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report of investigations 7433

# ON THE FUNCTION OF HYDROCARBON AND NITROGEN OXIDES IN PHOTOCHEMICAL-SMOG FORMATION

UNITED STATES DEPARTMENT OF THE INTERIOR

BUREAU OF MINES

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By Basil Dimitriades

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# ON THE FUNCTION OF HYDROCARBON AND NITROGEN OXIDES IN PHOTOCHEMICAL-SMOG FORMATION

by

Basil Dimitriades[1]

## ABSTRACT

The roles of hydrocarbons and nitrogen oxides in smog formation were investigated by the Bureau of Mines. Samples of automobile exhaust with varying HC and $NO_x$ levels were irradiated in a smog chamber under conditions that resulted in smog levels similar to those observed in the atmosphere. Results were used to define the patterns that describe the dependence of a number of smog manifestations on HC and on $NO_x$. Using these dependence data and some simplifying assumptions, estimates were made of the ranges within which HC and $NO_x$ must lie in order to obtain specified levels of air quality.

## INTRODUCTION

Since its inception, photochemical-smog abatement has been oriented toward reduction of hydrocarbon (HC) emissions in the atmosphere because it has been demonstrated that reduction of HC, one of the major photochemical-smog reactants, would be beneficial and because the technological problems in implementing such control were relatively simple. Conversely, control of the other major reactant, the nitrogen oxides ($NO_x$)--nitric oxide (NO) plus nitrogen dioxide ($NO_2$)--has not been applied primarily because of the uncertainty about its merits and secondarily because the related technological control problems are more difficult.

This report covers experimental work performed by the Bureau of Mines to determine relative contribution of HC and $NO_x$ in smog formation and to associate air quality with the HC:$NO_x$ ratio using current atmospheric quality criteria. This work is part of a major effort within the Bureau of Mines to study fuel technology and combustion phenomena, specifically, the photochemical-smog content of automotive emissions as a function of HC and $NO_x$ levels. Automobile exhaust was used because it is a readily available source of sample mixtures nearly identical in composition to that of the mixture in smog-infested atmospheres.

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The roles of HC and $NO_x$ in smog phenomena had been studied (3, 5, 17-19, 21-22)[2] with varied investigative approaches, experimental conditions, and apparatus. Clarification of the roles of HC and $NO_x$ was attempted using both atmospheric (22) and laboratory data. For the latter, samples of exhaust or synthetic HC-$NO_x$ mixtures were photoirradiated in environmental chambers where atmospheric conditions were simulated with varying degrees of proximity. In such studies, dilute automobile exhaust is considered a particularly appropriate sample mixture because its composition is similar to that of a typically polluted atmosphere. The unavoidable presence of $NO_x$ in exhaust, however, prohibits use of the $NO_x$ level as a truly independent variable. Because of this latter restriction, the HC:$NO_x$ ratio was varied by altering engine operating conditions; experimental data on dependence of exhaust reactivity on $NO_x$ were interpreted to represent not the effect of $NO_x$, but rather the effect of the overall change in exhaust composition that accompanies change in exhaust $NO_x$ (5, 19).

Other adopted investigative approaches are based on use of synthetic exhaust mixtures (21) or simple HC-$NO_x$ mixtures where $NO_x$ can be a truly independent variable (3, 16). These approaches, while appropriate for basic studies of reaction mechanisms, may, however, result in a picture of the HC and $NO_x$ effects that does not always agree with the inherently more valid conclusions from exhaust studies. Results of this and other research (2) have indicated such disagreement.

An understanding of the varied experimental methodology is important for the interpretation of experimental evidence in reports on studies of the HC and $NO_x$ roles. The typical apparatus used for measurement in such studies is an environmental chamber of several cubic feet capacity, in which the sample of diluted exhaust or synthetic HC-$NO_x$ mixture is irradiated with artificial sunlight. Results from such tests have involved extensive uncertainties introduced through inadvertent and little understood variation in experimental parameters in the reactivity measurement. Thus, intensity and spectral energy distribution of chamber radiation, nature and condition of wall surface, chamber surface-to-volume ratio, humidity, and background contamination are factors with effects which either are not fully understood or have not been adequately controlled. Furthermore, methods for measurement of smog manifestations in chamber studies have a rather short history of development, and for most methods, accuracy and precision are inadequate when concentrations of reactants in the chamber are as low as those typically present in the atmosphere. This difficulty and the unavoidable background contamination have led investigators to use reactant levels equivalent to several parts per million of total hydrocarbon--clearly much higher than the level in a typically polluted atmosphere--and to extrapolate their results or conclusions down to the concentration range of interest (21).

The discussion in preceding paragraphs points out that for a more complete understanding of the roles of HC and $NO_x$ in photochemical-smog formation, there is need for additional experimental evidence that would satisfy the following requirements:

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[2] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

1. Evidence must be obtained with test mixtures similar to those in the atmosphere rather than with synthetic simple mixtures of HC and $NO_x$.

2. HC and $NO_x$ levels in tests must be within a range that includes levels in current problem atmospheres as well as those anticipated as a result of control application.

3. Smog potential or reactivity of test mixtures must be measured in large environmental chambers capable of producing typical atmospheric levels of smog from typical early morning atmospheric levels of HC and $NO_x$.

This current research was performed to provide the needed information under the specified conditions. Exhaust mixtures were used to study reactivity as a function of HC and $NO_x$ at levels from 0.3 to 5.0 ppmC for total HC and from 0.08 to 1.4 ppm for $NO_x$. The experimental program incorporated findings from recent Bureau studies at the Bartlesville Petroleum Research Center about the effects of various experimental parameters upon chamber reactivity measurements. The internal consistency of chamber data obtained with these experimental systems has been demonstrated and reported (9, 11).

## EXPERIMENTAL WORK

The experimental program consisted of a series of chamber irradiation tests in which reactivity of exhaust was measured for varying levels of total HC and $NO_x$. These initial reactant levels are shown in the diagram of figure 1

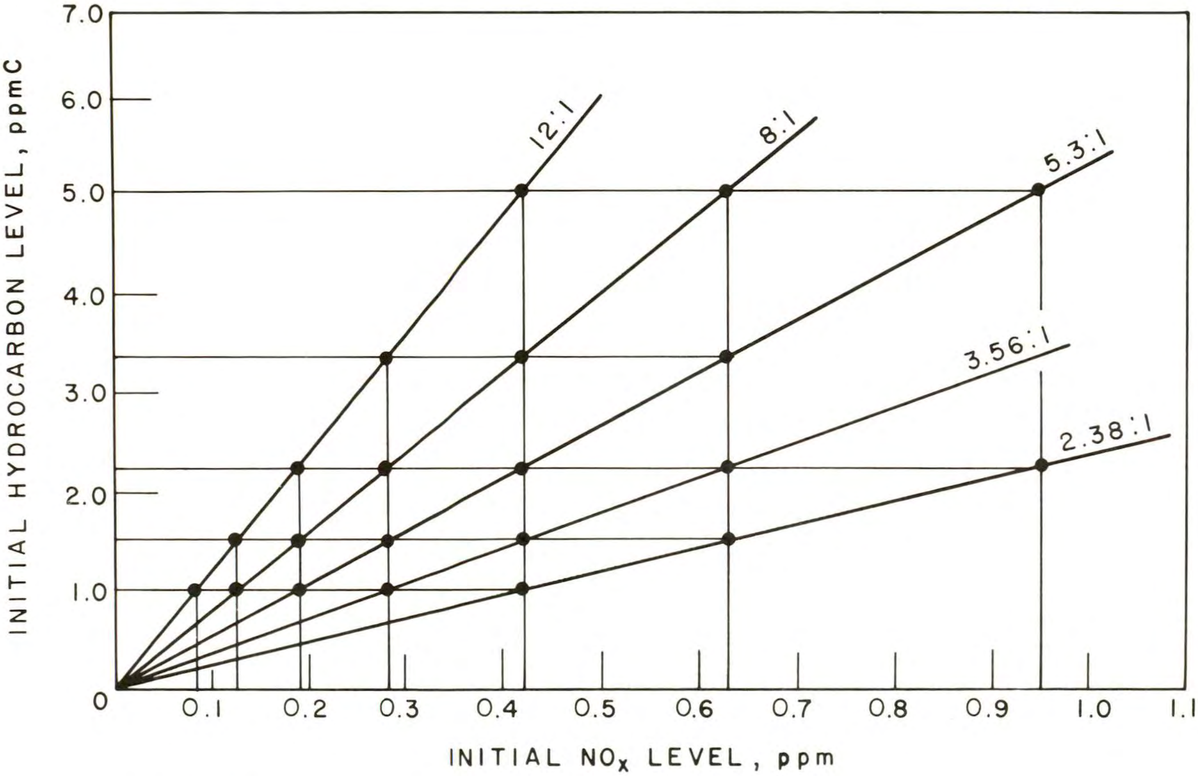

FIGURE 1. - Hydrocarbon and $NO_x$ Levels in Tested Exhaust Samples.

as points in the (HC, $NO_x$) plane. Points on horizontal lines represent conditions designed to determine the effect of $NO_x$ at constant HC; points on vertical lines represent conditions for determining the effect of HC at constant $NO_x$. Appropriately arranged in the two-dimensional space (fig. 1), these same points represent conditions for determining the effect of HC and $NO_x$ at a constant HC-$NO_x$ ratio. Reactivity was measured and expressed in terms of the rate of $NO_2$ formation (9) and oxidant, peroxyacetyl nitrate (PAN), formaldehyde (HCHO), and nitrogen dioxide ($NO_2$) dosage. Additionally, reactivity was expressed in terms of the same units used to express the California air quality standards for oxidant and $NO_2$ (7), namely, time during which oxidant exceeded 0.1 ppm and time during which $NO_2$ exceeded 0.25 ppm.

## Generation and Preparation of Exhaust Sample

Exhaust gas was generated using a 1963 automobile equipped with a 283-cu-in engine and operated to follow the seven-mode Federal test (26) cycle. The engine was fitted with a modified carburetor to allow wide-range adjustment of the air-to-fuel ratio (A/F). With normal carburetor settings, the HC-$NO_x$ ratio in exhaust was 6:1, approximately. To study ratio effect at ratios to 12:1, the A/F ratio was adjusted for a richer fuel mixture. Chromatographic analysis of exhaust hydrocarbons, before and after the carburetor adjustment, gave results shown in table 1. From these results, the effect of carburetor adjustment on composition of exhaust hydrocarbon was judged to be negligible.

TABLE 1. - Chromatographic composition of exhaust hydrocarbons under normal and under rich fuel-mixture conditions

| Carburetor conditions | Hydrocarbon component(s), mole fraction (v/v) | | | | | | Reactivity[1] |
|---|---|---|---|---|---|---|---|
| | $C_1$-$C_5$ paraffins | Total paraffins | Total olefins | Total aromatics | Acetylene | Ethylene | |
| Normal.... | 32.1 | 44.2 | 26.5 | 15.1 | 13.5 | 12.5 | 0.89 |
| Rich...... | 34.5 | 46.9 | 25.0 | 16.5 | 11.0 | 13.8 | .88 |

[1] Reactivity per mole of total hydrocarbon as defined and discussed in reference (10).

The exhaust stream was sampled with an all-heated, variable-rate proportional sampler, the output of which was received in a Tedlar[3] bag (13) covered with dark cloth and precharged with dry nitrogen. Resultant exhaust-to-$N_2$ ratio in the bag was approximately 1:5. Immediately following sample collection, the bag content was used to charge the chamber (a 10- to 15-minute operation) and to provide samples for chromatographic analysis. These chromatographic data were used to establish the extent to which composition of exhaust hydrocarbons varied unavoidably from test to test.

## Irradiation Chamber

Some design and performance characteristics of the irradiation chamber have been reported (11). The chamber (fig. 2) has a 100-$ft^3$ capacity and

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[3] Trade names are mentioned for identification only and do not imply endorsement by the Bureau of Mines.

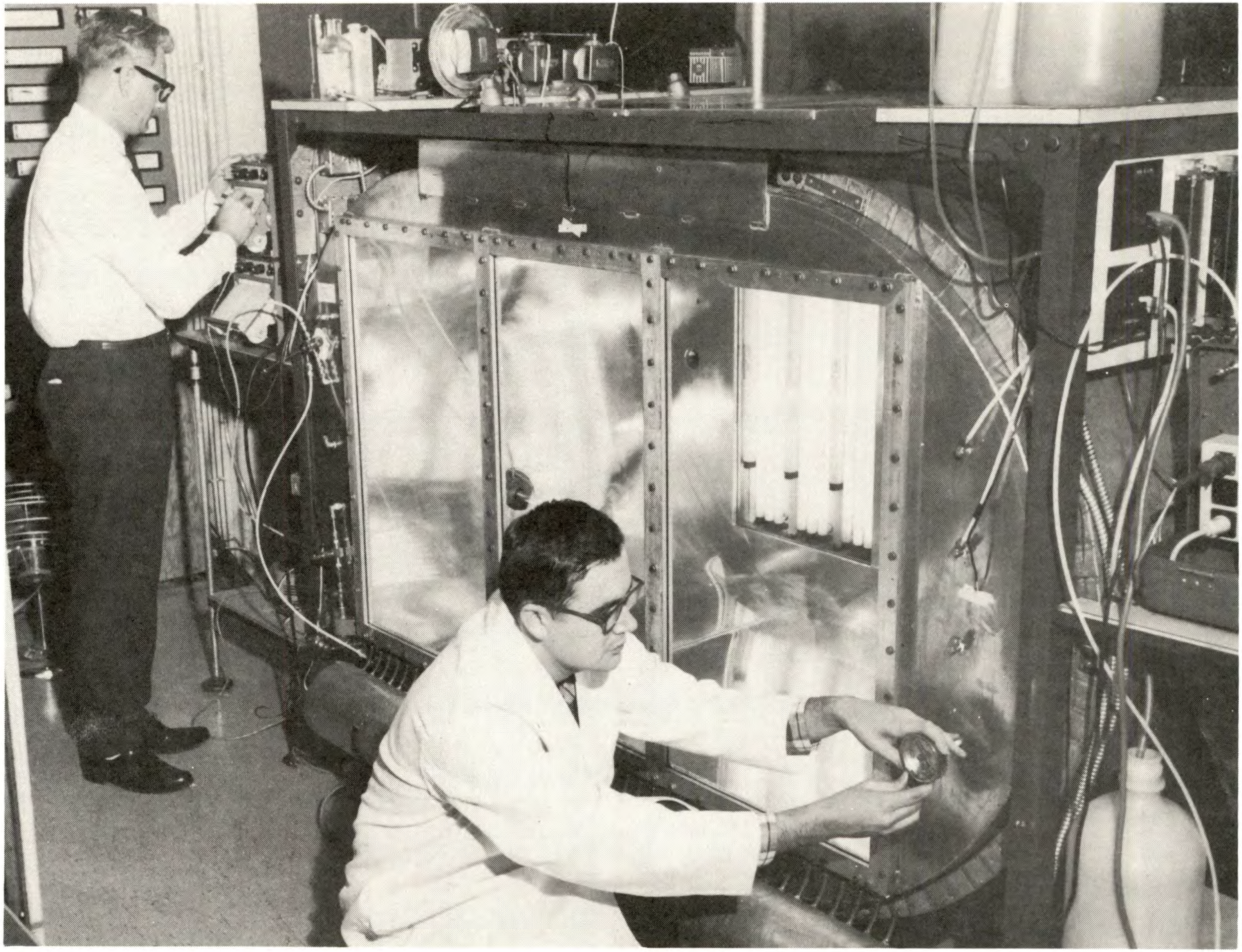

FIGURE 2. - The Smog Chamber.

125-ft$^2$ wall surface area of which 88 ft$^2$ is polished aluminum and 37 ft$^2$ is Pyrex glass (Corning No. 7740). Radiation is provided by 102 fluorescent lamps--56 blacklights (General Electric F30T8-BL), 28 blue lamps (Westinghouse F30T8/B), and 18 sunlamps (Westinghouse FS20)--powered by 51 6G100 ballasts. The Pyrex windows effectively filter out radiation of less than 2,800 Å wavelength and transmit about 90 percent of radiation of higher than 3,400 Å wavelength.

Relative light intensity is monitored by a photomultiplier tube (RCA 1P28) in line with an optical filter (Corning C 57-54). The photomultiplier-filter system is attached to the chamber so as to receive a beam of light that is reflected off a circular area of internal wall surface with a diameter of about 1 ft. Photomultiplier tube and optical filter were selected to respond to radiation ranging in wavelength from 2,800 to 4,000 Å, with maximum response at 3,400 Å.

