comparison. It would be improper to compare the data from the two balloon flights on a one-to-one basis for the temporal variation of NO concentration because of the different time of year when the two flights were carried out and, to some extent, because of the different geographical regions where the measurements were made. However, for the overlapping time when the NO measurements are available from the two flights it can be seen that the measured NO concentrations from the two flights are within the experimental error bars shown. More precise comparisons with respect to the exact local visible and UV sunrise will be published elsewhere (*7*).

We see from Fig. 1B that the maximum measured NO concentration occurred at ~15:00 M.S.T. (21:00 U.T.) and was $(22 \pm 6) \times 10^8$ molecule cm^{-3}. The slow rise of the NO concentration from ~11:00 to ~14:00 local time seen for the first balloon flight of fall 1973 is confirmed by the similar data from the second set of measurements. This slow rise is explained in terms of a slow dissociation of N_2O_5 and is not unexpected (*8*). A more dramatic event in the measured NO concentration is seen to occur at times starting ~18:00 M.S.T. (00:00 U.T.). Within a time period of about 1.5 hours, the NO concentration dropped from $\sim 20 \times 10^8$ to $< 3 \times 10^8$ molecule cm^{-3}. This drop is associated with the reduction in the solar UV radiation reaching the environs of the balloon because the solar radiation traverses longer and longer paths as the sun is setting. This reduction in solar UV radiation diminishes the NO production rate as seen from the reactions described in Eqs. 1 and 2. The recombination of NO with O_3 described in Eq. 3 is expected to remove the NO with a time constant of the order of 100 to 1000 seconds for generally accepted rate constants and an O_3 concentration of $\sim 10^{12}$ molecule cm^{-3}. With the sun completely set and all the solar UV radiation gone, all the NO is converted into NO_2 as is seen from Figs. 1B and 2B. The measured concentration of stratospheric NO and its remarkable temporal variation is the first direct confirmation of the importance of the dynamic NO catalytic cycle in the stratospheric O_3 balance.

A further objective of the present balloon flight was to attempt to obtain similar data at a lower altitude next morning, thus adding a set of data in the vertical profiling of the NO concentration temporal variation. However, as seen in Fig. 1A, the balloon and payload rapidly lost altitude after sunset. It was not possible to hold the altitude beyond midnight, and the mission for the next day was aborted at 02:30 M.S.T. It is, however, clear that further future flights of the experiment with improved balloon altitude control will allow us to obtain much needed data on the stratospheric chemistry. The intrinsic spectroscopic nature of the technique should allow measurements of a variety of gaseous species of interest by the proper choice of a tunable laser.

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9. We thank R. J. Kerl, J. S. Hasiak, C. Adams, and C. Pace of Bell Telephone Laboratories for technical assistance. We are also grateful to V. K. Smith, R. Myers, and A. C. Watts of Sandia Laboratories, Dr. H. Ballard of Atmospheric Sciences Laboratory, and A. Korn of the Air Force Cambridge Research Laboratory for enormous help given in this successful flight. Major B. B. Burnett of the Air Force Cambridge Research Laboratory, Holloman Air Force Base Balloon Branch, provided generous ground support for which we are grateful.

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Photochemical Smog Systems: Effect of Dilution on Ozone Formation

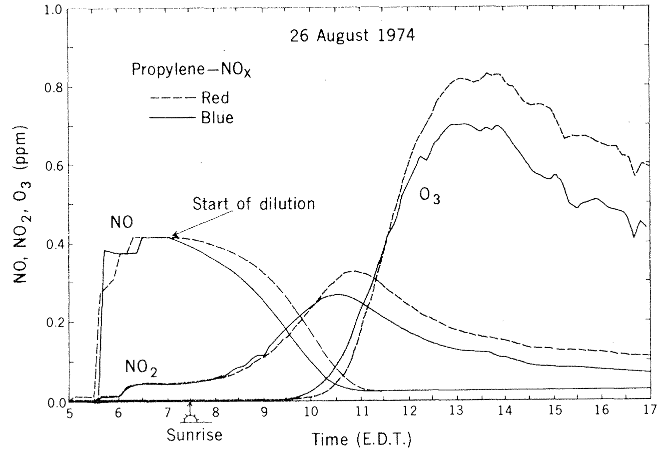
Abstract. *Dilution of a photochemical system containing hydrocarbons and oxides of nitrogen can lead to higher ozone concentrations than are observed in a static system. This effect was observed in an outdoor smog chamber with a hydrocarbon mix simulating urban systems.*

