Effects of Hydrocarbon and Nitrogen Oxides on Photochemical Smog Formation

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■ The role of hydrocarbon (HC) and nitrogen oxides (NO_x) in photochemical smog formation was investigated. Samples of automobile exhaust with varying HC and NO_x levels were irradiated in a smog chamber under conditions that resulted in levels of smog manifestations similar to those observed in the atmosphere. HC levels ranged from 0.3 to 5.0 ppmC, and NO_x levels ranged from 0.08 to 1.4 ppm. Photooxidation of nitric oxide (NO) and formations of oxidant, peroxyacyl nitrate (PAN), formaldehyde (HCHO), and nitrogen dioxide (NO_2) were used as smog manifestations. Results showed that except for the NO_2 yield, all smog manifestations were intensified by increasing HC; NO_x inhibited the oxidant, PAN, and HCHO yields but promoted the rate of NO oxidation and the NO_2 yield. By use of these data, it was estimated that to achieve an air quality equivalent to the current California standards for oxidant and NO_2, NO_x should be less than 0.33 ppm and HC less than 2.5 × (NO_x).

Since its inception, photochemical smog abatement has been oriented toward reduction of hydrocarbon emissions in the atmosphere. This approach to control has been taken because laboratory studies have demonstrated that reduction of one of the major photochemical smog reactants, the hydrocarbon (HC), 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)—i.e., nitric oxide (NO) plus nitrogen dioxide (NO_2), has not been applied as yet, primarily because of the uncertainty about its merits and, secondarily because the related technological problems are more difficult.

This report covers experimental work performed to determine the relative contribution of HC and NO_x in the atmospheric smog formation and to associate air quality with the HC:NO_x ratio using currently existent atmospheric quality criteria. This work comprised an experimental study of the photochemical smog potential of automotive emissions as a function of HC and NO_x levels. Automobile exhaust was used because it constitutes a readily available source of sample mixtures nearly identical in composition to that of the mixture in smog-infested atmospheres.

The role of HC and NO_x in smog phenomena had been studied (Altshuller et al., 1969; Buchberg et al., 1963; Glasson and Tuesday, 1966; Romanovsky et al., 1967; Hamming and Dickinson, 1966; Korth et al., 1964; Nicksic et al., 1966); however, interpretation of those earlier data was subject to uncertainty because test conditions and/or samples differed from those representing a typical urban atmosphere. In this study, composition and levels of the HC and NO_x reactants in the test mixtures were controlled to approximate pollutant makeup in present-day problem atmospheres and in atmospheres anticipated as a result of current controls. Further, a smog chamber was used in which irradiation of reactant mixtures similar to those in early morning atmospheres was found to result in levels of smog constituents comparable to levels observed in the atmosphere.

Experimental

The experimental program consisted of a series of chamber irradiation tests in which reactivity or smog potential of exhaust was measured for HC and NO_x levels ranging within 0.3 to 5.0 ppmC and 0.08 to 1.4 ppm, respectively. These initial reactant levels are shown in Figure 1 as points in the (HC, NO_x) plane. As arranged in the two-dimensional space (Figure 1), these points represent conditions appropriate for determining the effect of NO_x for constant HC, the effect of HC for constant NO_x, and the effect of HC and NO_x at a constant HC:NO_x ratio. Reactivity was measured and expressed in terms of five smog manifestations: Rate of NO_2 formation (Dimitriades, 1967) and oxidant, peroxyacetyl nitrate (PAN), formaldehyde (HCHO), and nitrogen dioxide dosages (Dimitriades, 1967). Additionally, reactivity was expressed in terms of the same units used to express the California air quality standards for oxidant and NO_2 (California State Air Resources Board, 1969), 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-in.^{3} engine and operated to follow the seven-mode California cycle. The engine was fitted with a modified carburetor for 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.