The light-monitor system is not calibrated and therefore cannot be used for daily corrections of reactivity data. However, it can be used to establish light-intensity changes over long periods of time and subsequent effects on reactivity-measurement results. For this purpose, light intensity and corresponding reactivity data were used from biweekly measurements of the reactivity of a standard ethylene-$NO_x$ mixture (at 3 ppmC/1 ppm). (Such measurements were conducted for the purpose of monitoring performance of entire chamber facility.) Results obtained in 1 year gave a correspondence between light-monitor response and rate-of-$NO_2$-formation reactivity shown in figure 3. The dark circles represent runs in which light intensity was changed artificially, either by shutting off 20 pct of the lights--and maintaining lamp type distribution--or by using aluminum reflectors to increase effective light intensity. Despite the large amount of scatter that probably resulted, at least in part, from variation in response of the uncalibrated monitor, the data in figure 3 show clearly that (a) ethylene reactivity varies proportionally with light monitor response, and (b) reactivity measurement results may vary over long periods by as much as plus or minus 20 pct. Such variation may be caused by random variation in lamp output and by changes in reflectivity of wall surface. During this study light-monitor response varied from test to test by about plus or minus 10 pct. Since the monitor was not calibrated, no correction of the reactivity data for light-intensity variation was attempted, other than the screening of tests in which the monitor response was clearly much higher or much lower than was the average level.

Further exploration of the stability of chamber light intensity revealed that the fluorescent lamp output varied significantly as a result of lamp-temperature variation. Figure 4 illustrates the magnitude of this temperature effect. The solid line of figure 4 shows change in light intensity with time when lamps were operated without cooling. When room air is rapidly circulated with a blower in the space between lamps and chamber walls, lamp output increases (see dashed line in fig. 4). While more detailed data on the correction of this problem are to be reported elsewhere, mention was made here in order to support the following assertions: (a) Lamp-temperature variation may account for part or all of random variation of light intensity; (b) with or without lamp cooling, light intensity is higher in the few minutes following

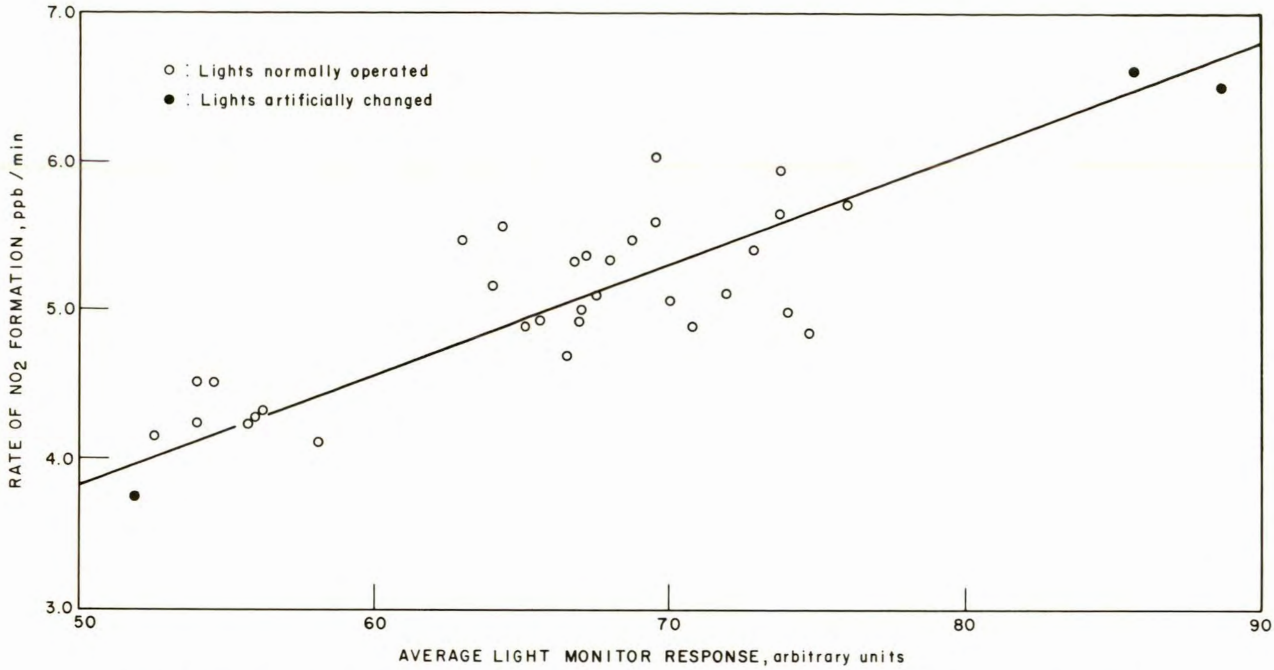

FIGURE 3. - Correlation of Ethylene Reactivity in Terms of Rate-of-$NO_2$ Formation and Light Monitor Response.

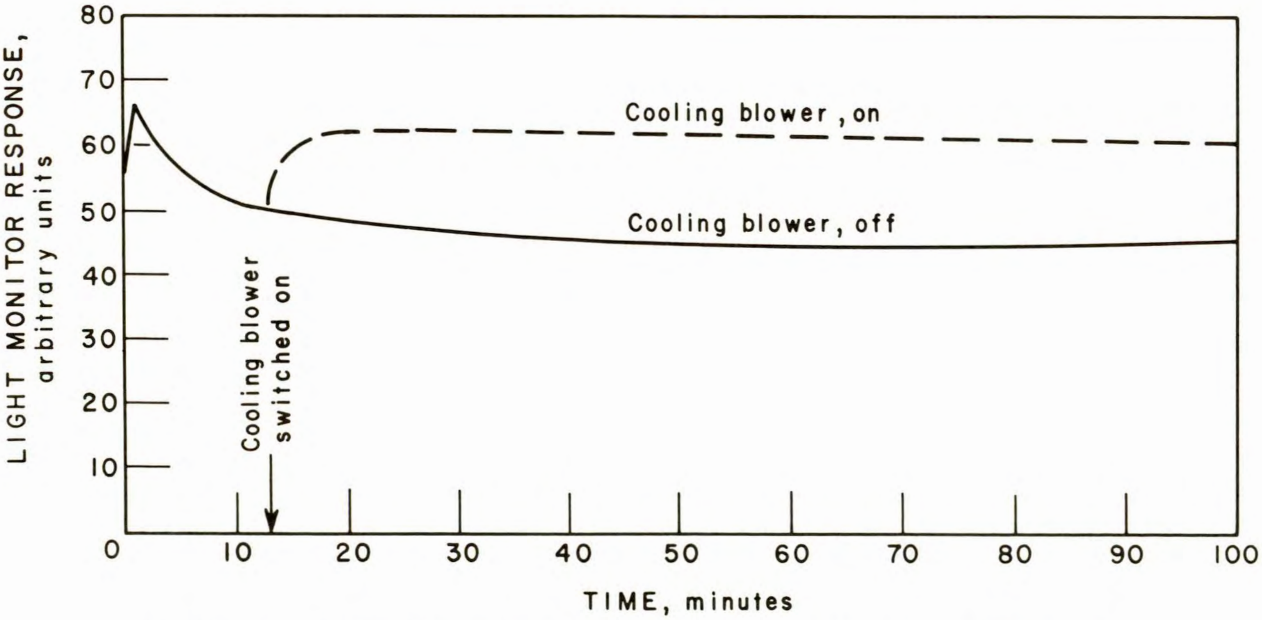

FIGURE 4. - Effect of Lamp Cooling on Lamp Output as Sensed by Light Monitor.

switch-on than in the remainder of the 6-hour test. In the chamber used in this study, the difference (expressed in terms of monitor response) was about 10 pct with lamp cooling and about 35 pct without lamp cooling.

The presence of lamp temperature effects suggests that the measurement of light intensity in the chamber by the commonly used method of $NO_2$ photolysis (25) is subject to uncertainty. This is so because the intensity is measured in the first 1 or 2 minutes after the lights are switched on and result is taken to represent light intensity level in the following several hours. Whereas, in fact, the measured level and the effective level differ to a degree that depends upon the change in lamp temperature during operation. The accuracy of the $NO_2$-photolysis method as applied to light intensity measurement is also questioned because the method ignores the contribution of secondary thermal reactions to $NO_2$ disappearance during photoirradiation (23). Disregard of the thermal-reaction contribution causes $NO_2$-disappearance data to reflect a higher rate of $NO_2$ photolysis--or higher "$k_D$" value--and, therefore, a higher level of light intensity. Finally, another question about the appropriateness of the $k_D$ method of measuring and expressing light intensity arises from comparison of data obtained with several large irradiation chambers. Such comparison indicates that the Bureau's chamber has comparable $k_D$ value ($0.44\ min^{-1}$) but significantly lower reactivity values for specified HC-$NO_x$ systems than have the other chambers.[4] In conclusion, the author feels that the $k_D$ method for measuring relative light intensities, although sound in concept, provides questionable results. For this reason, in this research light intensity in the chamber was evaluated by direct comparison with the intensity of natural sunlight, as described next.

The light intensity was measured by irradiating a standard HC-$NO_x$ mixture with natural sunlight and with the chamber lights. The standard mixture, purified air that contained propylene and NO at 1 ppm each, was contained in a 300-liter Tedlar bag, 2-mil thick, and was irradiated either inside the chamber or on a rooftop against a background of light gray concrete. During each 6-hour irradiation test, NO, $NO_2$, oxidant, and PAN were monitored, and results were expressed in terms of rate-of-$NO_2$-formation oxidant dosage, and PAN dosage (11). Table 2 summarizes detailed experimental conditions and test results. The difference in results between the two rooftop measurements was attributed to difference in experimental conditions that included partial overcast (clear to slightly cloudy) during the 6-hour tests. These results indicated that light intensity for this study was comparable to that of natural sunlight at the time and geographical location designated. Time, location, and overcast conditions for these tests are judged to be close to those that represent a typical "irradiation" day in the United States during the smog season.

## Analytical Methods

The chamber facility includes two Beckman 109 analyzers for measurement of total hydrocarbon ($HC_t$), two Mast meters for oxidant, and two Beckman

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[4] Data exchanged through private communications with National Air Pollution Control Administration, California Air Resources Board, General Motors Company, and Gulf Oil Company.

K-1008 analyzers for $NO_2$ and $NO_x$. Instrument duplication is a safeguard against instrument malfunction and improves reliability of analytical data. The $HC_t$ analyzers were calibrated at the beginning of the study with synthetic hydrocarbon mixtures of exhaustlike composition and daily with a standard propylene blend. The oxidant and $NO_x$ analyzers are calibrated weekly as described previously (10). Peroxyacetyl nitrate is measured by low temperature gas chromatography coupled with electron capture detection (10); the system is calibrated hourly with a standard blend of ethyl nitrate. Formaldehyde is measured by the chromotropic acid method (4) at the rate of two duplicate determinations each hour.

TABLE 2. - Data from light-intensity measurements using irradiation of propylene + NO mixtures in bags

| | Bag on rooftop | | Bag inside chamber | |
|---|---|---|---|---|
| Date | 9/12/69 | 9/18/69 | 9/17/69 | 9/19/69 |
| Irradiation source | Sun | Sun | Chamber lights | Chamber lights |
| Irradiation time, hours | 6 | 6 | 6 | 6 |
| Start time | 10:00 a.m. | 10:37 a.m. | - | - |
| Average bag temp., ° F | 91 | 78 | 92 | 92 |
| Ambient humidity: | | | | |
| Relative, percent | 64 → 33 | 77 → 53 | ~40 | ~40 |
| Absolute, percent | ~2.0 | ~2.0 | ~2.0 | ~2.0 |
| Initial HC, ppmC | 3.0 | 3.0 | 3.0 | 3.0 |
| Initial $NO_x$, ppm | 1.0 | 1.0 | 1.0 | 1.0 |
| Initial $NO_2$, ppm | .06 | .05 | .13 | .08 |
| $R_{NO_2}$, ppb/min | 6.2 | 8.3 | 8.4 | 8.6 |
| Oxidant dosage, ppm × min | 58 | 87 | 57 | 74 |
| PAN dosage, ppm × min | 28 | 43 | 30 | 36 |

## Test Procedure

In test preparation, the chamber is flushed for 3 hours with prepurified air under infrared lamp heating that results in a wall temperature of about 125° F. Next, the chamber is sealed, and chamber air is recirculated overnight through a catalytic combustor, a charcoal column, and a particulate filter. Chamber air, so purified, contains less than 0.2 ppmC of total organic material and less than 0.02 ppm $NO_x$. Levels of photochemical reactivity associated with such background contamination can be surmised from the results of this study.

For an irradiation test, the chamber air is first humidified by a stream of pure air that bubbles through heated distilled water; resultant relative humidity is 25 pct at 92° F. The chamber is then charged with the bag sample of exhaust plus $N_2$ to the desired $HC_t$ level, and additional NO and $NO_2$ are injected to attain the specified levels. Initial $NO_2$ level, $(NO_2)_i$, is adjusted to about 10 pct of initial $NO_x$ but not less than 0.03 ppm or more than 0.15 ppm. Tests showed that at extremely low levels, $(NO_2)_i$ affected the rate of NO photooxidation ($R_{NO_2}$). At levels above 0.03 ppm, $(NO_2)_i$ did not affect $R_{NO_2}$ but affected the appearance time for oxidant and PAN; however, such an effect was quantifiable and corrections for variation in $(NO_2)_i$ were easily made. Chamber wall temperature during run was maintained at 92 (±1)° F by circulating room air in the space between the chamber windows and the lights.

## RESULTS

### Treatment of Raw Experimental Data

Results from the exhaust reactivity measurements are given in table 3 along with detailed data on initial chamber charge. The data of table 3 represent results that were corrected as follows:

#### Correction for Variation in Exhaust Hydrocarbon Composition

Hydrocarbon composition was expressed in terms of a calculated reactivity value, R, defined by equation 1:

$$R = \sum_{i=1}^{i=n} X_i \; R_i , \tag{1}$$

where $X_i$ and $r_i$ designate mole fraction and specific rate-of-$NO_2$-formation reactivity (18), respectively, for ith component; n is the number of hydrocarbon components--165 in this case--that are normally "seen" chromatographically (11). With these R data, a correction factor was used, as shown by equation 2:

$$(R_{NO_2})_i^{\text{corrected}} = (R_{NO_2})_i^{\text{raw}} \times \frac{\overline{R}}{R_i} , \tag{2}$$

where $(R_{NO_2})_i$ designates rate of $NO_2$ formation for ith sample, and $R_i$ and $\overline{R}$ represent calculated reactivity values for ith sample and for the average of the exhaust samples of the study. The correction factor $\frac{\overline{R}}{R_i}$ ranged from 0.91 to 1.09. No analogous correction factor was developed for the oxidant, PAN, HCHO, and $NO_2$ dosage results.

#### Correction for Variation in $(NO_2)_i$

For reasons already discussed, only the oxidant and PAN yield data were corrected. To correct for $(NO_2)_i$ variation, a reference $(NO_2)_i$ level was defined. Either a fixed level or a fixed fraction of the $(NO_x)_i$ level could have been selected. Because $NO_2$ forms from NO, it is more rational to view emission discharges of varying $NO_x$ levels as having a fixed $NO_2$:$NO_x$ ratio rather than having a fixed $NO_2$ level. However, control of the $NO_2$:$NO_x$ ratio in the low $(NO_x)_i$-level runs of this program was experimentally impossible. Furthermore, at $(NO_2)_i$ levels below 0.03 ppm, reactivity measurement results are subject to varying and unpredictable effects from the unavoidably varying $(NO_2)_i$. In contrast, setting a low $(NO_2)_i$ limit (0.03 ppm) presents no experimental difficulty and permits correcting reactivity measurement results for $(NO_2)_i$ variation. Therefore, the reactivity results were corrected using a 0.03 ppm $(NO_2)_i$ reference level. The oxidant and PAN yield results were corrected whenever the sample's $(NO_2)_i$ was higher or lower than 0.03 ppm. Correction consisted of shortening or extrapolating--along the time axis--

the oxidant and PAN buildup curves for a time equal to that attendant $NO_2$ change from 0.03 ppm to $(NO_2)_i$ or from $(NO_2)_i$ to 0.03 ppm. Such corrections were from 0 to minus 10 pct with highest corrections applied to data from lowest $(NO_x)_i$-level runs. Effects of varying $(NO_2)_i$ on $NO_2$ and HCHO yields are generally of smaller magnitude and are not calculable; therefore, no such corrections were made.

