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HETEROGENEOUS REACTIONS OF NITROGEN OXIDES IN SIMULATED ATMOSPHERES

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HETEROGENEOUS REACTIONS OF NITROGEN OXIDES IN SIMULATED ATMOSPHERES

by

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ABSTRACT

A laboratory study has been conducted on heterogeneous reactions of nitrogen dioxide and nitric oxide to evaluate their potential role in reactions in polluted urban atmospheres. The results of this study suggest that nitrogen dioxide decomposes on a wide variety of solids likely to be found in urban environments. Measured reaction rates indicate these processes can be important in the atmosphere. Humidification of reaction mixtures leads to increased reactivities. It is concluded that heterogeneous reactions in the atmosphere are unimportant for the oxidation of nitric oxide.

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SECTION 1

INTRODUCTION

In recent years, considerable attention has been given to the study of aerosols in polluted urban atmospheres. This interest has arisen because of potential health effects, as well as the possibility that aerosols may play an active role in the physical and chemical processes taking place in the atmosphere. A well-known example of the latter phenomena is the oxidation of sulfur dioxide in water droplets (1-4).

Previously, through the use of a simple model and data from the catalyst literature, the conditions were outlined under which selected heterogeneous reactions involving urban aerosols could compete with gas phase reactions that are known or are postulated to occur (5). Although the model calculations suggested heterogeneous reactions could compete with homogeneous gas phase reactions, the major limitation to these conclusions lay in the fact that the literature data used were generally obtained from experiments conducted at considerably higher temperatures and reactant concentrations than those of interest in polluted atmospheres.

In this paper, results are presented from experiments, conducted under near-atmospheric conditions, on heterogeneous reactions of oxides of nitrogen. A wide variety of solids are found to be capable of decomposing NO_2. This is especially true when the reaction mixture is humidified (40-50% relative humidity). In fact, some materials found to be unreactive in the absence of added moisture reacted readily when water vapor was added. In the case of NO, except for reactions over MnO_2, only minimal activity was observed, and it was concluded that heterogeneous reactions of this gas are unimportant in polluted atmospheres.

Products formed during the heterogeneous decomposition of NO_2 consisted primarily of strongly adsorbed surface nitrogen compounds and gaseous NO.

Overall, the heterogeneous processes led to a substantial reduction of NO_x (i.e., $NO + NO_2$) in the gas phase.

Quantitatively, projection of our laboratory results for NO_2 to the atmosphere leads to the conclusion that NO_2 decomposition on the surface of airborne particles in polluted atmospheres can occur with a lifetime of ~0.5 to 5 hours. This compares favorably with observed NO_2 decay times of several hours (6,7) and suggests the potential importance of heterogeneous processes for the removal of NO_2. Moreover, although our results indicate only minimal heterogeneous activity toward NO, the latter species is rapidly converted to NO_2 in polluted atmospheres (7,8). Consequently, heterogeneous processes could also be important in the removal of NO_x emitted as NO.

SECTION 2

EXPERIMENTAL

MATERIALS

Solids used in the present study are listed in Table 1, along with their BET surface areas. These solids were supported on various pyrex cylinders or helices ranging from ∿1 cm in diameter x 10 cm long to 3.2 cm in diameter x 40 cm long. The helices were constructed from 3-mm pyrex rod with ∿3 mm between loops. The appropriate cylinder or helix was prepared by spraying a fluid suspension of the desired solid (water, acetone, alcohol, or mixtures of these were used as the fluid carrier) onto the cylinder or helix and allowing the wet film to dry in air before use. Typically, the net weight of the dry film was several hundred milligrams. The coated cylinder or helix was inserted concentrically into one of two cylindrical flow reactors and further dried under vacuum ($<10^{-2}$ Torr[1]) for 1 to 3 hours or in some cases overnight. (In the case of H_2SO_4, a cylinder was coated with the concentrated acid, inserted directly into the reactor, and used immediately without extensive evacuation.)

Gases used in these studies were obtained from Matheson. Gases were used as received, except for NO-N_2 or NO-Ar mixtures. The latter gases were passed through a molecular sieve column before use to decompose any residual NO_2. Various gas mixtures were prepared or humidified through the use of procedures described elsewhere (9,10).

REACTORS

Two different cylindrical flow reactors were used in these studies (10,11). The reactors differed principally in their modes of reactant and product analysis. The first reactor (11), designated reactor F (fluorescence detection), was used for detailed rate studies of the heterogeneous

[1] Torr = 1.33 22 E + 02 Newton/meter^2

TABLE 1. SOLIDS STUDIED AND PHYSICAL ADSORPTION SURFACE AREAS*

Material	Source	Area (m^2/g)
Al_2O_3†	Analabs, activated alumina no. 214-77	196
Al_2O_3	J.T. Baker, no. 0537	233 ± 7‡
Wood charcoal powder	Allied Chemical, no. 1567	40.7
Cement†	California Portland Cement	17.9
PbO	J.T. Baker, no. 2338 yellow powder	20.1
MnO_2	ROC/RIC, MN-37	109 ± 10‡
Fly ash	Western Coal Burning Power Plant	15.2
ZnO	New Jersey Zinc, SP500	22.2
Cu_2O	ROC/RIC, CU-33 red 99%	5.5 ± 3.0 ‡
Fe_2O_3	Commercial jeweler's rouge	27.3
Sand†	Baker and Adamson, no. 2171	7.3
V_2O_5	ROC/RIC V-15	14.1

*BET measurements using N_2 at -196 C, except for the case of MnO_2 where CO_2 was used at -78C. The following materials were also used, but their BET areas were not measured: $(NH_4)_2SO_4$, Al (powdered metal), CaO, $PbCl_2$, crushed oleander leaves, H_2SO_4, and soil (loam).

†Crushed to a fine powder before use. Other materials used as received.

‡Errors derived from estimates of error in reading pressure devices, i.e., Matheson 0-760 and voltmeter used with pressure transducer plus an 0.01 V/min drift noted.

decomposition of NO_2. Generally, NO_2-Ar mixtures were used in this reactor. An argon ion laser (488 nm) excited NO_2 fluorescence along the cylinder axis. This fluorescence was detected at right angles to the laser beam by a photomultiplier equipped with narrow slits. A narrow uncoated strip running the length of the cylinder on which the solid was supported permitted the fluorescence to reach the photomultiplier tube. The coated cylinder (with the uncoated strip) was mounted on a platform inside the reaction chamber. This platform was constructed such that the cylinder could be moved back and forth along the direction of the cylinder axis (11). This feature, along with the narrow laser excitation beam and the narrow slits on the photomultiplier, permitted the determination of NO_2 concentration gradients along the cylinder axis. The latter data, in conjunction with a mathematical analysis of the system (11, 12), were used to obtain the gas-solid reaction rate constants.

