Gas-phase oxidation and disproportionation of nitric oxide

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Title

(1) Title: Gas-phase oxidation and disproportionation of nitric oxide

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Introduction

Nitrogen and oxygen together comprise over 98% of the air we breathe. Nitric oxide (NO) is a simple molecule, consisting of a single nitrogen bonded to one oxygen atom, which makes its chemistry accessible to study in great detail.[1,2] However, it is only recently that mammalian cells were discovered to produce NO as a short-lived intercellular messenger.[3,4] NO participates in blood pressure control, neurotransmission and inflammation. Moreover, NO is the biologically active species released from a variety of cardiovascular drugs such as nitroglycerin and isosorbide dinitrate.[5] One important function of NO is in the macrophage-dependent killing of invaders, and possibly cancer cells, indicating the potential of this free radical to mediate cytotoxic and pathological effects.[6]

When inhaled, NO acts as a selective pulmonary vasodilator. There is intense clinical interest in inhalation of low doses of NO (less than 1 to 80 ppm) in the treatment of diseases characterized by pulmonary hypertension and hypoxemia (Table I).[7,8] The inhaled NO therapy is fairly inexpensive, but it seems that it is not indicated for everybody with regards to the paradigm of its efficiency and potential toxicity. NO reacts with O_2 in the gas phase to form nitrogen dioxide (NO_2):[1,2,9,10]

$$2NO\ (g) + O_2\ (g) = 2NO_2\ (g) \quad (1)$$
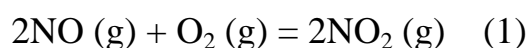
In this therapy, the inhaled NO_2 level must be kept as low as possible

because of its toxic pulmonary effects.[7,8]

Commercial NO, which is stored under compression, invariably contains impurities. Formation of the two main contaminants, NO_2 and nitrous oxide (N_2O), is due to a disproportionation reaction, whose rate is immaterially slow at 1 atm and below but becomes alarmingly high at elevated pressures:[2]

$$3NO \text{ (g)} = N_2O \text{ (g)} + NO_2 \text{ (g)} \quad (2)$$
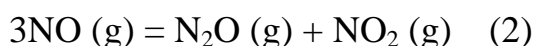
Potential adverse effects of N_2O are also a cause of concern in NO inhalation. N_2O, known as laughing gas, works both as an anesthetic and as an analgesic. Under most conditions N_2O appears to be inert, but prolonged exposure may produce myelotoxic, neurotoxic and reproductive adverse effects.[11] Therefore, a proper assessment of the chemical kinetics, i.e., rate law and the relevant rate constants, of Reactions (1) and (2) is indeed necessary in the medical community.

Reaction (2) must also be borne in mind when compressed NO in commercial cylinders is employed in high precision experiments. The presence of NO_2 in the compressed NO clearly creates difficulties in experimental studies of NO reactions and can pose explosion hazard when the gas is brought into contact with hydrocarbons.[2]

Our goal here is to provide an introduction to the reaction kinetics of gas-phase oxidation and disproportionation of NO, while emphasizing the prediction of NO_2 formation from Reactions (1) and (2).

Gas-phase oxidation of NO

Chemical kinetics of the reaction of NO with O_2

In the oxygenated gaseous environments the reaction of NO with O_2:

$$2NO + O_2 = 2NO_2 \quad (1)$$
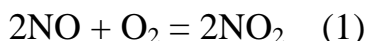
proceeds as a third-order reaction:[1,2,9,10]

$$-d[NO]/dt = +d[NO_2]/dt = 2k \cdot [NO]^2 \cdot [O_2] \quad (3)$$

Since the first chemical kinetic study of this reaction by Bodenstein and Wackenheim[12,13] 80 years ago, a majority of published experimental results supports the differential rate law (3) and the view that Reaction (1) is a homogeneous gas-phase reaction and does not require a participation of solid surfaces.[9,10] These results include the older data obtained with the NO pressures ranging from few torrs to a few hundred torrs and the more recent ones involving low NO concentrations down to the ppm level. In this section, we will briefly review the reaction mechanisms that have been proposed to explain the rate law (3).