TABLE 3. - Initial reactant levels and exhaust reactivity measurements

| Initial reactant levels | | | Reactivity measurements | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| $HC/NO_x$ | HC, ppmC | $NO_x$, ppm | Rate of $NO_2$ formation, $(R_{NO_2})$, ppb/min | $NO_2$ dosage, ppm x min | Oxidant dosage, ppm x min | PAN dosage, ppm x min | HCHO dosage, ppm x min | Time[1], min | Time[2], min |
| 0 | < 0.1 | .081 | - | 13.4 | 4.9 | 0.16 | 11.8 | 0 | 0 |
| 2.7 | .20 | .075 | - | 16.5 | 23.3 | .64 | 19.6 | 111 | 0 |
| 2.6 | .70 | .265 | 1.95 | 50.5 | 16.3 | .51 | 31.0 | 53 | 0 |
| 2.5 | 1.53 | .618 | - | 104.5 | 12.5 | .55 | 43.2 | 0 | 266 |
| 3.2 | .30 | .093 | 1.02 | 15.5 | 26.5 | 1.20 | 20.4 | 137 | 0 |
| 3.5 | .44 | .124 | 1.27 | 22.7 | 23.3 | 1.05 | 22.7 | 105 | 0 |
| 3.8 | .67 | .175 | - | 33.5 | 25.9 | 1.43 | 27.4 | 128 | 0 |
| 3.5 | .97 | .276 | 2.62 | 53.6 | 22.6 | 1.16 | 36.0 | 109 | 0 |
| 3.7 | 1.50 | .409 | 2.91 | 82.8 | 16.0 | 1.66 | 55.3 | 79 | 173 |
| 3.7 | 2.25 | .606 | 5.01 | 123.9 | 21.2 | 1.70 | 66.5 | 110 | 300 |
| 3.7 | 3.66 | .923 | 6.41 | 174.4 | 13.9 | 2.50 | 79.1 | 63 | 310 |
| 3.6 | 3.37 | .936 | 6.17 | 160.7 | 16.3 | 1.76 | 72.4 | 0 | 307 |
| 3.7 | 5.96 | 1.384 | 9.24 | 217.9 | 13.5 | 2.41 | 97.3 | 0 | 322 |
| 5.4 | .44 | .081 | 1.02 | 15.2 | 41.4 | 1.65 | 28.0 | 225 | 0 |
| 5.6 | .70 | .125 | 1.87 | 22.4 | 44.4 | 3.19 | 33.2 | 218 | 0 |
| 5.6 | .98 | .175 | 2.69 | 33.7 | 40.7 | 3.42 | 39.5 | 204 | 0 |
| 5.5 | 1.49 | .272 | 3.27 | 50.3 | 44.5 | 3.77 | 51.5 | 202 | 0 |
| 5.6 | 2.24 | .398 | 4.49 | 79.1 | 50.8 | 4.71 | 63.7 | 207 | 155 |
| 5.5 | 3.29 | .599 | 6.00 | 114.1 | 76.0 | 5.01 | 87.7 | 228 | 253 |
| 5.3 | 5.06 | .946 | 9.48 | 167.8 | 59.5 | 8.96 | 114.5 | 196 | 310 |
| 6.9 | .63 | .091 | 1.52 | 11.2 | 43.8 | 3.80 | 34.1 | 224 | 0 |
| 8.4 | 1.02 | .121 | 2.06 | 18.8 | 49.7 | 5.07 | 53.3 | 248 | 0 |
| 7.7 | 1.02 | .133 | 2.38 | 22.2 | 49.3 | 4.76 | 49.5 | 234 | 0 |
| 7.7 | 1.45 | .188 | 3.40 | 30.4 | 70.3 | 5.92 | 56.7 | 256 | 0 |
| 7.5 | 1.45 | .192 | 3.81 | 25.5 | 70.2 | 7.63 | 55.4 | 262 | 0 |
| 8.8 | 2.25 | .256 | - | 40.6 | - | 5.44 | 76.3 | - | 0 |
| 8.1 | 2.25 | .276 | - | 42.3 | - | 6.94 | 69.7 | - | 0 |
| 8.4 | 2.34 | .278 | 5.04 | 45.8 | - | - | 79.1 | - | 0 |
| 8.1 | 3.30 | .409 | - | 59.2 | 101.7 | 8.23 | 82.5 | 256 | 101 |
| 8.0 | 3.30 | .414 | 6.52 | 57.3 | 97.6 | 11.85 | 96.1 | 268 | 91 |
| 7.8 | 5.00 | .641 | 8.15 | 86.2 | 113.1 | 14.41 | 134.6 | 256 | 168 |
| 12.0 | 1.00 | .083 | 1.56 | 13.8 | 62.6 | - | 38.6 | 276 | 0 |
| 10.9 | 1.00 | .092 | - | 10.7 | 60.9 | 5.48 | 45.6 | 286 | 0 |
| 12.1 | 1.49 | .123 | 2.93 | 20.0 | 99.1 | - | 56.2 | 290 | 0 |
| 12.7 | 1.50 | .118 | 2.90 | 19.3 | 83.0 | 6.26 | 56.6 | 294 | 0 |
| 11.8 | 1.50 | .127 | - | 18.9 | - | - | 43.7 | - | 0 |
| 11.5 | 2.25 | .195 | 4.56 | 22.4 | 105.9 | 7.71 | 68.8 | 296 | 0 |
| 12.3 | 2.25 | .183 | 4.47 | 19.0 | 93.4 | 12.29 | 70.7 | 297 | 0 |
| 12.3 | 3.38 | .274 | 5.92 | 30.6 | 109.0 | 11.35 | 104.5 | 288 | 0 |
| 12.0 | 3.38 | .281 | 6.40 | 28.4 | - | 16.63 | 111.2 | - | 0 |
| 11.0 | 4.76 | .434 | 8.88 | 42.6 | 143.3 | 20.36 | 146.5 | 309 | 68 |
| 12.2 | 5.06 | .416 | 9.92 | 42.7 | 164.5 | 16.51 | 115.0 | 310 | 72 |

[1] Time during which oxidant exceeded 0.1 ppm.

[2] Time during which $NO_2$ exceeded 0.25 ppm.

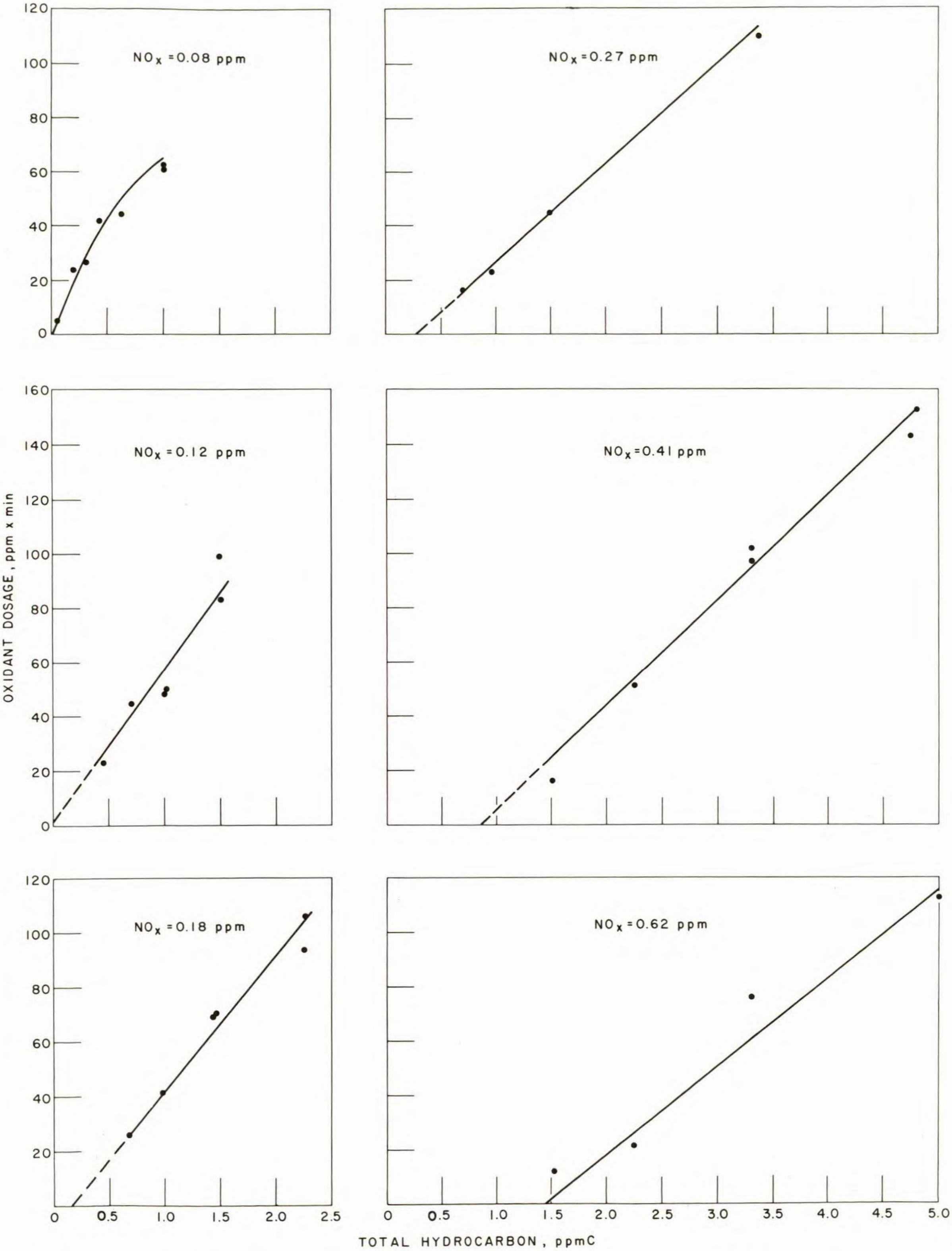

FIGURE 5. - Oxidant-Dosage Reactivity of Exhaust as a Function of Total Hydrocarbon at Various $NO_x$ Levels.

The data of table 3 have been plotted to depict each reactivity manifestation as a function of HC for constant $NO_x$ (fig. 5) and as a function of $NO_x$ for constant HC (fig. 6). Further data read off these plots were used to plot reactivity as a function of HC or $NO_x$ at constant HC-$NO_x$ ratios (figs. 7-8). Table 4 summarizes the data used to construct these latter plots. Graphical depiction of the HC and $NO_x$ effects was preferred to statistical analysis because it allowed some freedom in assessing reliability of the data individually. For example, the reliability of each oxidant yield value was judged by the consistency of the patterns that described dependence of oxidant on HC, dependence of oxidant on $NO_x$, correlation of oxidant and PAN yields, and by the agreement of results from the two oxidant measuring instruments.

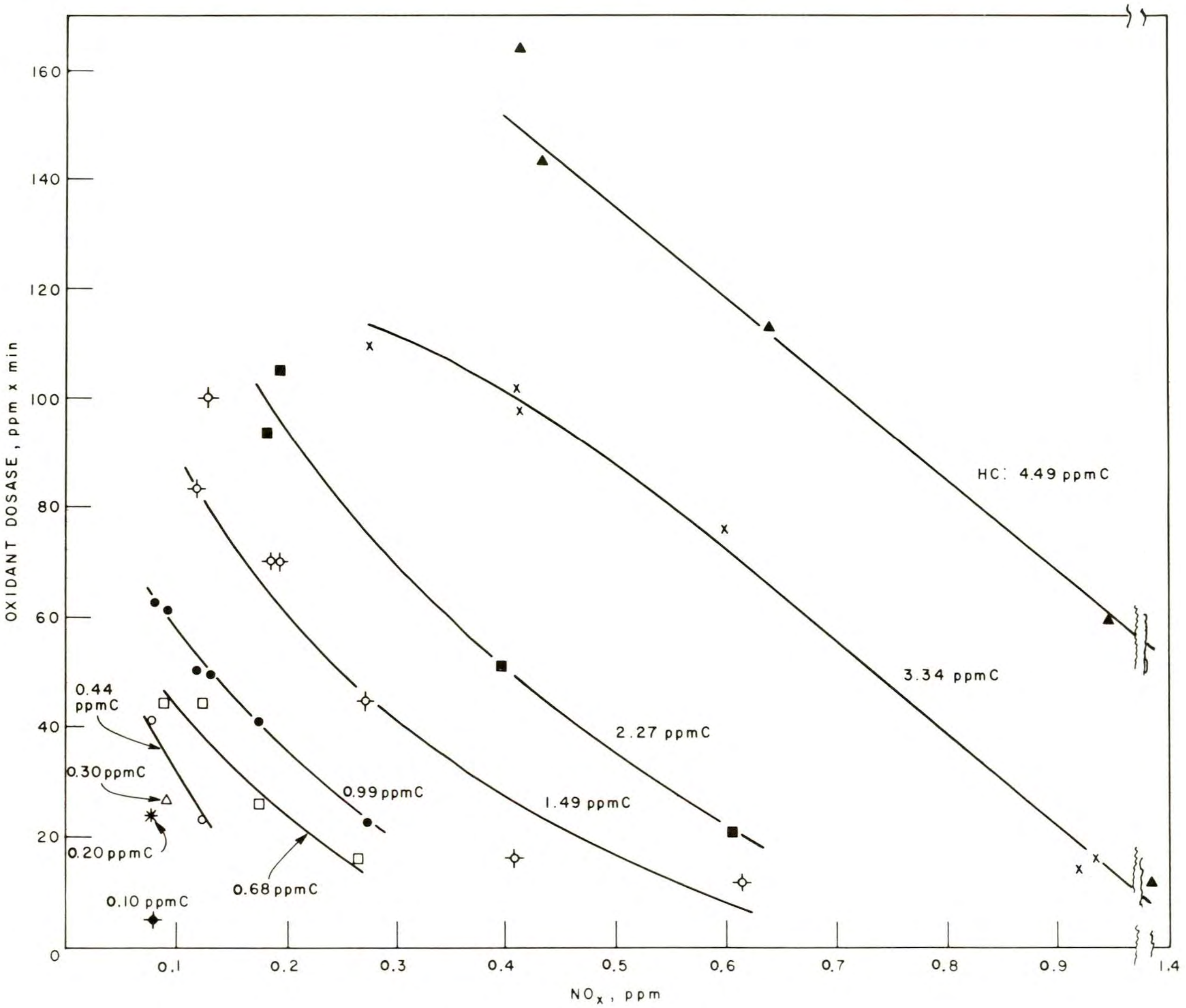

FIGURE 6. - Oxidant-Dosage Reactivity of Exhaust as a Function of $NO_x$ at Various HC Levels.

