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THE INTERACTION OF NITROGEN DIOXIDE WITH CARBON AND ALUMINA PARTICLES*

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Abstract

Laboratory studies have shown that NO_2 gas adsorbed without reaction on alumina particles. At $[NO_2] = 4$ ppm in air, 11-12% of the NO_2 was removed from the gas stream. The trapped gas appeared as equal amounts of NO_2^- and NO_3^- in water extracts of the particles. NO_2 reacted with activated carbon particles, forming NO, NO_2^-, and NO_3^-. The major product was NO_3^-. Carbon removed 95-96% of the NO_2 entering at 4 ppm in air. At this concentration of NO_2, the presence of water vapor in the air stream did not have much effect on the ability of either of these types of particles to interact with the gas. At $[NO_2] = 20$ ppm, alumina displayed the same behavior as at the lower gas concentration, except that its trapping capacity decreased in the presence of humid air. At the higher NO_2 concentration, carbon particles showed dramatically different product distributions, depending on the presence of water vapor. In dry air NO dominated, followed by NO_3^-. In humid air about equal concentrations of NO and NO_2^- were formed. These results are consistent with surface oxidation of carbon particles and formation of a surface nitrate. In the presence of water vapor, nitrous acid was formed from the interaction of NO and the surface nitrate.

Introduction

Because of the potential health effects of nitrogen oxides, their fate indoors has begun to receive attention recently. Some of these studies have indicated that surfaces of indoor materials can act as sinks for NO_2 (Spicer *et al.*, 1986, 1987) and as substrates for conversion of NO_2 to NO (D'Ottavio and Dietz, 1985; Nishimura *et al.*, 1986; Yanagisawa *et al.*, 1987). For example, Spicer *et al.* (1986, 1987) compared the ability of commonly used materials such as wall board and carpet to remove NO_2; and Nishimura *et al.* (1986) isolated a component of tatami (rush) mats that can convert NO_2 to NO.

Besides converting NO_2 to NO, surfaces may also generate nitrous and nitric acids in the presence of NO_2. A recent study of the behavior of reactive pollutants indoors indicated indirectly that surface reactions could be important for nitrogen oxides and oxy-acids (Nazaroff and Cass, 1986), but only gas-phase pollutants were monitored. Heterogeneous reactions involving NO_2 and water have been suggested to explain the formation of HNO_2 indoors (Pitts *et al.*, 1985).

The health consequences of the reaction pathways depend on the identity of the products. NO poses less of a risk than NO_2, so the ability of indoor surfaces to promote the conversion may be beneficial. However, both nitric and nitrous acids are quite reactive. HNO_3 corrodes surfaces, and HNO_2 can act as an oxidizing or reducing agent. Because

nitrous acid can react with ammonia to form nitrosamines, its presence indoors would present a health hazard. Under some conditions it may be photolyzed indoors to form OH radicals, thereby increasing the range of potential reactions. Not enough is known at present about heterogeneous NO_x chemistry to assess its role in the fate of nitrogen oxides indoors. A crucial and as yet unanswered question is whether significant amounts of HNO_2 and HNO_3 can be generated indoors through heterogeneous pathways.

Earlier work at Lawrence Berkeley Laboratory has shown that combustion appliances could raise NO_x levels up to two orders of magnitude above the outdoor level (Traynor *et al.*, 1983a,b). The ratio of NO to NO_2 indoors was always higher than outdoors (Traynor *et al.*, 1983a,b). When activated carbon was added to a room containing combustion appliances, the concentration of NO_2 dropped. Simultaneously the concentration of NO increased (Girman, 1986).

This paper describes laboratory studies of the interaction of NO_2 with activated carbon and alumina particles. Activated carbon may simulate combustion particles (soot) or dirty surfaces, while alumina may represent other types of porous surfaces. Besides monitoring NO and NO_2, we determined concentrations of nitrite and nitrate ions on the particles. The influence of water vapor on the distribution of reaction products has also been studied. The results have been interpreted with a mechanism that may apply to some other indoor surfaces.