Three mechanisms have been proposed.[10]

(i) Termolecular reaction: According to this view, two molecules of NO and one O_2 molecule simultaneously collide and form a transient complex, which thus takes a single step to form two molecules of NO_2. Although this reaction has long served as a classical example of termolecular reaction in chemistry textbooks, a majority of researchers in

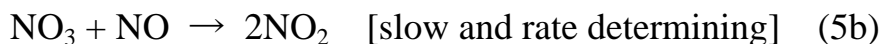recent years prefer the two-step mechanisms, as described below.

(ii) Pre-equilibrium mechanism with dimer of NO as an intermediate:

$$NO + NO \ \rightleftharpoons \ (NO)_2 \quad [fast] \quad (4a)$$

$$(NO)_2 + O_2 \ \rightarrow \ 2NO_2 \quad [slow \ and \ rate \ determining] \quad (4b)$$

$$-d[NO]/dt = k_1 \cdot k_2 \cdot [NO]^2 \cdot [O_2]/(k_{-1} + k_2 \cdot [O_2]) \quad (4c)$$

Equation (4c) results from the assumption that the rate constants k_1 and k_{-1} for the forward and reverse reactions of (4a) are significantly greater than that (k_2) of the second step, (4b). Since $[O_2]$ is only 0.041 $mol \cdot L^{-1}$ even in pure O_2 gas at 1 atm and 298 K, the relation $k_{-1} \gg k_2 \cdot [O_2]$ is assumed valid, thus making Equation (4c) take the form of Equation (3).

(iii) Pre-equilibrium mechanism with NO_3 as an intermediate:

$$NO + O_2 \ \rightleftharpoons \ NO_3 \quad [fast] \quad (5a)$$

$$NO_3 + NO \ \rightarrow \ 2NO_2 \quad [slow \ and \ rate \ determining] \quad (5b)$$

$$-d[NO]/dt = k_3 \cdot k_4 \cdot [NO]^2 \cdot [O_2]/(k_{-3} + k_4 \cdot [NO]) \quad (5c)$$

In Equation (5c), k_3 and k_{-3} are, respectively, the rate constants of the forward and reverse directions of (5a) and k_4 the constant for Reaction (5b). The molar concentration of NO is low even with the NO pressures at a few hundred torrs, and the expression (5c) converges to the form of Equation (3). NO_3 is a well-known intermediate in the decomposition of dinitrogen pentoxide to NO_2 and O_2.[14] Two structures for NO_3 are in the literature: (a) nitrogen trioxide, a nitrate-like planar trigonal structure, in which the N atom is surrounded by three equivalent O atoms;[1,15] and (b)

peroxynitrite radical, a bent-chain structure with an atomic sequence O-O-N-O.[1,16] Although peroxynitrite radical is more persuasive than nitrogen trioxide as an intermediate of Mechanism (iii), there is insufficient evidence to definitely favor one over the other. The formal oxidation state of the N atom in NO_3 is +6. At 298K the standard reduction potential E° for $ONOO\cdot + e^- \rightarrow ONOO^-$ is 0.4 V;[17] that is, peroxynitrite radical is more oxidative than peroxynitrite anion ($ONOO^-$), which itself is a strong oxidant: E° for $ONOO^- + 2H^+ + e^- \rightarrow NO_2 + H_2O$ is 1.4 V at pH 7.[17] For nitrogen trioxide, various estimates for E° of $NO_3 + e^- \rightarrow NO_3^-$ fall within a limit of 2.5 ± 0.2 V,[18] again indicating a highly oxidative nature of the intermediate of Mechanism (iii). Thus, the intermediate of the pathway (iii) could be biologically at least as damaging as $ONOO^-$ and more damaging than NO_2. However, reactivity and toxicity studies of NO_3 have largely escaped biologists' attention.

