

Gas-phase Disproportionation of Nitric Oxide at Elevated Pressures

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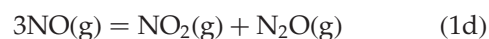
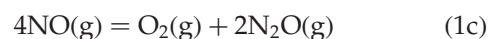
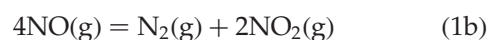
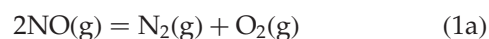
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T.P. Melia's chemical kinetics study of the disproportionation of nitric oxide (NO), $3\text{NO} \rightarrow \text{NO}_2 + \text{N}_2\text{O}$, (Melia, T.P. (1965) *J. Inorg. Nucl. Chem.*, **27**, 95-98), which is the most quoted quantitative investigation presently available, revealed a rather strong dependence of the effective rate constant, Kk' , of Melia's third-order rate law, $-d[\text{NO}]/dt = Kk'[\text{NO}]^3$, on the initial pressure of NO. In order to estimate extent of accumulation of NO_2 and N_2O as a function of time by integration of the rate law, we have evaluated the dependence of the effective rate constant as a function of pressure and thus as a function of time on the basis of the non-ideality of NO gas. Although our approach is crude in that the non-idealities of NO_2 and N_2O and other NO_x products and a probable deviation of the gas mixture from the Dalton's law have not been considered, it provides a means for approximately estimating the rate of accumulation of NO_2 and N_2O based on Melia's data. According to these calculations, the extent of the disproportionation is generally negligible at low initial pressures, e.g. 5 atm or less, while at 200 atm, the mole fractions of NO_2 and N_2O can become as high as 12-13% only after 10 days. These values are alarmingly high for handling pressured NO in N_2 -mixture in either research or clinical settings. This information must be borne in mind when compressed NO in commercial cylinders is employed in high precision experiments. Disproportionation of NO under pressure also deserves attention in inhalation of low doses of NO in the treatment of diseases characterized by pulmonary hypertension and hypoxemia.

Keywords: Chemical kinetics; Disproportionation; Nitric oxide; Nitrogen dioxide; Nitrous oxide; Rate constant

INTRODUCTION

Nitric oxide (NO) is thermodynamically unstable, as indicated by its large positive Gibbs energy of formation ($\Delta_f G_{298}^\circ = 86.32 \text{ kJ mol}^{-1}$). Despite the thermodynamic instability, decomposition and disproportionation of NO are kinetically hindered near the ambient temperature.^[1,2] Thus, none of the following reactions occur to any appreciable extent near the ambient temperature and near 1 atm pressure:



However, the rates of these reactions can be increased by the use of catalysts,^[3,4] high temperatures^[4,5] and elevated pressures.^[6-8] Briner *et al.*^[6,7] showed that, when stored under elevated pressures at room temperature, NO decomposes with the formation of nitrogen dioxide (NO_2), nitrous oxide (N_2O), nitrogen trioxide (N_2O_3), N_2 and O_2 . Melia^[8] reported that after having been stored in a cylinder under pressures between 50 and 100 atm and at

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temperatures near the ambient, freshly purified NO showed an increase of NO₂ and N₂O 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^[8] have been generally referred to in the contemporary review papers on the chemistry of NO gas.^[1,2,9]

Reaction (1d) above is probably the most predominant route for the appearance of nearly equimolar NO₂ and N₂O and loss of NO under pressure. This must be borne in mind when compressed NO in commercial cylinders is employed in high precision experiments. The presence of NO₂ 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. Furthermore, NO has recently been used in the medical community because it is a potent vasodilator.^[10–12] Serious diseases such as primary pulmonary hypertension and acute respiratory distress syndrome are being treated successfully by inhalation of NO.^[13,14] In NO inhalation therapy, the inhaled NO₂ level must be kept as low as possible because of its toxic pulmonary effects.^[13–15] N₂O, known as laughing gas, has also been used clinically as a general anesthetic and as an analgesic, and its potential adverse effects are also a cause of concern.^[12]

