is formed at a rate of $k(NO + Br_2^-) = (4.8 \pm 0.4) \times 10^9\ M^{-1}\ s^{-1}$ and decays to NOBr. The latter decays by a very complex mechanism which is dependent on such variables as pH, $[Br^-]_0$, etc. An in-depth study of this complex system is currently in progress.

Reaction of NO with $CO_3^{-\bullet}$ Radical. When N_2O-saturated solutions of 1 M Na_2CO_3 were pulse irradiated, $CO_3^{-\bullet}$ was formed by reactions 6 and 12:

$$CO_3^{2-} + OH \rightarrow CO_3^{-\bullet} + OH^- \qquad (12)$$

The $CO_3^{-\bullet}$ radical has an absorption peak at 600 nm with $\epsilon = (2200 \pm 200)\ M^{-1}\ cm^{-1}$ in agreement with earlier published values.[17] The $CO_3^{-\bullet}$ radicals decay by second-order kinetics with $2k = (4.0 \pm 0.4) \times 10^7\ M^{-1}\ s^{-1}$. Addition of 100 to 300 μM NO to this system accelerated the decay of $CO_3^{-\bullet}$. The decay at 600 nm was first order and linear with [NO]; $k_{14} = (3.5 \pm 0.5) \times 10^9\ M^{-1}\ s^{-1}$. We were unable to observe any absorption due to formation of an adduct or intermediate on the time scales ($t_{1/2} \geq 0.3\ \mu s$) available with our pulse radiolysis setup. The absorption of the $CO_3^{-\bullet}$ radical at 600 nm decays back to the base line, and there is no evidence of $N_2O_2^-$ or $N_2O_3^-$ formation, which we would have easily detected ($\epsilon(N_2O_2^-)_{380nm} \approx 3000\ M^{-1}\ cm^{-1}$ and $\epsilon(N_3O_3^-)_{380nm} \approx 4000\ M^{-1}\ cm^{-1}$).[11,12] As the endproduct of reaction between $CO_3^{-\bullet}$ and NO was identified as NO_2^-, two pathways are possible:

$$CO_3^{-\bullet} + NO \rightarrow CO_3^{2-} + NO^+ \qquad (13)$$

$$CO_3^{-\bullet} + NO \rightarrow CO_2 + NO_2^- \qquad (14)$$

If reaction 13 does occur, it would be impossible to observe the nitrosonium NO^+ ion as the reported rate constant for its aquation is diffusion controlled ($k_{15} = 1.1 \times 10^{10}\ M^{-1}\ s^{-1}$):[19]

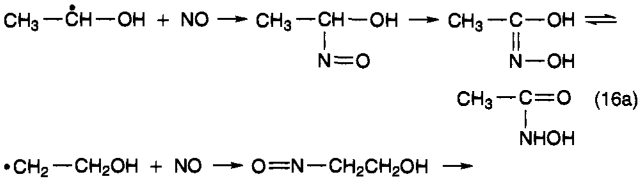
$$NO^+ + H_2O \rightleftharpoons H_2NO_2^+ \rightleftharpoons 2H^+ + NO_2^- \qquad (15)$$

Gratzel et al.,[20] using 1-μs electron pulses, studied the reaction of OH with NO in N_2O-saturated aqueous solutions. From absorbance changes in the UV they were able to show that NO_2^- had been formed quantitatively by the time the electron pulse ended; that is, all reactions were completed in less than 1 μs and there was no further change in absorbance. They concluded that NO^+ was not formed. To the best of our knowledge, direct spectrophotometric observation of NO^+ has been successful only in concentrated H_2SO_4 and $HClO_4$ (≈42.5 to 95.0% by wt).[21]

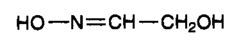
Reaction 14 suggests a O^- transfer from the $CO_3^{-\bullet}$ radical to NO, a reaction proposed earlier for a number of anions ($SO_3^{2-} \rightarrow SO_4^{2-}$; $NO_2^- \rightarrow NO_3^-$; etc.) by Henglein et al.[18,22] Overall, our results corroborate Henglein's findings, and we concur with his conclusion that the O^- transfer reactions may occur via a short-lived intermediate complex, a pathway that is facilitated by hydrolysis. While this pathway can apparently be distinguished by changes in electrical conductivity due to hydration of CO_2 following pulse irradiation, we were not able to verify this because the special pulse radiolysis conductivity cell is not available in our laboratory. In view of Henglein's earlier findings and the lack of evidence for NO^+ formation in the reaction of OH with NO, we favor reaction 14 as the most likely overall pathway.