Experimental Details

Figure 1 shows a schematic diagram of the apparatus. NO_2 (500 ppm in N_2) and clean dry air passed through mass flow controllers, mixed, and then passed through glass impingers that contained 20 mg chromatographic alumina (activity grade 1, from ICN Pharmaceuticals) or activated carbon particles (ground RB1, from American Norit Com-

pany) dispersed among 3-mm diameter glass beads. We measured NO and NO_2 concentrations downstream of the reaction vessel using a Thermo-Electron Model 14D/E Chemiluminescent NO-NO_2-NO_x Analyzer. The NO_2 level was 4 ppm or 20 ppm with total flow of 1 liter/min at atmospheric pressure. In some experiments we added humidified air just upstream of the reaction vessel. 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 wet-test meter.

After 10 min exposure to NO_2, the sample of particles was sonicated in 20 ml deionized water and filtered before determination of NO_2^- and NO_3^- by ion chromatography (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). We did not try to measure the amount of nitrous or nitric acid that may have desorbed from the surface of the particles.

Results and Discussion

Alumina. Table 1 shows the trapping capacity of the particles, and Fig. 2 presents the results as amount of each species as a fraction of NO_2 entering the reaction vessel. Alumina removed 12% of NO_2 when the initial concentration was 4 ppm. Less NO_2 was removed from the gas stream when water vapor was present. At 20 ppm about 5% of the NO_2 was removed from dry air; in humid air the amount trapped declined to 2%.

For both 4 and 20 ppm NO_2, the extracts showed approximately equal concentrations of NO_2^- and NO_3^-. This corresponds to reaction dissolution (Schwartz and White, 1981) according to Reaction (1):

$$2NO_2 + H_2O = HNO_2 + H^+ + NO_3^- . \quad (1)$$

Here the alumina or beads trapped some NO_2 that then reacted with water during extraction. The surface did not influence the ratio of nitrite to nitrate. When water vapor was present, it competed with NO_2 for adsorption sites and the total amount of NO_2 trapped declined. Most of the NO_2 passed through the reaction vessel unchanged. For all experiments the sum of the ionic products and the unreacted NO_2 gas was within 11% of the amount of NO_2 that entered the reaction vessel. This is reasonably good mass balance.

Carbon. The presence of carbon particles led to the generation of NO, which we detected downstream of the vessel. Table 2 contains the data on trapping capacity for carbon, and Fig. 3 expresses the results as amount of each species as a fraction of input NO_2. At $[NO_2] = 4$ ppm, the extract of the exposed particles contained about twice as much nitrate as nitrite, regardless of the presence of water vapor in the air stream, but less NO was generated in the humid experiments.

At $[NO_2] = 20$ ppm, the relative concentrations of nitrite and nitrate on the particles depended on the presence of water vapor. In dry air about three times more nitrate was formed than nitrite; NO was the dominant product. In humid air NO dropped while nitrite grew so that nitrite concentrations were more than double nitrate. Table 2 shows that the higher amounts of nitrite occurred at the expense of NO, for $[NO_2] = 20$ ppm in humid air.

We interpret these observations by suggesting that the carbon surface was oxidized by NO_2 to form an oxidized site, C_xO. This could oxidize NO_2, by forming a surface nitrate, causing nitrate ion to appear in the water extract:

$$NO_2 + C_x = NO + C_xO \quad (2)$$

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

At high concentrations of NO_2, another surface reaction occurred when water vapor was present in the gas stream, the interaction of NO with NO_2 to produce nitrous acid:

$$NO + NO_2 + H_2O = 2HNO_2 \,. \tag{4}$$

Nitric oxide could also react with the oxidized nitrogen already formed on the carbon surface to produce more nitrous acid:

$$2NO + C_xO{\cdot}NO_2 + H_2O = 3HNO_2 \,. \tag{5}$$

Both reactions (4) and (5) require NO and water at the surface. Reaction (5) explains the observed dominance of nitrite formation on the carbon surface that can occur when water vapor is present. If the NO_2 concentration is high enough to generate sufficient NO, then appreciable amounts of nitrous acid can be formed by Reaction (5). This reaction is analogous to a reaction that can occur on the walls of smog chambers (Besemer and Nieboer, 1985):

$$2NO + s{\cdot}HNO_3 = 3HNO_2 \,.$$

Here the surface is not carbon but the Teflon wall, and the surface species is adsorbed nitric acid.