Melia^[8] quantitatively studied the reaction kinetics and presented a pre-equilibrium mechanism:



for the overall reaction:



and the overall rate law:

$$-d[\text{NO}]/dt = k'[\text{NO}][\text{N}_2\text{O}_2] = Kk'[\text{NO}]^3 \quad (2d)$$

where K is the equilibrium constant for reaction (2a) and k' is the rate constant of reaction (2b). However, Melia reported only two values of Kk' at 303 K, i.e. $Kk' = (2.6 \pm 0.3) \times 10^{-5} \text{ l}^2 \text{ mol}^{-2} \text{ h}^{-1}$ when the initial pressure of NO was 200 atm and $(6.5 \pm 0.6) \times 10^{-5} \text{ l}^2 \text{ mol}^{-2} \text{ h}^{-1}$ when the initial pressure of NO was 400 atm. Thus, Melia's effective rate constant Kk' is highly dependent on the initial NO pressure at time zero. Because the NO pressure decreases as the disproportionation proceeds, Kk' in equation (2d) must be changing with time during the process since the initial NO pressure at time zero started. In essence then, equation (2d) cannot be integrated over a time period without knowledge of an explicit dependence of Kk' on the pressure.

A prime suspect of cause of such variation in Kk' is the non-ideality of NO gas. The purpose of the present work is evaluation of the pressure-dependence of Kk' from the viewpoint of the non-ideality with an aim to contribute to a (semi)-quantitative implication of this reaction in its relation to the medical and life sciences. It is our hope that the work presented here will provide an access to what Melia's data implies under various experimental conditions that have so far been inaccessible.

PROCEDURE

Non-ideality of 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. Since the non-ideality of NO plays a central role in our evaluation of quantitative implication of Melia's experimental results on reaction (2c), we will digress for a moment to explain the meaning of the various terms, e.g. ideality, non-ideality and compressibility.

An ideal gas consists of point-mass molecules and shows no intermolecular interaction, and thus obeys the ideal gas law at all temperatures and pressures:

$$PV_{\text{ideal}} = nRT, \quad PV_{\text{ideal}}/(nRT) = 1 \quad (3)$$

where P is the pressure, V the volume, n the number of moles of the gas molecules contained in the volume V , R the gas constant ($0.0820578 \text{ l atm mol}^{-1} \text{ K}^{-1}$) and T the absolute temperature. The subscript "ideal" indicates an ideal gas. Since this condition is not exactly met in reality, various equations of state other than the ideal gas law have been used for non-ideal gases. The van der Waals equation is one of the oldest and simplest equations that is still widely used:

For n moles,

$$\left\{ P + \left(\frac{n^2 a}{V_{\text{real}}^2} \right) \right\} (V_{\text{real}} - nb) = nRT \quad (4a)$$

or, for one mole,

$$PV_{\text{real}}^3 - (Pb + RT)V_{\text{real}}^2 + V_{\text{real}}a - ab = 0 \quad (4b)$$

where a and b are the van der Waals constants. The subscript "real" indicates a real gas. Equation (4b) is third order with respect to V_{real} . The term, nb , corrects for the total volume occupied by the bodies of n moles of the real molecules; nb is called the excluded volume. The term, $(n^2 a/V_{\text{real}}^2)$, is called the internal pressure; representing the effect of the intermolecular forces acting between the molecules of the real gas. The van der Waals constants of common gases

are well tabulated. For NO gas, $a = 1.340 \text{ l}^2 \text{ atm mol}^{-2}$ and $b = 0.02789 \text{ l mol}^{-1}$.^[16]

The simplest form of equations of state is in terms of the compressibility. The compressibility factor (denoted by z) is simply the ratio of PV_{real} and nRT :

$$z = PV_{\text{real}}/(nRT) = V_{\text{real}}/V_{\text{ideal}} \\ = [\text{NO}]_{\text{ideal}}/[\text{NO}]_{\text{real}} \quad (5)$$

where the square brackets denote the molar concentration; $z = 1$ for an ideal gas. As the behavior of a gas starts to deviate from the ideality with increasing pressure, the deviation is usually seen as a decreasing z from unity as a result of the intermolecular forces dominating over the excluded volume effect. Eventually, the excluded volume effect becomes significantly large to cause z to stop decreasing and, as the pressure increases further, z starts to increase. The up-turning pressure is sufficiently high for gases encountered under the ambient conditions, so that the compressibility factors are usually smaller than unity and becomes smaller with increasing pressure.

