

# Photofragment Detection of Nitrogen Dioxide

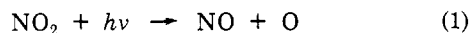
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Ambient-level concentrations of  $\text{NO}_2$  in air are measured at reduced pressures by photolyzing the  $\text{NO}_2$  and detecting the resultant O atoms by the chemiluminescence from their gas-phase reaction with nitric oxide. The intensity of chemiluminescence is a linear function of  $\text{NO}_2$  concentration over the range 1.0 to  $10^3$  ppb with an optimum photomultiplier response of 0.1 nA/ppb. Nonlinear response for concentrations greater than  $10^3$  ppb is due to the fast reaction between O atoms and  $\text{NO}_2$ . A mathematical model accurately predicts the experimental variations of photomultiplier response to system pressure, nitric oxide concentrations,  $\text{NO}_2$  concentrations, and photolysis source intensity. Interferences due to the O atom-hydrocarbon reactions are negligible for typical ambient-level concentrations of hydrocarbons. Using this detection scheme, both  $\text{NO}_2$  and  $\text{O}_3$  have been simultaneously measured at ambient-level concentrations.

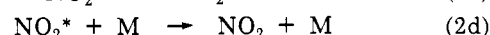
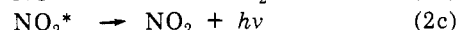
Recently, a new type of monitor for the gas-phase analysis of trace gases has been proposed (1). Photofragments of the molecular species of interest are formed by irradiation of a sample air stream and are subsequently detected by either a characteristic chemiluminescent emission, resonance absorption, or resonance fluorescence. A detection scheme for a single photofragment that is a product common to the photolysis of several trace gases serves to monitor all the parent species. The objectives of this paper are to communicate the results of experimental tests that have shown the feasibility of the method for  $\text{NO}_2$  and to present a discussion in terms of the fundamental processes involved.

The detection of  $\text{NO}_2$  is an example of the chemiluminescent type of photofragment detection that involves: (a) the selective photolysis of a trace gas in an irradiation chamber; (b) transfer of the photofragments through a light trap and into a reaction chamber; (c) recombination of the photofragments by gas-phase reaction with a pure mixer gas, resulting in the subsequent emission of a characteristic chemiluminescent spectrum; and (d) selective detection of all or a portion of this spectrum by a filter-photomultiplier combination. Specifically,  $\text{NO}_2$  molecules in a sample air stream are photolyzed at reduced pressures to produce O atoms.



The continuously flowing sample air stream carries the O atoms from the irradiation chamber through a light trap and into a closely coupled reaction chamber. The O atoms are detected by the chemiluminescence which occurs when they are mixed with nitric oxide. Pure NO is introduced into the reaction chamber at a rate typically less than a factor of  $10^{-2}$  of the sample stream flow rate. A portion of the O atoms collide with NO molecules, result-

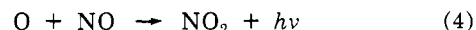
ing in a chemiluminescent emission. The chemiluminescent spectrum for this reaction extends from  $0.4 \mu\text{m}$  into the infrared with a maximum intensity at approximately  $0.65 \mu\text{m}$  (2). The reactions involved in the O + NO recombination are



where M denotes a third-body molecule in the reaction chamber. In steady state, Equations 2a, 2c, and 2d give

$$[\text{NO}_2^*] = \frac{k_a[\text{O}][\text{NO}][\text{M}]}{k_d[\text{M}] + k_c} \quad (3)$$

where  $k_a$ ,  $k_c$ , and  $k_d$  are the reaction rate constants for the reactions specified in Equation 2a, 2c, and 2d, respectively. Since  $k_d[\text{M}] \gg k_c$  for pressures in the Torr range, the intensity of chemiluminescence is experimentally indistinguishable from the value as deduced from the reaction



with reaction rate  $k_4$ .