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 Yanagisawa *et al.* (1987). They explained the source of NO in their experiments as decomposition of HNO_2, which was formed only in the presence of water vapor.

Mass balance. For alumina we found mass balance between products and reactants. For carbon particles we observed a product deficit that depended on the input NO_2 concentration. When the input NO_2 concentration was 4 ppm, unreacted NO_2 accounted for 4-5% of the initial amount; the reaction products NO, NO_2^-, and NO_3^-, and unreacted

NO_2 accounted for about two-thirds of the amount of NO_2 entering the reaction vessel, but we do not know the identity of the remainder. At 20 ppm unreacted NO_2 and the reaction products NO, NO_2^-, and NO_3^- accounted for only about 30% of the initial NO_2. One possible explanation is that not all the surface species were removed during extraction and thus were not detected. Another possibility is that gas-phase reaction products such as HNO_2 or HNO_3 were not detected by the NO_x analyzer.

Summary and Conclusions

These experiments show that NO_2 interacted quite differently for alumina and carbon particles. Our observations may represent two ways surfaces can influence indoor NO_x chemistry. Relative amounts of NO_2^- and NO_3^- depended on the type of surface, the amount of NO_2, and the presence of water vapor. Alumina particles adsorbed NO_2, which appeared as equal amounts of nitrite and nitrate ions in the water extract. This behavior is consistent with reactive dissolution of adsorbed NO_2. In the presence of water vapor, less NO_2 was trapped on alumina. However, NO_2 reacted with carbon particles, forming NO in addition to nitrite and nitrate ions. Carbon particles removed more NO_2 from the gas stream than alumina.

Our results suggest that NO_2 oxidized the surface of carbon particles while being reduced to NO. The amounts of nitrite and nitrate extracted from the particles depended on the initial concentration of NO_2 and the presence of water vapor. For $[NO_2] \leq 4$ ppm, about twice as much nitrate was formed as nitrite. At 20 ppm nitrite dominated only when water vapor was present; otherwise nitrate was the main product. These findings are consistent with the formation of a surface oxide that can convert NO_2 adsorbed on it to either nitric or nitrous acid, depending on the amounts of NO and H_2O available.

Implications for indoor chemistry. This research shows that NO_2 can be removed

from indoor air at surfaces by at least two pathways. The first is adsorption without chemical reaction, as observed on alumina. The second is chemical reaction, observed with carbon particles, in which NO was formed in addition to nitrite and nitrate ions. This work suggests that some indoor surfaces may be able to transform NO_2 to NO, and to nitrous and nitric acids. If these reactive acids desorb from the surfaces, they may continue to react in the indoor environment.

References

Besemer, A.C. and Nieboer, H. (1985) The wall as a source of hydroxyl radicals in smog chambers, *Atmos. Environ.* 19, 507-513.

D'Ottavio, T.W. and Dietz, R.N. (1985) Multizone NO_2 Reactivity in a Single Family Home. Brookhaven National Laboratory Report BNL 37497.

Girman, J. (1986) Personal communication.

Nazaroff, W.W. and Cass, G.R. (1986) Mathematical modeling of chemically reactive pollutants in indoor air, *Environ. Sci. Technol.* 20, 924-934.

Nishimura, H., Hayamizu, T. and Yanagisawa, Y. (1986) Reduction of NO_2 to NO by rush and other plants, *Environ. Sci. Technol.* 20, 413-416.