By solving equation (4b) for a value of V_{real} at a given P and T of NO and by applying the, thus, obtained V_{real} in equation (5), one can compute the compressibility factor of NO at various pressures and temperatures. We calculated the compressibility factor, z , of NO at 298 and 303 K and at 12 values of pressure (1, 2, 5, 10, 20, 50, 75, 100, 125, 150, 175 and 200 atm) and then least-squares fitted these z to a cubic function of pressure. The results are described below:

$$\text{At } T = 298 \text{ K, } z(P) = 0.998 - 0.001438P \\ - 0.000008488P^2 + 0.00000003735P^3 \quad (6a)$$

$$\text{At } T = 303 \text{ K, } z(P) = 0.998 - 0.001405P \\ - 0.000007175P^2 + 0.00000003199P^3 \quad (6b)$$

where P is in atm. These equations will be used in the following section.

Buildup of NO₂ and N₂O in Pressurized NO Gas

Now we will evaluate the mole fractions of NO, NO₂ and N₂O at time t after starting with pure NO gas with an initial pressure P_0 atm under a condition of constant total volume. The reaction responsible for the buildup of NO₂ and N₂O is, again:



and the corresponding rate law has been shown to be:

$$-d[\text{NO}]/dt = k'[\text{NO}][\text{N}_2\text{O}] = Kk'[\text{NO}]^3 \quad (2d)$$

Since $[\text{NO}]$ is $[\text{NO}]_{\text{real}}$:

$$-d[\text{NO}]_{\text{real}}/dt = Kk'[\text{NO}]_{\text{real}}^3 \quad (7)$$

Since $[\text{NO}]_{\text{real}} = (1/RT)(P/z)$ in which (P/z) is a function of P (cf. equations (5), (6a) and (6b)), equations (7) becomes:

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

which has a closed form of integration. Integration of this equation between $t = 0$ and $t = t$ yields:

$$(1/2)\{(z_f/P_f)^2 - (z_0/P_0)^2\} = \{Kk'/(RT)^2\}t \quad (8)$$

where the subscripts, "0" and "f", refer to the initial and final states, respectively. For a given P_0 , T and t , equation (8) can be solved by finding the value of P_f (and the corresponding z_f ; cf. equations (6a) and (6b)) that satisfy equation (8). 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.^[8]

Then, from the stoichiometry of reaction (2c), the number of moles of NO₂ and N₂O at time t is:

$$1/3 \cdot \{V/(RT)\} \cdot (P_0/z_0 - P_f/z_f)$$

TABLE I Mole fractions of NO₂ and N₂O at time t after starting with pure NO gas with an initial pressure P_0 atm at $T = 303 \text{ K}$ under a constant total volume: $Kk' = 2.6 \times 10^{-5} \text{ l}^2 \text{ mol}^{-2} \text{ h}^{-1}$

Time (h)	Initial pressure P_0 (atm)							
	200	100	50	20	10	5	2	1
1	0.0008	0.0002	0	0	0	0	0	0
3	0.0023	0.0005	0.0001	0	0	0	0	0
6	0.0046	0.0010	0.0002	0	0	0	0	0
12	0.0091	0.0021	0.0005	0.0001	0	0	0	0
24	0.0176	0.0041	0.0009	0.0001	0	0	0	0
48	0.0331	0.0080	0.0019	0.0003	0.0001	0	0	0
72	0.0471	0.0119	0.0028	0.0004	0.0001	0	0	0
240	0.1166	0.0363	0.0091	0.0014	0.0003	0.0001	0	0
720 (30 day)	0.2103	0.0881	0.0256	0.0042	0.0010	0.0003	0	0
8760 (1 year)	0.3925	0.2958	0.1660	0.0436	0.0120	0.0031	0.0005	0.0001