When studying urban photochemical smog systems with the use of chamber simulations, most researchers assume the worst case condition for O_3 production to be a system that is closed and static. This is not necessarily true under all conditions. Work described in this report shows that under some conditions a dynamically diluting system is capable of forming more O_3 than the static system, when each is charged with the same initial concentration of hydrocarbon and oxides of nitrogen ($NO_x = NO + NO_2$). This report shows the necessity of considering dilution, hydrocarbon reactivity, and diurnal solar radiation in photochemical smog reactions.

For the past 2 years the University of North Carolina has been operating a large dual-compartment (156 m^3 per side) outdoor smog chamber to investigate the effect of hydrocarbon control on afternoon concentrations of NO_2 and O_3. It was originally thought that the worst urban smog conditions could best be simulated in the outdoor chamber by a closed static system. This would represent an extremely stagnant air mass which could result in the maximum buildup of air pollutants over a city.

In order to evaluate this hypothesis, experiments were designed such that the same initial concentrations of nonmethane hydrocarbons (NMHC) and NO_x were introduced into both halves of the outdoor chamber. One side remained sealed off from the ambient atmosphere and was operated in the normal static mode, whereas the other side was slowly diluted with rural background air at a given time in the morning. The dilution air was not scrubbed to remove ambient hydrocarbons or oxides of nitrogen. At this location, background air has contained less than 0.02 part per million (ppm) of NO_x and has exhibited low reactivity (NO oxidation rate ≈ 0.2 part per billion per minute). The chamber halves have been labeled "red" and "blue" to help distinguish between the pollutant profiles graphically illustrated in Figs. 1 and 2. We discuss here two different dilution/static smog systems: (i) a reactive hydrocarbon-NO_x system (fast) with propylene as the hydrocarbon; dilution rate, 5.7 percent per hour (Fig. 1): and (ii) a less reactive hydrocarbon-NO_x system (slow) with urban mix as the hydrocarbon; dilution rate, 9.5 percent per hour (Fig. 2).

Let us consider first the reactive system. Both chamber sides have identical reactant profiles until 07:05 (Fig. 1), when dilution begins in the blue side. Propylene, NO_2, and NO are then slowly removed from the blue chamber by the dilution system. At the same time, however, NO_2 is being gen-



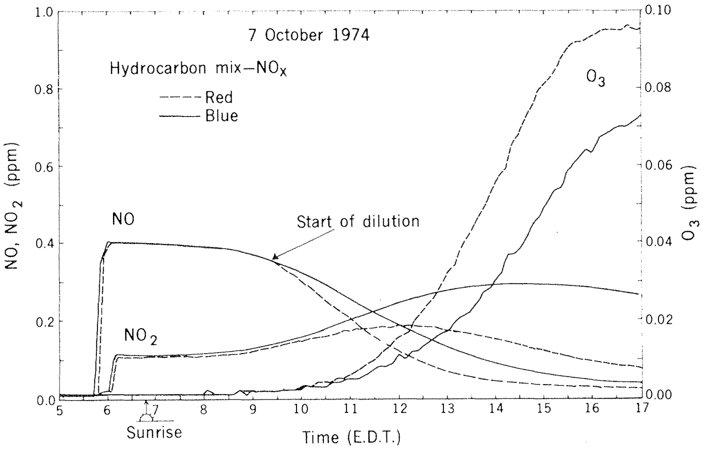


Fig. 1. Static/dilution experiment, with propylene as the hydrocarbon. Initial conditions: red side, 2.8 ppm of carbon NMHC and 0.45 ppm of NO_X; blue side, 2.6 ppm of carbon NMHC and 0.45 ppm of NO_X. Blue side diluted at 5.7 percent per hour. Fig. 2. Static/dilution experiment, with urban mix as the hydrocarbon. Initial conditions: red side, 2.4 ppm of carbon NMHC and 0.50 ppm of NO_X; blue side, 2.4 ppm of carbon NMHC and 0.50 ppm of NO_X. Red side diluted at 9.5 percent per hour.