In the second reactor (10), designated reactor A (absorption detection), NO_2 was monitored by its optical absorption (480 nm) along the cylinder axis. A chopped dual beam optical scheme was used for this purpose. Unlike reactor F, the coated cylinder (or helix, which was also used in this reactor) was not movable, and spatial discrimination of NO_2 along the cylinder axis was not obtained. However, other reactants or products (i.e., NO and O_2) and inert gases (i.e., N_2 and Ar) could be analyzed before entry into or after exit from the cylinder. Reactant or product NO was determined through a chemiluminscent reaction with O_3, while gas chromatography was used for the other gases (10).

The effects of moisture and simulated solar ultraviolet and visible radiation could be determined in reactor A. Reaction mixtures were humidified through the use of techniques similar to those described by Cheng et al. (9) and Hedgpeth et al. (10). A bank of daylight-type fluorescent lights surrounding the (pyrex) reactor was used to simulate solar radiation. In the latter experiments, the coated helix was used, since this configuration allowed for a more even light distribution inside the chamber. Additional details on this system are given by Hedgpeth et al. (10), while the procedures used for data analysis are described by Siegel et al. (12).

ANALYSIS OF SURFACE NITROGEN COMPOUNDS

In several experiments, the coated cylinders were removed from the reaction chamber upon completion of the experiment, washed with distilled water, and filtered, and the filtrate analyzed for NO_x^- (i.e., NO_2^- or NO_3^-). A wet chemical procedure or nitrate ion electrode (Beckman, model no. 39618) was used for NO_3^- analysis (12-13), while wet chemical techniques were employed for NO_2^- analysis (13). The latter test gives a positive result for both NO_2^- and gaseous NO_2 dissolved in solution. Consequently, the NO_2^- test cannot distinguish between adsorbed NO_2 and NO_2^-. An additional uncertainty in the analyses of NO_x^- lies in the possibility that NO_x^- could be formed from adsorbed NO_2 during the washing procedures.

In some cases, these experiments were run for short periods of time to avoid poisoning heterogeneous activity. In these experiments, the solid was removed in segments, washed, and filtered, and the individual filtrates analyzed for NO_x^-.

SECTION 3

RESULTS

DECOMPOSITION OF NO_2 IN DRY REACTION MIXTURES

Reactivities of Charcoal, Al_2O_3, and MnO_2

A series of experiments was conducted through the use of reactor F and NO_2-Ar mixtures to determine quantitatively the heterogeneous decomposition rates of NO_2 over charcoal, Al_2O_3, and MnO_2. Earlier experiments in reactor A had demonstrated that this reaction readily occurs in N_2-O_2-NO-NO_2 mixtures yielding surface nitrates, nitrites, and gaseous NO. Gas mixtures consisted of 0.05 to 5% NO_2 in Ar, with total pressures of 1 to 100 Torr. The NO_2 concentration, detected by laser-excited fluorescence, was measured as a function of distance along the axis of the cylindrical reactor.

Data from these experiments were analyzed through the use of model described by Stewart and Judeikis (11) and Siegel et al. (12). In this model, the rate of change of the NO_2 concentration at the walls is written in terms of duffusion of gaseous NO_2 to and from the walls of the coated cylinder, the gaseous flow rate through the cylinder, and the ratio k_r/k_c, where k_r is the rate constant for removal of NO_2 from the gas phase and k_c is the gas-solid collision rate constant. (Thus, k_r/k_c is the fraction of gas-solid collisions leading to removal of NO_2 from the gas phase.) Integration of the resulting differential equation yields a Bessel series solution for the spatial distribution of gaseous NO_2 in the cylinder. This series reduces to a single exponential term for large distances along the cylinder axis.

Results from a typical experiment with charcoal are illustrated in Figure 1. The data shown by the solid curve in the figure were calculated through the use of experimental parameters and a value of 0.0016 for k_r/k_c. An example of the exponential decay with distance at large distances is illustrated in Figure 2 for data from an experiment with MnO_2. The solid