The exhaust stream was sampled with a heated, variable-rate proportional sampler (Fleming et al., 1965), the output of which was received in a Tedlar bag that had been covered with dark cloth and precharged with dry nitrogen. Resultant exhaust-to-N_2 ratio in the bag was approximately 1:5. Immediately after sample collection, the bag content was used to charge the chamber (a 10- to 15-min operation) and to provide samples for chromatographic analysis. These chroma-

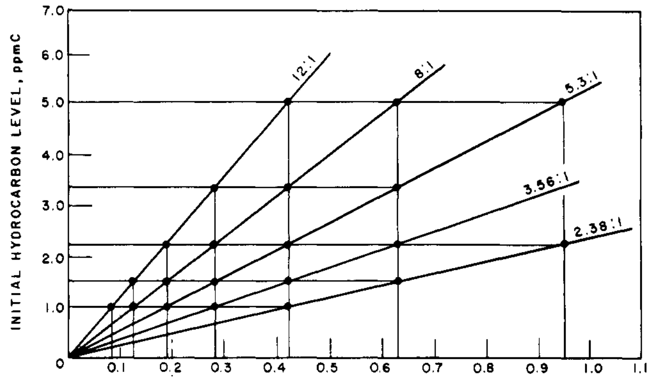

Figure 1. Hydrocarbon and NO_x levels in tested exhaust samples

Table I. 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, hr	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, %	64 → 33	77 → 53	≈40	≈40
Absolute, %	≈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	0.06	0.05	0.13	0.08
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

tographic data were used to establish the extent to which composition of exhaust hydrocarbons varied (unavoidably) from test to test.

Smog Chamber and Associated Instrumentation. Detailed description of the smog chamber has been reported (Dimitriades, 1967, 1970). Analytical instrumentation includes two Beckman 109 analyzers for measurement of total hydrocarbon, two Mast meters for oxidant, and two Beckman K-1008 analyzers for NO_2 and NO_x. Instrument duplication safeguards instrument malfunction and provides more reliable analytical data. The HC analyzers were calibrated at the beginning of the study with synthetic hydrocarbon mixtures of exhaustlike composition and daily with a standard propylene blend. Details on measurement of NO_2, NO_x, PAN, oxidant, and formaldehyde have been reported (Dimitriades, 1967).

Light-Intensity Measurement. It has been shown that measurement of light intensity in the chamber by the commonly used method of NO_2 photolysis (Tuesday, 1961) gives uncertain results (Dimitriades, 1970). For this reason, light intensity in this study was evaluated through direct comparison with natural sunlight. For this evaluation, a 300-liter Tedlar (2-mil thick) bag was charged with purified air containing propylene and NO at 1 ppm each and was irradiated inside the chamber and on a rooftop against a background of light grey concrete. During each 6-hr irradiation test, NO_2, NO_x, oxidant, and PAN were monitored and results were expressed in terms of rate-of-NO_2 formation, oxidant dosage, and PAN dosage. Table I summarizes detailed experimental conditions and test results. The difference between the two rooftop measurements was attributed to difference in experimental conditions that included partial overcast (clear to slightly cloudy) during the 6-hr tests. From these results, light intensity in the chamber was judged comparable to that of natural sunlight in a typical "irradiation" day in the United States during the smog season.

Variability of light intensity was investigated using data from biweekly measurements of the reactivity of a standard ethylene–NO_x mixture (at 3 ppmC/ppm) and parallel measurements of light intensity with a light monitor. Details from this investigation and results have been reported (Dimitriades, 1970). These results indicated that output of fluorescent lamps varied significantly as a result of lamp-temperature variation, and reactivity measurement results correlate well with the light monitor response data. From such light monitor response data it was deduced that during this study, light intensity in the chamber varied from test to test by about ±10%. No correction of the reactivity data for light intensity variation was attempted, other than screening off tests in which the monitor response was clearly much higher or much lower than the average level.

Test Procedure. In test preparation, the chamber is flushed for 3 hr with prepurified air (Dimitriades, 1967) under infrared lamps that heat the walls to about 125°F. Next, the chamber is sealed, the chamber air is recirculated overnight through a catalytic combustor, a charcoal column, and a particulate filter. Chamber air, so purified, contains less than 0.1 ppmC of total organic material and less than 0.02 ppm NO_x.