TABLE II Mole fractions of NO₂ and N₂O at time *t* after starting with pure NO gas with an initial pressure *P*₀ atm at *T* = 303 K under a constant total volume: $Kk' = 2.9 \times 10^{-5} \text{ l}^2 \text{ mol}^{-2} \text{ h}^{-1}$

Time (h)	Initial pressure <i>P</i> ₀ (atm)							
	200	100	50	20	10	5	2	1
1	0.0009	0.0002	0	0	0	0	0	0
3	0.0026	0.0006	0.0001	0	0	0	0	0
6	0.0051	0.0012	0.0003	0	0	0	0	0
12	0.0101	0.0023	0.0005	0.0001	0	0	0	0
24	0.0194	0.0045	0.0010	0.0002	0	0	0	0
48	0.0365	0.0089	0.0021	0.0003	0.0001	0	0	0
72	0.0516	0.0132	0.0031	0.0005	0.0001	0	0	0
240	0.1250	0.0399	0.0101	0.0016	0.0004	0.0001	0	0
720 (30 day)	0.2201	0.0953	0.0282	0.0046	0.0011	0.0003	0	0
8760 (1 year)	0.3977	0.3043	0.1756	0.0479	0.0133	0.0034	0.0006	0.0001

The total number of moles of NO, NO₂ and N₂O is:

$$1/3 \cdot \{V/(RT)\} \cdot \{2(P_0/z_0) + (P_f/z_f)\}$$

Then, the mole fractions, *x*, of the three gases at time *t* are:

$$x_{\text{NO}} = 3 \cdot (P_f/z_f) / \{2(P_0/z_0) + (P_f/z_f)\} \quad (9a)$$

$$x_{\text{NO}_2} = x_{\text{N}_2\text{O}}$$

$$= (P_0/z_0 - P_f/z_f) / \{2(P_0/z_0) + (P_f/z_f)\} \quad (9b)$$

These computations have been carried out at *T* = 303 K for eight initial NO pressures (1, 2, 5, 10, 20, 50, 100 and 200 atm) and for 10 reaction periods (1, 3, 6, 12, 24, 48, 72, 240, 720 and 8760 h). The combinations of higher initial pressures and longer reaction periods lead to the mole fractions of NO₂ and N₂O higher than a few percent. Under these conditions the non-idealities of NO₂ and N₂O and intermolecular reactions such as NO + NO₂ = N₂O₃ become somewhat significant, which the present treatment did not account for. In spite of this, we present results of calculation for all combinations of the eight initial NO pressures and 10 reaction periods, since they semiquantitatively demonstrate the degrees of importance of avoiding storage of NO under pressure. The results on the final mole fractions of NO₂ and N₂O based on Melia's data, $Kk' = 2.6 \times 10^{-5} \text{ l}^2 \text{ mol}^{-2} \text{ h}^{-1}$, are

summarized in Table I. Similar data for $Kk' = 2.9 \times 10^{-5} \text{ l}^2 \text{ mol}^{-2} \text{ h}^{-1}$ are presented in Table II. The second value of Kk' represents the upper limit of the value that Melia reported, $(2.6 \pm 0.3) \times 10^{-5} \text{ l}^2 \text{ mol}^{-2} \text{ h}^{-1}$.

RESULTS AND DISCUSSION

Buildup of NO₂ and N₂O in Pressurized NO Gas

The results of Tables I and II are for *T* = 303 K, the temperature of Melia's experiments, which is not the commonly accepted ambient temperature. Melia also carried out the experiments at 323 K and *P*₀ = 200 atm and reported a value of $Kk' = (2.7 \pm 0.3) \times 10^{-5} \text{ l}^2 \text{ mol}^{-2} \text{ h}^{-1}$. No direct experimental data were reported, which must have been used to estimate the Kk' -value at 323 K. Instead, it was simply stated, "The failure of the overall rate constant (Kk') to increase with increase in temperature would result from the increase in the true rate constant *k'* being offset by the decrease in concentration of N₂O₂ brought about by its thermal decomposition." This presumption by Melia has its parallel in the temperature effects on the rate of oxidation of NO, 2NO + O₂ = 2NO₂. In our recent review of this subject,^[9] we found that N₂O₂ is an intermediate product in one of acceptable mechanisms, which then reacts with O₂ in a rate-determining step.