TABLE 4. - Reactivity data for constant HC-$NO_x$ ratios--data were read from plots of reactivity versus HC or reactivity versus $NO_x$

| HC/$NO_x$ | $NO_x$, ppm | HC, ppmC | Dosage, ppm x min | | | | $R_{NO_2}$ ppb/min |
|---|---|---|---|---|---|---|---|
| | | | Oxidant | PAN | HCHO | $NO_2$ | |
| 1.0................. | 0.085 | 0.085 | 9.5 | 0.30 | 13.5 | 15.0 | 0.20 |
| | .124 | .124 | 8.0 | 0 | 15.0 | 22.0 | .40 |
| | .185 | .185 | 2.0 | 0 | 16.0 | 34.0 | .55 |
| | .273 | .273 | 0 | 0 | 18.0 | 53.0 | .80 |
| | .413 | .413 | 0 | 0 | 20.5 | 82.0 | 1.00 |
| | .616 | .616 | 0 | 0 | 25.5 | 124.5 | 1.57 |
| | .935 | .935 | 0 | 0 | 30.0 | 190.0 | 1.88 |
| | 1.384 | 1.384 | 0 | 0 | - | - | - |
| 2.5................. | .085 | .2125 | 21.0 | .85 | 18.0 | 15.0 | .56 |
| | .124 | .310 | 19.0 | .65 | 20.5 | 22.0 | .90 |
| | .185 | .463 | 18.5 | .25 | 24.0 | 34.0 | 1.40 |
| | .273 | .683 | 15.0 | 0 | 30.0 | 53.0 | 1.85 |
| | .413 | 1.033 | 7.0 | 0 | 36.0 | 82.0 | 2.77 |
| | .616 | 1.540 | 3.5 | 0 | 48.0 | 125.0 | 3.65 |
| | .908 | 2.270 | 0 | 0 | 56.0 | 186.0 | 5.00 |
| | 1.336 | 3.340 | 0 | 0 | 72.0 | - | 6.40 |
| 3.5................. | .085 | .298 | 27.5 | 1.25 | 21.0 | 15.0 | .80 |
| | .124 | .434 | 26.0 | 1.45 | 24.0 | 22.0 | 1.25 |
| | .185 | .648 | 25.0 | 1.30 | 29.0 | 34.0 | 1.90 |
| | .273 | .956 | 24.5 | 1.30 | 37.5 | 53.0 | 2.50 |
| | .413 | 1.446 | 23.0 | 1.35 | 46.5 | 83.0 | 3.00 |
| | .616 | 2.156 | 23.5 | 1.70 | 63.0 | 122.0 | 4.80 |
| | .954 | 3.340 | 13.0 | 1.70 | 78.0 | 181.0 | 6.33 |
| | 1.429 | 4.970 | 9.0 | 1.80 | 95.0 | - | 9.40 |
| 5.5................. | .085 | .468 | 40.2 | 2.05 | 26.5 | 15.0 | 1.17 |
| | .124 | .682 | 39.5 | 3.00 | 32.0 | 21.5 | 1.80 |
| | .185 | 1.018 | 43.5 | 3.50 | 40.0 | 33.0 | 2.72 |
| | .273 | 1.502 | 45.0 | 3.85 | 53.0 | 50.0 | 3.60 |
| | .413 | 2.272 | 54.0 | 5.20 | 67.0 | 75.0 | 4.58 |
| | .616 | 3.388 | 64.5 | 6.90 | 92.5 | 104.0 | 6.55 |
| | .907 | 4.990 | 67.0 | 8.70 | 115.0 | 141.0 | 9.40 |
| | 1.384 | - | - | - | - | - | - |
| 8.0................. | .085 | .680 | 52.5 | 3.15 | 34.0 | 14.0 | 1.42 |
| | .124 | .992 | 57.0 | 4.65 | 41.0 | 21.0 | 2.35 |
| | .185 | 1.480 | 67.0 | 6.20 | 52.5 | 29.0 | 3.57 |
| | .273 | 2.184 | 69.5 | 7.00 | 72.0 | 43.5 | 4.72 |
| | .413 | 3.304 | 95.0 | 10.10 | 92.5 | 60.5 | 6.50 |
| | .616 | 4.928 | 113.0 | 13.15 | 130.0 | 81.5 | 8.30 |
| | .935 | - | - | - | - | - | - |
| | 1.384 | - | - | - | - | - | - |
| 12.0................ | .085 | 1.020 | 66.0 | 5.90 | 45.0 | 13.0 | 1.56 |
| | .124 | 1.488 | 85.0 | 6.60 | 56.0 | 20.0 | 2.90 |
| | .185 | 2.220 | 104.0 | 10.50 | 73.5 | 21.5 | 4.48 |
| | .273 | 3.276 | 110.0 | 12.20 | 102.5 | 31.0 | 6.02 |
| | .413 | 4.956 | 160.0 | 17.90 | 134.0 | 41.0 | 9.55 |
| | .616 | - | - | - | - | - | - |
| | .935 | - | - | - | - | - | - |
| | 1.384 | - | - | - | - | - | - |

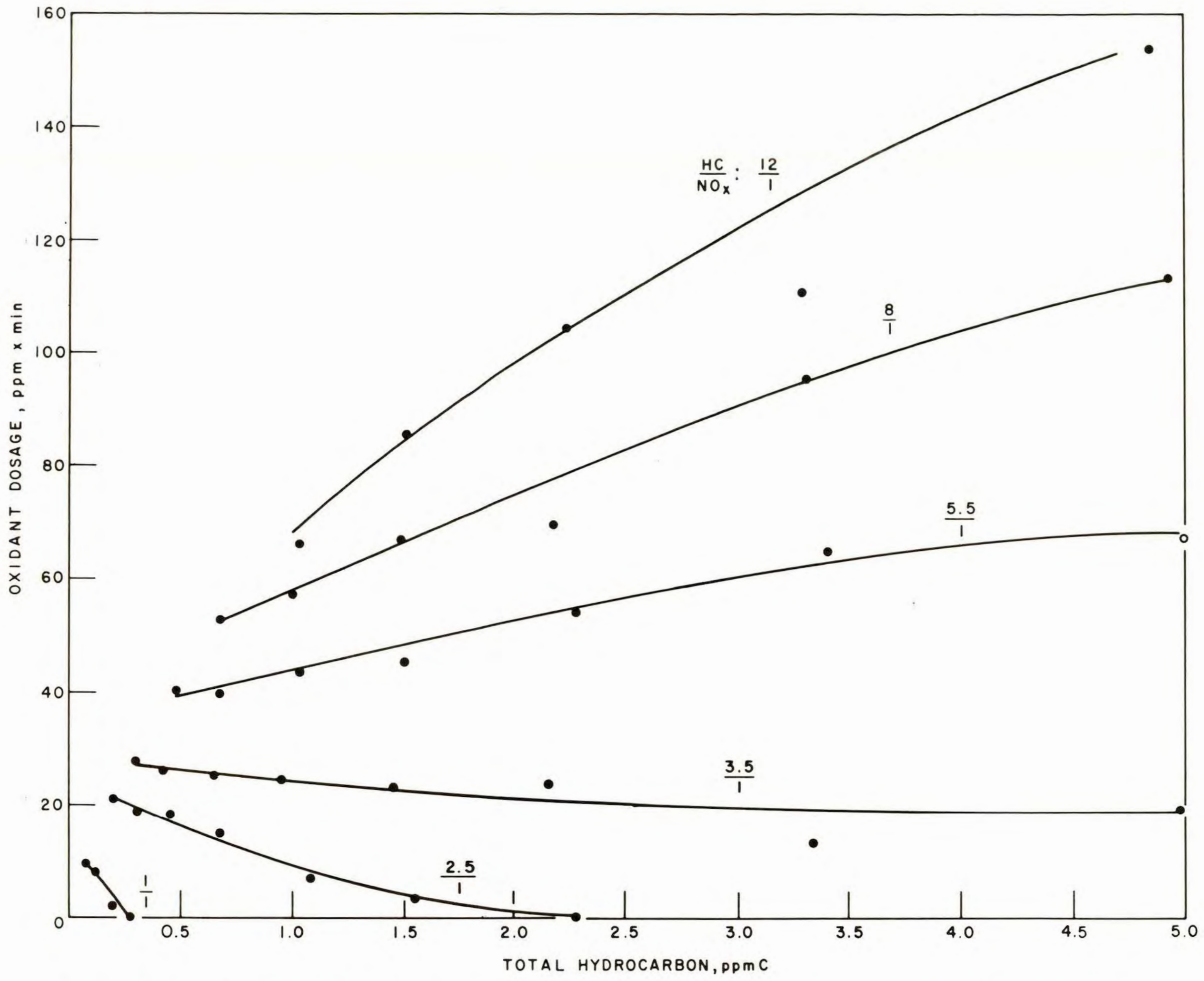

FIGURE 7. - Oxidant-Dosage Reactivity of Exhaust as a Function of Total Hydrocarbon at Various HC:$NO_x$ Ratios.

## Oxidant-Yield Reactivity

Of the reactivity data obtained in this study, those of oxidant and PAN yields seem to be the least precise. For oxidant, part of the observed imprecision was apparently caused by day-to-day variation of the Mast meter response to oxidant and to $NO_2$; daily instrument calibration would improve the data significantly. Furthermore, variation in light intensity and in composition of HC in tested samples could also have introduced variability.

Figures 5 through 8 show dependence of oxidant dosage on HC and $NO_x$. Diagrams in figure 6 show that change in $NO_x$ was never accompanied by a codirectional change in oxidant reactivity. This is contrary to what has been observed in irradiation of synthetic HC-$NO_x$ mixtures. Altshuller and coworkers (2) reported such data for hydrocarbons, including the fairly reactive propylene and xylene and the relatively unreactive toluene and butane.

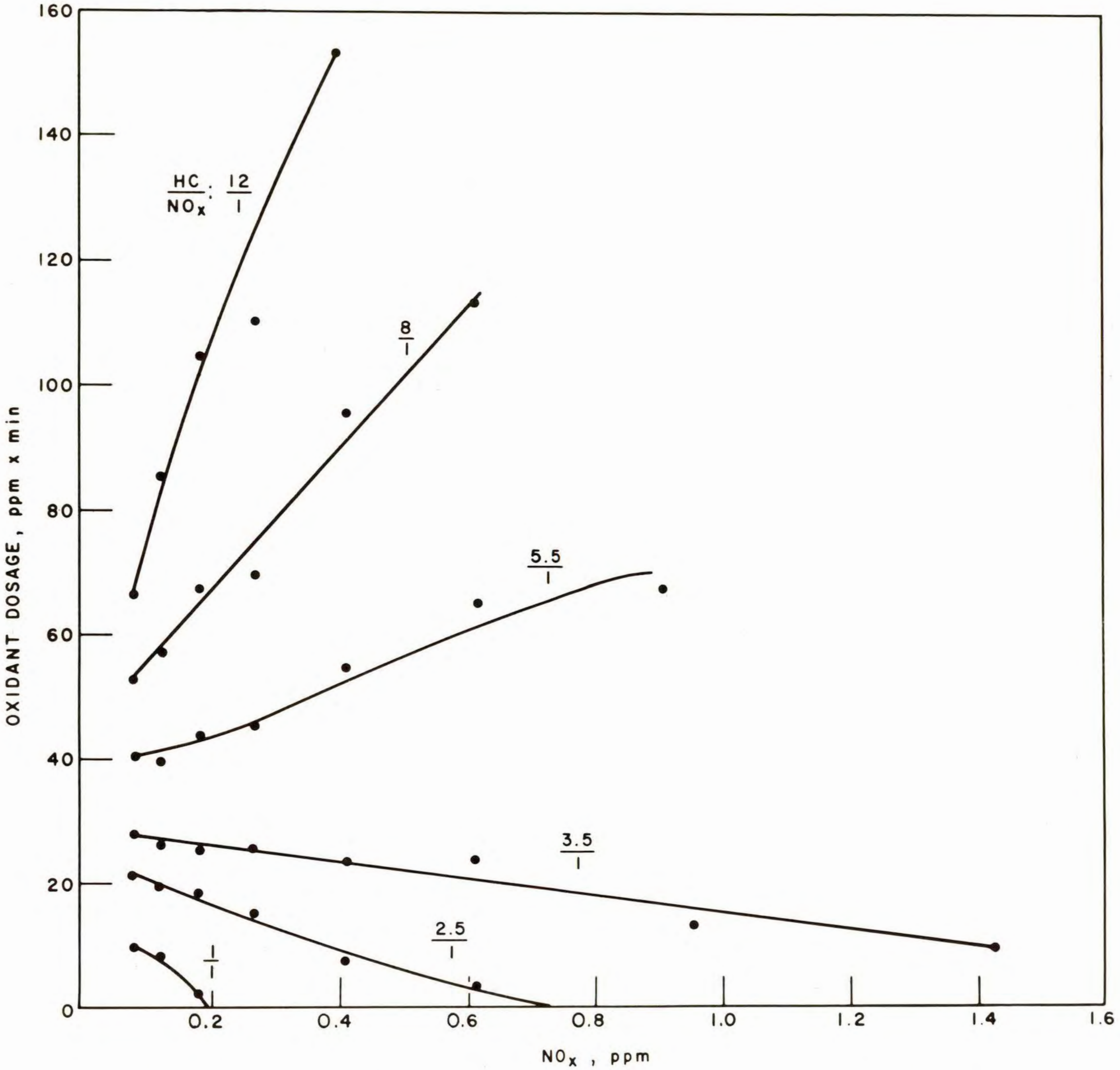

FIGURE 8. - Oxidant-Dosage Reactivity of Exhaust as a Function of $NO_x$ at Various HC:$NO_x$ Ratios.

Similar data were also reported by Glasson and Tuesday (16). These reported data show that the dependence of oxidant on $NO_x$ does show a maximum; however, the same data also seem to support the generalization that this oxidant maximum occurs at lower $NO_x$ levels for less reactive HC-$NO_x$ systems. Such oxidant maxima may, therefore, also exist in the exhaust system, but they occur at $NO_x$ levels lower than those used in this study. This, in turn, suggests that effect of $NO_x$ reduction on oxidant cannot be predicted by extrapolating the diagrams of figure 6 to lower $NO_x$ levels.

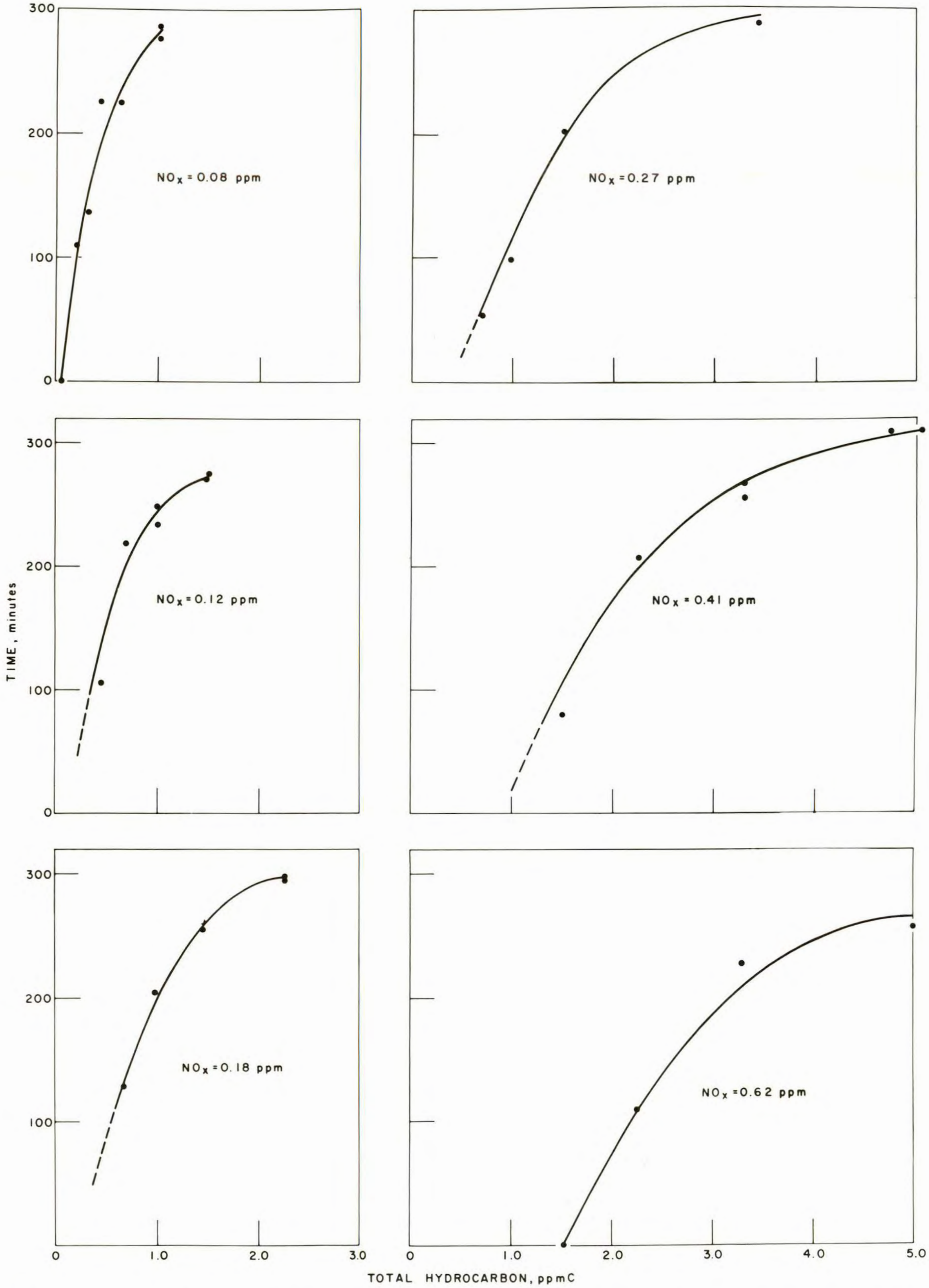

FIGURE 9. - Time During Which Oxidant Exceeded 0.1 ppm as a Function of Total Hydrocarbon at Various $NO_x$ Levels.