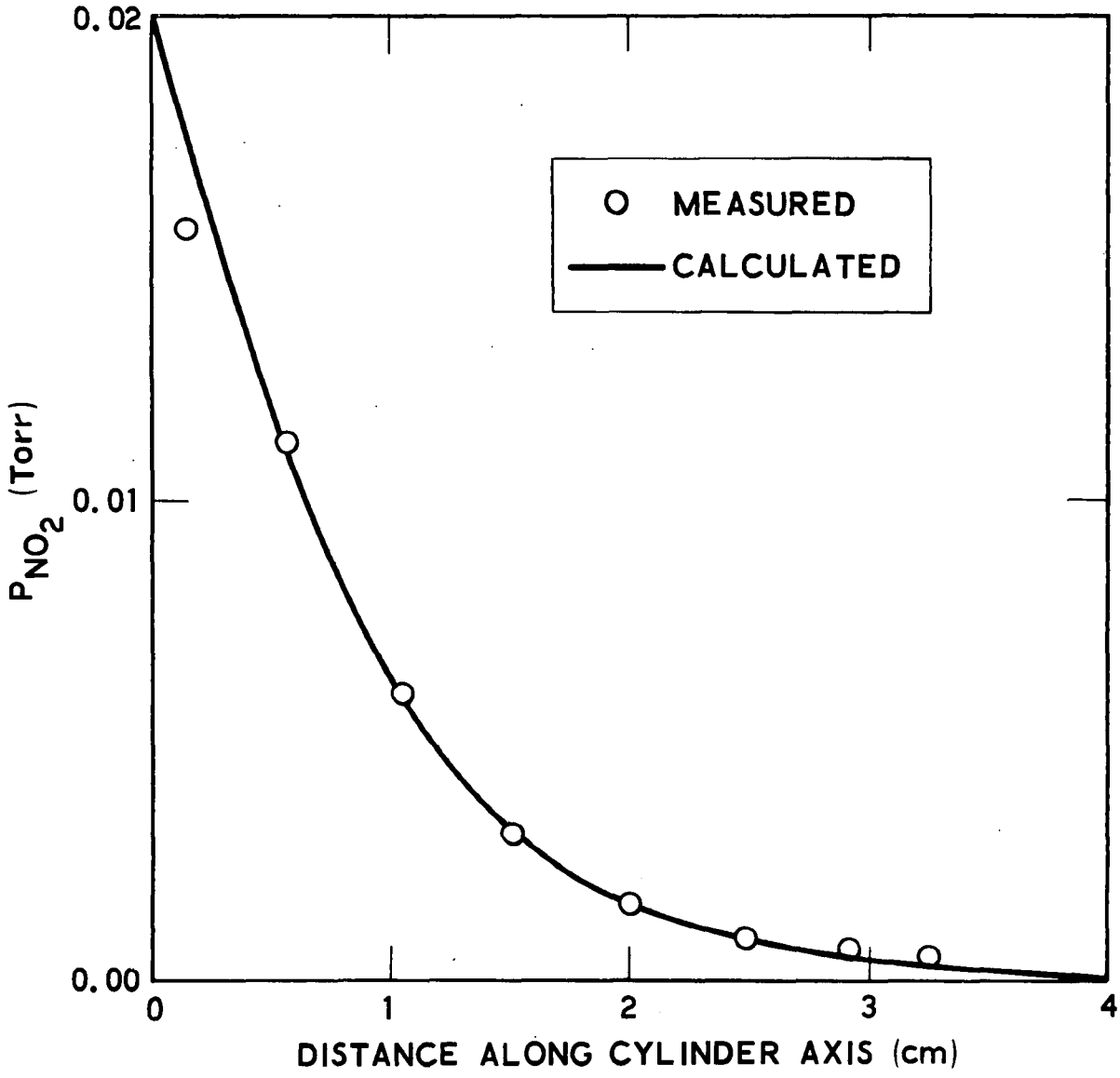

Figure 1. Decomposition of NO_2 over charcoal. Experimental conditions: 0.2% NO_2 in Ar (10 Torr total pressure), 23 ± 1 C, 1.7 cm^3/sec flow, and a cylinder radius of 0.95 cm.

curve in Figure 2 represents the limiting slope calculated for large distances through the use of the experimental parameters, a value of k_r/k_c of 0.0003, and the model described above.

Data from experiments in reactor F were analyzed through the use of the method indicated in Figure 2; i.e., the exponential decay with distance was fitted through the use of limiting slopes calculated from the model described by Stewart and Judeikis (11) and Siegel et al. (12). In general, slopes differing by about ±25% from the best fitting slope would give noticeable deviations from the experimental limiting slope. Examples of experimental reproducibility for NO_2 decomposition over charcoal as a function of cylinder radius, total pressure, and flow rate are given in Table 2. The average value of k_r/k_c for charcoal in these experiments was found to be 1.6×10^{-3} (standard deviation = $\pm 0.5 \times 10^{-3}$). Results from similar experiments with MnO_2 exhibited somewhat greater variations, and it is concluded that k_r/k_c = 0.3 to 3×10^{-3}, whereas for Al_2O_3 (Analabs) it is found that $k_r/k_c = (3 \pm 1) \times 10^{-4}$.

TABLE 2. DECOMPOSITION OF NO_2 OVER CHARCOAL*

Cylinder Radius (cm)	P_{total} (Torr)	Flow Rate (cm^3/sec)	$10^3 \times \frac{k_r}{k_c}$
0.50	1.0	17.5	2.6
	9.9	25.0	1.2
	10.2	16.5	1.4
0.95	1.0	0.4	1.5
	1.0	0.4	1.0
	9.8	1.7	1.6
	10.3	1.7	1.6

*Reaction mixture: 0.2% NO_2 in A (23 ± 1 C).

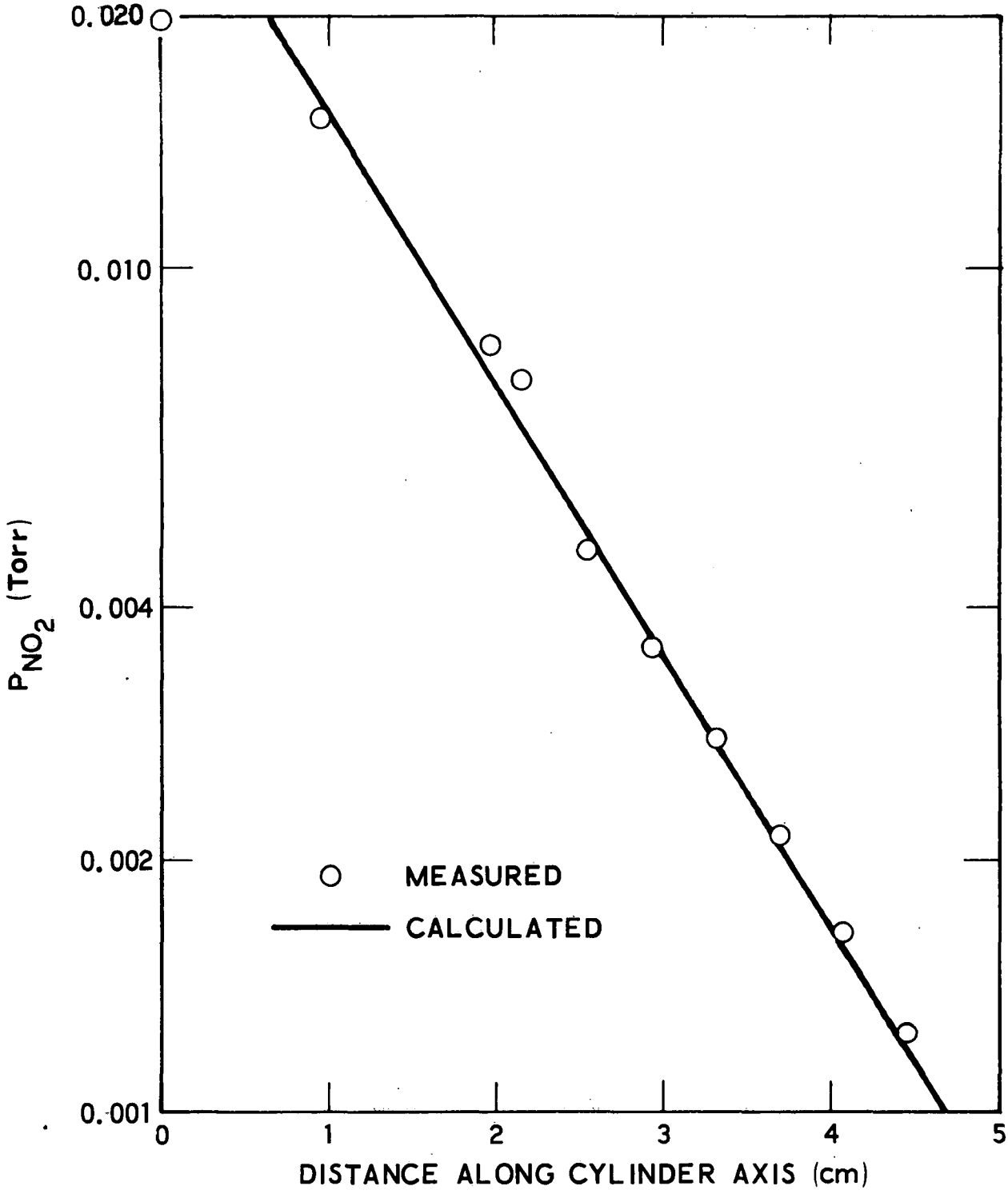

Figure 2. Decomposition of NO_2 over MnO_2. Experimental conditions: 0.2% NO_2 in Ar (10 Torr total pressure), 23 $\pm$ 1 C, 1.0 cm^3/sec flow, and a cylinder radius of 0.95 cm.

