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A STUDY OF THE INTERACTION OF NO_2 WITH CARBON PARTICLES*

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Abstract

The interaction of NO_2 in air (0.5-35 ppm) with carbon particles led to three products: NO gas, and NO_2^- and NO_3^-, removed from the particles by water extraction. At 4 ppm or below, in dry or humid air, the product distribution, in relative molar amounts, was $NO_3^- = 2NO_2^- = 2NO$. At 20 ppm and above, the relative amounts of products depended on the presence of water vapor. In dry air $NO = 3NO_3^- = 6NO_2^-$. In humid air $NO = NO_2^- = 2NO_3^-$. For carbon slurries in water, $[NO_2^-] = 6[NO_3^-]$ at an input concentration of NO_2 of 4 ppm. In comparison to carbon, alumina particles and glass beads removed NO_2 ineffectively. These results indicate that NO_2 oxidized the carbon particles while it was reduced to NO. NO_2 adsorbed at oxidized sites on the particles formed a surface species that was analyzed as nitrate. At high enough concentration of NO_2 (20 ppm and above), the interaction of NO and water vapor with the surface nitrate produced NO_2^-. In slurries NO, generated from interaction of NO_2 with carbon, reacted with surface nitrate or nitric acid in solution to form the relatively large quantities of nitrite. This work suggests that NO_x reactions with carbon in droplets or on wet surfaces could be important sources for the production of nitrous acid in the environment.

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Introduction

This study examines the interaction of activated carbon particles with NO_2 in air. Its aim is to identify heterogeneous reactions involving NO_x species that may be important in the atmosphere and in indoor environments. Earlier work indicates that carbon can react quickly and irreversibly with NO_2. Charcoal led a group of more than a dozen kinds of particles in ability to decompose NO_2 in a flow reactor (Judeikis et al., 1979). In an indoor air quality study, Girman (1986) added activated carbon to a room and observed simultaneous decreases in NO_2 and increases in NO concentrations. Akhter et al. (1984) found that NO_2 reacted rapidly with hexane soot, resulting in the formation of surface species C—ONO and C—NO_2. Indoor surfaces such as wallboard and carpet can also act as sinks for NO_2 (Spicer et al., 1986, 1987) and as substrates for the conversion of NO_2 to NO (D'Octavio and Dietz, 1985; Nishimura et al., 1986; Yanagisawa et al., 1987).

Recent studies indicate that heterogeneous reactions involving NO_2 and water may be responsible for the formation of significant amounts of HONO in nighttime polluted air (Harris et al., 1982; Pitts et al., 1984a). Measurements of the rate of formation of HONO on the walls of environmental (smog) chambers (Sakamaki et al., 1983; Pitts et al., 1984b; Svensson et al., 1987) and in a simulated indoor environment (Pitts et al., 1985) support this interpretation. Apparently HNO_3 was also formed in these experiments, but it remained on the walls. Because the measured rates cannot account for all the observed ambient HONO (Heikes and Thompson, 1983), other as yet undiscovered processes, possibly involving ambient particles, may be important, as suggested by Sakamaki et al. (1983). Modeling studies of the fate of NO_2 and other pollutants indoors by Nazaroff and Cass (1986) also pointed to the potential importance of heterogeneous NO_x reactions.

This work concentrates on the interaction of ppm levels of NO_2 with carbon particles and compares the relative activities of activated carbon, alumina, and glass to convert NO_2 to NO, NO_2^-, and NO_3^-. The influence of both water vapor and liquid water on product distributions has also been studied.

Experimental Details

Experiments were performed with gas-particle and gas-liquid water-particle systems. Figure 1 shows a schematic diagram of the apparatus used for two-phase experiments (NO_2 + particles in air). NO_2 (500 ppm in N_2, obtained from Scott-Marrin, Inc., Riverside, California) and clean dry air passed through mass flow controllers, mixed, and entered glass impingers that contained 20 mg activated carbon particles (ground RB1, from American Norit Company) or alumina (chromatographic activity grade 1, from ICN Pharmaceuticals). All experiments were conducted at room temperature. The particles were dispersed among 20 ml 3-mm diameter glass beads by vigorous shaking. Blank measurements were performed using glass beads alone. The activated carbon for these experiments has been chosen because in previous studies of the rate of oxidation of $SO_3^=$ (Gundel et al., 1985), this carbon (RB1) was found to be the most active.

A Thermo-Electron Model 14D/E Chemiluminescent NO-NO_2-NO_x Analyzer monitored NO and NO_2 concentrations downstream of the reaction vessel. Upstream NO_2 concentration ranged from 0.5 to 35 ppm, with a typical total flow of 1 liter/min at atmospheric pressure through the reaction vessel. Before the start of experiments, NO_2 in air at about 20 ppm passed through the tubing leading to the apparatus for an hour. With this preconditioning, NO was always less than 2% of NO_2; otherwise, up to 10% of the total NO_x was NO.

In some experiments humidified air entered the system just upstream of the reaction vessel, after passing through a temperature-controlled impinger that contained 10 ml water. The resulting relative humidity was 50% as measured by a dew point hygrometer (General Eastern Model 1200 AP). For dry experiments this auxiliary flow line was kept dry, but air passed through it at the same rate. Flow rates were measured with a calibrated wet-test meter.

After a 10-minute exposure to NO_2, the sample of particles was sonicated in 20 ml deionized water and filtered through pre-extracted 0.22-μm pore size cellulose acetate filters (Millipore Corp.) before determining NO_2^- and NO_3^- by ion chromatography (IC) (Dionex Auto-Ion System 12 Analyzer). Because

the eluent was basic ([HCO_3^-] = 3.0 mM and [$CO_3^=$] = 2.4 mM), this analytical method could not distinguish between HNO_2 (nitrous acid) and NO_2^- (nitrite ion) or between HNO_3 (nitric acid) and NO_3^- (nitrate ion). Freshly prepared $NaNO_2$ and $NaNO_3$ solutions were used as standards. Background concentrations of nitrite and nitrate on the particles were determined by passing air alone through loaded reaction vessels for 10 min and then extracting as usual. pH measurements were performed on some of the filtered extracts after IC analysis.