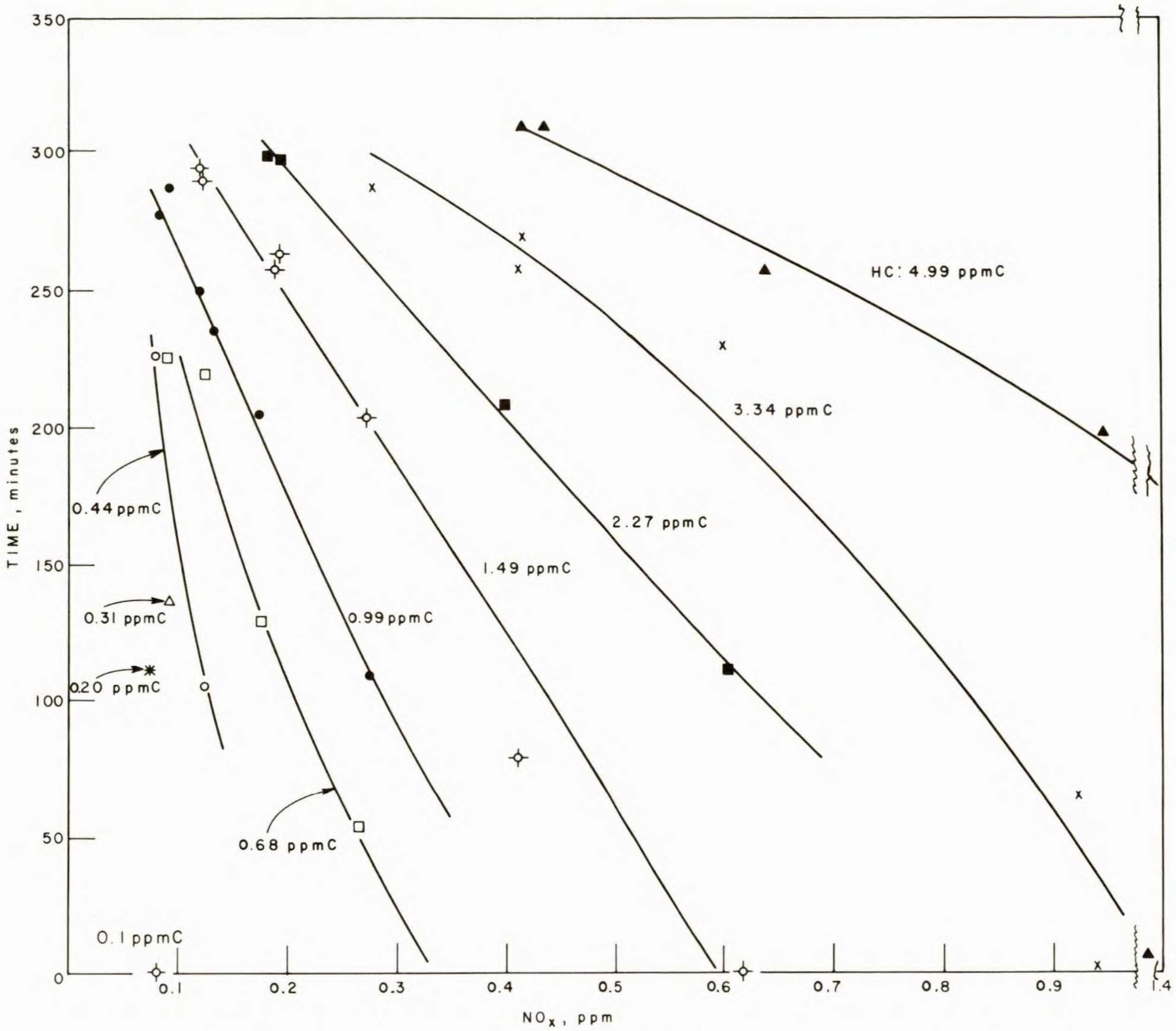

FIGURE 10. - Time During Which Oxidant Exceeded 0.1 ppm as a Function of $NO_x$ at Various HC Levels.

Figures 9 and 10 show the dependence of oxidant yield on HC and $NO_x$; oxidant yield in these figures is expressed as time during which oxidant exceeded 0.1 ppm. These dependence patterns are similar to those shown by the oxidant dosage data.

## PAN-Yield Reactivity

Of the known PAN-compound family, only the first member, peroxyacetyl nitrate, was measured routinely. The presence of peroxypropionyl nitrate (PPN) and peroxybenzoyl nitrate ($PB_zN$) in the irradiated exhaust samples was also occasionally checked. Results showed undetectable levels of $PB_zN$ and PPN levels equivalent to 10 to 20 pct of those of PAN. Figure 11 shows that PAN yields follow the same patterns of dependence on HC and $NO_x$ as oxidant

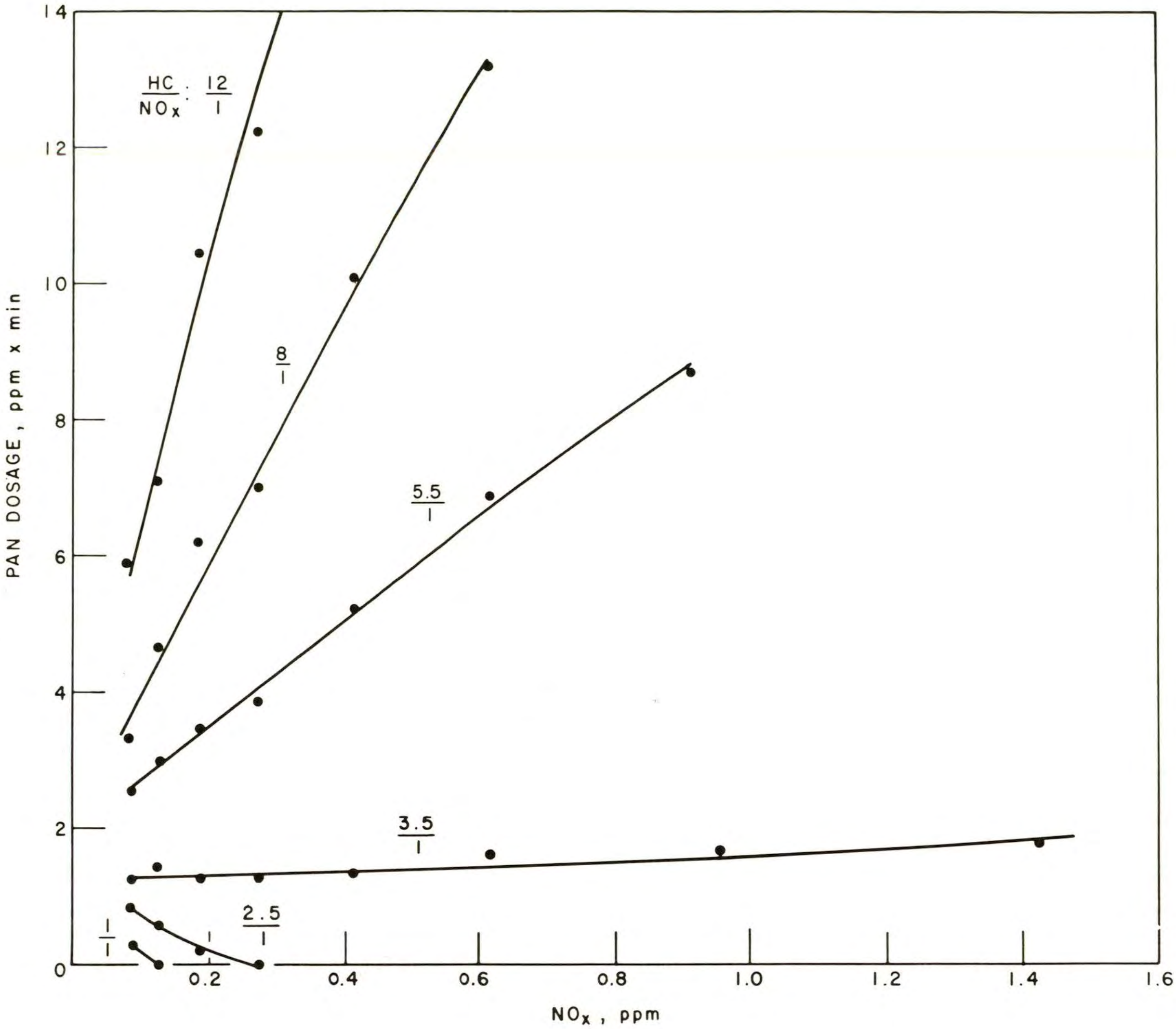

FIGURE 11. - PAN-Dosage Reactivity of Exhaust as a Function of $NO_x$ at Various $HC:NO_x$ Ratios.

yields. Figure 12 shows more clearly the close correlation of PAN and oxidant yields. Also, the approximate 1:10 ratio of PAN to oxidant dosage can be estimated from figure 12; this compares well with the level of ratios found in the atmosphere: 1:5 to 1:10.

## HCHO-Yield Reactivity

Formaldehyde yields showed extremely well defined dependencies on HC and $NO_x$. A typical example is given in figure 13. Formaldehyde dosage appears to be a linear function of HC, with slope depending slightly on $NO_x$. The effect of $NO_x$ is inhibitive, as shown by the following tabulation:

| $(NO_x)_1$, ppm.......... | 0.08 | 0.12 | 0.18 | 0.27 | 0.41 | 0.62 |
|---|---|---|---|---|---|---|
| Intercept[1].......... | 11 | 11 | 11 | 11 | 10 | 10 |
| Slope[1].............. | 33 | 31 | 28 | 27 | 25 | 23 |

[1] Units are the same as those used in diagram of figure 13.

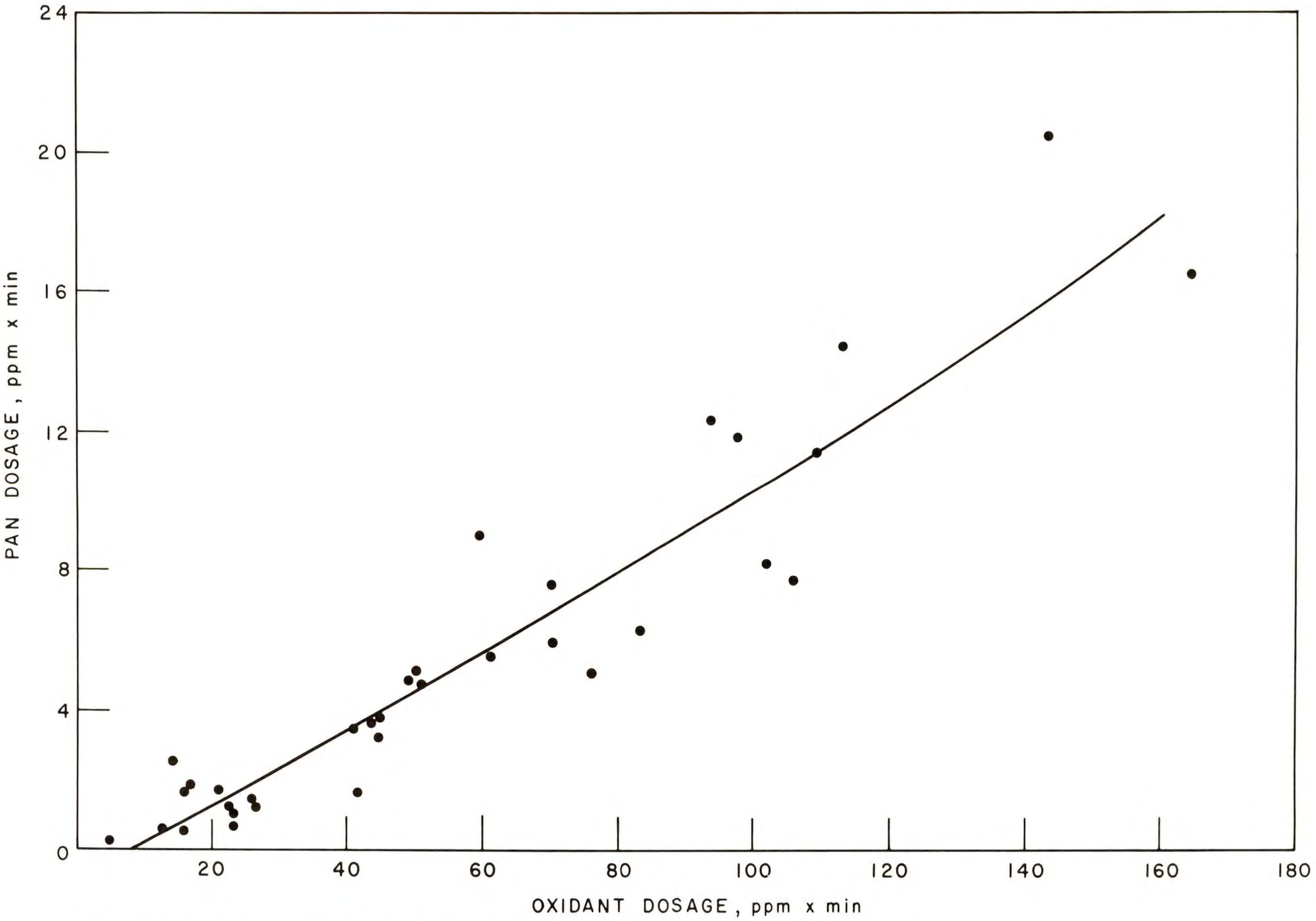

FIGURE 12. - Correlation of Oxidant and PAN Dosages in Irradiated Exhaust Samples of Varying HC:$NO_x$ Ratios.

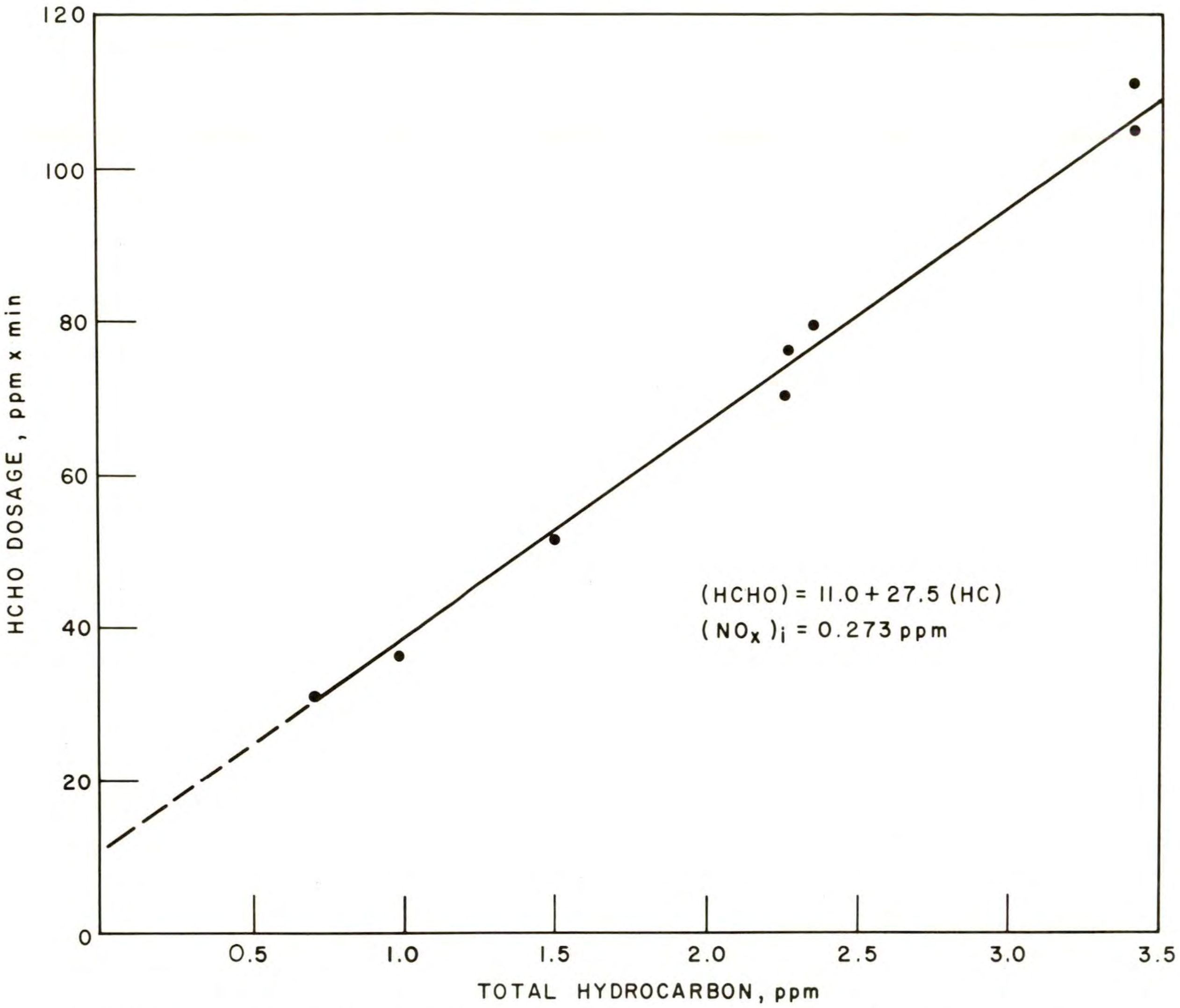

FIGURE 13. - Formaldehyde-Dosage Reactivity of Exhaust as a Function of Total Hydrocarbon at $NO_x$ = 0.273 ppm.