Additional Experiments in Reactor A

An additional sequence of experiments with dry NO_2-N_2 or NO_2-Ar mixtures was carried out in reactor A. The purpose of these experiments was to screen other solids for reactivity toward NO_2, analyze gaseous and adsorbed reaction products, measure overall capacities for reaction, and examine the effects of simulated solar radiation. Because of pressure and flow rate limitations, however, only minimum reactivities could be determined for solids that efficiently removed NO_2. This was because, for $k_r/k_c \geq 10^{-4}$, reactions were limited by diffusion of gaseous NO_2 to the cylinder walls in this system.

In addition to those materials discussed in the preceding section, the following solids were found to exhibit substantial reactivity ($k_r/k_c \geq 10^{-4}$) toward NO_2 decomposition: Al_2O_3 (Baker), cement, PbO, fly ash, and CaO. The remaining materials in Table 1 exhibited only minimal activity ($k_r/k_c < 3 \times 10^{-7}$) or no activity within experimental error toward <u>dry</u> NO_2 reaction mixtures.

Results from representative experiments in reactor A are illustrated in Figure 3. These results are from experiments in which glass helices (3.2 cm in diameter x 40 cm long) were used to support PbO and cement. In addition, a 1-mil sheet of DuPont Kapton was placed between the fluorescent lamps and reactor to filter wavelengths responsible for direct photolysis of NO_2 (10).

Experimentally, dry nitrogen was passed through the chamber at the desired flow and pressure until the gas flow stabilized. Then valves were rapidly switched to admit NO_2-N_2 mixtures at the same pressures and flows. This procedure avoided pressure surges in the system and required only a few minutes for the NO_2-N_2 flow to stabilize (see blank run in Figure 3).

In the case of PbO and cement, the initial nonzero values for the average NO_2 pressured after stabilization are due to the reaction mixtures filling the space between the gas inlet and leading edge of the helices, as well as partially penetrating into the helices before NO_2 diffuses to the helix walls and reacts. Over long periods of time ($\sim$ 400 min in the experiments illustrated), the NO_2 concentrations slowly increased as the activities of the solids gradually diminished, and ultimately ($t > 400$ min) reached the

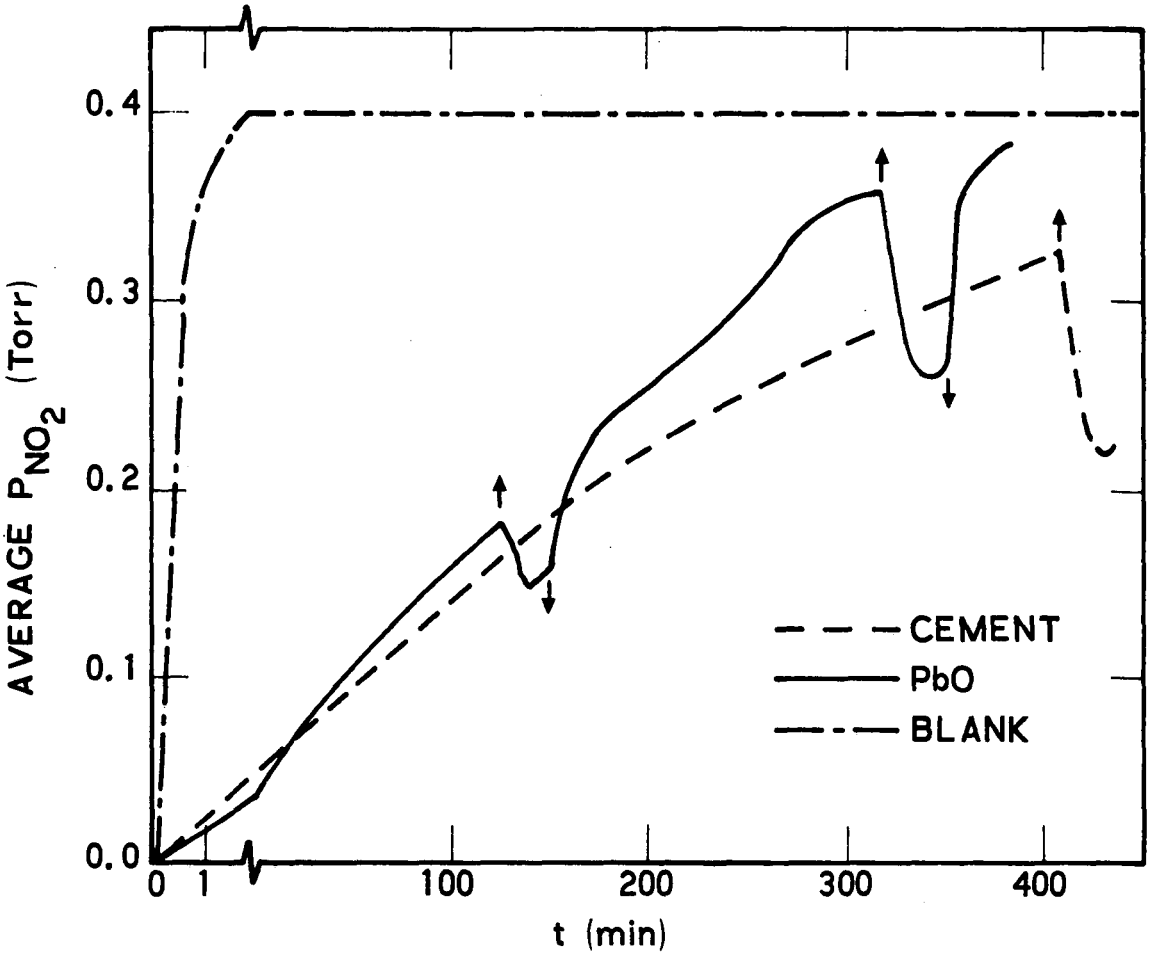

Figure 3. Decomposition of NO_2 over PbO and cement. Experimental conditions: 0.2% NO_2 in N_2 [total pressures of 191 Torr (PbO) and 200 Torr (cement)], 23 ± 1 C, and flow rates of 9.5 cm^3/sec (PbO) and 11.6 cm^3/sec (cement). The remaining curve in the figure is for a blank experiment conducted in the absence of added solids with the same experimental conditions as for PbO. Arrows indicate where fluorescent lamps (∿3 equivalent suns) were turned on (↑) or off (↓).

levels obtained in the absence of added solids when the activities of the PbO and cement were completely destroyed (not shown).

From the flow rates, weights of solids, and time to poisoning, the capacities of the solids to destroy NO_2 can be calculated. The results for the experiments discussed above, as well as experiments in which other solids were investigated are given in the first column of Table 3. Once poisoned, exposure of the solid to vacuum for periods up to several hours did not restore any substantial activity. Also, introduction of O_2 during or after the experimental had little effect on the results, which indicated poisoning was not due to depletion of surface oxygen.