Two types of interference occur in the detection of  $\text{NO}_2$  by this scheme. One involves the loss of O atoms by ways other than that specified by Equation 4 and the second involves the chemiluminescence of NO with other molecular or atomic species, notably  $\text{O}_3$ , that are carried in the sample stream. Thus, reaction 2b eliminates O atoms at a rate

$$\frac{d[\text{O}]}{dt} = k_b[\text{NO}][\text{O}][\text{M}] \quad (5)$$

The ratio of this loss rate to the one corresponding to reaction 4 is  $k_b[\text{M}]/k_4 = 3.54 \times 10^{16} p k_b/k_4$  where  $p$  is the reaction chamber pressure in Torr. Using the reaction rates  $k_b = 6.8 \times 10^{-32} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$  (3) and  $k_4 = 6.4 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$  (2), the reaction specified in Equation 5 is at least two orders of magnitude more efficient in eliminating O atoms at pressures greater than 3 Torr. Appreciable losses of O atoms also can occur by reaction with  $\text{NO}_2$  and with certain hydrocarbons. The former process



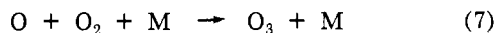
can affect the linearity of the signal response at sufficiently high  $\text{NO}_2$  concentrations, while the latter process can

(1) J. A. Hodgeson and W. A. McClenny, 164th National Meeting of the American Chemical Society New York, N. Y., Aug 30, 1972, Paper No. Watr-60.

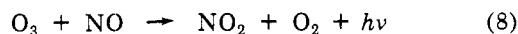
(2) A. Fontijn, C. B. Meyer, and H. I. Schiff, *J. Chem. Phys.*, **40**, 64 (1964).

(3) F. Kaufman, *Proc. Roy. Soc., Ser. A*, **247**, 123 (1958).

both alter the sensitivity of the system and make the system linearity a temporal function of the concentration of the hydrocarbons. It will be established that the concentration of hydrocarbons necessary to constitute an important interference is much larger than that ordinarily encountered in ambient air. The reaction rate of O atoms with molecular oxygen to form ozone



with a reaction rate of  $5.6 \times 10^{-34} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$  (4) is important at pressures of a few Torr and will be accounted for in the analytical treatment of the system. A final source of O atom destruction is the loss due to heterogeneous recombination on the walls. The reaction



results in a strong chemiluminescent signal that has been successfully used to measure NO concentrations at ambient levels (5). Obviously, in the present case, the reaction can be used to monitor the  $\text{O}_3$  concentration. The chemiluminescent spectrum extends from  $0.6 \mu\text{m}$  into the infrared with a peak emission at  $1.2 \mu\text{m}$ . Because of the overlap in spectra, this reaction constitutes an interference with the measurement of O atoms unless an appropriate combination of photomultiplier and filter is used. In lieu of decreasing the system sensitivity by filtering, the photolysis source can be alternately switched on and off giving readings due to  $(\text{NO}_2 + \text{O}_3)$  and  $\text{O}_3$ , respectively. The difference in these readings corresponds to the  $\text{NO}_2$  concentration alone. Thus measurements of  $\text{O}_3$  and  $\text{NO}_2$  can be made with the same system. Relative sensitivity can be altered by varying the intensity of the photolysis source and the spectral sensitivity of the detector.

## EXPERIMENTAL

A schematic of the experimental system is shown in Figure 1. As part of the feasibility tests, gas cylinders (Air Products and Chemicals, Inc.) containing predetermined concentrations of  $\text{NO}_2$  were further diluted to give concentrations in a range extending from 1 ppb to several ppm.  $\text{NO}_2$  concentrations were checked by both the Saltzman wet chemical method (6) and a chemiluminescent method (7) involving the pyrolytic conversion of  $\text{NO}_2$  to NO and the subsequent detection of the light intensity resulting from the reaction given in Equation 8. The sample stream could be passed through an ozonator (8) to create known concentrations of  $\text{O}_3$ .

The flow rate through the system was established by a Welch Duo Seal Vacuum Pump (Model 1397, 1 hp) with a free air capacity of  $500 \text{ l. min}^{-1}$ . The relationship between system pressure and flow rate was linear ( $0.5 \text{ l./Torr}$ ) and typical flow rates were 1 to 5 l. (STP)  $\text{min}^{-1}$ . System pressure was monitored on a Wallace-Tiernan gauge which was calibrated with a McLeod gauge. Mixer gas flow rate was measured with a Hastings mass flowmeter. Silver wool was placed at the exit port of the reaction chamber to destroy any remaining O atoms.