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% of 92°F. The chamber is then charged with the bag sample of exhaust + N_2 to the desired HC_t levels, 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% of initial NO_x (from about 5%, as present in the bag mixture) 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 II along with detailed data on initial chamber charge. The data of Table II represent results that were corrected for unavoidable variation in exhaust hydrocarbon composition and in $(NO_2)_i$ (Dimitriades, 1970). In each case the correction ranged from 0 to 10%.

For interpretation, the data of Table II have been plotted (Figures 2 and 3) to depict reactivity as a function of HC for constant NO_x and as a function of NO_x for constant HC [more complete plots can be found (Dimitriades, 1970)]. Graphical depiction of the HC and NO_x effects was preferred to statistical

Table II. 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 × min	Oxidant dosage, ppm × min	PAN dosage, ppm × min	HCHO dosage, ppm × min	Time,[a] min	Time,[b] min
0	<0.1	0.081	...	13.4	4.9	0.16	11.8	0	0
2.7	0.20	0.075	...	16.5	23.3	0.64	19.6	111	0
2.6	0.70	0.265	1.95	50.5	16.3	0.51	31.0	53	0
2.5	1.53	0.618	...	104.5	12.5	0.55	43.2	0	266
3.2	0.30	0.093	1.02	15.5	26.5	1.20	20.4	137	0
3.5	0.44	0.124	1.27	22.7	23.3	1.05	22.7	105	0
3.8	0.67	0.175	...	33.5	25.9	1.43	27.4	128	0
3.5	0.97	0.276	2.62	53.6	22.6	1.16	36.0	109	0
3.7	1.50	0.409	2.91	82.8	16.0	1.66	55.3	79	173
3.7	2.25	0.606	5.01	123.9	21.2	1.70	66.5	110	300
3.7	3.66	0.923	6.41	174.4	13.9	2.50	79.1	63	310
3.6	3.37	0.936	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	0.44	0.081	1.02	15.2	41.4	1.65	28.0	225	0
5.6	0.70	0.125	1.87	22.4	44.4	3.19	33.2	218	0
5.6	0.98	0.175	2.69	33.7	40.7	3.42	39.5	204	0
5.5	1.49	0.272	3.27	50.3	44.5	3.77	51.5	202	0
5.6	2.24	0.398	4.49	79.1	50.8	4.71	63.7	207	155
5.5	3.29	0.599	6.00	114.1	76.0	5.01	87.7	228	253
5.3	5.06	0.946	9.48	167.8	59.5	8.96	114.5	196	310
6.9	0.63	0.091	1.52	11.2	43.8	3.80	34.1	224	0
8.4	1.02	0.121	2.06	18.8	49.7	5.07	53.3	248	0
7.7	1.02	0.133	2.38	22.2	49.3	4.76	49.5	234	0
7.7	1.45	0.188	3.40	30.4	70.3	5.92	56.7	256	0
7.5	1.45	0.192	3.81	25.5	70.2	7.63	55.4	262	0
8.8	2.25	0.256	...	40.6	...	5.44	76.3	...	0
8.1	2.25	0.276	...	42.3	...	6.94	69.7	...	0
8.4	2.34	0.278	5.04	45.8	...	...	79.1	...	0
8.1	3.30	0.409	...	59.2	101.7	8.23	82.5	256	101
8.0	3.30	0.414	6.52	57.3	97.6	11.85	96.1	268	91
7.8	5.00	0.641	8.15	86.2	113.1	14.41	134.6	256	168
12.0	1.00	0.083	1.56	13.8	62.6	...	38.6	276	0
10.9	1.00	0.092	...	10.7	60.9	5.48	45.6	286	0
12.1	1.49	0.123	2.93	20.0	99.1	...	56.2	290	0
12.7	1.50	0.118	2.90	19.3	83.0	6.26	56.6	294	0
11.8	1.50	0.127	...	18.9	...	...	43.7	...	0
11.5	2.25	0.195	4.56	22.4	105.9	7.71	68.8	296	0
12.3	2.25	0.183	4.47	19.0	93.4	12.29	70.7	297	0
12.3	3.38	0.274	5.92	30.6	109.0	11.35	104.5	288	0
12.0	3.38	0.281	6.40	28.4	...	16.63	111.2	...	0
11.0	4.76	0.434	8.88	42.6	143.3	20.36	146.5	309	68
12.2	5.06	0.416	9.92	42.7	164.5	16.51	115.0	310	72

[a] Time during which oxidant exceed 0.1 ppm.
[b] Time during which NO_2 exceeded 0.25 ppm.