Exposure of samples to visible light during experiments led to brief decreases or increases in NO_2, which suggested a slight restoration of solid activity in the former case, or photodesorption of adsorbed NO_2 in the latter. However, these changes were short-lived (Figure 3) and had little effect on the overall activity or capacity of the solid. Exposure to visible light after the solid had been poisoned frequently led to brief, large increases in NO_2, probably because of photodesorption. Here also, the overall effects on reactivity and capacity were small.

Reaction Products

In selected experiments, solids were removed from the reactor upon completion of the experiment, washed with distilled water, and filtered, and the filtrate analyzed for NO_x^- (see Section 2 for discussion of uncertainties). Results from these experiments are given in Table 4. The results indicate that both NO_2^- and NO_3^- are formed, the dominant specie depending on the solid used. The identity of the NO_x^- formed appeared to be independent of the length of time the experiment was run.

In the case of Al_2O_3, the Analabs material gave predominantly NO_2^-, while the Baker Al_2O_3 gave mostly NO_3^-. Elemental and x-ray analysis of these two solids indicated slight differences. Thus, elemental analysis gave higher percentages of Si, Fe, and Na in the Analabs material (0.1 - 0.3% versus 0.002 - 0.08%). In addition, although the dominant x-ray patterns from both materials were similar (boehmite), the Analabs material gave several extra (unidentified) peaks not observed for the Baker Al_2O_3.

TABLE 3. DECOMPOSITION OF NO_2 OVER VARIOUS SOLIDS*†

	Dry Reaction Mixtures		Humidified Reaction Mixtures††	
	Capacity	NO_x^- Formed	Capacity	NO_x^- Formed
PbO	0.05	-	>0.23	-
Cement	0.05	-	>0.37	-
Al_2O_3§	0.07 ± 0.02	0.03 ± 0.01	0.21 ± 0.01	0.11 ± 0.01
Charcoal	0.12 ± 0.03	0.03 ± 0.01	0.24 ± 0.09	0.09 ± 0.05
MnO_2	0.04		>0.41	

*Capacities refer to the grams of NO_2 decomposed per gram of solid, while NO_x^- formed refers to the grams of NO_2 converted to surface NO_x^- per gram of solid.

†Uncertainties are standard deviations from 3 to 5 experiments. Results expressed without uncertainties are from single experiments (see Figure 6).

††44% relative humidity

§Baker.

TABLE 4. ANALYSIS OF SURFACE NITROGEN COMPOUNDS

Solid	Surface Nitrogen Compounds		Total as NO_2 (mg)	
	NO_3^-	NO_2^-	NO_x^-	NO_2 Lost
Al_2O_3*	Small	Large	24	24
			19	14
			0.8	1.0
Al_2O_3†	Large	Small	-	-
Charcoal	Large	Small	-	-
MnO_2	Large	Small	-	-
PbO	Small	Large	-	-

*Analabs.

†Baker.

Experiments were also conducted to quantitatively determine NO_x^-. Experiments run for short periods of time to avoid poisoning indicated a quantitative conversion of NO_2 to NO_x^-. This is illustrated for Al_2O_3 in the last two columns of Table 4. The NO_2 lost was determined from the gas pressures, flow rates, and duration of the experiment. In several of these experiments, adsorbed NO_x^- was analyzed as a function of distance along the cylinder. Results from a typical experiment are shown in Figure 4. After the experiment, the Al_2O_3 was removed in sections, and the NO_x^- was analyzed in each section. The model described by Stewart and Judeikis (11) and Siegel et al. (12) was used to determine the calculated concentration profile, which was normalized through the use of the gas flow data and under the assumption that $k_r/k_c \geq 10^{-4}$, which is the diffusion limit in this experiment. Thus, the calculated and experimental results may be quantitatively compared. The major discrepancy, which occurs near $z = 0$, is probably due to edge effects.

Additional experiments were conducted for longer periods of time to investigate changes that might occur as the solid activity poisons. Results from these experiments are given in the third column of Table 3 and indicate that the $NO_2 \rightarrow NO_x$ conversion becomes less than quantitative. In order to establish a material balance for the NO_2 lost, several experiments were conducted with Al_2O_3 (Baker) and MnO_2 to determine if gaseous products were formed. Results from one such experiment for NO_2 decomposition over Al_2O_3 are shown in Figure 5. The production of gaseous NO (measured in the exit stream) is apparent. Integration of the NO produced and NO_2 lost indicates a 62% conversion of NO_2 to NO. The remaining 38% can be accounted for, to within experimental error, by NO_x^- formed on the Al_2O_3 surface. Similar results were obtained for MnO_2 with a 71% $NO_2 \rightarrow$ NO conversion. In the case of MnO_2, a distinct induction period was observed for NO formation even though NO_2 was destroyed. The latter observation may be due in part to removal of product NO by MnO_2 (see Section 3--Reactivity of NO).

DECOMPOSITION OF NO_2 IN MOIST REACTION MIXTURES

The effects of moisture on the decomposition of NO_2 were quite dramatic and are illustrated in Figure 6. In the experiments illustrated, only the first several centimeters of the cylinder were coated with the indicated solids. Dry reaction mixtures were passed through the chamber until