Pitts, Jr., J.N., Wallington, T.W., Bierman, H.W. and Winter, A.T. (1985) Identification and measurement of nitrous acid in an indoor environment, *Atmos. Environ.* 19, 763-767.

Schwartz, S.E. and White, W.H. (1981) Kinetics of Reactive Dissolution of Nitrogen Oxides into Aqueous Solution, in *Trace Atmospheric Constituents: Properties, Transformations, and Fates, Wiley, New York, pp. 1-116.*

Spicer, C., Coutant, R.W. and Ward G.F. (1986) Investigation of Nitrogen Dioxide Removal from Indoor Air. GRI Report GRI-86/0303.

Spicer, C.W., Coutant, R.W., Gaynor, A.J. and Billick, I.H. (1987) Rates and Mechanisms of NO_2 Removal from Indoor Air by Residential Materials in *Proceedings of the 4th International Conference on Indoor Air Quality and Climate, Berlin (West), 17-21 August 1987, Vol. 1,* Institute for Water, Soil and Air Hygiene, Berlin, pp. 371-375.

Traynor, G.W. *et al.* (1983) Indoor Air Pollution Due to Emissions from Unvented Gas-Fired Space Heaters: A Controlled Field Study. Lawrence Berkeley Laboratory Report LBL-15130.

Traynor, G.W. *et al.* (1983) Indoor Air Pollution from Portable Kerosene-Fired Space Heaters, Wood Burning Stoves and Wood Burning Furnaces, in *Proceedings, Residential Wood and Coal Combustion,* Air Pollution Control Association, Pittsburgh, pp. 253-263.

Yanagisawa, Y., Fasano, A.M., Spengler, J.D. and Billick, I.H. (1987) Removal of Nitrogen Dioxide by Indoor Materials, in *Proceedings of the 4th International Conference of Indoor Air Quality and Climate, Berlin (West), 17-21 August 1987, Institute for Water, Soil and Air Hygiene, Berlin, pp. 376-380.*

Table 1. Alumina + NO_2
Amounts of Nitrogenous Species Observed[a]

Particle	NO_2^-	NO_3^-	NO	NO_2 (out)[b]
	Micromoles/g particles			
	[NO_2 in] = 4 ppm			
Dry air	4.8	4.2	0	73
Humid air	4.1	4.0	0	68
	[NO_2 in] = 20 ppm			
Dry air	10.55	9.9	0	388
Humid air	2.35	4.0	0	432

[a] Air containing NO_2 passed through 20-mg particles for 10 minutes.

[b] Total amount of NO_2 detected downstream of the reaction vessel, normalized to mass of particles.

Table 2. Carbon + NO_2
Amounts of Nitrogenous Species Observed[a]

Particle	NO_2^-	NO_3^-	NO	NO_2 (out)[b]
	Micromoles/g particles			
	[NO_2 in] = 4 ppm			
Dry air	10.9	21.0	14.4	3.0
Humid air	13.4	25.4	10.8	3.8
	[NO_2 in] = 20 ppm			
Dry air	9.6	28.8	83.5	10.5
Humid air	44.0	18.6	46.0	4.8

[a]Air containing NO_2 passed through 20-mg particles for 10 min.