The irradiation source was an Oriel Optics Model C-30 arc housing with a 200-W Hg-Xe lamp. The collimated beam diameter was approximately 1.75 in. in diameter; it was filtered with a Corning 0-54 glass filter with a  $e^{-1}$  short wavelength cutoff at  $3150 \text{ \AA}$ . Light output in the region between  $3150 \text{ \AA}$  and the dissociation limit for  $\text{NO}_2$  which corresponds to a wavelength near

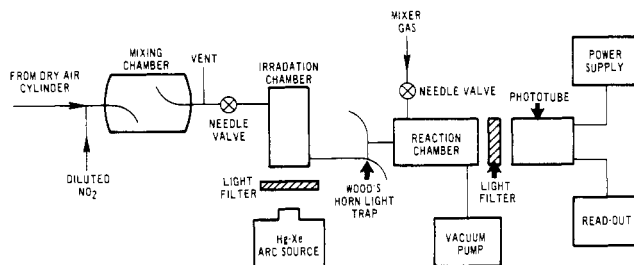


Figure 1. Experimental system for photofragment detection of  $\text{NO}_2$

$4000 \text{ \AA}$  was approximately 48 mW as given by source specifications. Filtering of the source was effective in eliminating major interferences resulting from the photolysis of ozone and molecular oxygen. Photolysis of  $\text{NO}_2$  occurred in a cylindrical irradiation chamber of Pyrex glass, 6 in. in length, 1.75 in. in diameter, and capped on each end by a quartz window. A front surface silvered mirror was placed at the end of the chamber to reflect the source light beam.

Photofragments were channeled into the reaction chamber through 8-mm i.d. Pyrex tubing and a double Wood's horn light trap. A stainless steel ball joint in the connecting line reduced source light that was otherwise ducted into the reaction chamber. The leakage light for this arrangement produced a signal of typically 2.5 nA and could be further reduced by filtering the source for a long wavelength cutoff near  $4000 \text{ \AA}$  and by filtering the detector with a short wavelength cutoff near  $4000 \text{ \AA}$ . The reaction chamber was a glass cylinder 1.75 in. in diameter and 10 in. long, capped at the detector end by a quartz window. Magnesium oxide powder was packed around the cylinder and inside an aluminum housing to ensure efficient light transfer to a photomultiplier that viewed the cylinder end-on. Both 9558QA and 6256S EMI photomultipliers at  $10^\circ \text{C}$  were used to detect chemiluminescence inside the reaction chamber. A combination of a 6256S tube and a Bausch and Lomb filter (90-1-600) was used to discriminate against the chemiluminescence from the ozone-nitric oxide reaction and thus to make the system specific to  $\text{NO}_2$ . The 9558QA tube was sensitive to chemiluminescence from both the ozone-nitric oxide reaction and the oxygen atom-nitric oxide reaction. Signals were recorded by a Heath Model EU 20-11 amplifier recorder.

## MATHEMATICAL DEVELOPMENT

**Correspondence between  $[\text{NO}_2]$  and System Response.** The intensity,  $I$ , of the photolysis source after passing through a length  $x$  of the irradiation chamber can be approximated by  $I_0 \exp(-[\text{NO}_2]\sigma x)$ , where  $\sigma$  denotes the average microscopic cross section for absorption by  $\text{NO}_2$ , and  $I_0$  denotes the source intensity over the spectral bandwidth causing photolysis. Using typical values of  $\sigma = 2.5 \times 10^{-19} \text{ cm}^2$  (9), a concentration of 1 ppm at 8 Torr, and a length of 15.24 cm, then  $I/I_0 \approx \exp(-10^{-6})$ . The source is essentially unattenuated.