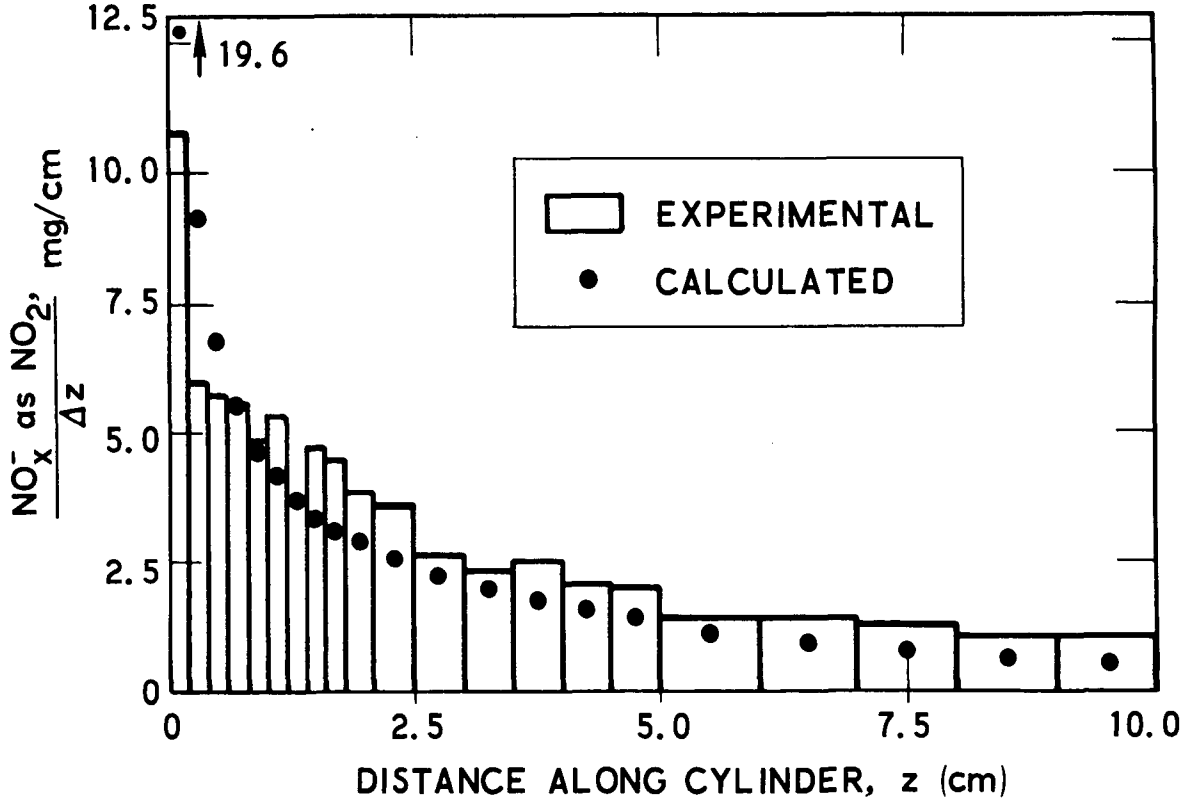

Figure 4. Surface nitrogen compounds measured after NO_2 decomposition over Al_2O_3 (Baker). Experimental conditions: 0.2% NO_2 in N_2 (700 Torr total pressure), 23 $\pm$ 1 C, flow rate = 10 cm^3/sec, and cylinder radius = 2.0 cm.

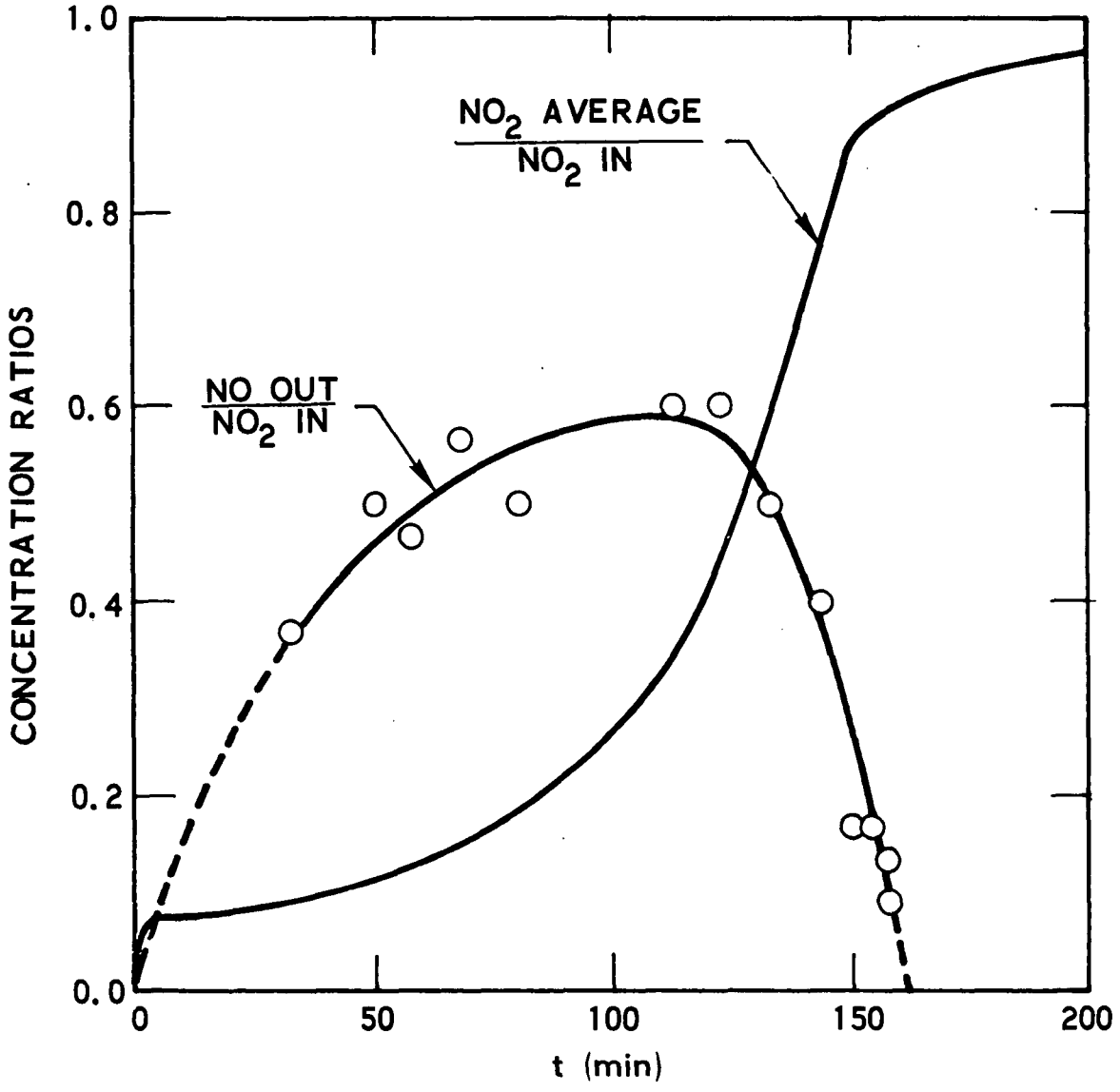

Figure 5. Decomposition of NO_2 over Al_2O_3 (Baker). Experimental conditions: 0.05% NO_2 in N_2 (180 Torr total pressure), 23 ± 1 C, flow rate = 9.2 cm^3/sec, and cylinder radius = 2.0 cm.