erated in the blue side at a faster rate than it is being removed by dilution and actually appears almost as fast as NO_2 in the red (undiluted) chamber. This creates a situation in which the ratio of NO_2 to NO is higher in the blue chamber than in the red. If one assumes that pseudophotostationary equilibrium can be used to approximate the O_3 concentration at each point in time (Eq. 1), then the ratio of the NO_2 concentration to the NO concentration governs the O_3 concentration at a given light intensity.

$$\frac{[NO_2]}{[NO]} = \frac{k_3}{k_1}[O_3] \qquad (1)$$

where k_1 (Φk_a for NO_2) is the rate constant for the reaction

$$NO_2 + h\nu - NO + O$$

and k_3 is the rate constant for the reaction

$$NO + O_3 \rightarrow NO_2 + O_2$$

In the reactive system (Fig. 1) O_3 is initially generated more quickly in the diluted side. However, NO_X is being removed by dilution and the potential NO_2 peak is therefore greater in the undiluted side. Hence, a higher ratio of NO_2 to NO is ultimately reached in the undiluted side during that period of the day when the solar intensity is greatest (that is, greater value for k_1) and is accompanied by a faster O_3 generation rate and higher O_3 concentrations.

The less reactive smog system can be analyzed in a similar manner. Both sides initially contain an urban hydrocarbon mix consisting of 2.4 ppm of carbon and 0.5 ppm of NO_X (20 percent (NO_2). Dilution begins in the red side at about 09:00 (Fig. 2), and, soon after, this side is generating O_3 faster than the static side. The major difference between this less reactive system and the reactive propylene system is that for the less reactive system a higher ratio of NO_2 to NO is not reached in the undiluted side until the sun is beginning to set. The net effect is lower and lower values of k_1 during the greatest period of potential O_3 generation for the undiluted side.

In summary, the effect of different dilution rates and time at which dilution begins cannot be quantified at this time. However, on the basis of the two experiments that have been presented here, certain phenomena of dilution/static smog systems may be elucidated. Reactive systems, which would normally achieve maximum oxidant values during the early afternoon, may initially generate oxidant faster under dilution conditions but probably will not reach the oxidant concentrations generated by static systems. By contrast, less reactive systems under certain dilution conditions may actually generate more oxidant. In the experiment considered here, the oxidant concentration of the diluted side actually exceeded the federal air quality standard (0.08 ppm) (*1*) although that of the undiluted side did not. Greater control of the hydrocarbon content as compared to the NO_X content tends to shift the urban atmosphere in the direction of one containing less reactive mixtures. Dilution as opposed to static experimental conditions may prove to be more important if smog chamber data are to be used as guides in developing certain future control strategies.

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Behaviorally Evoked Hippocampal Theta Waves: A Cholinergic Response

Abstract. *Forced running in a treadmill results in the instantaneous appearance of a synchronous electroencephalographic pattern in the dorsal hippocampus of the rat. A similar bioelectric response in the absence of movement is induced by physostigmine. Both responses are blocked with scopolamine. Lesions of the medial septal nucleus abolish hippocampal theta waves induced by forced running or physostigmine.*

There is substantial evidence that the hippocampal theta pattern recorded from the unanesthetized, unrestrained mammal is associated with the initiation of movement (*1–4*). This bioelectric pattern can be elicited instantaneously and maintained indefinitely by placing the animal upon a moving treadmill (*4*). The amplitude of these behaviorally evoked hippocampal theta waves varies directly with the speed of movement (*4*).

Earlier electrophysiological experiments with acute, immobilized preparations have demonstrated that hippocampal theta patterns can be obtained with either high-frequency electrical stimulation of the brainstem reticular formation or with systemic administration of physostigmine, a cholin-