The intercept point on the HCHO-dosage axis is constant and equal to 11 ppm x min; this latter level was attributed to contaminants in background air. The formaldehyde level naturally present in exhaust is too low to affect appreciably the results obtained on HCHO dosage; therefore, the effect from such formaldehyde on observed patterns should be unimportant. At constant HC:$NO_x$ ratios, the dependence of HCHO dosage on HC or $NO_x$ is shown in figure 14.

## $NO_2$-Yield Reactivity

In this study, the $NO_2$ dosage appeared to be the only manifestation that was inhibited, although only slightly, by HC. The inhibitive effect of HC was shown more clearly at the higher HC levels (figs. 15-16) and presumably was

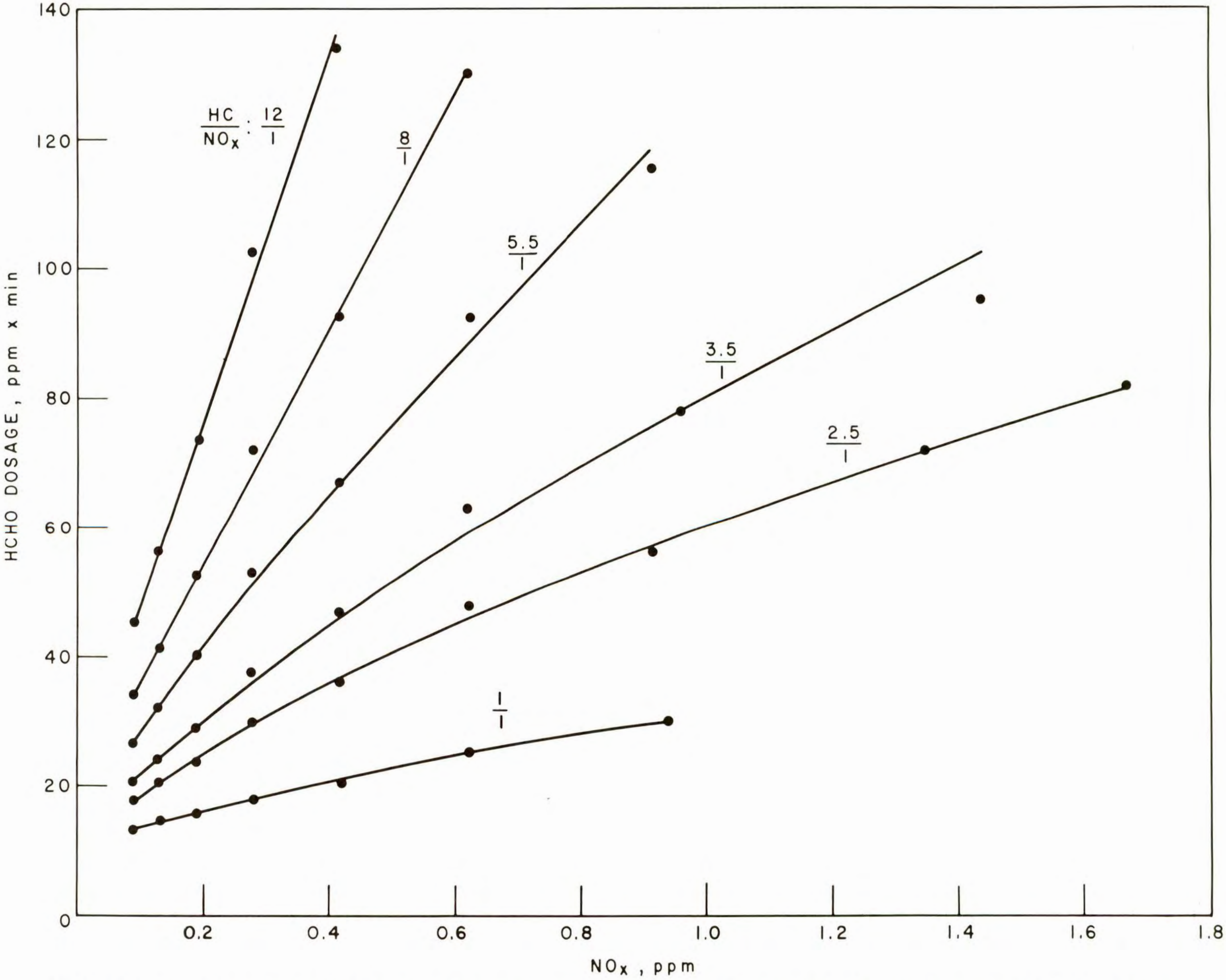

FIGURE 14. - Formaldehyde-Dosage Reactivity of Exhaust as a Function of $NO_x$ at Various HC:$NO_x$ Ratios.

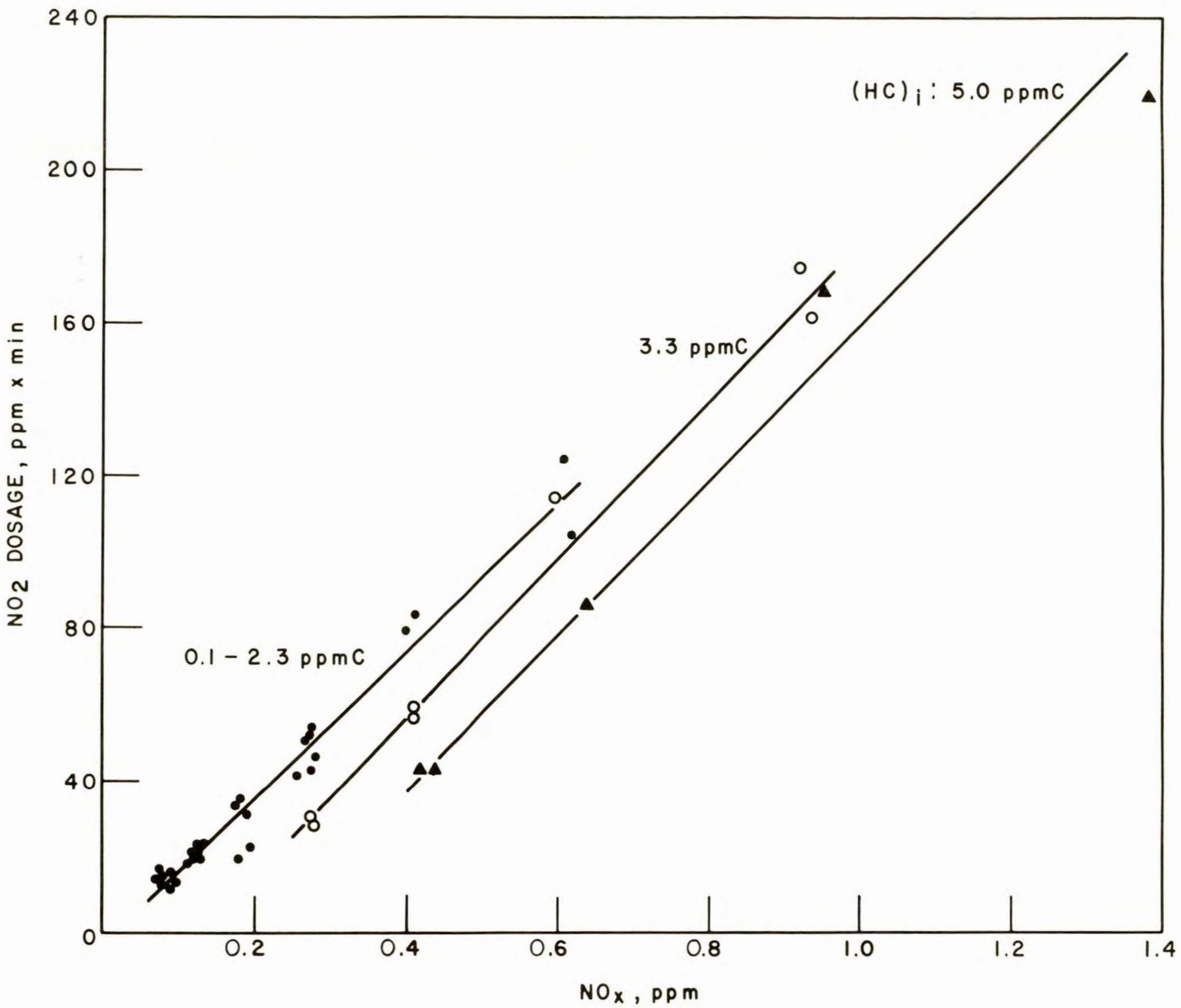

FIGURE 15. - Nitrogen Dioxide-Dosage Reactivity of Exhaust as a Function of $NO_x$ at Various HC Levels.

caused by accelerated consumption of $NO_2$ in reactions with oxidant and to a lesser extent with hydrocarbons. Similar patterns were revealed when $NO_2$ yield was expressed as time during which $NO_2$ exceeded 0.25 ppm (fig. 17).

Nitrogen dioxide accounted for less than one-half of the $NO_x$ present in the initial chamber charge. Of the nitrogen compounds known to form in such reaction systems (namely, peroxyacyl, alkyl, and inorganic nitrates), only PAN, PPN, and inorganic nitrates were expected to affect nitrogen balance significantly (2, 14). The ratio of $NO_2$ dosage to PAN dosage varied from 200:1 in the low HC:$NO_x$ ratio samples to 2:1 with the highest HC:$NO_x$ ratio samples. The sum of $NO_2$, PAN, and PPN levels at the end of irradiation ranged from 20 to 60 pct of the sum of initial NO and $NO_2$; therefore, much of the $NO_x$ initially present must have been converted to nitric acid and nitrate.

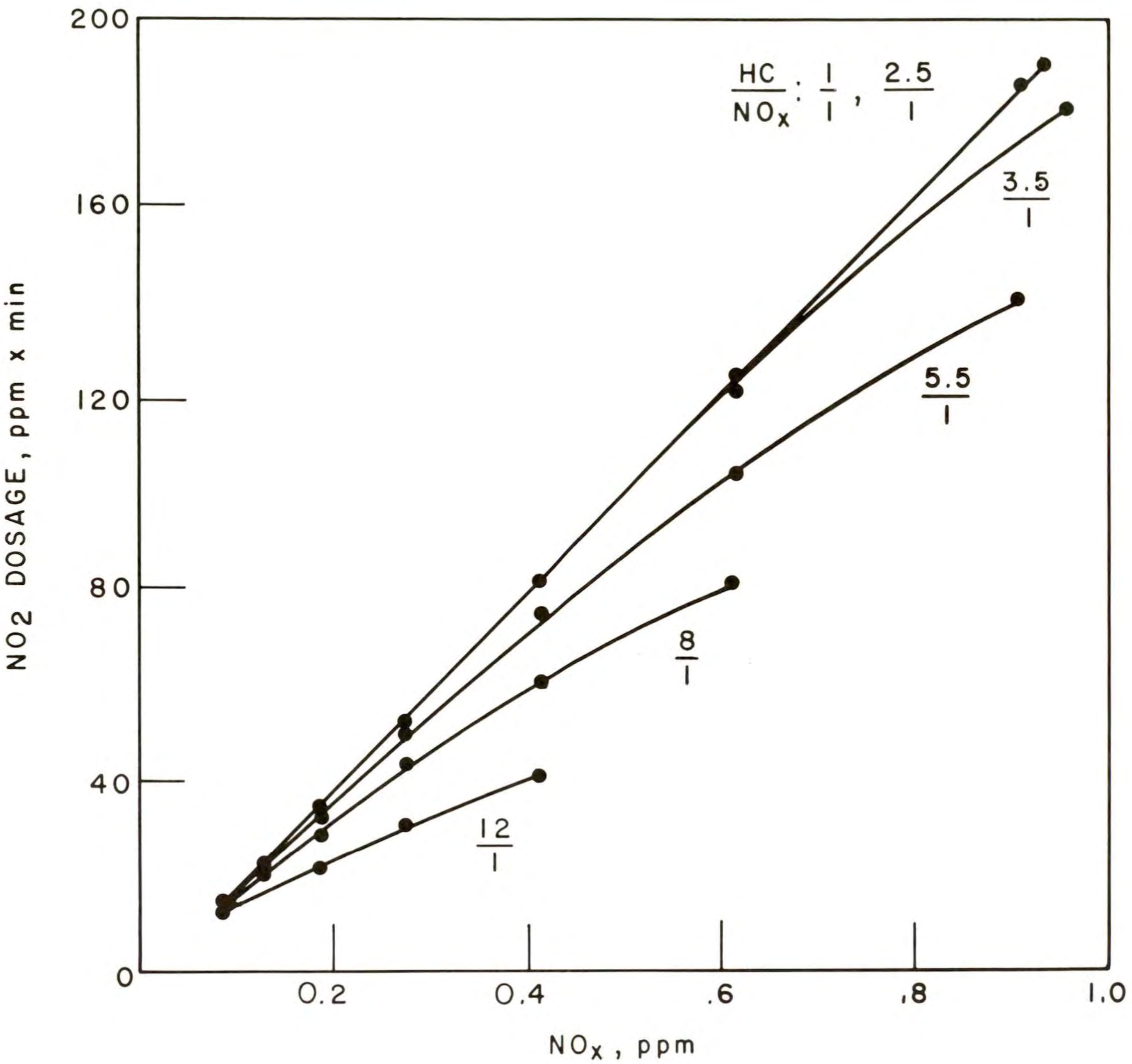

FIGURE 16. - Nitrogen Dioxide-Dosage Reactivity of Exhaust as a Function of $NO_x$ at Various HC:$NO_x$ Ratios.

Evidence that nitric acid or its anhydride, $N_2O_5$, forms at significant levels was also provided by experimental data on oxidant measured by the Mast method and by an NO-titration technique. The latter method involved NO injection in the chamber at the end of each run and invariably gave higher oxidant results by 0 to 0.15 ppm. The difference, called nonozone oxidant, was attributed to $N_2O_5$ that reacts with NO to $NO_2$ but fails to cause response to the Mast instrument because of nearly total loss in the sampling line. Final levels of such nonozone oxidant or $N_2O_5$ were related to initial HC and $NO_x$ levels in a fairly well defined and unique pattern (figs. 18-19). Specifically, diagrams of figures 18 and 19 show that the dependence of $N_2O_5$ on either HC or $NO_x$ shows a maximum suggesting that, within the concentration ranges used in this study, both HC and $NO_x$ can either promote or inhibit $N_2O_5$ yield. Considering the inadequacies of the analytical method used to measure $N_2O_5$, these results are submitted merely as evidence to suggest that significant

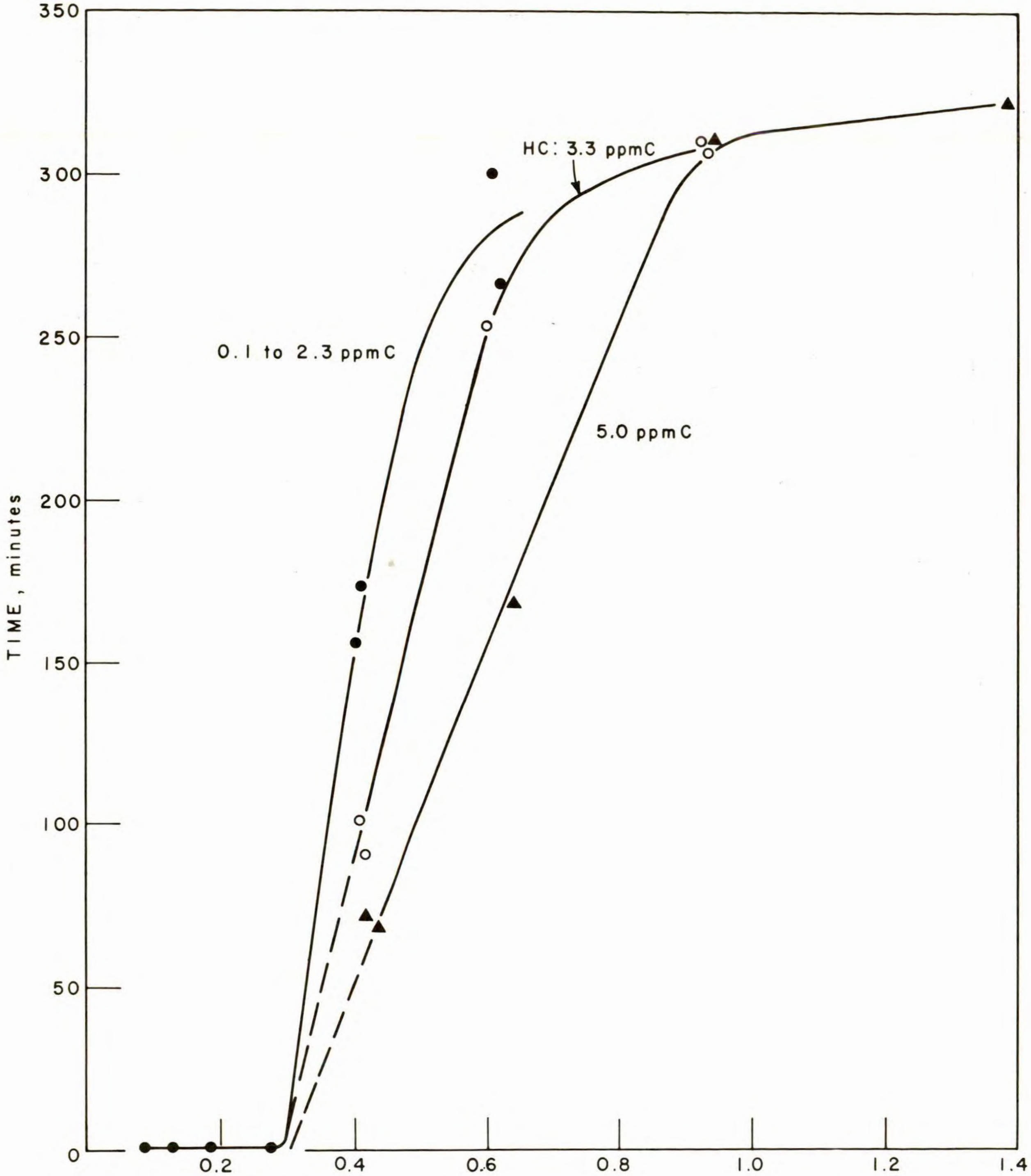

FIGURE 17. - Time During Which $NO_2$ Exceeded 0.25 ppm as a Function of $NO_x$ at Various HC Levels.