TABLE III Mole fractions of NO₂ and N₂O at time *t* after starting with pure NO gas with an initial pressure *P*₀ atm at *T* = 298 K under a constant total volume: $Kk' = 2.6 \times 10^{-5} \text{ l}^2 \text{ mol}^{-2} \text{ h}^{-1}$

Time (h)	Initial pressure <i>P</i> ₀ (atm)							
	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
12	0.0093	0.0021	0.0005	0.0001	0	0	0	0
24	0.0181	0.0042	0.0010	0.0002	0	0	0	0
48	0.0341	0.0083	0.0019	0.0003	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 (30 day)	0.2133	0.0903	0.0264	0.0043	0.0011	0.0003	0	0
8760 (1 year)	0.3941	0.2984	0.1689	0.0449	0.0124	0.0032	0.0001	0.0001

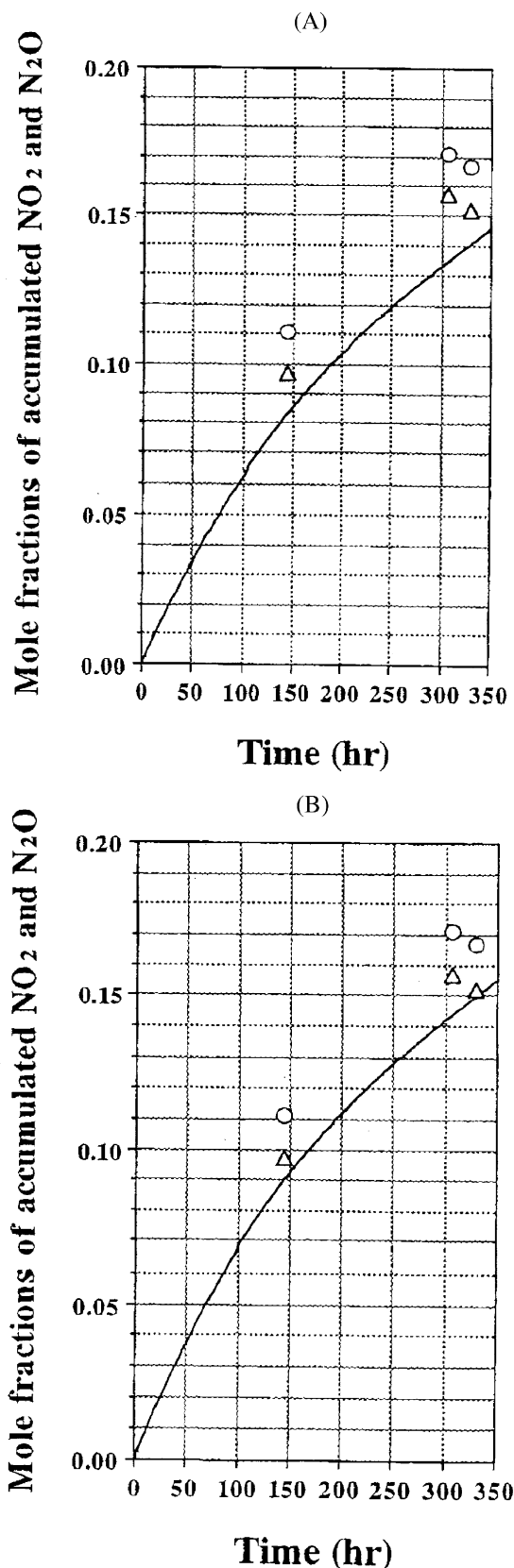


FIGURE 1 Mole fractions of accumulated NO₂ and N₂O plotted against the elapsed time using the overall rate constant $Kk' = 2.6 \times 10^{-5} \text{ l}^2 \text{ mol}^{-2} \text{ h}^{-1}$ (A) and $Kk' = 2.9 \times 10^{-5} \text{ l}^2 \text{ mol}^{-2} \text{ h}^{-1}$ (B) at $T = 303 \text{ K}$: Comparison with Melia's three data points.^[8] Initial pressure of NO is 200 ppm. The smooth line is our calculated results. O, Data points for NO₂ from Melia's data; Δ, Data points for N₂O from Melia's data.