The effects of varying flow rate through the reaction vessel were not investigated extensively. Future studies will vary the flow rate to determine whether the contact time between NO_2 and particles influences observed product distributions.

Three-phase experiments were conducted using the apparatus shown in Fig. 2. NO_2 (1 to 25 ppm) in air passed through 10-ml aliquots of water slurries of particles (1 mg/ml). To assure that NO_2 could dissolve in water during its residence time in the reaction vessel (Schwartz and White, 1981), a lower flow rate was used, typically 0.15 liter/min. This resulted in a residence time of 4 sec. After 10 minutes the slurries were filtered and analyzed by IC.

Particles were precleaned before use. A batch of about 10 g carbon was ground in an agate ball mill overnight and then washed three times in boiling deionized water, filtered through porous glass, dried overnight at 110°C, and reground in a small agate mortar. Earlier work with this type of activated carbon showed that this heating had no effect on its ability to oxidize $SO_3^=$ (Gundel et al., 1985). The principal contaminant measured after this treatment was $SO_4^=$, at about 2 μmoles/g C. Alumina was ground by hand in an agate mortar to a fine powder before extraction in boiling water. Filtration and air drying at 110°C followed. Glass beads, filters, and syringes were sonicated in deionized water and dried before use.

Results

Carbon. Figure 3 shows the amounts of NO, NO_2^-, and NO_3^- generated when NO_2 passed through carbon particles for initial NO_2 concentrations between 0.5 and 35 ppm. The results are expressed in

micromoles per gram C. These units adjust for differences in flow rates between experiments. The upper part of the figure contains data for NO_2 in dry air; the lower part shows the product distribution for humid air.

In dry air a significant part of the initial NO_2 was converted to NO. Above an upstream concentration of about 100 μmoles NO_2/g C, NO was the principal product; but at all concentrations of NO_2, the particles contained significant amounts of NO_2^- and NO_3^-. About half as much nitrite was formed as nitrate. A saturation effect occurred for each product: for the ionic species, the slope flattened above 80 μmoles/g C; for NO the saturation did not appear until the initial NO_2 concentration was over 400 μmoles/g C.

When the air stream contained water vapor at 50% relative humidity, the relative amounts of the products differed from the distribution in dry air. Throughout the concentration range of the experiments, approximately equal amounts of NO and NO_2^- were formed. Compared to carbon particles in dry air, this was an increase in production of nitrite at the expense of NO. At low NO_2 concentrations, nitrate was most abundant, as in dry air. Above 80 μmoles NO_2/g C, the yield of nitrate remained constant, while NO_2^- and NO continued to increase with increasing initial NO_2. About half as much nitrate was formed as in the dry NO_2 air mixture.

Figure 4 shows the amounts of NO_2^- and NO_3^- found in carbon slurries vs. amounts of NO_2 that entered the reaction vessel. Data are expressed in micromoles per gram C. Figure 5 contains data in micromoles per liter for experiments in which NO_2 passed through pure water in the impinger. Because the carbon concentration was 1 g/liter for the data shown in Fig. 4, the units of these figures are equivalent. The input NO_2 concentrations ranged from 1 to 25 ppm in these experiments.

About a third more NO_2 was trapped in carbon slurries than in pure water, and for carbon most of this was detected as nitrite. At 24 μmoles NO_2/g C (4 ppm) $[NO_2^-]$ was about 6 times $[NO_3^-]$. Above 100 μmoles NO_2/g C (~ 16 ppm), 95% of the NO_x^- was NO_2^-. Water alone contained equal amounts of nitrite and nitrate after NO_2 passed through it. The slopes of curves drawn in Figs. 4 and 5 decreased as initial

NO_2 increased, indicating saturation effects occurred, even in pure water.

Mass balance. At 40 μmoles NO_2/g C, the products and unreacted NO_2 accounted for 81% of the amount entering the reaction vessel. At 730 μmoles/g C, only about 20% of the input NO_2 could be accounted for. Slightly lower recoveries were observed for experiments conducted in humid air. The missing species may have reacted at or been adsorbed on the tubing walls downstream of the reaction vessel. Another possibility is conversion to nitrogenous species that were not detected or that remained on the carbon surface after extraction. Mass balance calculations could not be made for slurries because the NO_x sampling port was upstream of the reaction vessel in those experiments.

Alumina. Figure 6 shows the results for the interaction of NO_2 with alumina particles for both dry and humid air streams. No NO was produced, and for all values of entering NO_2 concentration, approximately equal amounts of NO_2^- and NO_3^- were found on the particles. Unreacted NO_2 was detected in large amounts downstream of the reaction vessel. The sum of nitrite, nitrate, and downstream NO_2 concentrations accounted for between 93 and 108% of the NO_2 that entered the impinger. At high NO_2 concentrations, the presence of water vapor depressed the ability of alumina to trap NO_2^- and NO_3^- by about a factor of three.

Alumina slurries trapped NO_2 only slightly more efficiently than water. Figure 7 shows amounts of nitrite and nitrate found, along with a comparison with water, for low levels of NO_2. No experiments were done with alumina at NO_2 concentrations higher than 50 μmoles/g alumina. Although NO_2^- concentrations were somewhat higher than NO_3^-, the differences were not so pronounced as in carbon slurries, where NO_2^- clearly dominated.

Glass beads. Below 80 μmoles NO_2 per liter of beads (equivalent to 80 μmoles/g of particles because 20 mg of particles were disbursed among 20 ml of glass beads), the beads contained no nitrite or nitrate above blank values. This was true for dry and humid gas streams. In dry and humid air, above 400 μM NO_2/liter about 0.3% and 0.7% respectively of the NO_2 was extracted from the beads as equal amounts of NO_2^- and NO_3^-. This represents less than 2% of the amounts removed from carbon, and 10 to

50% of the amounts removed from alumina.