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 the agreement of results from the two oxidant-measuring instruments.

Oxidant Yield. 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 caused by day-to-day variation of the Mast meter response to oxidant and to NO_2. Furthermore, variation in light intensity and in composition of HC in tested samples could also have introduced variability.

Figures 2 and 3 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. Similar dependence patterns were shown by the oxidant dosage data.

Diagrams in Figure 3 show that change in NO_x was never accompanied by a codirectional change in oxidant reactivity.

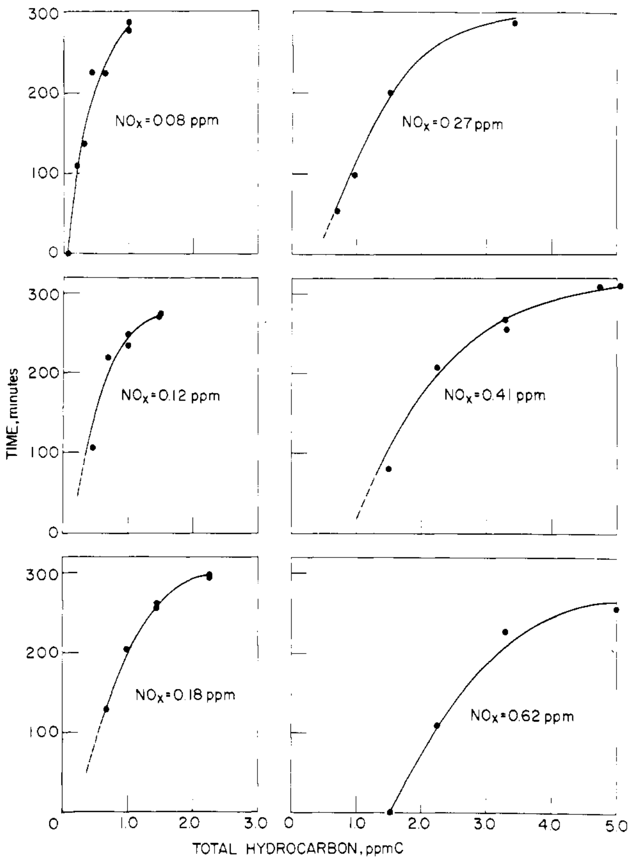

Figure 2. Time during which oxidant exceeded 0.1 ppm as a function of total hydrocarbon at various NO_x levels

This is contrary to what has been observed in irradiation of synthetic HC:NO_x mixtures. Altshuller et al. (1970) reported such data for hydrocarbons, including the fairly reactive propylene and xylene and the relatively unreactive toluene and butane. Similar data were also reported by Glasson and Tuesday (1970). 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 3 to lower NO_x levels.

PAN Yield. Of the known PAN compound family, only the first member, peroxyacetyl nitrate was measured routinely. The presence of peroxypropionyl nitrate (PPN) and peroxybenzoyl nitrate (PBZN) in the irradiated exhaust samples was also occasionally checked. Results showed undetectable levels of PBZN and PPN levels equivalent to 10 to 20% of those of PAN. The PAN yields, in general, follow the same patterns of dependence on HC and NO_x as oxidant yields. Also, the ratio of PAN to oxidant dosages was 1:10, approximately; this compares well with the level of ratios found in the atmosphere—1:5 to 1:10.

Table III. Slope and Intercept Values of the HCHO Dosage Vs. HC Lines for Varying $(NO_x)_i$

	$(NO_x)_i$, ppm					
	0.08	0.12	0.18	0.27	0.41	0.62
Intercept[a]	11	11	11	11	10	10
Slope[a]	33	31	28	27	25	23

[a] Units are the same as those used in diagram of Figure 4—i.e., ppm × min for HCHO dosage (ordinate) and ppmC for HC (abscissa).