To calculate the O atom concentration,  $[\text{O}]_{\text{ex}}$ , at the exit to the irradiation chamber, the rate equation can be used in the form

$$\frac{d[\text{O}]}{dt} = \frac{\phi I_0 \sigma [\text{NO}_2]}{A_1} - k_6 [\text{NO}_2][\text{O}] - k_7 [\text{O}_2][\text{M}][\text{O}] - \beta [\text{O}] \quad (9)$$

where  $\phi$  denotes the average quantum yield for photolysis,  $k_6$  and  $k_7$  are the reaction rates for Equations 6 and 7, respectively,  $A_1$  denotes the cross sectional area of the photolysis chamber, and  $\beta$  denotes the rate coefficient for wall recombination. The first source term represents the rate of formation of O atoms.  $[\text{NO}_2]$  is established by the equation

(9) T. C. Hall, Jr., and F. E. Blacet, *J. Chem. Phys.*, **20**, 1745 (1952).

- (4) R. E. Huie, J. T. Herron, and D. D. Davis, *J. Chem. Phys.*, **76**, 2653 (1972).
- (5) R. K. Stevens, T. A. Clark, C. E. Decker, and L. F. Ballard, Preprint, EPA, Research Triangle Park, N. C., Presented at 1972 APCA Meeting, Miami, Fla., June, 1972, Paper No. 72-13.
- (6) B. E. Saltzman, *Anal. Chem.*, **26**, 1949 (1954).
- (7) J. A. Hodgeson, J. P. Bell, K. A. Rehme, K. J. Krost, and R. K. Stevens, Preprint, Presented at 1972 APCA Meeting, Miami, Fla., June, 1972, Paper No. 72-12.
- (8) J. A. Hodgeson, R. K. Stevens, and B. E. Martin, *ISA Trans.*, **11**, 161 (1972).

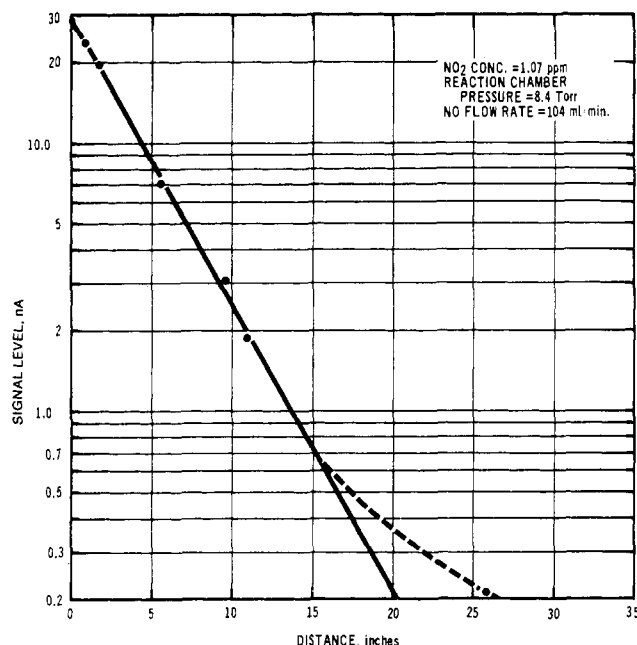


Figure 2. Oxygen atom losses by wall recombination

$$\frac{d[\text{NO}_2]}{dt} = \frac{\phi I_0 \sigma [\text{NO}_2]}{A_i} \quad (10)$$

Integrating over the residence time,  $V_i/F_i$ , where  $F_i$  denotes the flow rate and  $V_i$  denotes the irradiation chamber volume which is the product of  $A_i$  and the chamber length  $L_i$ , the  $\text{NO}_2$  concentration is

$$[\text{NO}_2] = [\text{NO}_2]_0 \exp(-\phi I_0 \sigma L_i / F_i) \quad (11)$$

which for typical values gives a concentration change of less than 0.01%. Hence,  $[\text{NO}_2] = [\text{NO}_2]_0$  in Equation 9. The second and third source terms represent the loss rates resulting from the fast reaction between  $\text{NO}_2$  and O atoms and from the formation of ozone, respectively. Obviously, additional terms can be included to account for other reactions that eliminate O atoms. The last term represents the rate of O atom losses by wall recombination by assuming a first-order dependence on concentration. Equation 9 has the solution

$$\frac{[\text{O}]_{\text{ex}}}{\phi I_0 \sigma [\text{NO}_2]_0 (1 - \exp(-(k_6[\text{NO}_2]_0 + k_7[\text{O}_2][\text{M}] + \beta)V_i/F_i))} = \frac{A_i(k_6[\text{NO}_2]_0 + k_7[\text{O}_2][\text{M}] + \beta)}{\quad} \quad (12)$$