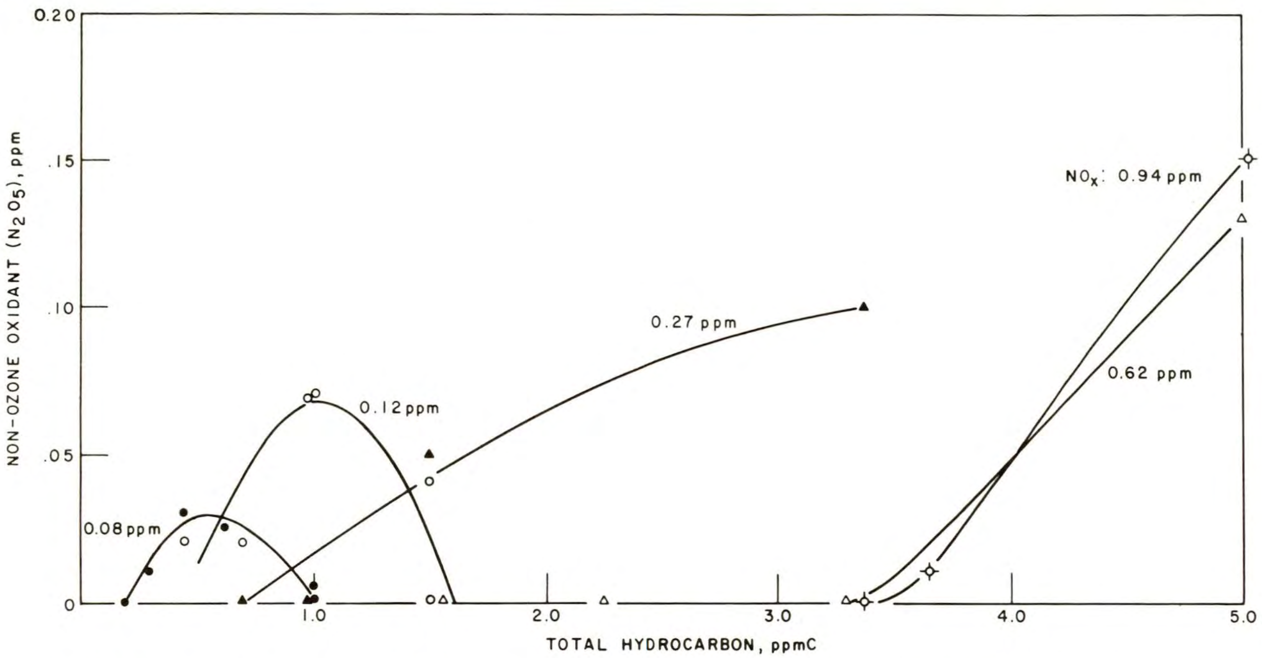

FIGURE 18. - Final Level of Non-Ozone Oxidant as a Function of Total Hydrocarbon at Various $NO_x$ Levels.

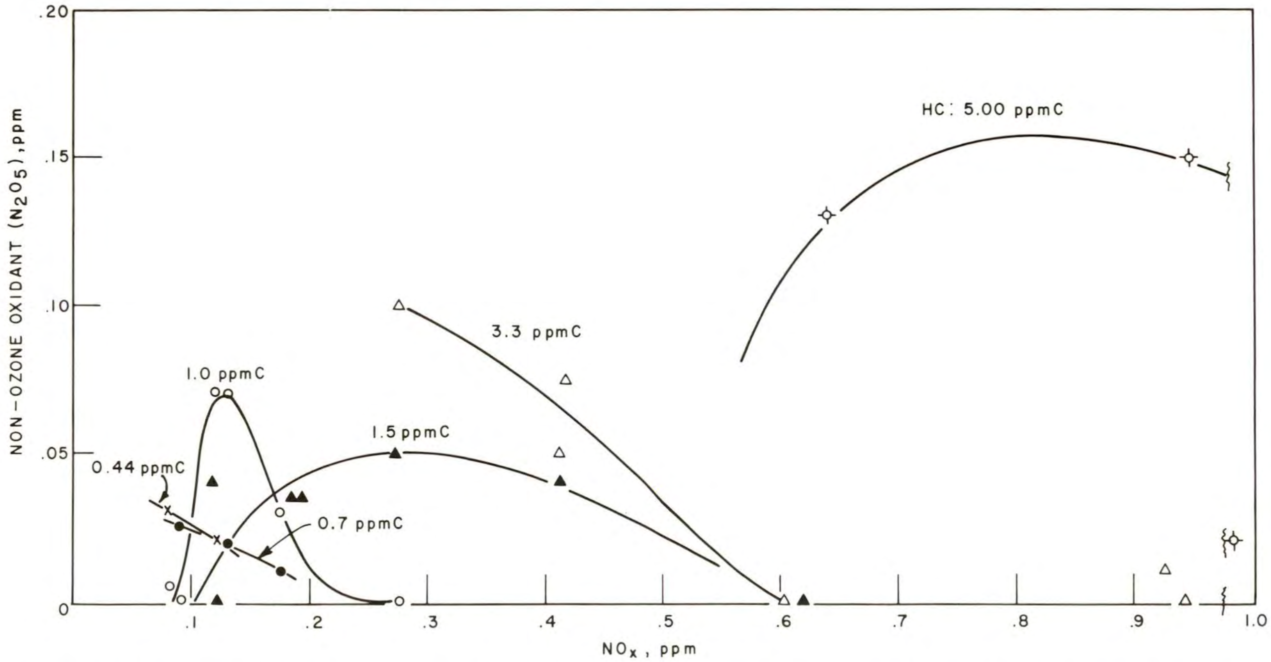

FIGURE 19. - Final Level of Non-Ozone Oxidant as a Function of $NO_x$ at Various HC Levels.

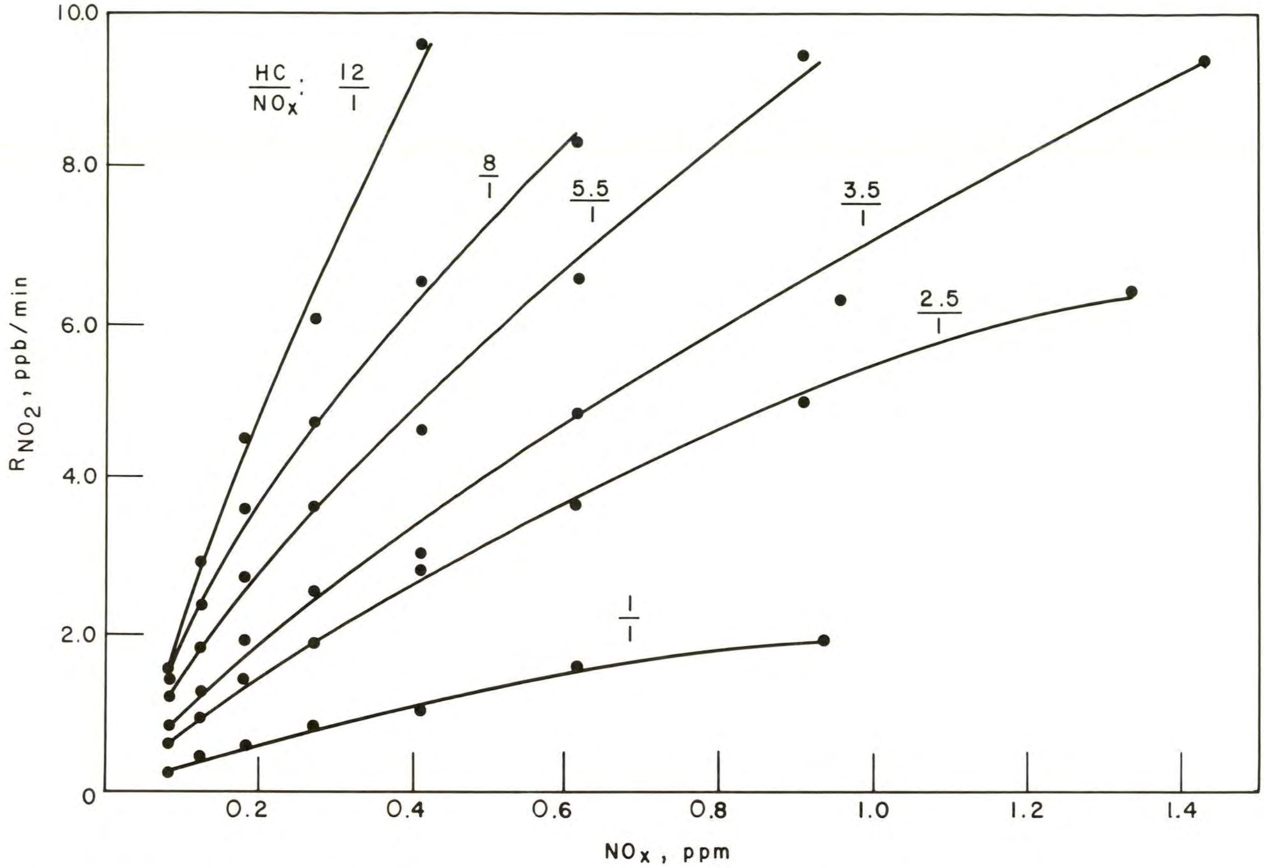

FIGURE 20. - Rate-of-$NO_2$-Formation Reactivity of Exhaust as a Function of $NO_x$ at Various HC:$NO_x$ Ratios.

levels of inorganic nitrates should be expected to form in ordinary polluted atmospheres, and that the dependence of such nitrate yields on reactant HC and $NO_x$ does not parallel those established for other smog manifestations.

### Rate-of-$NO_2$-Formation Reactivity

Rate-of-$NO_2$ formation ($R_{NO_2}$) was strongly dependent on HC and, at $NO_x$ levels lower than 0.2 ppm, on $NO_x$ also. At higher $NO_x$ levels, $R_{NO_2}$ was insensitive to $NO_x$ variations. At constant HC:$NO_x$ ratio $R_{NO_2}$ increased with increasing $NO_x$ (fig. 20) because of the HC effect. Such dependence of $R_{NO_2}$ on HC and $NO_x$ was similar to reported patterns (15) for single hydrocarbon-$NO_x$ systems.

## DISCUSSION

### Comparison of Smog Levels in Real and in Simulated Atmospheres

Considering the differences between the experimental system of this study and the natural atmosphere, it would be of interest to compare smog levels observed in this study with smog levels in the atmosphere, for similar mixtures of pollutants. For such comparison it is necessary to use atmospheric data that are not readily attainable, for example, HC and $NO_x$ levels in an air parcel during early morning hours and levels of smog in the same air parcel after several hours of sun irradiation.

Alternatively, the necessary data can be obtained by measuring smog levels in an atmospheric sample directly, and obtaining data on the sample's initial levels of HC and $NO_x$ indirectly. This latter approach is applicable only to samples of atmospheres for which the sources and detailed compositions of atmospheric pollutants have been established. Such information is currently being pursued, and in at least one instance, data have been reported that led to establishment of corresponding values for initial atmospheric levels of reactants--HC and $NO_x$--and resultant levels of smog (24). Specifically, the reported information included data on oxidant and PAN levels in an atmospheric sample taken in Riverside, Calif., at 4:10 p.m. on a smoggy day. Total HC and $NO_x$ levels in the unreacted sample were also estimated by the use of established compositional patterns in the sampled atmosphere and knowledge of relative hydrocarbon reactivities. Table 5 summarizes resultant data and corresponding data from this research.

TABLE 5. - Comparison of smog levels from an atmospheric sample and a chamber sample that contain the same initial reactant levels

| Sample | Initial reactant levels | | Smog levels | |
|---|---|---|---|---|
| | Total nonmethane hydrocarbon, ppmC | $NO_x$, ppm | Oxidant, ppm | PAN, ppm |
| Atmosphere (Riverside, Calif., 10/24/68)........................ | 3.05 | 0.30 | - | - |
| At 16:10 PST................... | - | - | 0.40 | 0.034 |
| Smog chamber...................... | 3.13 | .27 | - | - |
| After 2-hr irradiation......... | - | - | .26 | .034 |
| After 4-hr irradiation......... | - | - | .49 | .047 |
| After 6-hr irradiation......... | - | - | .49 | .044 |

The data of table 5 show general good agreement in observed smog levels. Note that atmospheric hydrocarbons mostly originate from automotive exhaust but include also emissions from natural gas, oilfields, and gasoline evaporation (24). The predominant hydrocarbon from these secondary sources, however, is methane with zero reactivity; the average reactivity of the others is comparable to that of exhaust. Therefore, with methane excluded, the comparison of the atmospheric and chamber data shown in table 5 is valid because distribution of reactive hydrocarbons in the compared systems can be reasonably assumed to be the same. The good agreement between data from the chamber and the data associated with one atmospheric sample (table 5) certainly does not resolve the issue of comparability (of atmospheric system and smog chamber system), but it does add an element of realism to the experimental data of this study in that both the reactants and the products are present at levels close to those in smoggy atmospheres.

Quantitative comparison of results from this study with those from similar exhaust studies conducted elsewhere is inappropriate because of different experimental conditions. Qualitative patterns, however, can be compared with some significant results.

First, comparison of results from this research with those from an earlier exhaust reactivity study by the Bureau (27) revealed the following: (a) The rate-of-$NO_2$-formation reactivity values were almost identical for the two studies. (b) The oxidant-yield values from this research were more than twice as high as those from the earlier study. This last difference was attributed to difference in surface effects between the two chambers. This was concluded by excluding other conceivably present effects. Thus, engine and fuel used to generate the exhaust samples were the same for the two studies. Furthermore, levels and spectral energy distribution of radiation could not be responsible for observed differences because they were closely similar for the two chambers; such similarity was expected by design, and was verified by the nearly identical rate-of-$NO_2$-formation values obtained with the two chambers. On the other hand, difference in surface effects was indicated by the difference in ozone stability between the two chambers; namely, in this research ozone half-life under irradiation in the chamber was nearly 7 hours compared to 3.5 hours in the chamber of the previous study. These results suggest that surface-to-volume ratio and condition of chamber wall surface may affect the various chamber reactivity manifestations in a nonuniform manner.

Comparison of patterns that described oxidant and PAN dependence on HC and $NO_x$ shows a striking disagreement in results between this exhaust study and reported studies of simple HC-$NO_x$ mixtures. Specifically, in the exhaust study, the oxidant dependence on $NO_x$ did not show a maximum within the range of HC:$NO_x$ ratios used (fig. 6). In contrast, the propylene-$NO_x$ and xylene-$NO_x$ systems at comparable HC-$NO_x$ ratios do show such maxima, a pattern that is probably real because it has been verified by several independent studies (2, 16, 21). Therefore, we must conclude that use of simple HC-$NO_x$ systems, for example, propylene plus $NO_x$, as substitutes for exhaust or atmospheric samples is invalid. Exhaust behavior can probably be simulated in synthetic mixtures; however, such mixtures should be carefully designed and should be tested by direct comparison to exhaust at various HC:$NO_x$ ratios before they are accepted as exhaust substitutes.