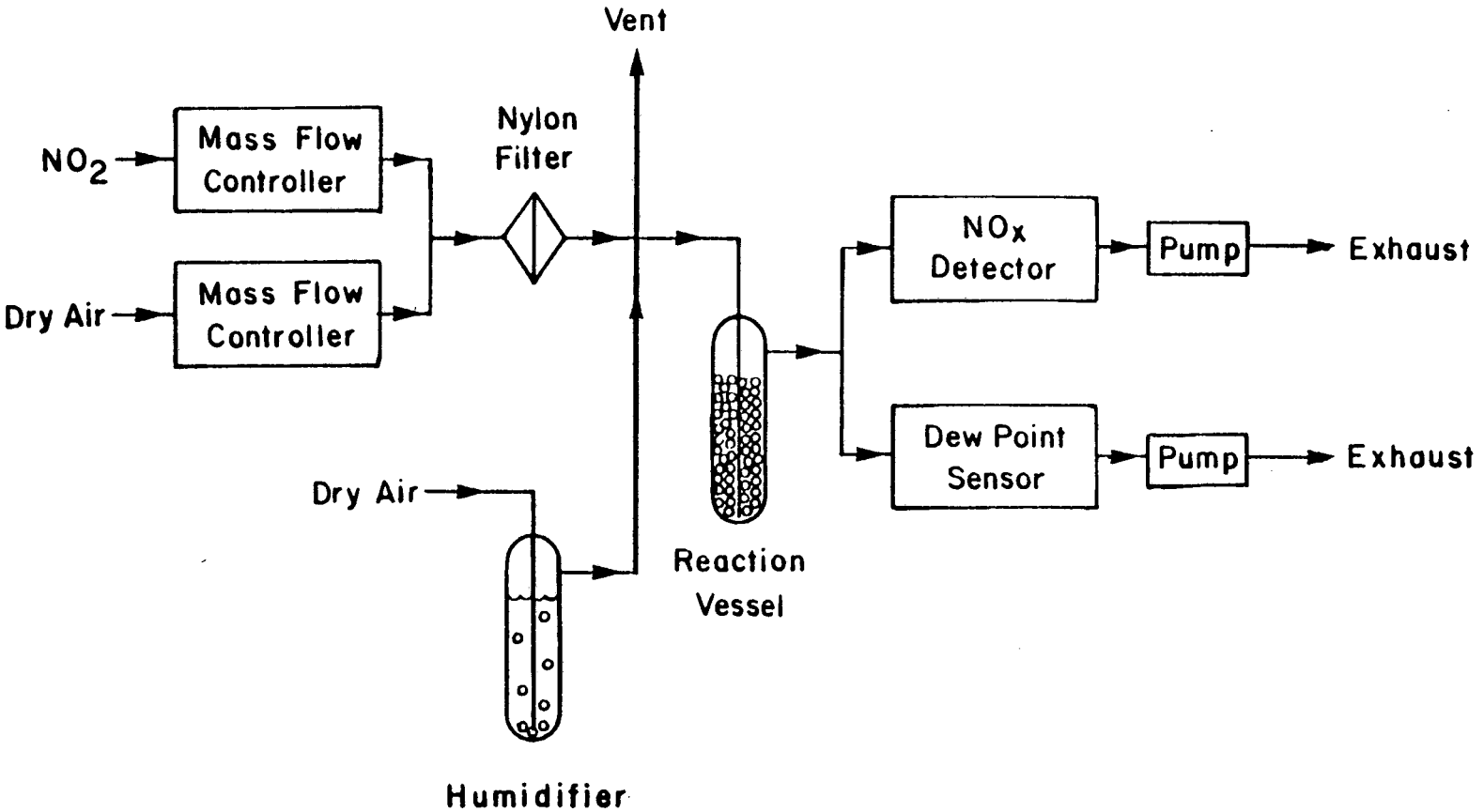
[b]Total amount of NO_2 detected downstream of the reaction vessel, normalized to mass of particles.

Figure Captions

Figure 1. Schematic diagram of the apparatus used to study the interaction of carbon and alumina particles in air. (XBL 8712-5307)