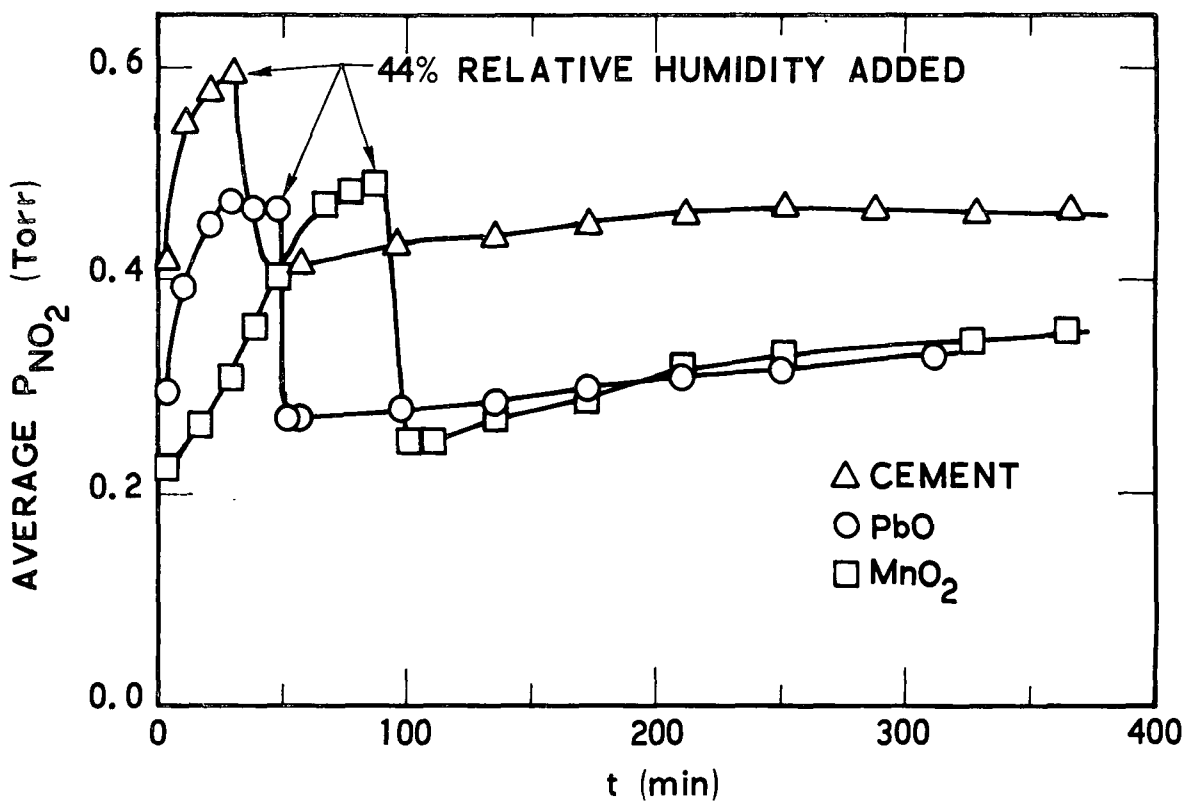

Figure 6. Decomposition of NO_2 over selected solids. Effects of added moisture. Experimental conditions: 0.2% NO_2 in Ar (∿200-300 Torr total pressures), 23 ± 1 C, flow rates ≈10 cm^3/sec, and cylinder radius = 2.0 cm.

reactivity was destroyed. At that point moisture was added (44% relative humidity), and the activity was restored. Separate experiments in the absence of added solids indicated gas phase reactions between NO_2 and H_2O were unimportant below 50% relative humidity. From Figure 6, it will be noted that the total activity (before poisoning) is substantially increased when moisture is added. Similar results were obtained when moisture was present initially in the reaction mixture. Qunatitative values for capacities in moist systems are given in the last two columns of Table 3. Diffusion limited reaction rates were obtained in the presence of moisture ($k_r/k_c \geq 10^{-4}$) for the first seven materials listed in Table 1 and for CaO, all of which were reactive in dry systems.

An equally significant result was that materials found to be unreactive in the absence of moisture reacted readily when moisture was added (44% relative humidity). The following values were measured for k_r/k_c in these experiments: $\geq 10^{-4}$ (ZnO), 3×10^{-5} (Cu_2O, Fe_2O_3), 1×10^{-5} (sand), and 1×10^{-6} [V_2O_5, $(NH_4)_2SO_4$, H_2SO_4]. The remaining materials in Table 1 were not examined in these experiments.

Glass filter paper of the type used in high-volume samplers for collecting airborne particles was also examined. While this material was unreactive with dry NO_2-N_2 mixtures, the addition of moisture led to extensive decomposition of NO_2 ($k_r/k_c \geq 10^{-4}$). This could have serious consequences in the interpretation of particulate data if surface NO_x^- compounds are formed. Some discrepancies between particles collected on various types of filters have been noted (14).

In one case (Fe_2O_3), reactivity was examined as a function of relative humidity (rh). The results obtained for k_r/k_c were: $< 10^{-7}$ (0-7% rh), $\sim 5 \times 10^{-6}$ (14% rh), $\sim 1.6 \times 10^{-5}$ (28% rh), and $\sim 3 \times 10^{-5}$ (44% rh). Attempts to conduct experiments at higher relative humidities were unsuccessful because of gas phase (or wall) reactions involving NO_2 and H_2O.

The increased reactivity and capacity in the presence of moisture led to the exploration of the possibility that surface nitrogen compounds formed in the presence of water might volatilize as the corresponding acids. In experiments with MnO_2 and Al_2O_3 (Baker), effluent gas from the reactor was

bubbled through a water solution, and the solution analyzed at intervals for NO_3^- and pH. (Under the experimental conditions, NO_2 was completely destroyed in transit through the reactor being converted, in part, to gaseous NO.) In the case of MnO_2, NO_3^- was observed even in dry reaction mixtures and increased when moisture was added. (Separate experiments bubbling NO through the water gave a negative NO_3^- test). In the presence of moisture, the NO_3^- analysis and pH indicate that ∿2 to 3% of the NO_2 lost is ultimately converted to volatile HNO_3 in the effluent stream. For Al_2O_3, no NO_3^- was observed in the effluent stream.

REACTIVITY OF NO

A number of experiments was conducted in reactor A with $NO-O_2-N_2$ mixtures to determine the reactivity of NO toward various solids. The conditions of these experiments were such that ∿10 to 20% of the NO was converted to NO_2 during passage through the reactor by the termolecular gas phase reaction between NO and O_2 (7-8). Several of the materials listed in Table 1, notably V_2O_5 and ZnO, appeared to exhibit some activity toward oxidation (photo-oxidation in the case of ZnO) of NO to NO_2, as evidenced by increased NO_2 yields. However, $k_r/k_c \approx 10^{-7}$ for these cases. In the case of MnO_2, charcoal, and Al_2O_3, NO_2 yields were sharply decreased. Separate experiments with $NO-N_2$ mixtures indicated that, except for MnO_2, this decrease was due to NO_2-solid interactions and not NO-solid interactions. For MnO_2, both NO and NO_2 were reactive with $k_r/k_c \geq 10^{-4}$. The remaining materials listed in Table 1 exhibited no reactivity toward NO to within experimental error and $k_r/k_c < 10^{-7}$.

Additional experiments were carried out with humidified (44% relative humidity) $NO-N_2$ mixtures to determine the effects of moisture on reactivities. The materials examined were Al_2O_3, charcoal, ZnO, and V_2O_5. Unlike the case of NO_2, moisture had no effect on the NO-solid interactions to within the limits of experimental detectability ($k_r/k_c < 10^{-7}$).