Bodenstein considered both Mechanisms (ii) and (iii) as possible explanations of his experimental results.[12,13] More recent investigations compared the two mechanisms and concluded that both have equal merits.[9,19,20]

Rate constant for oxidation of NO to NO$_2$

Equation (3) defines the rate constant k for Reaction (1), which will be used in this section. Experimental results from 22 investigations on the rate constant k for the oxidation of NO have recently been

summarized.[10] In these investigations, the concentration of NO ranged over five orders of magnitude from 8.2×10^{-8} to 1.8×10^{-2} mol·L^{-1} and the temperature from 225 to 843 K. In many recent studies N_2 gas was used as a diluent. Most of the kinetic studies agree that the rate constant k is independent of variations in the total pressure (from less than 20 torr to atmospheric pressure) and the absolute NO concentration or the $NO:O_2$ ratio (up to a thousandfold variation) and that the logarithm of the rate constant is inversely proportional to the absolute temperature. The addition of N_2, CO_2, methane and olefins, or moisture (up to 90% relative humidity) has no apparent effect on the order and rate constant for the reaction of NO and O_2. Since water reacts with NO_2 but not with NO in the absence of dissolved O_2, it is expected that the presence of water in the NO/O_2 reaction systems will shift the final equilibrium toward the products, including oxyacids of nitrogen and their anions, but it will not change the rate with which NO is oxidized.

The best accepted temperature-dependence of k in T = 273 to 600 K is represented by an Arrhenius-type equation:[9,10]

$$k \; (L^2 \cdot mol^{-2} \cdot s^{-1}) = 1.2 \times 10^3 \, e^{530/T} = 1.2 \times 10^3 \times 10^{230/T} \quad (6)$$

where T is the absolute temperature. It is noted that the rate constant of Reaction (1) has a negative temperature coefficient. In summary, k = 7.0×10^3 $L^2 \cdot mol^{-2} \cdot s^{-1}$ near the ambient temperature (~ 298 K) and decreases by only 0.04×10^3 $L^2 \cdot mol^{-2} \cdot s^{-1}$ per degree of rise in the

temperature. Thus, the rate constant is rather insensitive to changes of temperature over a wide range.

Prediction of NO_2 formation using the rate constant k

In the setting of NO inhalation environment as well as of ambient atmospheres, NO is present in much lower concentrations than O_2, and it can be assumed that $[O_2]$ remains unchanged. Therefore, a pseudo-second-order kinetics can be applied to Reaction (1). Integration of Equation (3) yields:

$$1/[NO]_t - 1/[NO]_0 = 2k \cdot [O_2] \cdot t \quad (7a)$$

where $[NO]_t$ represents the molar concentration of NO after a residence time t and $[NO]_0$ is the initial NO concentration. Since the difference between $[NO]_0$ and $[NO]_t$ is $[NO_2]$,

$$t = \{1/(2k \cdot [O_2] \cdot [NO]_0)\} \cdot [NO_2]/([NO]_0 - [NO_2]) \quad (7b)$$

$$t = \{1/(2k \cdot [O_2] \cdot [NO]_0)\} \cdot f/(1-f) \quad (7c)$$

where f is the fraction of NO that has become NO_2 in time t (i.e., f = $[NO_2]/[NO]_0$) and $k = 7.0 \times 10^3 \ L^2 \cdot mol^{-2} \cdot s^{-1}$ near the ambient temperature. It is evident from Equation (7c) that the time required for the conversion of a certain fraction of NO to NO_2 is inversely proportional to the initial NO concentration and the rate constant k. Equation (7c) can be used to calculate the time to reach a certain concentration of NO_2 for any concentrations of initial NO in O_2 (Table II).

The initial rate of production of NO_2 is proportional to the square of

the initial concentration of NO. Thus, gas-phase oxidation of NO is slow at very low concentrations of NO in ambient atmospheres. For example, about 6 h is required for 50% oxidation of 10 ppm NO. Conversely, with high-inspired O_2, a small error in the initial timing of NO inhalation could lead to a larger error in the exposure to the undesirable NO_2. Under a condition of inspired O_2 fraction = 1.0, the concentration of NO_2 reaches 52, 8.8, 2.3, 0.57 and 0.023 ppm in the first 10 sec of inhalation of 500, 200, 100, 50 and 10 ppm NO, respectively. At high NO concentrations, even a 1-sec error in the timing could cause serious consequences.