Comparison. To enable comparison of the interaction of NO_2 with various substrates, Table 1 contains data for two-phase experiments at 4 ppm (about 75 μmoles NO_2/g) and three-phase experiments at 8 ppm (about 50 μmoles NO_2/g). For carbon in dry or humid air, about twice as much NO_3^- was formed as NO_2^-, and amounts of NO equalled amounts of NO_2^-. Carbon trapped about 6 times as much NO_2 as alumina. Glass beads were inert. Carbon slurries contained 9 times as much nitrite as nitrate. At 8 ppm NO_2, the total NO_x^- in solution was twice that in alumina slurries or water alone.

Discussion

Both alumina and glass beads trapped small amounts of NO_2 that appeared as equal amounts of nitrite and nitrate in water extracts. The same behavior appeared in alumina and pure water slurries. Observation of equal amounts of NO_2^- and NO_3^- suggests that reactive dissolution of NO_2 occurred according to reaction (1) (Schwartz and White, 1981):

$$2NO_2 + H_2O \rightarrow HNO_2 + H^+ + NO_3^- . \qquad (1)$$

Here the alumina or beads adsorbed some NO_2, which then reacted with water during extraction. The alumina and glass surfaces did not influence the ratio of nitrite to nitrate, and no NO was generated. Water vapor competed with NO_2 for adsorption sites on alumina, and the total amount of NO_2 trapped declined when water vapor was present. For both alumina and glass beads, most of the NO_2 passed through the reaction vessel unchanged. Adding alumina to water did not lead to increased amounts of nitrite and nitrate, compared to water alone, suggesting that the alumina surface was inactive in water.

In contrast to the behavior seen on alumina and glass surfaces, chemical reactions occurred on carbon particles. NO resulted from the reduction of NO_2 as it oxidized the surface. If an oxidized site C_xO was created, reaction (2), it could oxidize NO_2 and cause nitrate ion to appear in the water extract, reaction (3):

$$NO_2 + C_x \rightarrow NO + C_xO \qquad (2)$$

$$NO_2 + C_xO \rightarrow C_xO{\cdot}NO_2 \text{ (analyzed as } NO_3^-) . \quad (3)$$

The relatively high yields of NO_3^- found at low NO_2 concentrations may also reflect the formation of the oxidized species by reaction (3) on previously formed C_xO sites, i.e. those already present on the particles before exposure to NO_2. At high concentrations of NO_2, another surface reaction could occur when water vapor was present in the gas stream -- the interaction of NO with NO_2 to form nitrous acid:

$$NO + NO_2 + H_2O \rightarrow 2HNO_2 . \quad (4)$$

The homogeneous version of reaction (4) is too slow to be important in the gas phase (Heikes and Thompson, 1983; Pitts et al., 1984b). Nitric oxide could also react with the oxidized nitrogen already formed on the carbon surface to yield more nitrous acid:

$$3NO + C_xO{\cdot}NO_2 + 2H_2O \rightarrow 4HNO_2 + C_x. \quad (5)$$

The indicated stoichiometry of this reaction is probably not too meaningful. Both reactions (4) and (5) require NO and water at the surface, and they explain the observed dominance of nitrite formation on carbon in the presence of water vapor. When the NO_2 concentration was high enough to generate sufficient NO, appreciable amounts of nitrous acid could be formed by these reactions. Reaction (5) is somewhat similar to a reaction that can occur on the walls of smog chambers (Besemer and Nieboer, 1985):

$$2NO + s{\cdot}HNO_3 + H_2O \rightarrow 3HNO_2 . \quad (6)$$

Here the surface is not carbon but the Teflon wall, and the surface species is adsorbed nitric acid, shown in (6) as $s{\cdot}HNO_3$. In carbon slurries surface-generated NO may react with surface nitrate, reaction (5), or with nitrate in solution:

$$2NO + HNO_3 + H_2O \rightarrow 3HNO_2 . \quad (7)$$

Reaction (7) can explain the observed prevalence of NO_2^- in carbon slurries.

Comparison to Other Work

The mechanism proposed here to explain the generation of NO from the carbon surface does not require the presence of water. This contrasts with the reaction scheme proposed by Nishimura et al.

(1986) and by Yanagasawa et al. (1987), who explained the source of NO in their experiments as decomposition of HNO_2 in a study of the interaction of NO_2 with indoor materials such as rush mats and gypsum wall board. These authors suggested that the HNO_2 was formed from reaction (1) and decomposed in the reverse of reaction (4).

Adsorption of NO_2 on carbon particles without reaction probably also occurred because some nitrite was formed even with no water vapor present. The source of this HNO_2 was reactive dissolution of adsorbed NO_2, reaction (1).

In studies of the reaction of NO_2/N_2O_4 with hexane soot, Akhter et al. (1984) found infrared evidence for formation of C-NO_2 and C-ONO groups on the soot surface. Absorbance for each species grew at the same rate. The C-ONO group may correspond to a surface product or intermediate whose decomposition leads to formation of NO in our work:

$$NO_2 + C_x = C_x{\cdot}ONO = C_xO + NO \tag{2a}$$

The C-NO_2 group may correspond to adsorbed NO_2 on the surface, which decomposes in water to form equal amounts of nitrite and nitrate:

$$NO_2 + C_x = C_x{\cdot}NO_2 \tag{1a}$$

$$2C_xNO_2 + H_2O = 2C_x + HNO_2 + H^+ + NO_3^- . \tag{1b}$$

The results of this study cannot be extrapolated directly to atmospheric chemistry because activated carbon particles may not simulate the behavior of combustion soot, and ambient NO_2 levels are much lower than those used here (parts per billion rather than parts per million).

Conclusions

This work identifies a new pathway for transformation of NO_2: reaction at the surface of carbon particles to produce NO, nitrite, and nitrate. The results of this study indicate that all these products can form easily and quickly on activated carbon particles, although no rates of generation were measured.

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Table 1. Comparison of the interactions of NO_2 with carbon, alumina, glass, and water.