Furthermore, the overall rate constant is rather insensitive to changes in temperature over a wide range. It was shown in our review^[9] that the insensitivity is due to the counteracting effects of temperature in the pre-equilibrium constant against the increase in the rate constant of the reaction, $\text{N}_2\text{O}_2 + \text{O}_2 \rightarrow 2\text{NO}_2$.

To obtain data at a more standard temperature (298 K), we calculated NO₂ and N₂O accumulation at $T = 298 \text{ K}$, assuming that $Kk' = 2.6 \times 10^{-5} \text{ l}^2 \text{ mol}^{-2} \text{ h}^{-1}$ itself is unchanged between 298 and 303 K. The results are summarized in Table III.

Either at $T = 298$ or 303 K, it can be seen from Tables I, II and III that formation of NO₂ and N₂O 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 lower, while they can become as high as 12–13% in the same period when $P_0 = 200 \text{ atm}$. Even when pure NO is stored under an initial pressure 50 atm, the mole fractions of NO₂ and N₂O can reach as high as 17–18% after 1 year. Our results appear consistent with Melia's view that freshly prepared NO, on storage in a cylinder under pressures between 50 and 100 atm, shows an increase in NO₂ and N₂O contents at a rate of 2–3% per month.^[8]

The reverse reaction of the disproportionation reaction, $3\text{NO} = \text{NO}_2 + \text{N}_2\text{O}$, would have been our concern, because accumulation of NO₂ and N₂O might not proceed forward forever. However, the equilibrium constant K for this reaction is $K = 6.19 \times 10^{18}$ at 298 K, since the standard Gibbs energy of formation is: $\Delta G_f^\circ = 87.6 \text{ kJ mol}^{-1}$ for NO, $\Delta G_f^\circ = 51.3 \text{ kJ mol}^{-1}$ for NO₂ and $\Delta G_f^\circ = 104.2 \text{ kJ mol}^{-1}$ for N₂O.^[16] The magnitude of this K is so large that the equilibrium is overwhelmingly lopsided to the right. We conclude that disproportionation of NO should go virtually to completion, as previously pointed out by Addison and Barrer^[3], and that we do not have to worry about the reverse reaction.

Comparison with Melia's Experimental Results

Next, we are going to compare our calculations of the mole fractions with Melia's experimental results, which are shown in Table I of Melia's paper (three data points $t = 145, 306$ and 330 h with an initial NO pressure = 200 atm and at $T = 303 \text{ K}$). For Fig. 1A, the mole fractions of accumulated NO₂ and N₂O using $Kk' = 2.6 \times 10^{-5} \text{ l}^2 \text{ mol}^{-2} \text{ h}^{-1}$ have been plotted against the elapsed time and compared with Melia's three data points. We also performed similar comparisons, in case Kk' is at the upper limit ($2.9 \times 10^{-5} \text{ l}^2 \text{ mol}^{-2} \text{ h}^{-1}$) of Melia's Kk' at 303 K

(Fig. 1B). We note, in Fig. 1, inconsistencies in Melia's own data points. That is, the mole fractions of NO₂ and N₂O at 306 h are slightly higher than those at a later time (330 h). This tends to show the extent of precision of Melia's data. The disagreement of our calculations with Melia's experimental results at $Kk' = 2.6 \times 10^{-5} \text{ l}^2 \text{ mol}^{-2} \text{ h}^{-1}$ (Fig. 1A) is rather large, but the results with $Kk' = 2.9 \times 10^{-5} \text{ l}^2 \text{ mol}^{-2} \text{ h}^{-1}$ (Fig. 1B) yield a better agreement with them.