Gas-phase disproportionation of NO

Chemical kinetics and rate constant of the disproportionation of NO

NO is thermodynamically unstable, as indicated by its large positive Gibbs energy of formation ($\Delta_f G^o_{298}$ = 86.32 kJ·mol^{-1}).[1,2] Despite the thermodynamic instability of NO, its decomposition and disproportionation are kinetically hindered near the ambient temperature. The following reaction does not occur to any appreciable extent near the ambient temperature and near 1 atm pressure:[2,21]

$$3NO\ (g) = N_2O\ (g) + NO_2\ (g) \quad (2)$$
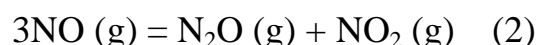
However, the rate of this reaction can be increased by the use of catalysts[22] and elevated pressures.[23] Melia[23] reported that after having

been stored in a cylinder under pressures between 50 and 100 atm and near the ambient temperature, freshly purified NO showed an increase of NO_2 and N_2O contents at a rate of 2-3 % per month. Although the above observations are the only quantitative experimental data available until now, and the experiments were performed at temperatures above the ambient and under relatively high pressures, the data of Melia[23] have been generally referred to in the contemporary review papers on the chemistry of NO gas.[2,10,21]

It has been proposed that under elevated pressures, NO undergoes disproportionation proceeding by the following pre-equilibrium mechanism:[2,21,23]

$$2NO \rightleftarrows (NO)_2 \quad [fast] \quad (8a)$$

$$NO + (NO)_2 \rightarrow NO_2 + N_2O \quad [slow \ and \ rate \ determining] \quad (8b)$$
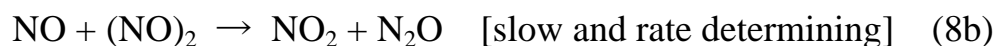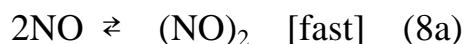
and the overall rate law:

$$-d[NO]/dt = k'[NO][(NO)_2] = Kk'[NO]^3 \quad (8c)$$

where K is the equilibrium constant for Reaction (8a), and k' the rate constant of Reaction (8b). Melia[23] concluded that in the temperature range, 303 to 323 K, and at pressures up to 400 atm, the overall reaction for the disproportionation of NO obeys the third-order kinetics. Melia gave the overall rate constant $Kk' = 2.6 \times 10^{-5} \ L^2 \cdot mol^{-2} \cdot hr^{-1}$ at T = 303 K and $Kk' = 2.7 \times 10^{-5} \ L^2 \cdot mol^{-2} \cdot hr^{-1}$ at T = 323 K, with an initial pressure $P_0 = 200$ atm. According to Melia the insensitivity of Kk' to changes of

temperature in this range appears to result from the increase in the rate

constant k' being offset by the decrease in concentration of $(NO)_2$

brought about by its thermal decomposition.

Buildup of NO_2 and N_2O in pressurized NO gas

At very low pressures, the behavior of a real gas approaches the

ideality. At higher pressures, however, the physical properties of a real

gas may deviate substantially from the ideality. In Melia's equations

(8a-c), [NO] is the molar concentration of NO as a real gas (NO_{real}) and

not an ideal gas (NO_{ideal}). Keeping in mind that the non-ideality of NO

plays a central role in the evaluation of quantitative implication of

Melia's experimental results on Reaction (2), we calculated the

compressibility factor, defined as $z = [NO_{ideal}]/[NO_{real}]$, of NO at 298 K

and at 12 values of pressure (from 1 to 200 atm) using the ideal gas law

and van der Waals equation, and then least-squares fitted these z to a

cubic function of pressure:

$$z (P) = 0.998-0.001438P-0.000008488P^2+0.00000003735P^3$$

where P is the pressure (in atm).