The absence of an intermediate in the reaction of NO with $CO_3^{-\bullet}$ is different from the reactions with O_2^-, CO_2^-, Br_2^-, and $(SCN)_2^-$, which form relatively long-lived adducts with nitric oxide.

Reaction of NO with Ethanol Radical. Upon irradiation of N_2O-saturated 1 M ethanol, all primary radicals are converted into the α- and β-ethanol radicals. In the presence of nitric oxide the ethanol radicals form NO adducts which can be observed at 270 nm where both the ethanol radicals and their derivative adducts absorb. The rate of this reaction in 0.025 M phosphate (pH 6.8) was found to be $k(R^\bullet + NO) = (3.0 \pm 1.0) \times 10^9\ M^{-1}\ s^{-1}$, which is most probably the rate of formation of the nitroso ethanol compounds. This value is an average of the rate constants for both the α- and β-ethanol radicals as it was impossible to separate the respective kinetic parameters. On a much longer time scale, this absorption decays by two first-order processes which are independent of [NO]. As no absorption was observed at 380 nm, one can conclude that neither $N_2O_2^-$ nor $N_3O_3^-$ is formed. The two first-order decay reactions measured ($k = (8.0 \pm 0.8)\ s^{-1}$ and $k = (0.4 \pm 0.1)\ s^{-1}$) are most likely parallel reactions of the α- and β-nitroso ethanol. It is expected that NO will form with the alcohol radicals nitroso compounds which are known to isomerize into oximes or dimerize. As the observed decays at 270 nm are true first-order reactions (a best fit was obtained when the data were analyzed as two first-order processes), the dimerization process must be negligible. Hence the observed decays most probably represent the isomerization of the corresponding nitroso compounds to oximes and/or hydroxamic acids:



$$CH_3{-}\dot{C}H{-}OH + NO \rightarrow CH_3{-}\underset{\displaystyle N{=}O}{\underset{|}{C}H}{-}OH \rightarrow CH_3{-}\underset{\displaystyle N{-}OH}{\underset{\|}{C}}{-}OH \rightleftharpoons CH_3{-}\underset{\displaystyle NHOH}{\underset{|}{C}}{=}O \qquad (16a)$$



$$\bullet CH_2{-}CH_2OH + NO \rightarrow O{=}N{-}CH_2CH_2OH \rightarrow HO{-}N{=}CH{-}CH_2OH \qquad (16b)$$

This assumption is supported by the fact that the relative absorptions of the two transients vary with wavelength as the two derivative transients have most likely different spectra.

Reaction of NO with CO_2^- Radical. When NO-saturated 10 mM formate is pulse irradiated at pH 6.6, an intermediate is

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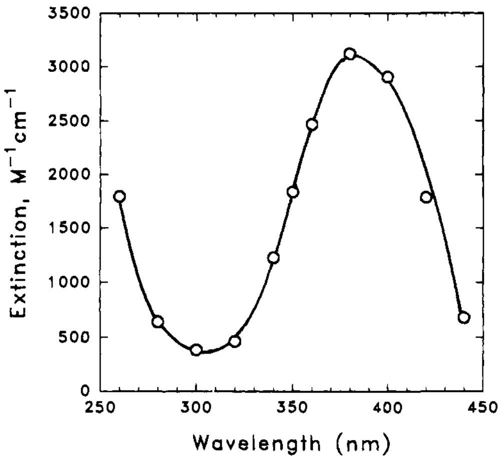

Figure 2. Spectrum of products of NO + CO_2^- reaction 1 ms after the pulse in 0.01 M formate saturated with NO.

observed on a longer time scale (total time 1 ms). This intermediate has an absorption peak at 380 nm ($\epsilon = 3280 \pm 300\ M^{-1}\ cm^{-1}$) and exhibits a continuous increase in absorbance with decreasing wavelength in the lower UV (Figure 2). This spectrum is very similar to earlier reported spectra of $N_2O_2^-$ and $N_3O_3^-$ which have absorption maxima at 380 nm ($\epsilon(N_2O_2^-) = 2850$ and $\epsilon(N_3O_3^-) = 3300\ M^{-1}\ cm^{-1}$)[11] and ($\epsilon(N_2O_2^-) = 3300$ and $\epsilon(N_3O_3^- = 4000\ M^{-1}\ cm^{-1}$).[12]

Irradiation of 0.1 M $HCOO^-$ containing 0.013 M N_2O in the presence of $[NO]_0 < 100\ \mu M$ yields initially the UV spectrum of CO_2^- which is identical with the spectrum obtained in absence of NO. Upon reaction with NO, the absorbance of CO_2^- at 250 nm decays partially to a transient ($NOCO_2^-$) which has a weaker absorbance at this wavelength (see Figure 3).