	Condition[a]	NO_2 (in) ppm	NO_2 (in)	NO_2 (out)	NO	NO_2^-	NO_3^-	Sum/NO_2 (in) %
				μmoles/g				
Carbon	Dry	4	80.1	2.7	14.6	12.2	22.7	65
	Humid	4	73.4	2.3	11.5	10.7	21.3	62
	Slurry	8	51.6	b	b	6.5	0.76	-
Alumina	Dry	4	75.4	72.6	c	4.8	4.2	108
	Humid	4	75.4	67.8	c	4.1	4.0	101
	Slurry	8	49.6	b	b	2.2	1.8	-
Glass beads	Dry	4	75.4	75.4	c	c	c	100
	Humid	4	75.4	75.4	c	c	c	100
Liquid water	Liquid[d]	8	48.8	b	b	2.1	1.9	-

[a]Averaged data from duplicate experiments, when available.

[b]No data available.

[c]Below the limit of detection.

[d]Micromoles per liter.

Figure Captions

Figure 1. Schematic diagram of the apparatus used to study the interaction of NO_2 with carbon and alumina particles. For experiments in dry air, the auxiliary line was used as shown, but the humidifier vessel was empty.

Figure 2. Schematic diagram of the apparatus used to study the interaction of NO_2 with carbon and alumina particles in water.

Figure 3. Amounts of nitrogenous species resulting from the interaction of NO_2 with carbon particles in two-phase experiments vs. initial amount of NO_2. Upper: NO_2 in dry air; lower: NO_2 in humid air (50% relative humidity). Solid line and □, NO; dashed line and cross, NO_2^-; dotted line and ∇, NO_3^-; hexagon - NO_2 measured downstream of the reaction vessel.

Figure 4. Amounts of NO_2^- and NO_3^- determined in carbon slurries vs. amount of NO_2. Dashed line and O, NO_2^-; dotted line and ∇, NO_3^-; solid line and □, $NO_2^- + NO_3^-$.

Figure 5. Amounts of NO_2^- and NO_3^- determined in water vs. initial amount of $NO_2(g)$. Dashed line and O, NO_2^-; dotted line and ∇, NO_3^-; solid line and □, $NO_2^- + NO_3^-$.

Figure 6. Amounts of nitrogenous species resulting from the interaction of NO_2 with alumina particles in two-phase experiments vs. amount of $NO_2(g)$. Upper: NO_2 in dry air; lower: NO_2 in humid air (50% relative humidity). □ - NO; cross - NO_2^-; ∇ - NO_3^-.

Figure 7. Upper: amounts of NO_2^- and NO_3^- in alumina slurries (1 g/liter) vs. amount of NO_2. Dashed line and O, NO_2^-; dotted line and ∇, NO_3^-; solid line and □, $NO_2^- + NO_3^-$. Lower: Amounts of NO_2^- and NO_3^- in pure water vs. amount of NO_2.