The O atom concentration is further depleted by wall recombination in passing from the irradiation chamber to the reaction chamber. Experimental data relating the signal response of the system to the length of tubing between the two chambers are given in Figure 2. The exponential decay as a function of length is taken to indicate the effect of the number of collisions between O atoms and the tubing wall. Since changing the flow time inside the tubing is essentially equivalent to changing the number of collisions per transit, the O atom concentration to the entrance to the reaction chamber  $[\text{O}]_r$  is:

$$[\text{O}]_r = [\text{O}]_{\text{ex}} \exp(-\gamma v_t / F_t) \quad (13)$$

where  $v_t/F_t$  is the residence time with  $v_t$  the volume of

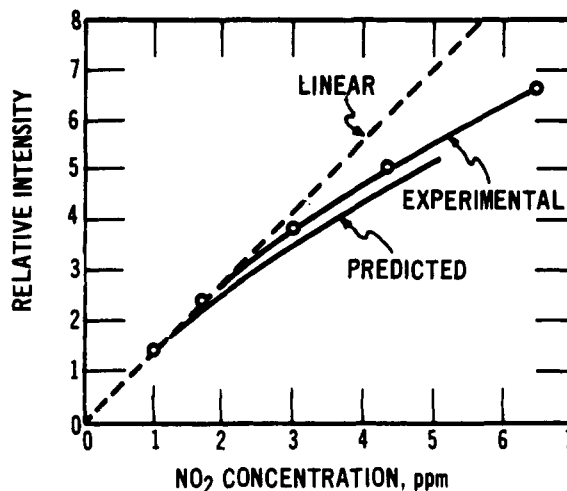


Figure 3. System response to high  $\text{NO}_2$  concentrations

the connecting tubing and  $F_t$  the flow rate.  $F_t$  and  $F_i$  are the same if the small pressure drop along the connecting tubing is neglected. The value of  $\gamma$  as established from Figure 2 and experimental flow rates is  $0.84 \times 10^{-3} \text{ sec}^{-1}$ , which gives an approximate survival percentage of 12% for O atoms at a system pressure of 8 Torr.

Once inside the reaction chamber, [O] is reduced by the recombination of O atoms with NO. Neglecting wall losses, the photomultiplier output,  $I_{\text{pm}}$ , is obtained by integrating over the reaction chamber volume,  $V_r$

$$I_{\text{pm}} = A_m G \int k_c [\text{NO}_2^*] dV_r \quad (14)$$

where  $A_m$  denotes the product of the photomultiplier quantum efficiency and amplification, and  $G$  denotes a geometrical factor that corresponds to the changing efficiency of collection as the spatial emission pattern changes with pressure and to the particular characteristics of the mixing process between the NO mixer gas stream and the sample stream. If all the emitted light were collected,  $G = 1$ ; however, light originating from more remote regions is often reflected in reaching the photomultiplier and, hence, is reduced in intensity. The value for  $[\text{NO}_2^*]$  has been given in Equation 3 in terms of the density of O atoms and of NO molecules. In order to simplify the expression for  $I_{\text{pm}}$ , [NO] will be assumed constant throughout the reaction chamber and [O] will be assumed to vary only along the length of the reaction chamber. The first assumption is quite reasonable since the NO concentration is several orders of magnitude greater than the O atom concentration; the second assumption is correct to a degree depending on the actual mixing configuration.

The variation in the density of O atoms is determined primarily by the reactions given in Equations 2b and 7 with a contribution from the reaction specified in Equation 6 if the  $\text{NO}_2$  concentration is sufficiently high. Thus, the O atom concentration along the length of the tubing,  $[\text{O}]_l$ , is

$$[\text{O}]_l = [\text{O}]_r \exp(-\delta l) \quad (15)$$

where  $\delta = ((1 + (k_6[\text{NO}_2] + k_7[\text{O}_2][\text{M}]/k_b[\text{M}] \cdot [\text{NO}]))k_6 \cdot [\text{M}][\text{NO}]/A_r F_r)$ , in which  $A_r$  denotes the reaction chamber cross sectional area. Typically at a system pressure of 8 Torr, the O atom density at the exit to the reaction chamber has decreased to 1.5% of its initial value. Using this expression in Equation 14, the signal response of the system, subject to the stated assumptions is