Since $[NO] = (1/RT)(P/z)$ in which R is the gas constant (0.08206

$L \cdot atm \cdot mol^{-1} \cdot K^{-1}$), T the absolute temperature and (P/z) a function of P,

Equation (8c) becomes:

$$-\{1/(P/z)^3\}d(P/z) = \{Kk'/(RT)^2\}dt$$

Integration of this equation between t = 0 and t = t yields:

$$(1/2)\{(z_f/P_f)^2 - (z_0/P_0)^2\} = \{Kk'/(RT)^2\}\cdot t \quad (9)$$

where the subscripts, "0" and "f", refer to the initial and final states, respectively. For a given P_0, T and t, Equation (9) can be solved by finding the value of P_f (and the corresponding z_f) that satisfy Equation (9). Between t = 0 and t = t, the number of moles of NO decreases from $n_0 = \{V/(RT)\}\cdot(P_0/z_0)$ to $n_f = \{V/(RT)\}\cdot(P_f/z_f)$, where V is the internal volume of a container that has been assumed unchanged. Then, from the stoichiometry of Reaction (2), the number of moles of NO_2 and N_2O at residence time t is $1/3\cdot(V/RT)\cdot(P_0/z_0 - P_f/z_f)$ and the total number of moles of NO, NO_2 and N_2O is $1/3\cdot(V/RT)\cdot\{2(P_0/z_0) + (P_f/z_f)\}$. Consequently, the mole fractions, x, of the three gases at time t are:

$$x_{NO} = 3\cdot (P_f/z_f)/\{2(P_0/z_0) + (P_f/z_f)\} \quad (10a)$$

$$x_{NO2} = x_{N2O} = \{(P_0/z_0 - P_f/z_f)\}/\{2(P_0/z_0) + (P_f/z_f)\} \quad (10b)$$

These computations have been carried out at T = 298 K for 8 initial NO pressures (from 1 to 200 atm) and for 8 reaction periods (from 1 to 8,760 hours). The results on the final mole fractions of NO_2 and N_2O based on Melia's data, Kk' = 2.6 x 10^{-5} $L^2\cdot mol^{-2}hr^{-1}$, are summarized in Table III.[21] This value of Kk' is for T = 303 K, but Kk' is very insensitive to the changes in temperature. A similar calculation done at T = 303 K has yielded a practically same result.[21]

It can be seen from Table III that formation of NO_2 and N_2O due to the disproportionation of NO is generally negligible at low initial

pressures, but becomes higher at elevated pressures. After 10 days of storage, the mole fractions of these contaminants are 0.01 % or lower under an initial pressure 5 atm or below, while they can become as high as 12 % in the same period when $P_0 = 200$ atm. Even when pure NO is stored under an initial pressure = 50 atm, the mole fractions of NO_2 and N_2O can reach as high as 17 % after 1 year.

Threshold for the exposure to NO_2

The USA Occupational Safety and Health Administration has set the permissible limits for NO not to exceed 25 ppm for an 8-hr time-weighted average period and NO_2 not to exceed 5 ppm during any part of the working day.[7,8] On the other hand, the USA National Institute for Occupational Safety and Health has set the recommended exposure limit for NO_2 not to exceed 1 ppm for a 15-min exposure and a maximum inhaled NO_2 level of 5 ppm. Public Safety agencies from other countries have adopted similar or lower levels. However, these recommendations are intended for healthy workers and not for patients (especially neonates) with serious diseases, although some guidelines regarding the use of NO in patients have been based on these recommendations.[24,25] In addition, inhaled NO therapy must frequently be continued for prolonged periods ranging from several hours to several weeks.

The national ambient air quality standard for the annual NO_2 level in USA is 0.05 ppm.[26] A "safe" level of NO_2 is difficult to determine. NO_2 levels of less than 0.5 ppm may enhance human airway hyperreactivity. Toxic pulmonary effects of breathing NO_2 at or below 5 ppm have been reported.[7,26] These include altered surfactant chemistry and metabolism, epithelial hyperplasia of terminal bronchioles and increased cellularity of alveoli in rats, as well as diffuse inflammation and hyperreactivity. At higher inhaled doses, pulmonary edema and death have been reported.