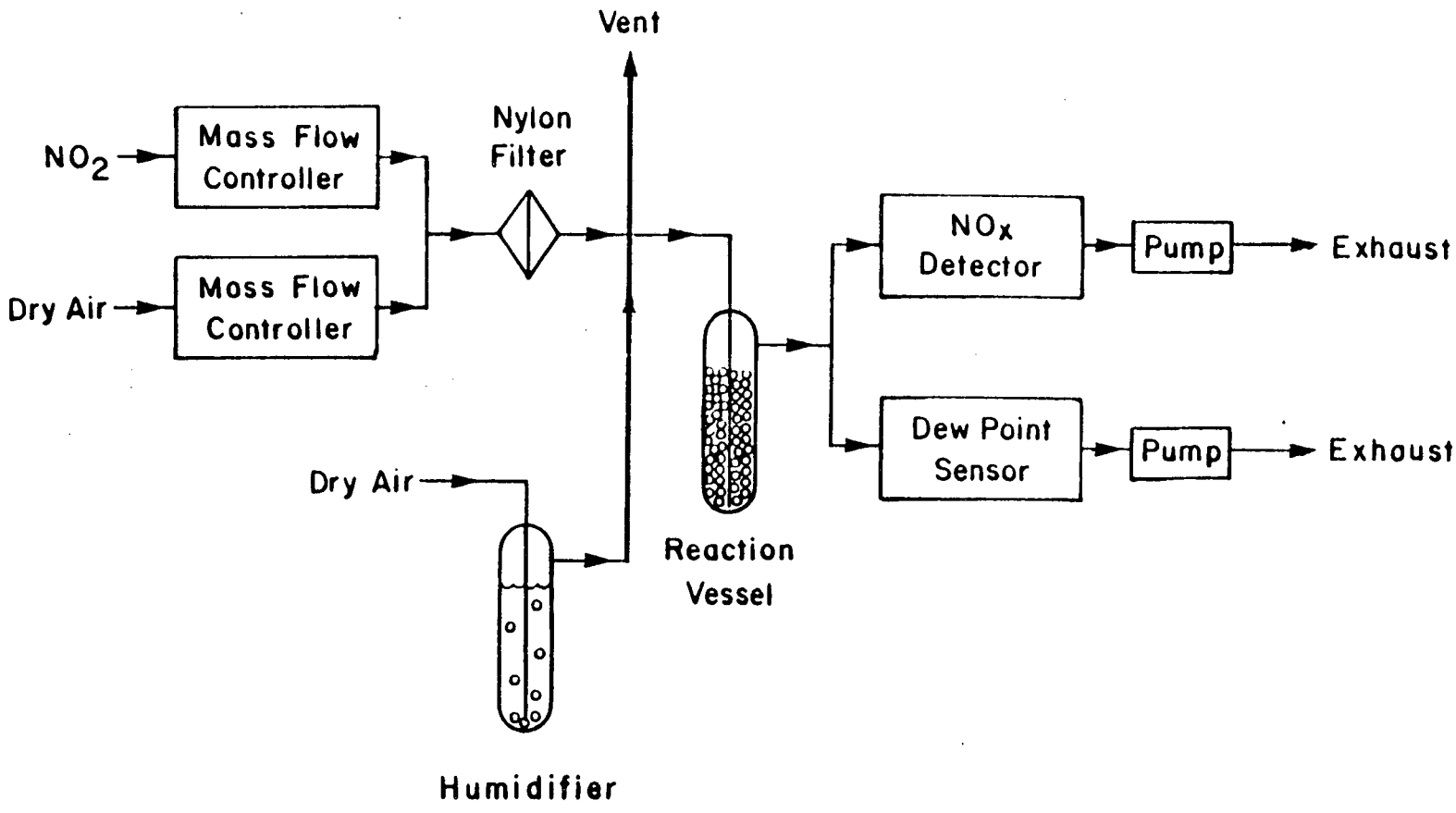

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Figure 1

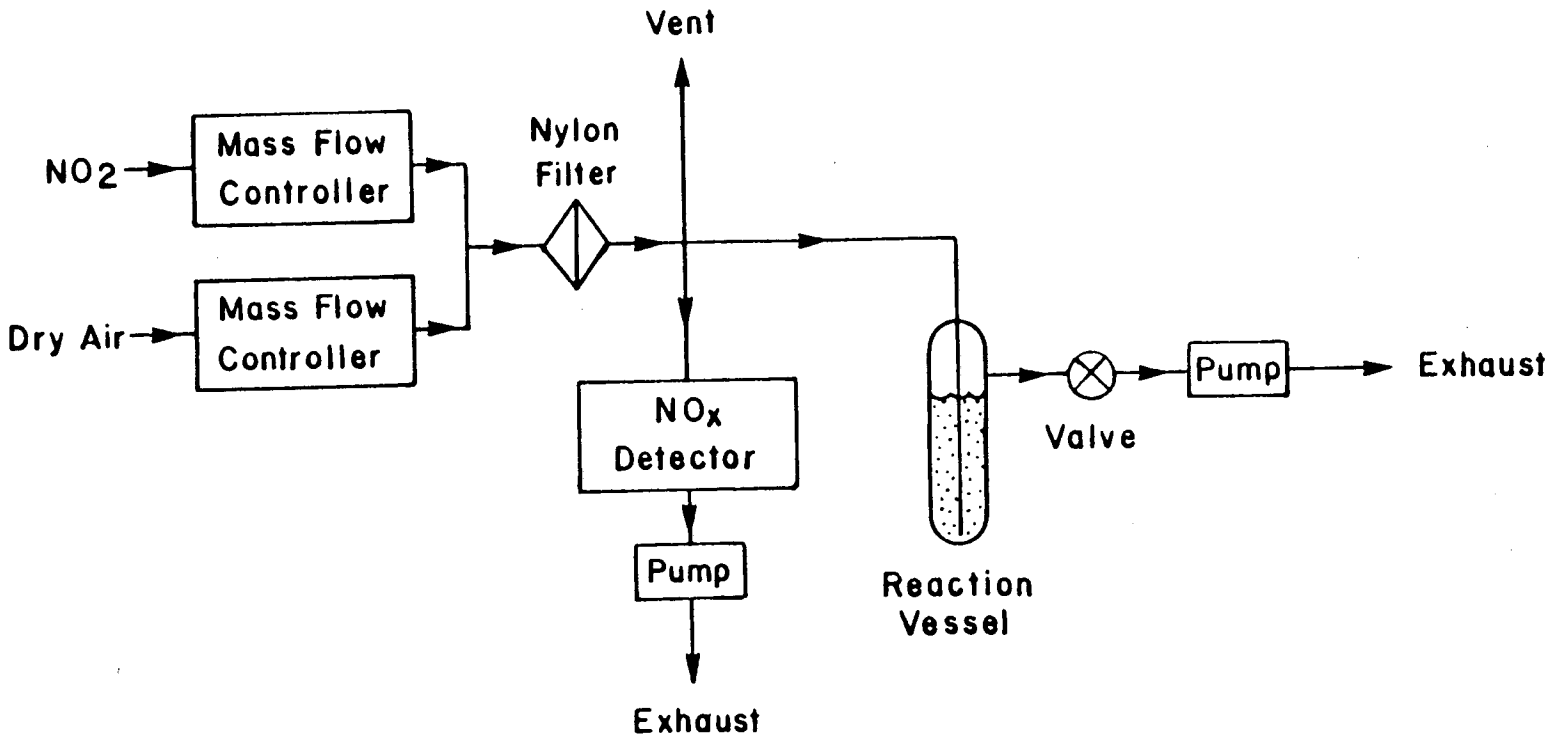

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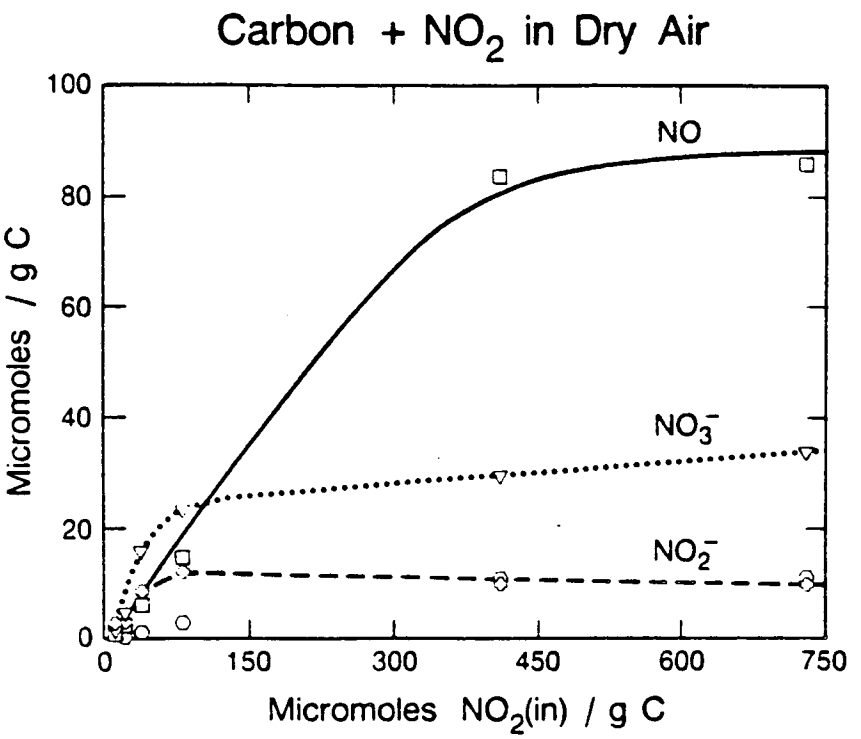
Figure 2