$$I_{pm} = \frac{Cl_0 F_r [NO_2]_0 \exp(-\gamma v_t / F_i) (1 - \exp(-(k_6 [NO_2]_0 + k_7 [O_2] [M] + \beta) V_i / F_i))}{(k_6 [NO_2]_0 + k_7 [O_2] [M] + \beta) (1 + (k_6 [NO_2]_0 + k_7 [O_2] [M] / k_b [NO] [M]))} \times \\ (1 - \exp(-(1 + k_6 [NO_2]_0 + k_7 [O_2] [M] / k_b [NO] [M])) k_b [M] [NO] V_r / F_r)) \quad (16)$$

where  $C = A_m G k_c k_a \phi \sigma / k_d k_b A_i [M]$ .

## RESULTS AND DISCUSSION

**Linearity.** Figure 3 shows the signal response as a function of  $NO_2$  concentration and the transition from a linear response to a nonlinear one for a system pressure of 8 Torr and for a mixer gas flow rate of 10 ml/min. The predicted values are obtained by normalizing the concentration dependent terms in Equation 16 to the experimentally observed value at 1 ppm. Relative values are calculated using  $k_6 = 5.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$  (10) and  $\beta = 0$ . For  $NO_2$  concentrations less than 1 ppm at 8 Torr, the system response is observed to be proportional to the  $NO_2$  concentration. For higher concentrations, the fast reaction between  $NO_2$  and O atoms eliminates some of the O atoms and a departure from linearity occurs.

**Sensitivity.** Signal values obtained using the system previously described indicate a sensitivity of approximately 0.1 nA/ppb and allow for a minimum detectable limit of 1 ppb. Since only a fraction of 0.01% of the  $NO_2$  concentration is being photolyzed, the ultimate sensitivity can essentially be established by whatever light source is deemed practical for continuous monitoring. Further enhancement of sensitivity could occur by reduction of O atom losses between the two chambers, possibly by use of tubing material of lower recombination coefficient. There is also a possibility of photolyzing within the reaction chamber (*in situ* photofragment detection), thereby eliminating wall recombination losses.

**Variation of System Pressure and NO Flow Rate.** The last term in Equation 16 contains the only dependence on the mixer gas flow rate. The value of this term gives the fraction of O atoms which react within the reaction chamber. With other quantities constant and a system pressure of 4.5 Torr, the variation of the NO flow rate is reflected in the variation of  $I_{pm}$ . The experimental and predicted variations of  $I_{pm}$  with NO flow rate are shown in Figure 4 with  $I_{pm}$  normalized to the asymptotic value. Although the system response is insensitive to fluctuations in NO flow rate for the higher values, most experiments were performed with a flow rate of less than 10 ml/min to minimize the NO contribution to the system exhaust.

The variation of  $I_{pm}$  with pressure is a function of the combined effect of the last three terms in Equation 16. Loss of O atoms by wall recombination as represented by the term  $\exp(-\gamma v_t / F_i)$  preferentially modifies the signal response at low pressures leading to a less pronounced response. This effect is evident in Figure 5 in which a comparison of the experimental data with the predicted pressure variation is given. Predicted values were normalized to the experimental value at 7 Torr.

**Interferences.** The interferences caused by hydrocarbons can be estimated by reference to Equations 9 and 15. Oxygen atom loss rates in the irradiation chamber attributable to the presence of hydrocarbons are represented by an additional loss  $(\Sigma k_{HC} [HC]) [O]$  in Equation 9, the inclusion of which modifies  $[O]_{ex}$  as given in Equation 12 to