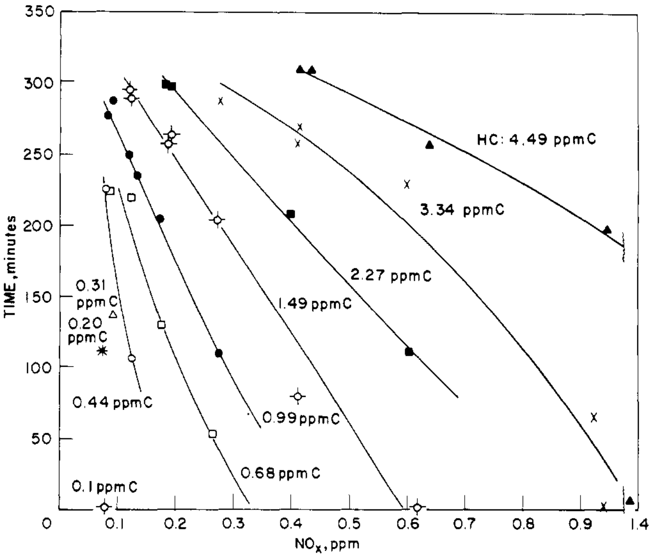

Figure 3. Time during which oxidant exceeded 0.1 ppm as a function of NO_x at various HC levels

HCHO Yield. Formaldehyde yields showed extremely well-defined dependencies on HC and NO_x. A typical example is given in Figure 4. 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 in Table III. The intercept point on the HCHO-dosage axis is constant and equal to 11 ppm × 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.

NO_2 Yield. The NO_2 yield, in terms of time during which NO_2 exceeded 0.25 ppm, appeared to be the only manifestation that, within the confines of this study, was inhibited, although only slightly, by HC. The inhibitive effect of HC was shown more clearly at the higher HC levels (Figure 5) and pre-

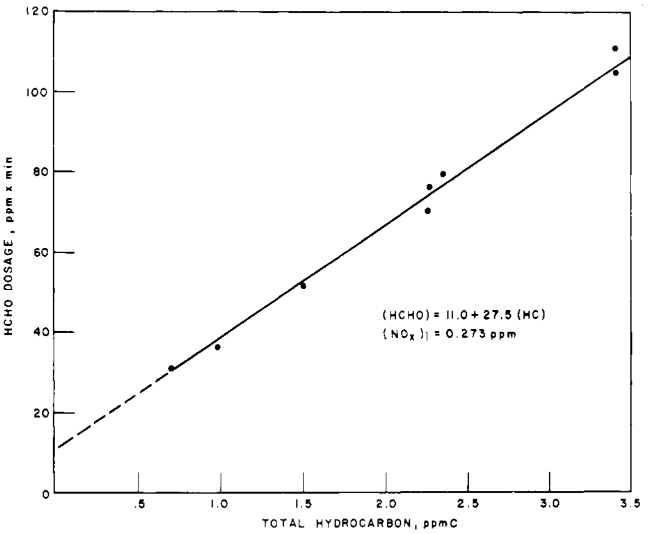

Figure 4. Formaldehyde-dosage reactivity of exhaust as a function of total hydrocarbon at NO_x = 0.273 ppm