Patterns that describe dependence of other reactivity manifestations on HC and $NO_x$ were generally in good agreement with those reported (2, 3, 5, 15, 19, 21). Within the range of initial concentration levels used in this research, these dependencies are as follows: (1) At low $NO_x$ levels the $NO_2$ dosage is nearly proportional to initial $NO_x$ level and is slightly inhibited by HC at higher HC levels. (2) The HCHO dosage is nearly proportional to HC levels and slightly inhibited by $NO_x$. (3) Rate of $NO_2$ formation is nearly proportional to HC and varies similarly with $NO_x$ in the lower $NO_x$ level range; at higher $NO_x$ levels $R_{NO_2}$ is nearly independent of $NO_x$.

## Air Quality Benefits from HC and $NO_x$ Reduction

Data from this study can be used to estimate benefits attendant to HC reduction from current atmospheric levels but are not sufficiently complete to estimate effect of $NO_x$ reduction. Thus, for a typically polluted atmosphere assumed equivalent to an exhaust-air mixture that contains 5 ppmC HC and 0.4 ppm $NO_x$, the resultant HC:$NO_x$ ratio of 5:0.4 is approximately equal to the highest (12:1) ratio used in the study. Further, higher-than-12:1 ratio data, needed to estimate $NO_x$ reduction benefit, cannot be obtained through extrapolation of low HC:$NO_x$ ratio data because the dependence of some reactivity manifestations on the HC:$NO_x$ ratio is not adequately established, as was pointed out previously. These problems evidently do not exist in estimating benefits from HC reduction and such benefits can be computed readily from this study's data. However, since the issue of interest here is the relative effects of HC and $NO_x$ reduction, data on benefit from HC reduction alone would be of no particular use. Instead, the following statements are the author's interpretations of evidence developed in this research for relative effects of HC and $NO_x$ reduction:

1. Reduction of HC (from present atmospheric levels) would be accompanied by a reduction in intensity of all smog manifestations, except for the $NO_2$ yield and perhaps the inorganic nitrate yield.

2. As HC levels are reduced--as a result of HC-emission control--the benefits attendant to a specified level of $NO_x$ reduction are lessened.

3. Significant levels of oxidant can be produced by HC at less than 1 ppmC if the HC and $NO_x$ are at appropriate ratio.

An alternative way of relating the results of this study to relative benefits from HC and $NO_x$ reduction is illustrated by using these results to estimate the HC and $NO_x$ levels necessary to meet the California air quality standards for oxidant and $NO_2$. Such estimates were obtained as follows: First, from the diagrams in figure 9, combinations of HC and $NO_x$ were defined that result in an oxidant yield equal to the California standard, namely, 0.1 ppm for 1 hour. For example, from figure 9, it is seen that for $(NO_x)_i$ = 0.08 ppm, $(HC)_i$ should be equal to or less than 0.13 ppmC in order that resultant oxidant exceed 0.1 ppm for 1 hour or less. Such optimum $(HC)_i$ and $(NO_x)_i$ values are given in table 6 and were also used to draw the equal-response line aeb in figure 21.

TABLE 6. - Paired values of $(NO_x)_i$[1] levels and $(HC)_i$[1] levels corresponding to oxidant yield equivalent to the California air quality standard for oxidant

| Time during which oxidant exceeded 0.1 ppm, min | $(NO_x)_i$, ppm | $(HC)_i$, ppmC |
|---|---|---|
| 60 | 0.08 | 0.13 |
| 60 | .12 | .25 |
| 60 | .18 | .40 |
| 60 | .27 | .70 |
| 60 | .41 | 1.23 |
| 60 | .62 | 1.90 |

[1] Subscript designates level in initial chamber charge.

Points above the equal-response line aeb represent values of $(HC)_i$ and $(NO_x)_i$ that meet the California standard for oxidant; points below correspond

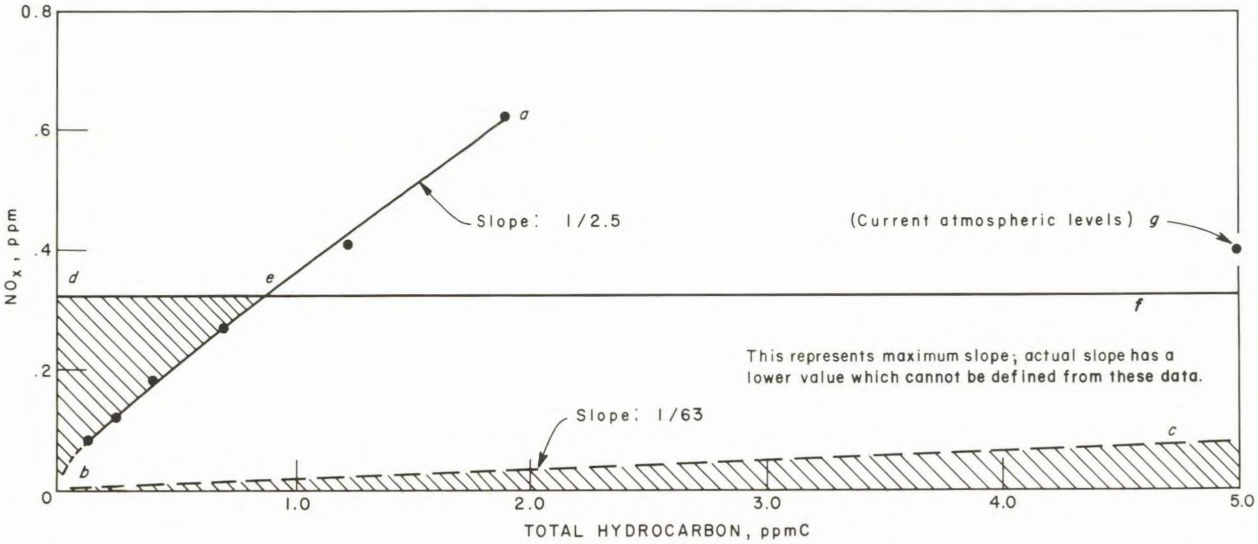

FIGURE 21. - Equal Response Lines Representing Combinations of Total Hydrocarbon and $NO_x$ Corresponding to Oxidant and $NO_2$ Yields Equal to the California Standards.

to high oxidant yields in general except for those that represent extremely low $NO_x$ levels. For those $NO_x$ levels, experimental data on oxidant yields are not available, however, gross approximations can be made. These approximations are based on the assumption that the oxidant dependence on $NO_x$ (fig. 10) has a maximum and that at sufficiently low $NO_x$ levels--lower than those used in this study--oxidant increases with $NO_x$. Thus, assuming that oxidant dependence on $NO_x$, for HC at 5 ppmC, has a maximum at $NO_x$ = 0.4 ppm (see fig. 10) and that oxidant yield is proportional to $NO_x$ within the range 0 to 0.4 ppm, then the $NO_x$ level corresponding to the California oxidant standard is estimated (from fig. 10) to be 0.08 ppm, yielding an HC:$NO_x$ ratio of 4.99:0.08 or 62. In actuality, the oxidant maximum would probably occur at $NO_x$ less than 0.4 ppm resulting in a ratio higher than 62. When similar treatment was applied upon the oxidant-$NO_x$ curves (fig. 10) for 3.34 ppmC, 2.27 ppmC, 1.49 ppmC, and 4.99 ppmC, resultant ratio values were 61, 64, 60, and 67, respectively.

These results suggest that within the concentration ranges of this study, the California standard for oxidant can be met when the HC:$NO_x$ ratio is about 63 or higher. HC and $NO_x$ levels at this ratio are represented by points that comprise line bc in figure 21. Unlike line ab, line bc is shown as a dashed line to designate that the associated data were, in part at least, deduced through use of assumptions rather than obtained experimentally. To summarize, line aebc in figure 21 is an equal-response line consisting of (HC,$NO_x$) points that correspond to an oxidant yield equal to the California standard. Points above aeb and below bc represent HC and $NO_x$ levels corresponding to oxidant yields lower than the California standard.

To meet the California standard for $NO_2$, additional restrictions must be placed upon the HC and $NO_x$ levels. From figure 17, it can be estimated that for any HC level, the California $NO_2$ standard is met simply when $NO_x$ is 0.33 ppm or less. HC and $NO_x$ levels satisfying this condition are represented by points that comprise line def in figure 21. All points below line def--obviously including those below line bc--correspond to $NO_2$ yields lower than the California standard. The resultant line debc in figure 21 outlines an area (shaded) in the (HC,$NO_x$) plane, within which lie all HC-$NO_x$ combinations that correspond to air quality meeting the California standards. Point g was also included in figure 21 to show the currently typical levels of HC and $NO_x$ in atmosphere, relative to the desired levels.

From diagrams such as figure 21, it is possible to estimate the direction and extent to which current atmospheric levels need to be modified to achieve a specified air quality level. To illustrate this, such estimates of optimum HC and $NO_x$ levels were obtained for different sets of air quality standards, existent and hypothetical, and are listed in the following tabulation.

| 1. Standards (Existent) | Optimum $NO_x$ and HC Levels | | |
|---|---|---|---|
| Oxidant: Not to exceed 0.1 ppm for more than 1 hour. | $NO_x$: $\le 0.08$ ppm<br>HC: $\ge 62 \times (NO_x)$ | or | $NO_x$: $\le 0.33$ ppm<br>HC: $\le 2.5 \times (NO_x)$ |
| $NO_2$: Not to exceed 0.25 ppm for more than 1 hour. | (Requires at least 80 pct $NO_x$ reduction and no HC reduction from current levels) | | (Requires at least 15 pct $NO_x$ reduction and drastic HC reduction from current levels) |
| 2. Standards (Hypothetical) | | | |
| Oxidant: Not to exceed the dosage level of 0.1 ppm × hour | $NO_x$: $\le 0.017$<br>HC: $\ge 300 \times (NO_x)$ | or | $NO_x$: $\le 0.10$ ppm<br>HC: $\le (NO_x)$ |
| $NO_2$: Not to exceed the dosage level of 0.25 ppm × hour | (Requires drastic $NO_x$ reduction and no HC reduction) | | (Requires at least 65 pct $NO_x$ reduction and drastic HC reduction) |
| 3. Standards (Hypothetical) | | | |
| Oxidant: Not to exceed the dosage level of 0.25 ppm × hour | $NO_x$: $\le 0.04$ ppm<br>HC: $\ge 125 \times (NO_x)$ | or | $NO_x$: $\le 0.10$ ppm<br>HC: $\le 2.0 \times (NO_x)$ |
| $NO_2$: Not to exceed the dosage level of 0.25 ppm × hour | (Requires drastic $NO_x$ reduction and no HC reduction) | | (Requires at least 65 pct $NO_x$ reduction and drastic HC reduction) |
| 4. Standards (Hypothetical) | | | |
| Oxidant: Not to exceed the dosage level of 0.25 ppm × hour | $NO_x$: $\le 0.04$ ppm<br>HC: $\ge 125 \times (NO_x)$ | or | $NO_x$: $\le 0.25$ ppm<br>HC: $\le 2.5 \times (NO_x)$ |
| Daily maximum $NO_2$ or $NO_x$: Not to exceed 0.25 ppm | (Requires drastic $NO_x$ reduction and no HC reduction) | | (Requires at least 30 pct $NO_x$ reduction and drastic HC reduction) |

The estimates given are based directly or indirectly on exhaust reactivity data obtained in this study. Application of these estimates to the actual atmospheric system is valid depending on the extent to which the following conditions are satisfied:

1. Interdependence of initial reactants and resultant smog levels is the same in the smog chamber as it is in the atmosphere.

2. Hydrocarbon composition is the same in exhaust as it is in the atmosphere.

3. Change in HC:$NO_x$ ratio in the atmosphere is not accompanied by unavoidable change in hydrocarbon composition.

Comparison of the reactants-smog interdependencies in the chamber and in the atmosphere cannot be made easily, and it is likely that agreement will not be achieved for all smog manifestations. An approach, however, for such comparison is available, and the data of table 5 suggest that at least for some smog manifestations, the atmospheric reactant-smog interdependency can be reproduced in smog chambers.

Hydrocarbon composition in the atmosphere is closely similar to that in exhaust, except for the relatively higher atmospheric levels of methane, ethane, propane, and some heavier hydrocarbons that result from gasoline evaporation. Stephens and coworkers (24) have, however, demonstrated that these composition differences can be defined quantitatively and that the portion of the total atmospheric HC level which originates from exhaust can be calculated. Furthermore, the reactivities of the methane, ethane, and propane, under ordinary HC:$NO_x$ ratios, are zero, whereas, the reactivity of gasoline evaporative emissions, under summer temperature conditions, is comparable to that of exhaust (12). All in all, exhaust HC and atmospheric HC values can be used almost indistinguishably if methane, ethane, and propane are not included in the expression for total HC. Optimum levels of atmospheric HC can then be obtained from the optimum levels of exhaust HC by addition of the levels of methane, ethane, and propane typically present in the atmosphere.

A change of HC:$NO_x$ ratio in the atmosphere as a result of emission controls may or may not be accompanied by a change in hydrocarbon composition, depending on the control method used. Use of devices currently produced by automobile manufacturers for exhaust hydrocarbon control does not seem to affect composition of exhaust hydrocarbons (1). Composition of hydrocarbons in exhausts from $NO_x$-controlled autos may, however, depend decidedly upon whether $NO_x$ control is effected by catalytic treatment of the exhaust stream or by other methods, such as exhaust recirculation and modification of spark schedule or carburetion. For example, catalytic $NO_x$ control was found drastically to alter hydrocarbon composition by preferentially removing reactive hydrocarbons (28). The other control methods are not expected to have an important effect. Because no $NO_x$-control method has been specified for application, compositional effects that will unavoidably accompany the effect of $NO_x$ reduction cannot be predicted or even studied at this time.

## The Problem of Measuring Hydrocarbon Reactivity

Results from this and other studies show clearly that the hydrocarbon reactant promotes most smog manifestations. In contrast, $NO_x$ can either promote or inhibit smog formation; furthermore, the smog-$NO_x$ interdependence pattern differs with drastically different HC-$NO_x$ systems. This suggests that to evaluate or compare samples of organic emissions for smog potential, reactivity data obtained for several $NO_x$ levels must be used. Also, the HC and $NO_x$ levels should be comparable to those in typically polluted atmospheres. For example, in evaluation of automobile emissions, appropriate levels of HC and $NO_x$ in the initial chamber charge would be 1.5 ppm for HC and 0.25, 0.50, and 1.00 ppm for $NO_x$. For more complete information, reactivity data would be necessary also for HC at 0.75 ppm and $NO_x$ at 0.12, 0.25, and 0.50 ppm. When the HC:$NO_x$ ratio in the test sample is lower than the recommended values because of lean engine operation, the A/F can be adjusted to increase HC/$NO_x$ without significant alteration of the hydrocarbon composition. Another reported approach is based on separation of $NO_x$ from the exhaust stream (8); however, the reported evidence regarding the method's success is limited at this time.

Another problem relevant to measuring smog potential in irradiation chambers is the definition and measurement of background reactivity. Demonstrations have shown that in most smog chambers, irradiation of background air produces certain smog manifestations. Even though such reactivity is generally believed to be caused by background organic contaminants, the only unequivocal available evidence is for the rate-of-$NO_2$-formation type of reactivity (6). In a clean chamber, the level of rate-of-$NO_2$-formation reactivity is essentially zero (6). A previous Bureau of Mines study showed that irradiation of chamber air that contained less than 0.1 ppmC of hydrocarbon contaminant and less than 0.003 ppm $NO_x$ failed to produce detectable levels of oxidant. However, because this study revealed that oxidant forms at extremely low levels of HC and $NO_x$ and that oxidant yields depend critically upon the HC:$NO_x$ ratio, the observed zero oxidant yield may reflect an unfavorable HC:$NO_x$ ratio rather than absence of background hydrocarbon reactivity. These observations support the assertion (10) that the rate of $NO_2$ formation is an appropriate index of background reactivity, but oxidant yield is not.

## SUMMARY AND CONCLUSIONS

1. The roles of HC and $NO_x$ in smog formation were investigated by photoirradiating samples of automobile exhaust at levels equal to or lower than those in a typically polluted atmosphere.

2. Smog levels observed in the smog chamber were comparable to those in the atmosphere for similar levels of reactants.

3. Data were developed which showed that use of simple HC-$NO_x$ systems, for example, propylene/$NO_x$, as substitutes for natural atmosphere or exhaust is invalid.

4. The relative effects of HC and $NO_x$ reduction were discussed in terms of modifications of atmospheric HC:$NO_x$ ratios required to meet the currently existent as well as some hypothetical atmospheric air-quality standards.

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