$$[O]_{ex} = \frac{\phi I_0 \sigma [NO_2]_0 V_i Q}{A_i F_i} \quad (17)$$

where  $Q$  is a dimensionless factor which denotes the frac-

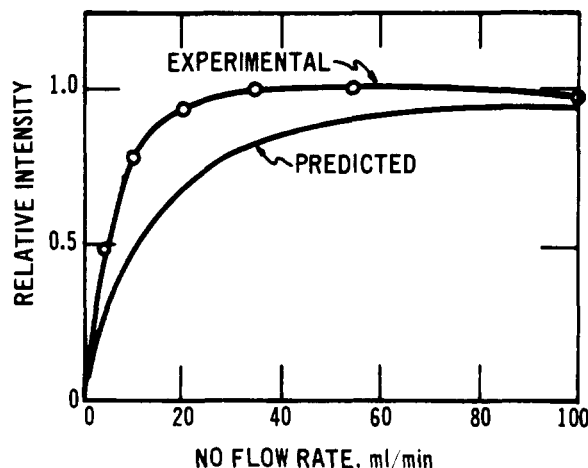


Figure 4. System response to variations in mixer gas flow rate

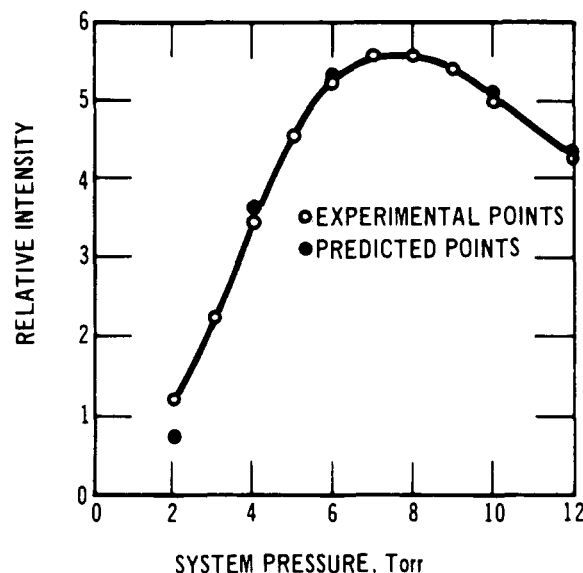


Figure 5. System response to variations in system pressure

tion of O atoms which are eliminated in the irradiation cell due to the presence of both  $NO_2$  and hydrocarbons.  $Q$  is given by

$$Q = \frac{(1 - \exp(-(k_7 [O_2] [M] (1 + R) + \beta) V_i / F_i))}{(k_7 [O_2] [M] (1 + R) + \beta) V_i / F_i} \quad (18)$$

where  $R = (k_6 [NO_2] + k_{HC} [HC]) / k_7 [O_2] [M]$ . A criterion for hydrocarbon interference was obtained by equating the fractional departure from linearity in the signal response,  $Q/Q(R=0)$ , to a fractional value less than 1.0 that is agreed to constitute the maximum negligible departure from linearity. This value is taken to be 0.95. For a system pressure of 8 Torr and for  $k_6 [NO_2] \ll k_{HC} [HC]$ , with  $\beta = 0$ , the maximum allowable product summation,  $\Sigma k_{HC} [HC]$ , is equal to  $2.25 \text{ sec}^{-1}$ . Using an average value for  $k_{HC}$  of  $10^9 \text{ l. mol}^{-1} \text{ sec}^{-1}$ , which is typical of the olefinic hydrocarbons, a value of  $[HC]$  corresponding to 4.5 ppm is obtained. This must be compared to the equivalent hydrocarbon concentration  $[HC]$  encountered in the ambient air.

$$k_{\text{ref}}^{-1} \Sigma k_{\text{HC}}[\text{HC}] = [\overline{\text{HC}}] \quad (19)$$

where  $k_{\text{ref}} = 10^9 \text{ l. mol}^{-1} \text{ sec}^{-1}$ . A reasonable limit for  $[\overline{\text{HC}}]$  can be determined by considering recent values of hydrocarbon concentrations in the urban atmosphere (11) and the reaction rates of O atoms with the various individual hydrocarbons (12). This gives a limit of  $[\overline{\text{HC}}] \approx 0.25 \text{ ppm}$ . Hence, in the case where  $k_6[\text{NO}_2] \ll k_{\text{HC}}[\text{HC}]$ , average ambient levels of equivalent hydrocarbons are approximately an order of magnitude less than the levels needed to cause nonlinearity.

