EPA-AA-TSS-PA-84-6

Technical Report

Reactivity of Methanol Exhaust: A Smog Chamber Study

Project Officer: Craig A. Harvey

Technical Representative: Penny M. Carey

November 1984

NOTICE

Technical Support Staff
Emission Control Technology Division
Office of Mobile Sources
Office of Air and Radiation
U. S. Environmental Protection Agency

Reactivity of Methanol Exhaust

Memorandum of Results

H.E. Jeffries, K.G. Sexton
R.M. Kamens, M.B. Holleman

Department of Envr. Sci. and Eng.
University of North Carolina
Chapel Hill, N.C., 27514
(919)-966-5451

A memorandum of results was furnished to the Environmental Protection Agency by the University of North Carolina, Department of Environmental Sciences and Engineering, in fulfillment of Task Specification 22 of EPA Contract No. 68-03-3162 with Southwest Research Institute. This edited version of the memorandum of results has been released by EPA to report technical data of interest and to facilitate information exchange. Readers should be aware that the data reported here are preliminary. Detailed data analysis will be performed and a complete report issued at a later date.

Reactivity of Methanol Exhaust

Memorandum of Results
September 26, 1984

Introduction

This memorandum summarizes the experimental results from a three month program conducted in the University of North Carolina Outdoor Dual Smog Chamber. The detailed experimental work has been described in a planning memorandum (Jeffries, July 16), and two monthly progress reports (Jeffries *et al.*, July, August). In addition, a half-day seminar was present by Jeffries at the EPA offices in Ann Arbor.

Purpose of Work

The purpose of this research was to conduct outdoor smog chamber experiments to test whether chemical mechanisms that are likely to be used in control strategy calculations accurately predict the compositional effects caused by large scale use of neet methanol as a fuel instead of gasoline.

The basic tests consisted of side-by-side experiments in which the chemistry of a typical synthetic auto-exhaust or synthetic urban-like hydrocarbon mixture, at typical HC-to-NO_x ratios, was compared with the chemistry of a mixture in which one-third of the original mixture is substituted by a synthetic methanol-exhaust mixture. In these so called "substitution" experiments, the overall reactivity of the original auto-exhaust mixture is compared with the reactivity of the methanol-exhaust substituted mixture.

The tests were conducted at four hydrocarbon (HC) concentrations: 0.6, 1.0, 2.0, and 3.0 parts per million Carbon (ppmC), and at 0.35 ppm oxides of nitrogen (NO_x). Substitution was performed at the 1 and 3 ppmC level. The degree of substitution was always 1:2 (33% substitution). The composition of the synthetic methanol-fuel exhaust was 1% methyl nitrite ($MeNO_2$), 0–20% formaldehyde (HCHO), and 79–99% methanol (MeOH). The standard mixture was 10% formaldehyde.

Conclusions

The major initial conclusions that can be drawn from this study are:

- Synthetic methanol exhaust substitution in these experiments never resulted in an increase in reactivity, even for a fuel composition having 20% formaldehyde.
- At the 9-to-1 HC-to-NO_x ratio for the synthetic auto-exhaust, the synthetic methanol exhaust is as reactive as the mixture; although the peak ozone is essentially independent of the formaldehyde content, the rise of ozone is delayed slightly as formaldehyde is decreased from 20% (almost no delay) to 0% (about 60 minutes delay).
- At the 3-to-1 HC-to-NO_x ratio for the synthetic auto-exhaust, there was a 33% reduction in peak ozone when synthetic methanol exhaust containing 10% formaldehyde was substituted for 1/3 of the mixture.
- At the 9-to-1 HC-to-NO_x ratio, for the much less reactive synthetic urban mixture, the synthetic methanol exhaust, at the 10% formaldehyde level, is as reactive as the urban mixture; at the 0% formaldehyde level, however, there was a 17% decrease in ozone maximum for a 33% substitution of methanol.
- At the 3-to-1 ratio, for the synthetic urban mixture, there was also an 18% decrease in peak ozone when methanol fuel (10% formaldehyde) was substituted.

Summary of Results

Level of Effort

This project clearly met its goals in terms of producing quality experiments designed to address the issue of methanol-exhaust reactivity:

1. Twenty-three dual smog chamber runs were conducted. Ten of these experiments are nearly ideal for model testing, in close agreement with the estimates made in the planning memorandum. The other 13 experiments, while having poorer sunlight which complicates the model testing, are quite useful to support the trends or directional effects of the substitution.
2. Three different hydrocarbon mixtures were used:
   - **UNCMIX**, a well-studied paraffin and olefin mixture;
   - **SynAuto**, a 13-component mixture developed by a series of direct comparisons of the mixture with automobile exhaust in side-by-side chamber experiments; and
   - **SynUrban**, an 18-component mixture that conforms with the EPA recommended "default" mixture composition for use with the Carbon Bond Model in urban ozone control calculations.