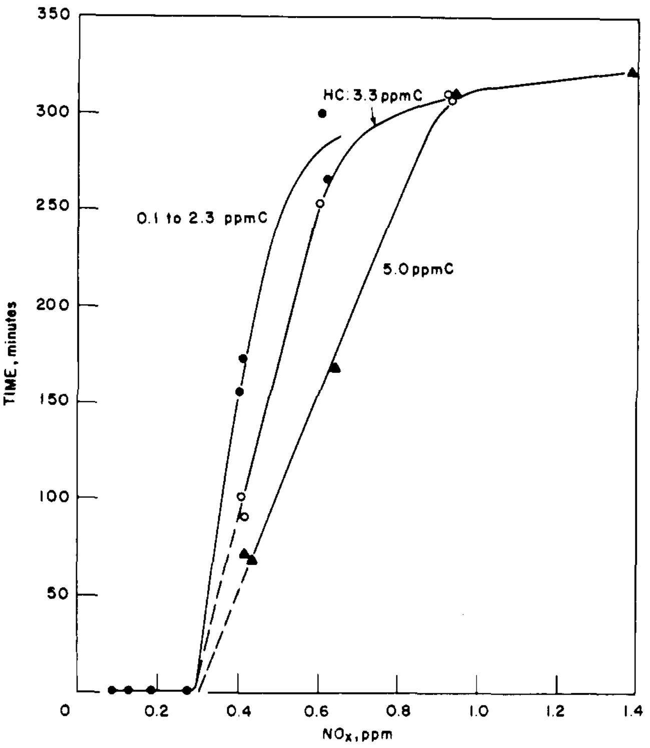

Figure 5. Time during which NO_2 exceeded 0.25 ppm as a function of NO_x at various HC levels

sumably was caused by accelerated consumption of NO_2 in reactions with oxidant and to a lesser extent with hydrocarbons. Similar patterns were shown by the NO_2 dosage data.

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 (Altshuller et al., 1970; Gay and Bufalini, 1969). The ratio of NO_2 dosage to PAN dosage ranged 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% 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.

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 fairly well-defined and unique patterns (Figures 6–7). Specifically, diagrams of Figures 6 and 7 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 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. 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 because of the HC effect. Such dependence of R_{NO_2} on HC and NO_x was similar to reported patterns (Glasson and Tuesday, 1966) for single HC:NO_x systems.

Discussion

Comparison of Smog Levels in Real and 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, atmospheric data not readily attainable must be used; 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 (Stephens and Burleson, 1969). 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

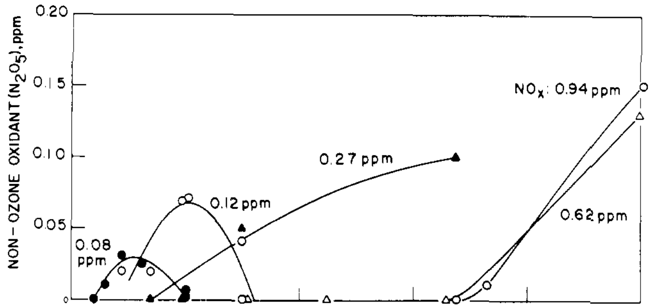

Figure 6. Final level of nonozone oxidant as a function of total hydrocarbon at various NO_x levels

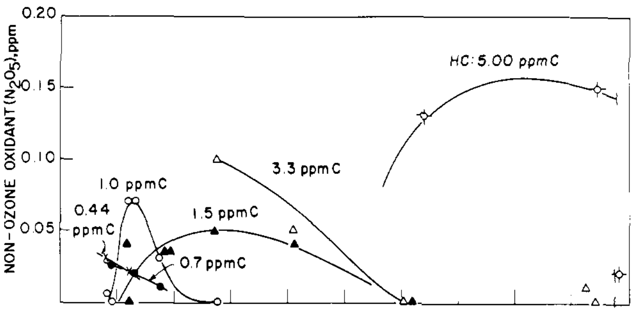

Figure 7. Final level of nonozone oxidant as a function of NO_x at various HC levels

Table IV. Comparison of Smog Levels from an Atmospheric Sample and a Chamber Sample that Contain the Same Initial Reactant Levels

	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	0.27		
After 2-hr irradiation			0.26	0.034
After 4-hr irradiation			0.49	0.047
After 6-hr irradiation			0.49	0.044

Table V. Values of $(NO_x)_i$[a] Levels and $(HC)_i$[a] 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	0.12	0.25
60	0.18	0.40
60	0.27	0.70
60	0.41	1.23
60	0.62	1.90

[a] Subscript designates level in initial chamber charge.

the use of established compositional patterns in the sampled atmosphere and knowledge of relative hydrocarbon disappearance rates. Table IV summarizes resultant and corresponding data from this research. The data of Table IV show generally 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 (Stephens and Burleson, 1969). 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 IV 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 IV) certainly does not resolve the issue of comparability (of atmospheric and smog chamber systems), 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.