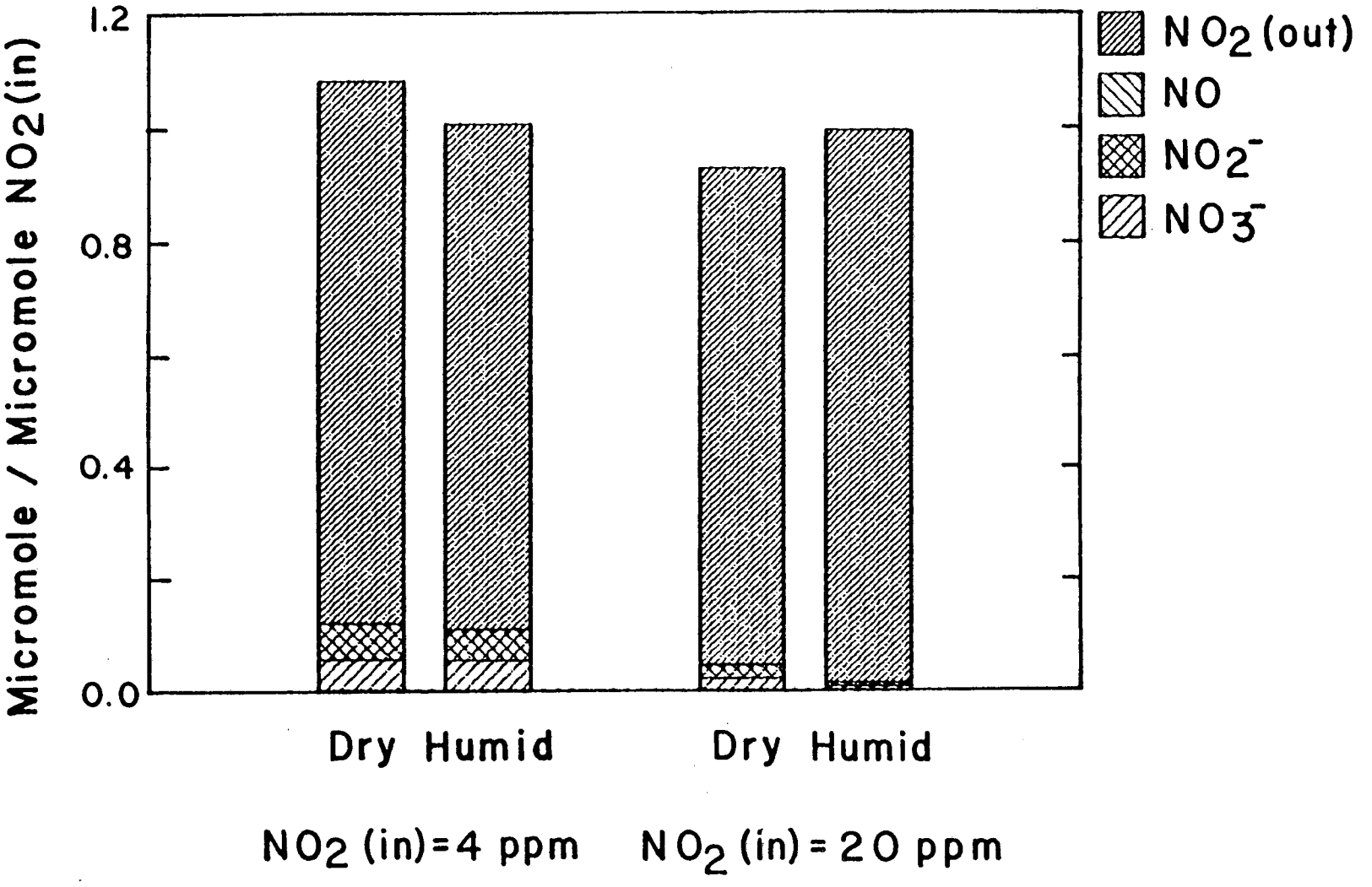
Figure 2. Interaction of NO_2 with alumina particles. Amounts of nitrogenous species as fractions of the amount of NO_2 that entered the reaction vessel. For experiments conducted in humid air, the relative humidity was 50%. (XBL 8712-5408)

Figure 3. Interaction of NO_2 with carbon particles. Amounts of nitrogenous species as fractions of the amount of NO_2 that entered the reaction vessel. For experiments conducted in humid air, the relative humidity was 50%. (XBL 8712-5409)