Obviously, if the  $\text{NO}_2$  concentration is high, it cannot be neglected.  $R$  can be written as

$$R = \frac{k_{\text{ref}}[\overline{\text{HC}}]}{k_7[\text{O}_2][\text{M}]} (1 + (3.4f_{\text{NO}_2}/f_{\text{HC}})) \quad (20)$$

where  $f_{\text{NO}_2}$  and  $f_{\text{HC}}$  denote ppm of  $\text{NO}_2$  and HC, respectively. Hence, if both hydrocarbon and  $\text{NO}_2$  concentrations are high, then the value of  $Q$  is reduced; i.e., for 1 ppm  $\text{NO}_2$  and 1 ppm equivalent hydrocarbon concentration, the value of  $Q$  is 0.95. If, however, the equivalent hydrocarbon concentration is less than 0.25 ppm, the system response should not be affected over a typical ambient range of  $\text{NO}_2$  concentrations from 0 to 0.5 ppm. Preliminary experiments with several olefinic hydrocarbons have shown that the fractional departure from linearity as given in Equation 18 can be used to predict the experimental values within a few per cent using reaction rate values given in ref 12.

The reaction of O atoms and hydrocarbons can also decrease the sensitivity of the system by changing the steady-state O atom concentration profile in the reaction chamber. This profile is otherwise established as given in Equation 15. Thus, if  $\Sigma k_{\text{HC}}[\text{HC}]$  is comparable to  $k_b[\text{M}][\text{NO}]$ , then the sensitivity is decreased. The criterion for alteration of sensitivity is taken to be

$$\Sigma k_{\text{HC}}[\text{HC}] = 0.1k_b[\text{M}][\text{NO}] \quad (21)$$

For a system pressure of 8 Torr, this relationship is satisfied if the atmospheric concentration of the equivalent hydrocarbons is greater than 10 ppm.

(11) S. L. Kopczynski, W. A. Lonneman, F. D. Sutterfield, and P. E. Darley, *Environ. Sci. Technol.*, **6** (4), 342 (1972).

(12) P. A. Leighton, "Photochemistry of Air Pollution," Academic Press, New York, N. Y., 1961, p 142.

The presence of  $\text{O}_3$  in the sample air stream leads to the photolysis of  $\text{O}_3$  and the creation of O atoms that are sensed along with those resulting from the photolysis of  $\text{NO}_2$ . Experimentally, it has been determined that the sensitivity of the present system to  $\text{O}_3$  via O atoms created by photolysis is approximately 2% of that caused by O atoms created by  $\text{NO}_2$  photolysis. A reduction in this interference is possible by restricting the spectral passband of the source so that the low wavelength cutoff is increased.

## CONCLUSIONS

The method herein described for measuring the  $\text{NO}_2$  concentrations in ambient air has been shown to give sensitivities as high as 0.1 nA/ppb using an unfiltered 9558QA EMI photomultiplier. Since the fraction of  $\text{NO}_2$  photolyzed is negligible, the sensitivity is limited by the intensity of the photolysis source. While linear at ambient concentrations, the system response becomes nonlinear above 1 ppm of  $\text{NO}_2$  or at sufficiently high concentrations of hydrocarbons. The equivalent hydrocarbon concentrations calculated as necessary to cause nonlinearity are approximately one order of magnitude higher than those ordinarily encountered in ambient monitoring. A trade-off between sensitivity and linearity is obvious by altering the volume of the irradiation chamber or the flow rate (pumping speed) through it. Equivalent hydrocarbon concentrations 40 times higher than ambient levels are calculated to be sufficient to cause slight changes in the sensitivity of the system. Interference from the photolysis of ozone using the spectral region of 3150 to 4000 Å from a 200-W Hg-Xe arc source has been found experimentally to be approximately 2% for equal concentrations of  $\text{NO}_2$  and  $\text{O}_3$ . Both  $\text{NO}_2$  and  $\text{O}_3$  can be measured in the present experimental arrangement by mechanically chopping the light source. A signal from  $\text{O}_3$  alone is obtained by blocking the source while a signal from both  $\text{O}_3$  and  $\text{NO}_2$  is recorded when photolysis of  $\text{NO}_2$  occurs. A modified form of this system to monitor ambient levels of  $\text{NO}_2$  is being used and will be reported subsequently.

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