   The composition of these mixtures is given in Table 1.
3. The composition of the synthetic methanol-fuel exhaust was 1% methyl nitrite ($MeNO_2$) 0-20% formaldehyde (HCHO), and 79-99% methanol (MeOH). The standard mixture was 10% formaldehyde.
4. Three dual experiments were conducted with UNCMIX; six dual experiments were conducted with the SynUrban mixture; and 14 dual experiments were conducted with the SynAuto mixture.

Experimental Results

Table 2 summarizes the major results for maximum O_3 produced. The dependence of O_3-maximum on HC at constant NO_x is shown graphically in Figure 1. Profile plots for NO_x and O_3 for four of the days are shown in Figures 2-5.

The SynAuto Runs

Table 2 shows that for the SynAuto mixture, the 3 ppmC pure SynAuto runs all made approximately 0.8 to 0.9 ppm O_3. The variation is due to daily and monthly variation in sunlight and temperature.

The 2 ppmC pure SynAuto run (Aug. 6) also made essentially the same O_3, only a little later. The 1 ppmC pure SynAuto runs made a little more than half the O_3 of the 3 ppmC runs. The 0.66 ppmC run made about half the O_3 as that of the 1 ppmC runs and about one-third the O_3 of the 3 ppmC runs.

For the SynAuto substituted runs at the 3 ppmC level, the amount of O_3 produced was essentially the same as the pure SynAuto mixture; there was a small dependence O_3 rise time upon the amount of HCHO present in the methanol exhaust.

For the SynAuto substituted runs at the 1 ppmC level, there was a 33% reduction in maximum O_3. This compares with a 42% reduction for simply removing one-third of the carbon.

The SynUrban Runs

Table 2 shows that the SynUrban mixture is significantly less reactive than the SynAuto mixture. At 3 ppmC pure SynUrban, the maximum O_3 is approximately equal to that in the 1 ppmC SynAuto run. At the 1 ppmC level, the SynUrban ozone is less than 20% of the SynAuto ozone.

Substitution at the 3 ppmC level shows a small effect in O_3 maximum and shows a dependence upon the degree of formaldehyde substitution. Without formaldehyde in the methanol exhaust, there was a 17% reduction in ozone maximum for a 33% substitution.

Substitution at the 1 ppmC level also shows approximately the same effect: 18% reduction in ozone maximum. Removing 1/3 of the carbon at this level, however, has a very large effect on O_3 production—a decrease of 80%.

Table 1. Composition of Hydrocarbon Mixtures.

Compound	UNCMIX	SYNAUTO	SYNURBAN
butane		0.0391	0.1000
pentane	0.2531		0.1367
isopentane	0.1484	0.0519	0.0801
2-methylpentane	0.0996		0.0538
2,4-dimethylpentane	0.0864		0.0467
2,2,4-trimethylpentane	0.1202	0.1121	0.0347
ethylene	0.1167	0.2391	0.0630
propylene	0.0524	0.0416	0.0238
1-butene	0.0254	0.0196	0.0137
trans-2-butene		0.0196	
cis-2-butene	0.0313		0.0169
2-methyl-1-butene	0.0347		0.0187
2-methyl-2-butene	0.0317		0.0171
benzene		0.0538	0.0331
toluene		0.2115	0.1304
m-xylene		0.1026	0.0633
o-xylene		0.0481	0.0296
1,2,4-trimethylbenzene		0.0564	0.0347
formaldehyde		0.0200	0.0200
total paraffin	0.7077	0.2031	0.5404
total olefin	0.2922	0.3199	0.1546
total aromatic	0.0000	0.4724	0.2854

Table 2
Maximum Ozone for Methanol Reactivity Program.