SECTION 4

DISCUSSION AND CONCLUSIONS

The results for NO_2 suggest that this pollutant could be heterogeneously destroyed in the atmosphere on a wide variety of airborne solids likely to be found in urban environments. The heterogeneous decomposition is greatly facilitated by the presence of moisture. In fact, many solids that were unreactive in the absence of moisture readily decomposed NO_2 when water vapor was added. The striking effects of water suggest the involvement of surface OH groups in the heterogeneous processes.

Initially, the decomposition reactions quantitatively convert NO_2 to adsorbed NO_x^-. With time, the conversion becomes less than quantitative, and gaseous NO is formed. Overall, ∿20 to 30% of the NO_2 lost is converted to adsorbed NO_x^-. Although volatilized HNO_3 was observed in one case (MnO_2), this product accounted for only ∿2 to 3% of the NO_2 lost. The possibility exists that HNO_2 or HNO_3 formed in the presence of moisture could react with a number of the oxides investigated in this study. Solution of the metal ions and reactions in surface water films would then be possible. A similar suggestion has been made for oxidation of SO_2 to H_2SO_4 in the presence of moisture over various solids (15).

Based on the initial reactivities observed in these studies, it is estimated that fresh aerosol in an urban atmosphere could remove NO_2 with a lifetime of 1/2 to 5 hours. This projected lifetime is based on the model described by Judeikis and Siegel (5) and assumes a particle loading of 100 $\mu g/m^3$ and the reactivities measured in these experiments (e.g., if it is assumed that particles had the same reactivity as charcoal, MnO_2, or Al_2O_3, the calculated particle limited half-lives are 1, 1/2 to 5, and 5 hours respectively). The projected lifetimes could be shorter in the presence of moisture. As the aerosols age, the net removal of NO_2 is formed as the

the reaction continues. The latter species is rapidly converted to NO_2 in urban atmospheres during daylight hours (8).

The projected particle limited lifetimes compare favorably with observed diurnal variations in NO_x (6-7). They are longer than the noontime photolytic lifetime of 3 min for NO_2 in the atmosphere (8); however, the heterogeneous processes lead to a net reduction in oxidant ($NO_2 + O_3$), as well as NO_x, while the photolytic process does not. Moreover, since the photolytic process is not operable during the night, heterogeneous reactions could be the dominant nighttime sink for NO_2.

Only airborne particulate matter has been considered in our modeling. Consideration of ground-level surfaces could greatly enhance total reactivity. Moreover, reactions taking place on the latter surfaces could lead to concentration gradients near the ground, depending upon the amount of transport and mixing taking place. These gradients could be significant in accurately assessing pollution-related health hazards.

Finally, except for MnO_2, NO exhibits only minimal activity toward solids examined in this study. Based on quantitative rate measurements, it is concluded that heterogeneous atmospheric processes of NO are probably unimportant. However, as noted earlier, NO is rapidly converted to NO_2 in urban atmospheres (8), and heterogeneous removal of the latter product could act as the ultimate sink for NO_x emitted as NO.

REFERENCES

1. Johnstone, H.F., and D.R. Coughanowr. Adsorption of Sulfur Dioxide from Air. Ind. Eng. Chem., 50:1169-1172, 1958.

2. Urone, P., H. Lutsep, C.M. Noyes, and J.F. Parcher. Static Studies of Sulfur Dioxide Reactions In Air. Environ. Sci. Technol., 2:611-618, 1968.

3. Matteson, M.J., W. Stöber, and H. Luther. Kinetics of the Oxidation of Sulfur Dioxide by Aerosols of Manganese Sulfate. Ind. Eng. Chem. Fundamentals, 8:677-687, 1969.

4. Carabine, M.D. Interactions in the Atmosphere of Droplets and Gases. Chem. Soc. Rev., 1:411-432, 1972.

5. Judeikis, H.S., and S. Siegel. Particle-Catalyzed Oxidation of Atmospheric Pollutants. Atmospheric Environment, 7:619-631, 1973.

6. Pitts, J.N. Environmental Appraisal: Oxidants, Hydrocarbons, and Oxides of Nitrogen. J. Air Pollut. Control Ass., 19:658-667, 1969.

7. Altshuller, A.P., and J. Bufalini. Photochemical Aspects of Air Pollution: A Review. Photochem. Photobiol., 4:97-146, 1965.

8. Shuck, E.A., and E.R. Stephens. Oxides of Nitrogen. In: Advances in Environmental Sciences, Vol.1, J.N. Pitts and R.L. Metcalf, eds. Wiley-Interscience, New York, New York, 1969. pp. 73-118.

9. Cheng, R.T., J.O. Frohliger, and M. Corn. Aerosol Stabilization for Laboratory Studies of Aerosol-Gas Interactions. J. Air Pollut. Control Ass., 21:138-142, 1971.

10. Hedgpeth, H., S. Siegel, T. Stewart, and H.S. Judeikis. Cylindrical Flow Reactor for the Study of Heterogeneous Reactions of Possible Importance in Polluted Atmospheres. Rev. Sci. Instrum., 45(3): 344-347, 1972.

11. Stewart, T.B., and H.S. Judeikis. Measurements of Spatial Reactant and Product Concentrations in a Flow Reactor Using Laser-Induced Fluorescence. Rev. Sci. Instrum., 45(12):1542-1545, 1974.

12. Siegel, S., H.S. Judeikis, and C. Badcock. The Role of Solid-Gas Interactions in Air Pollution. EPA-650/3-74-007, U.S. Environmental Protection Agency, Washington, D.C., 1974.

13. Feigl, F. Spot Test in Inorganic Analysis. Ed. 5. El Sevier Publishing Co., New York, New York, 1958. pp. 326-332.

14. Muller, P.K., S. Twiss, and G. Sanders. Selection of Filter Media: An Annotated Outline. Paper presented before 13th Conference on Methods Air Pollution and Industril Hygiene Studies, Berkeley, California, October 30-31, 1972.

15. Foster, P.M. The Oxidation of Sulphur Dioxide in Power Station Plumes. Atmospheric Environment, 3:157-175, 1969.

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15. SUPPLEMENTARY NOTES

16. ABSTRACT

A laboratory study has been conducted on heterogeneous reactions of nitrogen dioxide and nitric oxide to evaluate their potential role in reaction in polluted urban atmosphere. The results of this study suggest that nitrogen dioxide decomposes on a wide variety of solids likely to be found in urban environments. Measured reaction rates indicate these processes can be important in the atmosphere. Humidification of reaction mixtures leads to increased reactivities. It is concluded that heterogeneous reactions in the atmosphere are unimportant for the oxidation of nitric oxide.

17. KEY WORDS AND DOCUMENT ANALYSIS

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