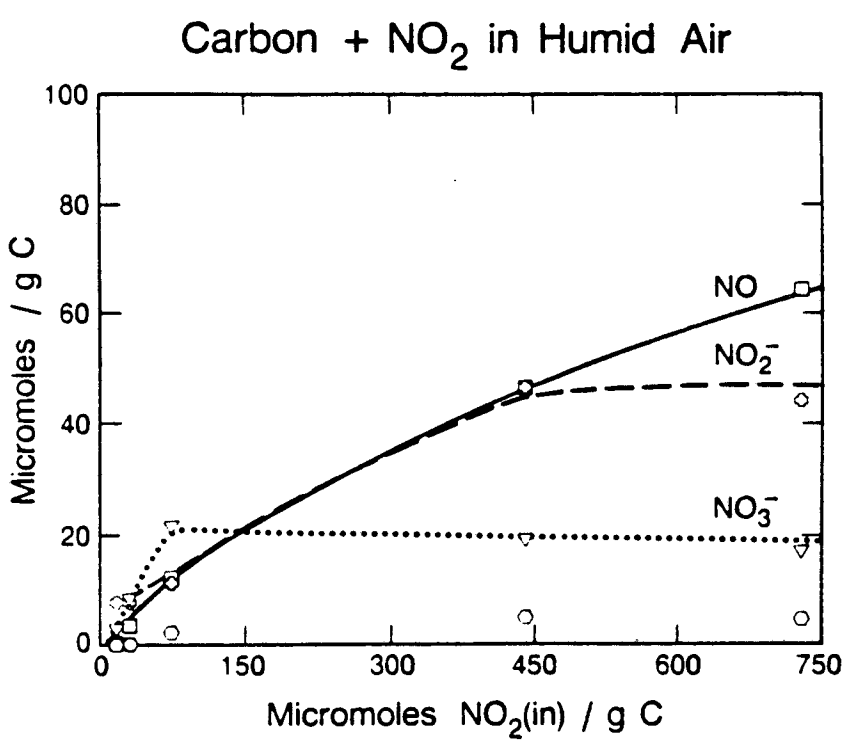


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Figure 3

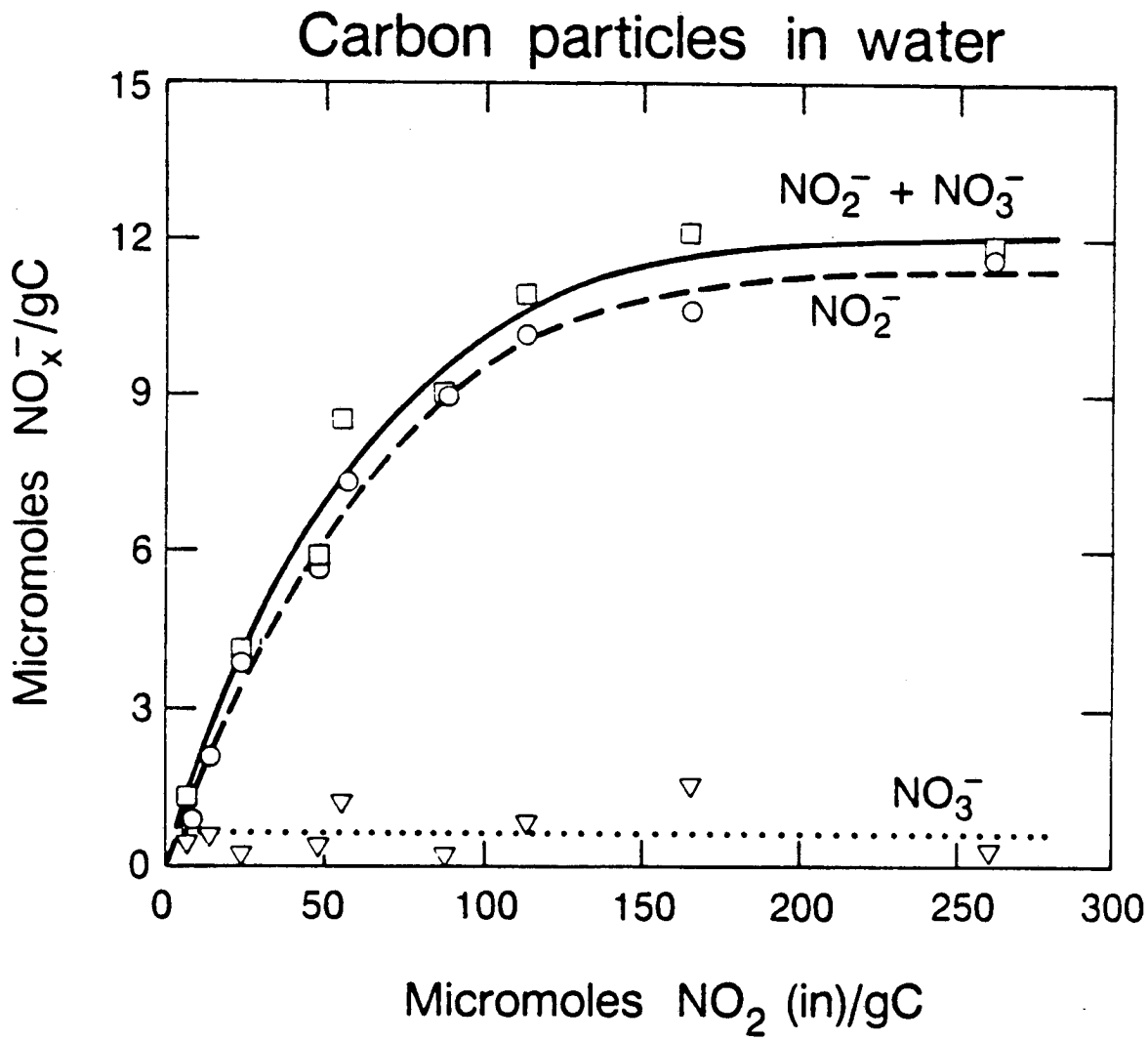

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Figure 4