Preparation, storage and application of ultrahigh-purity NO

Disproportionation of NO under pressure must be born in mind when compressed NO in commercial cylinders is employed, as described above. For this reason, purification of commercial NO, most particularly for removal of NO_2, is essential to its use in either research or clinically.[2]

The normal (1 atm) melting and boiling temperatures are 109 K and 121 K for NO, 262 K and 294 K for NO_2, and 182 K and 185 K for N_2O, respectively.[1] In our laboratory, NO is purified by a repeated bulb-to-bulb distillation at the cryogenic temperatures as follows. The all-borosilicate glass purification system has been designed to provide the bulb-to-bulb distillation in a most effective manner (Figure 1). When the gas mixture is evaporated from Trap 1 to Trap 2, the NO_x impurities, which are all higher-boiling than NO, tend to condense on the walls of

Trap 2 near the entrance to the trap, while NO tends to condense on the walls deeper down the trap. When the condensates are evaporated from Trap 2 back to the (degassed) Trap 1, the pathway between the two traps are built in such a way that NO leaves Trap 2 while the majority of NO_x impurities remain trapped in Trap 2. If the impurities ever leave Trap 2 for Trap 1, they must be the last ones to leave Trap 2. This procedure can be repeated to remove completely the impurities and to obtain ultrahigh-purity NO. The final ultrahigh-purity NO can be transported through the high vacuum system from Trap 2 to the storage tank (Type-316 stainless steel), which is put in a liquid N_2 trap during the transfer. Once purified, NO can be safely stored in the storage tank at low pressures (e.g., 5 atm or below).

NO gas is colorless, and the solid and liquid forms exhibit very faint blue, which can be taken as being colorless. The condensates of dinitrogen trioxide (N_2O_3) is bright blue, so that some regards the faint blue color of condensed NO as evidence of NO_2 since NO and NO_2 readily react to form N_2O_3 at the cryogenic temperatures.[1] The melting and boiling temperatures of N_2O_3 are 162 K and 275 K, respectively. When more NO_2 is present, the condensates' color becomes greenish.

In the study of aqueous NO systems it is important that the solvent be thoroughly deoxygenated. NO readily reacts with O_2 to form NO_2 and, further, N_2O_3 and dinitrogen tetroxide (N_2O_4). NO_2, N_2O_3 and N_2O_4 will

form the nitroxy anions on interaction with water causing side reactions, some of them catalytic. Inert gas-bubble-purging is one of the most effective deoxygenation methods, as long as the gas is sufficiently pure. In our laboratory, N_2 is purified by passage through activated charcoal and silica gel and then through copper metal-turnings heated red-hot in a silica tube furnace to remove NO_x (e.g., $2NO + 2Cu \rightarrow N_2 + 2CuO$) and O_2 (i.e., $O_2 + 2Cu \rightarrow 2CuO$). Preparation of ultra-pure water involves a two-step purification process. The first step yields the water, which we may call acid-permanganate distillation water, which is free of all impurities with an exception of O_2 (Figure 2).[27] The second step is removal of dissolved O_2 by purging with the ultra-pure N_2 in a specially built all-borosilicate glass apparatus. This water is used throughout our investigation in aqueous solutions.

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Table I.   Potential clinical uses for inhaled NO.

Persistent pulmonary hypertension of the newborn

Primary pulmonary hypertension

Acute respiratory distress syndrome

Pulmonary hypertension following cardiac surgery

Cardiac transplantation

Lung transplantation

Congenital heart disease

Congenital diaphragmatic hernia

Chronic obstructive pulmonary disease

Bronchospasm

Table II.   Time (min) to yield 5 ppm NO_2 from Reaction: $2NO + O_2 = 2NO_2$ at T = 298 K under a constant total volume.