Comparison of patterns that describe 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 (Figure 3). 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 (Romanovsky et al., 1967; Altshuller et al., 1970; Glasson and Tuesday, 1970). Therefore, we must conclude that use of simple HC:NO_x systems, for example, propylene + NO_x, as substitutes for exhaust or atmospheric samples is unrealistic. 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 (Altshuller et al., 1969; Buchberg et al., 1963; Glasson and Tuesday, 1966; Korth et al., 1964; Altshuller et al., 1970; Stephens and Burleson, 1969). Within the range of initial concentration levels used in this research, these dependencies are as follows: At low NO_x levels, the NO_2 dosage is nearly proportional to NO_x and is slightly inhibited by HC at higher HC levels, the HCHO dosage is nearly proportional to HC level and slightly inhibited by NO_x, and 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. Results from this study can be used to define the dependence of certain types of air quality on HC and NO_x. This 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 2, 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 hr. For example, for $(NO_x)_i = 0.08$ ppm, $(HC)_i$ should be 0.13 ppmC or less in order that resultant oxidant exceed 0.1 ppm for 1 hr or less. Such optimum $(HC)_i$ and $(NO_x)_i$ values (listed in Table V) were used to draw the equal-response line *aeb* in Figure 8. Points above this equal-response line represent values of $(HC)_i$ and $(NO_x)_i$ that meet the California standard for oxidant; points below correspond 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 (Figure 3) 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 Figure 3) and that oxidant yield is proportional to NO_x within the range 0–0.4 ppm, then the NO_x level corresponding to the California oxidant standard is estimated (from Figure 3) to be

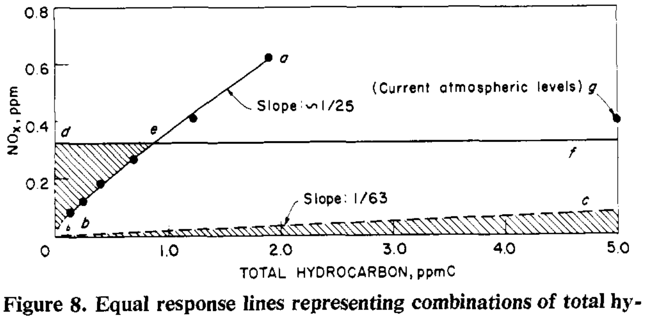

Figure 8. Equal response lines representing combinations of total hydrocarbon and NO_x corresponding to oxidant and NO_2 yields equal to the California standards

Shaded area represents all points in the (HC, NO_x) plane that meet the California oxidant and NO_2 standards of air quality

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 and yield a ratio higher than 62. When similar treatment was applied on the oxidant-NO_x curves (Figure 3) 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 8. 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 8 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 on the HC and NO_x levels. From Figure 5, 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 8. 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 8 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 8 to show the currently typical levels of HC and NO_x in atmosphere, relative to the desired levels.

From diagrams such as Figure 8, it is possible to estimate the direction and extent to which current atmospheric levels must 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 Table VI.

The estimates given in Table VI 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:

- Interdependence of initial reactants and resultant smog levels are the same in the smog chamber as in the atmosphere
- Hydrocarbon composition is the same in exhaust as in the atmosphere
- 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 unlikely that agreement will be achieved for all smog manifestations. An approach, however, for such comparison is available, and the data of Table IV 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 Burleson (1969) 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 (Eccleston et al., 1970). 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.