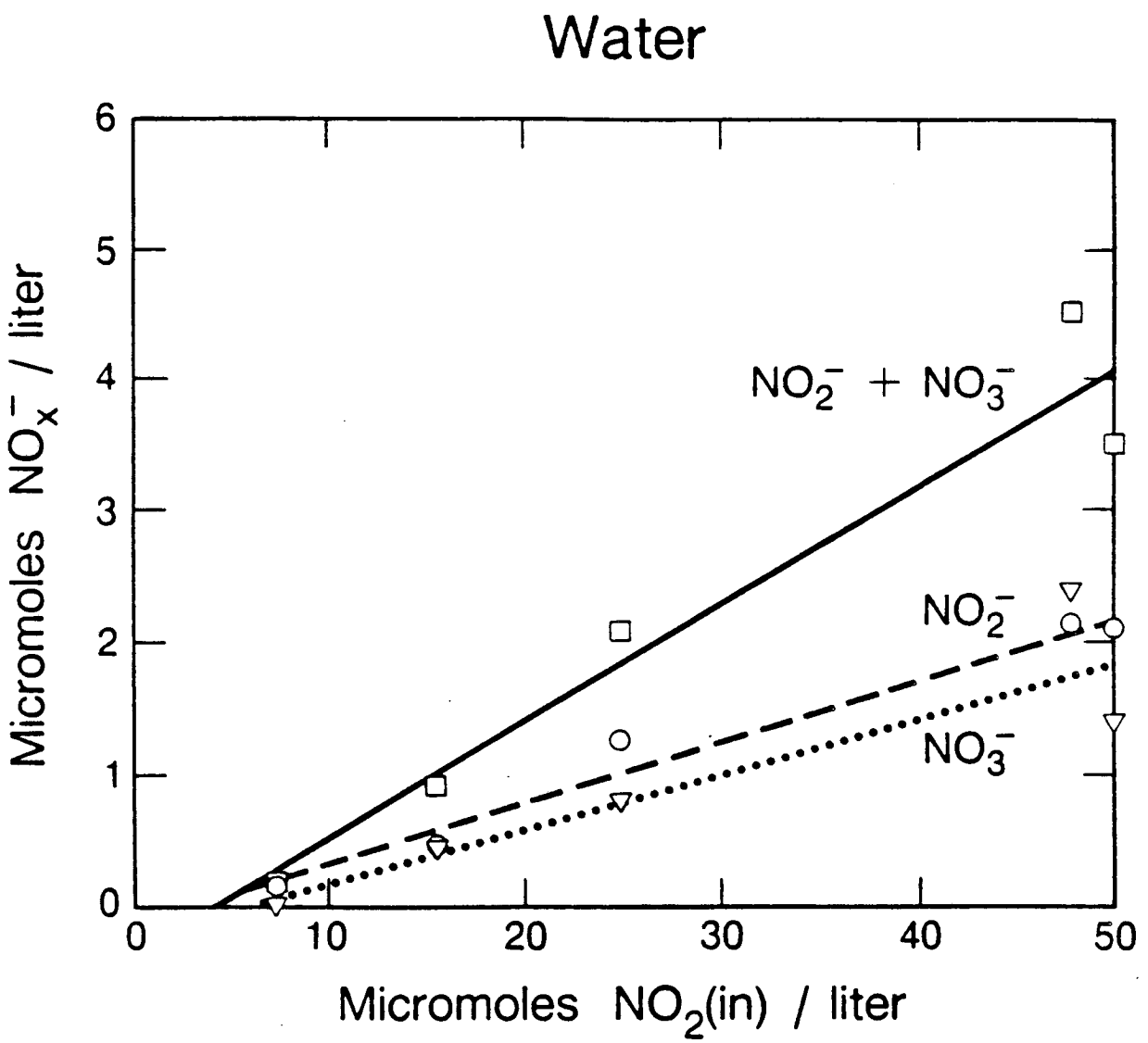

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Figure 5

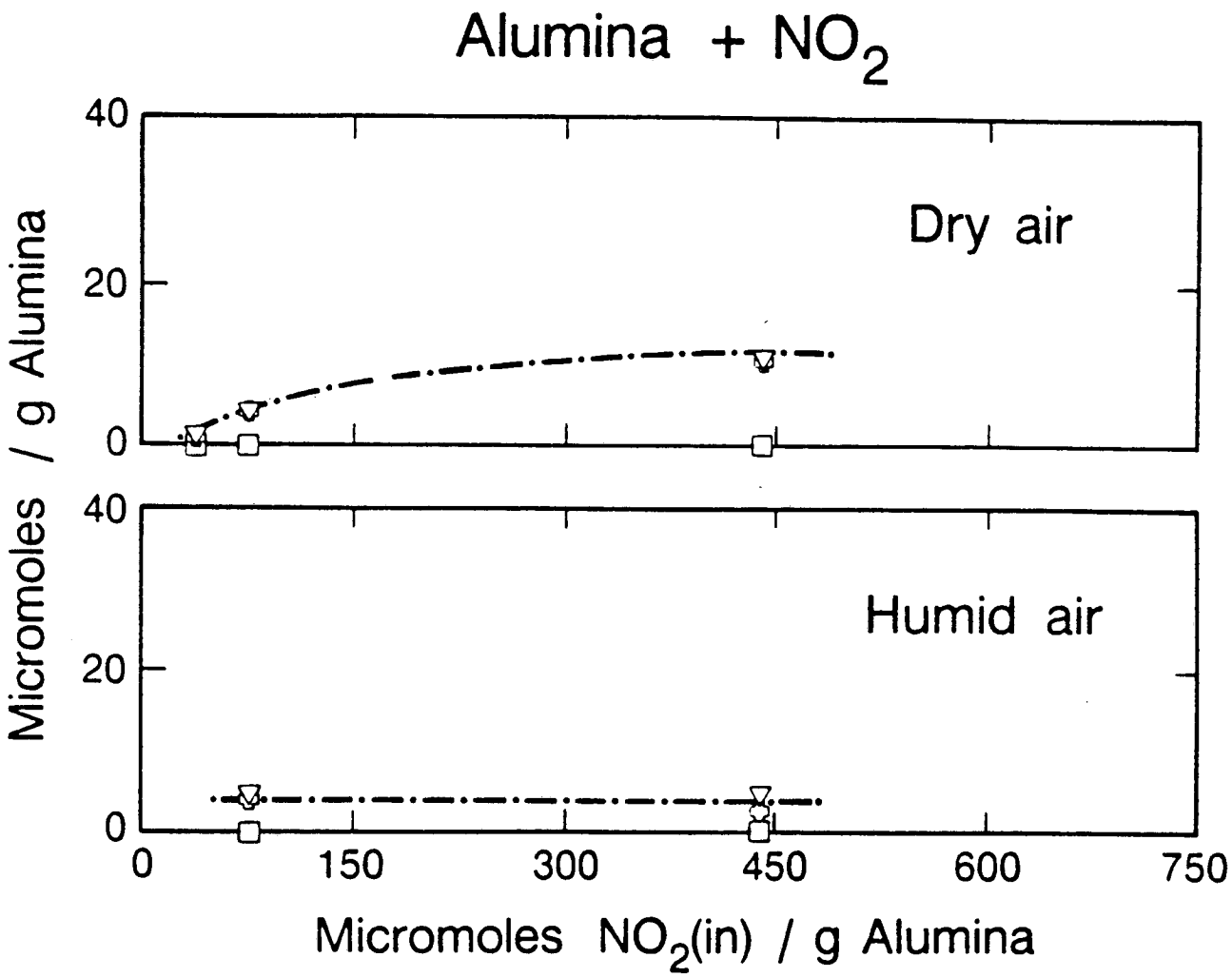

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