Melia also reported an increase in Kk' from $(2.6 \pm 0.3) \times 10^{-5} \text{ l}^2 \text{ mol}^{-2} \text{ h}^{-1}$ ($P_0 = 200 \text{ atm}$) to $(6.5 \pm 0.6) \times 10^{-5} \text{ l}^2 \text{ mol}^{-2} \text{ h}^{-1}$ ($P_0 = 400 \text{ atm}$) at $T = 303 \text{ K}$. A significant portion of the pressure-dependence of Kk' is due to an increase in the deviation of NO gas from the ideality. The higher the pressure, the higher the intermolecular attraction, thus causing an increase in the molecular density and the N₂O₂ dimer concentration. Since we hardly use such a high-pressured NO gas in either research or clinical settings, we have not attempted to reproduce this increase in Kk' using the computational method. Finally, we did not consider Table II in Melia's paper, because the temperatures used (i.e. from 443 to 513 K) do not match our purpose.

Practical Implications

Formation of the two main contaminants, NO₂ and N₂O, will be negligible at low initial pressures, e.g. 5 atm or below, near the ambient temperature, but become alarmingly high at elevated pressures, e.g. 50 atm or above. For these reasons, purification of commercially available NO, most particularly for removal of NO₂, is essential in its use in either research or clinical situations. Once purified, NO can be safely stored in vessels at low pressures, employing vacuum line and/or septum and gas-tight syringe methodology for access.^[1,2]

Although the United States Occupational Safety and Health Administration has set safety limits for NO₂ at 5 ppm, airway reactivity and parenchymal lung injury have been reported with inhalation of as little as 2 ppm.^[15] N₂O has been widely used in medical and dental anesthesia. Low potency, low solubility and rapid induction as well as rapid recovery account for the widespread acceptance of N₂O as one of the safest and least toxic of the inhaled anesthetics.^[12] Under most conditions N₂O appears to be inert, but prolonged exposure may produce myelotoxic, neurotoxic and reproductive adverse effects.^[17] In addition, N₂O has recently been shown to modulate *N*-methyl-D-aspartic acid receptor function.^[18] N₂O is generated from NO by the cytosolic fraction of hepatocytes, suggesting the possible formation of this gas in mammalian cells.^[19]

In NO inhalation therapy, NO is typically supplied from a cylinder with a high NO concentration in N₂.^[13,14] It is then diluted with N₂, air or O₂ before

delivery to the patient. The choice of cylinder concentration is determined by safety and convenience. A higher concentration would be convenient (fewer cylinder changes and/or smaller cylinders) but increase the risk of exposure to high NO and its disproportionation products (for both the patient and bedside care providers). A source gas with a higher NO concentration would also allow delivery of a higher fraction of inspired O₂ due to less dilution from the NO source.

In spite of these conveniences, the workshop sponsored by the National Heart, Lung and Blood Institute in 1993 suggested that stock NO concentration should not exceed 1000 ppm for NO inhalation therapy.^[13] Even if the total pressure of NO- in N₂-mixture reaches 100 atm in the stock cylinder, the partial pressure of NO will not exceed 0.1 atm. Our theoretical calculations reveal that in such a condition, NO gas can be stored without detectable disproportionation.

Concluding Remarks

We reviewed the chemical kinetics, i.e. rate law and the relevant rate constant values Kk' , for the gas-phase reaction $3\text{NO} = \text{NO}_2 + \text{N}_2\text{O}$, and made (semi-) quantitative estimates for the disproportionation of NO and accumulation of NO₂ and N₂O in pressured NO gas over wide ranges of initial pressure and reaction period. These are conservative estimates and, yet, the orders of magnitude of the accumulation of NO₂ and N₂O are alarming. It is strongly recommended that the researchers take appropriate precautions, e.g. using up purified NO within a short time after purification or storing the purified gas under low pressures. Manufacturers of inert gas-diluted NO should take similar precautions with yet-undiluted NO.

The present computations have been carried out using meager experimental data that exist today. A lot is to be desired for a high precision data for more reliable estimates. It is prudent to be cautious until a more comprehensive data become available.

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