The decay kinetics of the CO_2^- radical and the formation of a transient ($NOCO_2^-$) in reaction 17 were monitored in the range between 250 and 300 nm and found to be wavelength independent. The disappearance of CO_2^- follows first-order kinetics and the rate is linearly dependent upon $[NO]_0$. Most measurements were taken at 250 nm, where the system gave the best signal to noise ratio, yielding $k_{17} = (2.9 \pm 0.5) \times 10^9\ M^{-1}\ s^{-1}$:

$$CO_2^- + NO \rightarrow NOCO_2^- \quad (17)$$

$$CO_2^- + NO \rightarrow NO^- + CO_2 \quad (18)$$

The transient formed in reaction 17 decays by two consecutive reactions, (19) and (3). As NO^-, $N_2O_2^-$, and $N_3O_3^-$ have similar absorbances at 250 nm,[11,12] the decay of $NOCO_2^-$ was studied at 380 nm where only $N_2O_2^-$ and $N_3O_3^-$ absorb. The buildup of absorbance at 380 nm, following an electron pulse, is illustrated in Figure 4 under conditions where formate solutions contain either NO/N_2O or NO/Ar. In the NO/N_2O experiments (Figure 4A), no absorbance is observed at the end of the pulse suggesting that no $N_2O_2^-$ or $N_3O_3^-$ is formed. Therefore, under these conditions only the adduct $NOCO_2^-$ is formed (eq 17) and reaction 18 is ruled out, as $t_{1/2}$ of formation of $N_2O_2^-$ from NO^- (eq 2) would be less than 1 μs and show an initial absorbance after the pulse. These observations also show that $NOCO_2^-$ does not absorb at 380 nm.

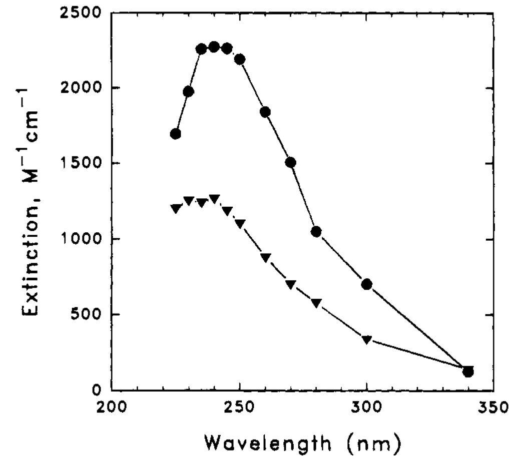

Figure 3. Spectrum of CO_2^- (O) and of its reaction product with NO (▼) in 50 mM formate, 0.013 mM N_2Om, 50 μM NO at pH 6.6. The CO_2^- spectrum was taken at the end of a 600-ns electron pulse while that of the product was determined 60 μs after the pulse.

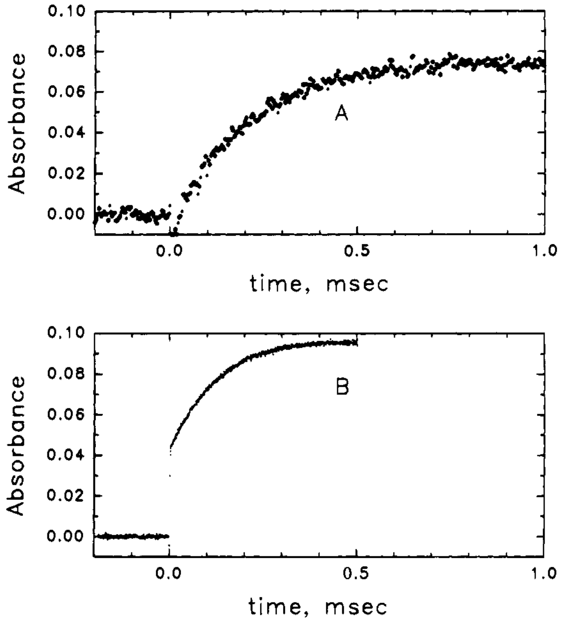

Figure 4. Change in absorbance at 380 nm in a 50 mM $HCOO^-$ solution (50 mM phosphate, pH 6.7) following a 900-ns electron pulse: (A) 13 mM N_2O and 0.5 mM NO; (B) argon and 1.0 mM NO.