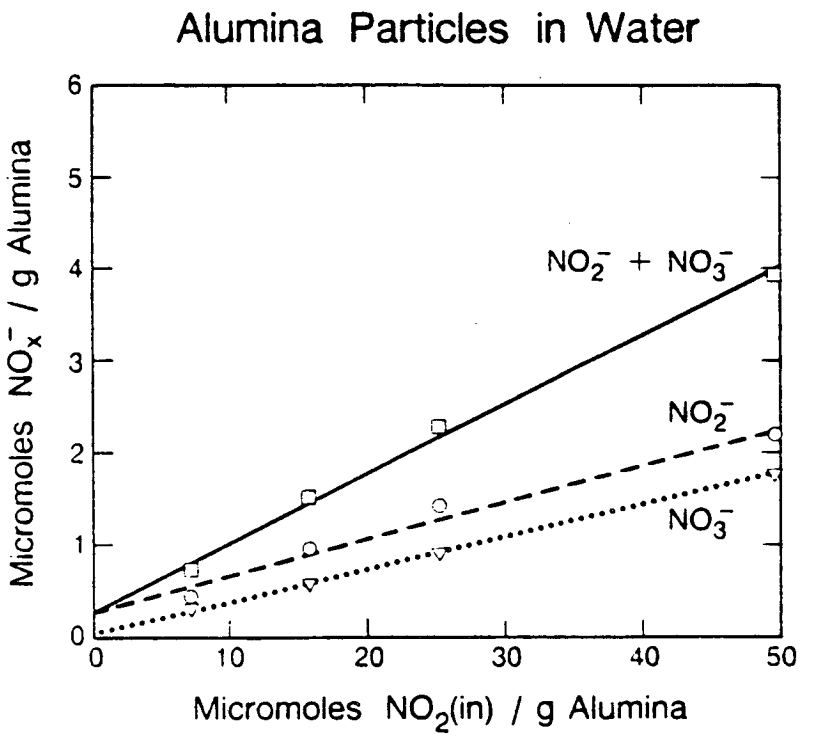
Figure 6



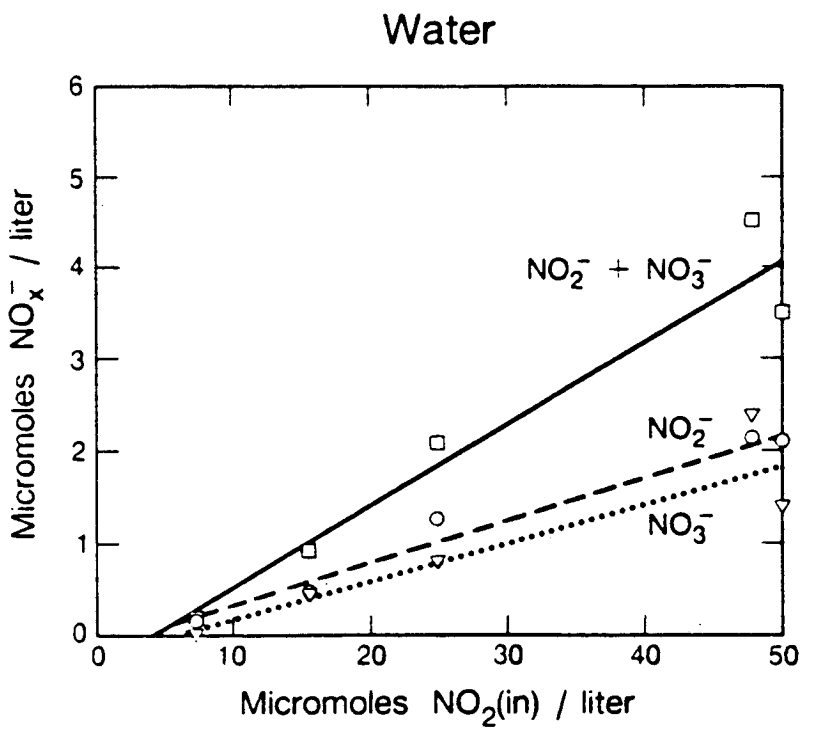


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Figure 7

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