XBL 8712-5307

Figure 1



XBL 8712-5408

Figure 2

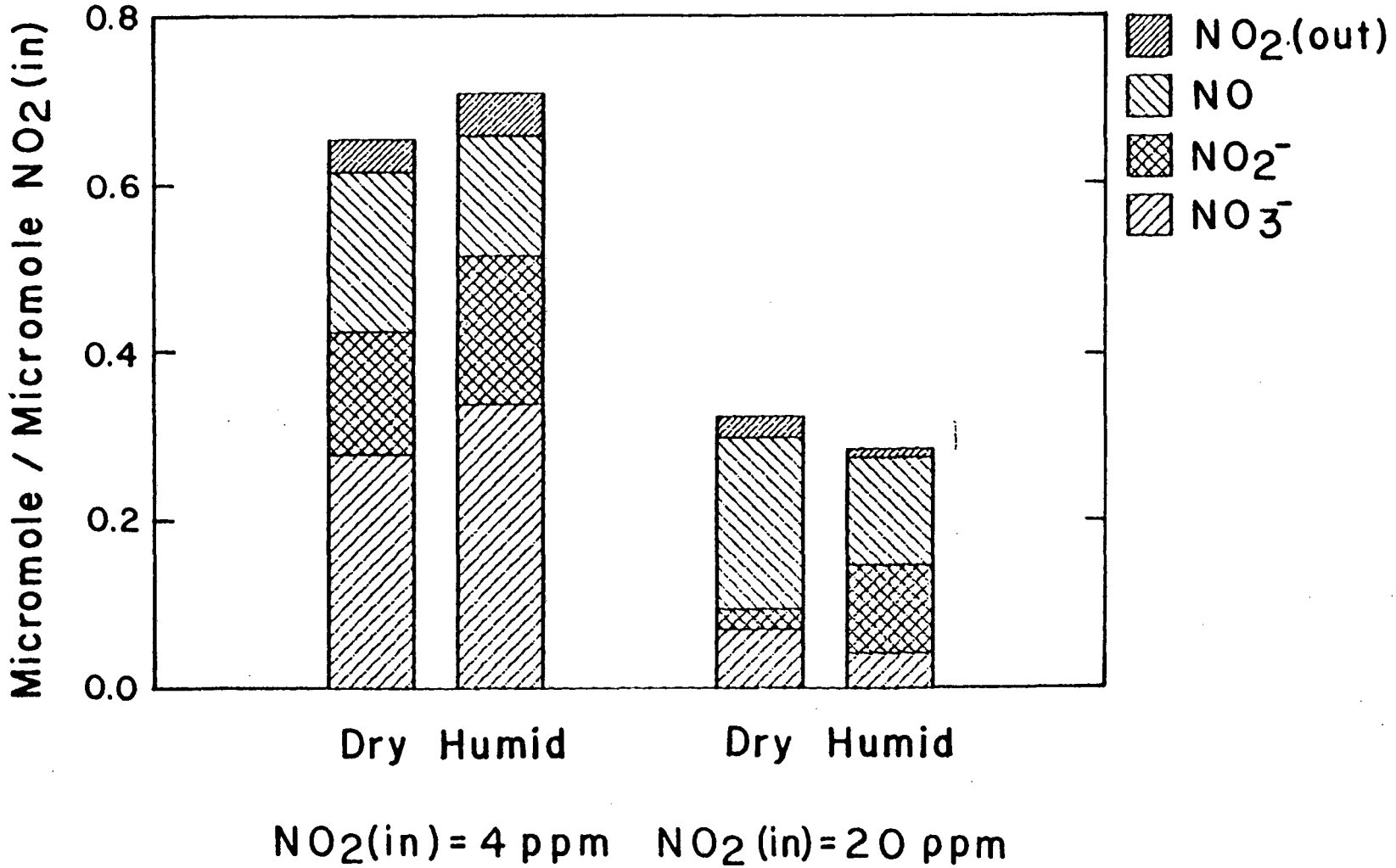


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Figure 3

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