				NO (ppm)			
O_2 (%)	10	20	40	80	200	400	800
20	355.83	59.31	12.71	2.97	0.456	0.113	0.028
30	236.64	39.44	8.45	1.97	0.303	0.075	0.019
40	177.48	29.58	6.34	1.48	0.228	0.056	0.014
50	141.99	23.66	5.07	1.18	0.182	0.045	0.011
60	118.80	19.80	4.24	0.99	0.152	0.038	0.009
70	101.77	16.96	3.64	0.85	0.130	0.032	0.008
80	89.01	14.84	3.18	0.74	0.114	0.028	0.007
90	79.10	13.18	2.83	0.66	0.101	0.025	0.006
100	71.17	11.86	2.54	0.59	0.091	0.023	0.006

Threshold values of NO_2 have been set at 5 ppm or lower for permissible exposure limit for workers.[7,8] Therefore, we have calculated the time to reach 5 ppm NO_2 from NO concentrations of 10 to 800 ppm in O_2 concentrations of 20 to 100 %.

Table III.   Mole fractions of NO_2 and N_2O formation from Reaction:

$3NO = N_2O + NO_2$ at T = 298 K under a constant total volume.

Initial pressure (atm)

Time (hr)	200	100	50	20	10	5	2	1
1	0.0008	0.0002	0	0	0	0	0	0
3	0.0024	0.0005	0.0001	0	0	0	0	0
6	0.0048	0.0011	0.0002	0	0	0	0	0
24	0.0181	0.0042	0.0010	0.0002	0	0	0	0
72	0.0484	0.0123	0.0029	0.0004	0.0001	0	0	0
240	0.1192	0.0373	0.0094	0.0014	0.0004	0.0001	0	0
720	0.2133	0.0903	0.0264	0.0043	0.0011	0.0003	0	0
(30 days)								
8,760	0.3941	0.2984	0.1689	0.0449	0.0124	0.0032	0.0001	0.0001
(1 year)								

Figure 1. Procedure for bulb-to-bulb distillation of pure NO.

Step	A	B	C	D	E	F	G	H	J	Trap 1	Trap 2	Purpose
1	O	O	O	O	O	O	O	C	O	--	--	Evacuate.
2	O	C	C	O	C	O	C	C	C	LN$_2$	--	NO to Trap 1.
3	C	C	O	C	O	O	C	C	C	S[a]	LN$_2$	NO to Trap 2.
4	C	C	C	O	C	C	O	O	C	HW[b]	LN$_2$	NO$_x$ from Trap 1 to Waste Disposal. NO remains in Trap 2.
5	C	C	C	O	C	O	O	C	C	--	LN$_2$	Degas Trap 1.
6	C	O	C	O	C	O	C	C	C	LN$_2$	S	NO to Trap 1.
7	C	C	C	C	O	C	O	O	C	LN$_2$	HW	NO$_x$ from Trap 2 to Waste Disposal. NO remains in Trap 1.
8	C	C	C	C	O	O	O	C	C	LN$_2$	--	Degas Trap 2.
9	C	C	O	C	O	O	C	C	C	S	LN$_2$	NO to Trap 2.
10	(Go back to Step 4, if necessary)											

Abbreviations: O, open; C, closed; LN$_2$, liquid nitrogen. [a]Slurry of organic solid in its own liquid. Choose a preferably non-flammable compound whose melting temperature is above the boiling temperature of NO but below the melting temperatures of other NO$_x$. [b]Hot water (~ 50°C), which will evaporate all NO$_x$. *Traps 3 and 4 are always kept in LN$_2$ during the procedure.

Figure 2.   Water distillation apparatus.

Water is distilled from 10^{-3} M permanganate solution in 10^{-2} M H_2SO_4 at a rate of 150 mL/hr

for at least 24 hr, during which the distillate is continuously fed back to the still by gravity.

This is then followed by a period of withdrawal of product water at a rate of 150 mL/hr. The

still is a 5-L round-bottom flask with three tapered ground points. Water vapor from the still

passes through two liquid traps, which catch spatters of permanganate solution. The system

is continuously purged by a stream of specially purified N_2 (cf. Section, "Preparation, storage

and application of ultrahigh-purity NO," of this article) to carry the gaseous impurities out of

the apparatus through a "vent," a poly(perfluoroethylene) check valve.