Under conditions where the solutions contain NO/Ar, an initial absorbance at the end of the pulse is observed (see Figure 4B). This absorbance is due to $N_2O_2^-$, which is formed by the rapid reaction of e_{aq}^- with NO ($k = 2.3 \times 10^{10}\ M^{-1}\ s^{-1}$)[23] followed by $NO^- + NO$ ($k_2 = 1.7 \times 10^9\ M^{-1}\ s^{-1}$).[12] The slower increase that follows is due to reactions 19 and 3 as described below. The extinction coefficients $\epsilon_{380nm}(N_2O_2^-) = (2900 \pm 150)\ M^{-1}\ cm^{-1}$ and $\epsilon_{380nm}(N_2O_3^-) = (4133 \pm 100)\ M^{-1}\ cm^{-1}$ observed in this study are in fair agreement with earlier reported values: $(\epsilon(N_2O_2^-)_{380nm} = 2800\ M^{-1}\ cm^{-1}$ and $\epsilon(N_3O_3^-)_{380nm} = 3750\ M^{-1}\ cm^{-1})$[11] and $(\epsilon(N_3O_3^-)_{380nm} = 3300\ M^{-1}\ cm^{-1}$ and $\epsilon(N_3O_3^-) = 4000\ M^{-1}\ cm^{-1})$.[12]

In the NO/N_2O solutions the buildup in absorption at 380 nm is due to the simultaneous formation of $N_2O_2^-$ and $N_3O_3^-$ by reactions 19 and 3:

$$NOCO_2^- + NO \rightarrow N_2O_2^- + CO_2 \quad (19)$$

$$N_2O_2^- + NO \rightarrow N_3O_3^- \quad (3)$$

The kinetics for reactions 19 and 3 could not be resolved into

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two components. The overall observed decay is linear with $[NO]_0$ and is the same for the NO/N_2O and NO/Ar systems ($k_{obs} = (6.8 \pm 0.2) \times 10^6$ M^{-1} s^{-1}). Following the buildup, $N_3O_3^-$ decays on a slower time scale by a true first-order process that is $[NO]_0$ independent. The corresponding rate constant, $k_4 = (235 \pm 25)$ s^{-1}, falls between two earlier reported values (87 s^{-1} and 3300 s^{-1}).[11,12]

One could argue whether NO reacts directly with the NO adduct by reaction 19 or whether the following equilibrium is established:

$$NOCO_2^- \rightleftharpoons NO^- + CO_2 \qquad (20, -20)$$

If equilibrium 20, −20 exists, then NO and CO_2 compete for NO^- in reactions 2 and −20, respectively. But since under our experimental conditions $[NO]_0 \gg [CO_2]_{formed}$ and $k_2 = 1.7 \times 10^9$ M^{-1} s^{-1}, k_{-20} would have to exceed diffusion-controlled limits. Therefore, the existence of equilibrium 20, −20 is ruled out and reaction 19 is accepted as the true pathway.

Summary and Conclusions

This study examined the reaction of nitric oxide with a variety of simple oxidizing and reducing radicals. With some simple oxidizing free radicals ($(SCN)_2^-$, Br_2^-), NO forms adducts (NOX_2^-) that hydrolyze to yield ultimately NO_2^-. Reducing radicals ($\bullet CH_2CH_2OH$, $CH_3\dot{C}HOH$) derived from ethanol form adducts that rearrange to yield stable oximes and/or hydroxamic acids. The superoxide radical, as was shown in other laboratories, reacts with NO by forming the adduct pernitrous acid (^-OONO).[8-10] The relatively strong reducing agent CO_2^- ($E^0 = -1.9$ V)[24] forms the $NOCO_2^-$ adduct which reacts with excess NO forming $N_2O_2^-$. The latter reacts further with NO to yield $N_3O_3^-$ which hydrolyzes to the stable products N_2O and NO_2^-.

Although $CO_3^{-\bullet}$ appears to transfer an $O^{-\bullet}$ to NO in a single step (no transient was observed) with formation of $NO_2^{-\bullet}$, a very short-lived transient adduct on the nanosecond time scale cannot be ruled out. This type of reaction has been reported from another laboratory for a number of compounds[18] and in the case of NO appears to be similar to the reaction with the OH radical[25] as both yield NO_2^-.

Overall, the examples given here illustrate the rich chemistry of the NO radical and are intended to serve as models for the different reactions nitric oxide can undergo with free radicals that may be relevant to atmospheric and biological processes.

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