Table VI. Optimum NO_x and HC Levels to Meet Prescribed California Air Quality Standards

Standards (existent)			
Oxidant not to exceed 0.1 ppm for more than 1 hr NO_2 not to exceed 0.25 ppm for more than 1 hr	NO_x: ≤ 0.08 ppm HC: $\geq 62 \times (NO_x)$ (Requires at least 80% NO_x reduction and no HC reduction from current levels)	or	NO_x: ≤ 0.33 ppm HC: $\leq 2.5 \times (NO_x)$ (Requires at least 15% NO_x reduction and drastic HC reduction from current levels)
Standards (hypothetical)			
Oxidant not to exceed the dosage level of 0.1 ppm × hr NO_2 not to exceed the dosage level of 0.25 ppm × hr	NO_x: ≤ 0.017 ppm HC: $\geq 300 \times (NO_x)$ (Requires drastic NO_x reduction and no HC reduction)	or	NO_x: ≤ 0.10 ppm HC: $\leq (NO_x)$ (Requires at least 75% NO_x reduction and drastic HC reduction)
Oxidant not to exceed the dosage level of 0.25 ppm × hr NO_2 not to exceed the dosage level of 0.25 ppm × hr	NO_x: ≤ 0.04 ppm HC: $\geq 125 \times (NO_x)$ (Requires drastic NO_x reduction and no HC reduction)	or	NO_x: ≤ 0.10 ppm HC: $\leq 2.0 \times (NO_x)$ (Requires at least 65% NO_x reduction and drastic HC reduction)
Oxidant not to exceed the dosage level of 0.25 ppm × hr Daily maximum NO_2 or NO_x not to exceed 0.25 ppm	NO_x: ≤ 0.04 ppm HC: $\geq 125 \times (NO_x)$ (Requires drastic NO_x reduction and no HC reduction)	or	NO_x: ≤ 0.25 ppm HC: $\leq 2.5 \times (NO_x)$ (Requires at least 30% NO_x reduction and drastic HC reduction)

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 (Altshuller, 1968). Composition of hydrocarbons in exhaust from NO_x-controlled autos may, however, depend decidedly on 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 to alter hydrocarbon composition drastically by preferentially removing reactive hydrocarbons (Weaver, 1969). The other control methods are not expected to have a drastic effect. Because no NO_x-control method has been specified for application, no compositional effects that would unavoidably accompany the effect of NO_x reduction can be predicted or even studied at this time.

Summary and Conclusions

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.

Smog levels observed in the smog chamber were comparable to similar atmospheric levels of reactants.

Data were developed which showed that use of simple HC:NO_x systems—e.g., propylene/NO_x, as substitutes for natural atmosphere or exhaust is unrealistic.

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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Nitrogen Removal from Municipal Waste Water by Columnar Denitrification

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■ Among the available methods to remove nitrogen from waste water, the biological method of denitrification appears most promising. The work reported herein describes the results of a pilot plant investigation of columnar denitrification on three sizes of inert media, utilizing methanol as a substrate for the biochemical reduction of the nitrate ion. These studies were conducted on the nitrified effluent of a municipal waste treatment plant receiving sewage of domestic origin. The work was directed toward extending the state of the art of columnar denitrification and to specifically define the optimum conditions for this process. The effects of media size, gradation, column porosity, and contact time, and the effect of influent dissolved oxygen on nitrate reduction efficiency were determined. Hydraulic characteristics and solids removal efficiencies were examined for each column. Results indicated that greater than 90% denitrification was achieved at methanol/nitrate ratios of 2.50/1.0 and 2.75/1.0 at contact times of 5 min for coarse sand and 15 min for $^3/_4$-in. stone.

Nitrogen, in its many forms, has long played a fundamental role in the aquatic environment. It is now apparent that ecological imbalances in the natural environment have been caused, in part, by the excessive discharges of nitrogenous materials into natural waterways. Although phosphorus has been identified more frequently than nitrogen as the limiting algal nutrient, field studies have shown that, under certain circumstances, nitrogen occupies a critical role in the eutrophication of lakes (Dean, 1970). For instance, it has been demonstrated that nitrogen is the critical element causing eutrophication of the upper San Francisco Bay. In addition to the nutrient value of nitrogen, the oxygen demand of reduced nitrogen forms in treated municipal effluents can represent as much as 70% of the total oxygen demand of these effluents.

The State of Maryland now sets a limit of 1 mg/l. ammonia in effluents discharged into the Patuxent River. The Potomac Enforcement Conference requires 85% removal of the total

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