(clear sky conditions only, units are ppm)

Mixture	Initial HC, ppmC (mix/methanol)											
	3		2/1			2		1		0.6/0.3		0.6
SynAuto	Jul 25	0.75	Jul 25	0.75	(10%)			Aug 5	0.55			Aug 5 0.32
	Jul 26	0.72	Jul 26	0.72	(0%)			Aug 7	0.60	Aug 7	0.40 (10%)	
	Aug 6	0.90				Aug 6	0.86					
	Aug 8	0.85	Aug 8	0.85	(20%)							
SynUrban	Aug 22	0.68	Aug 22	0.65	(10%)			Aug 25	0.11	Aug 25	0.09 (10%)	
	Sept 1	0.66	Sept 1	0.55	(0%)			Sept 2	0.11			Sept 2 0.02

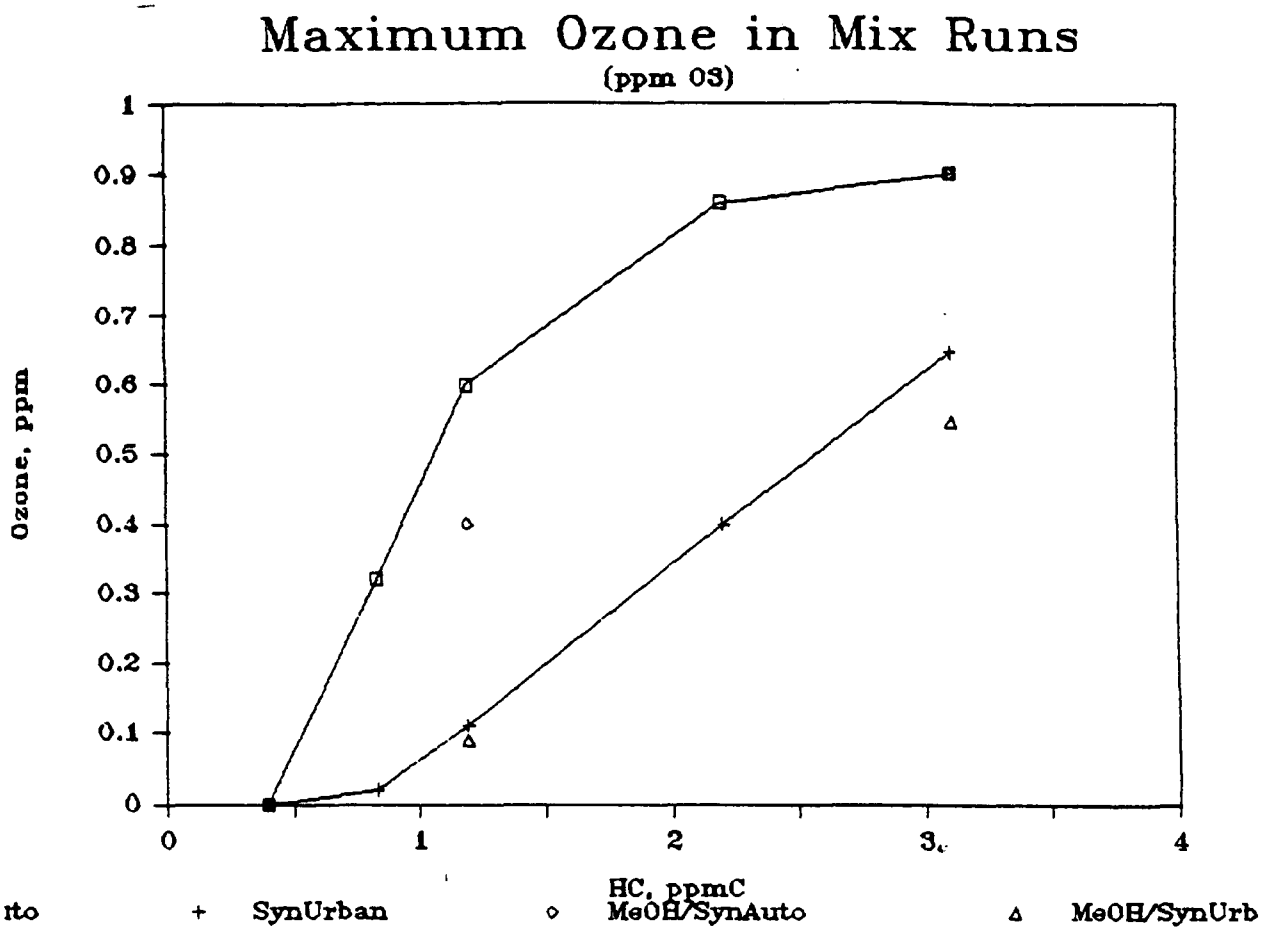

Figure 1. Maximum ozone concentrations as a function of initial hydrocarbon for SynAuto mixture (top line) and for SynUrban mixture (bottom line). Individual points are for 33% methanol/HCHO substitution.

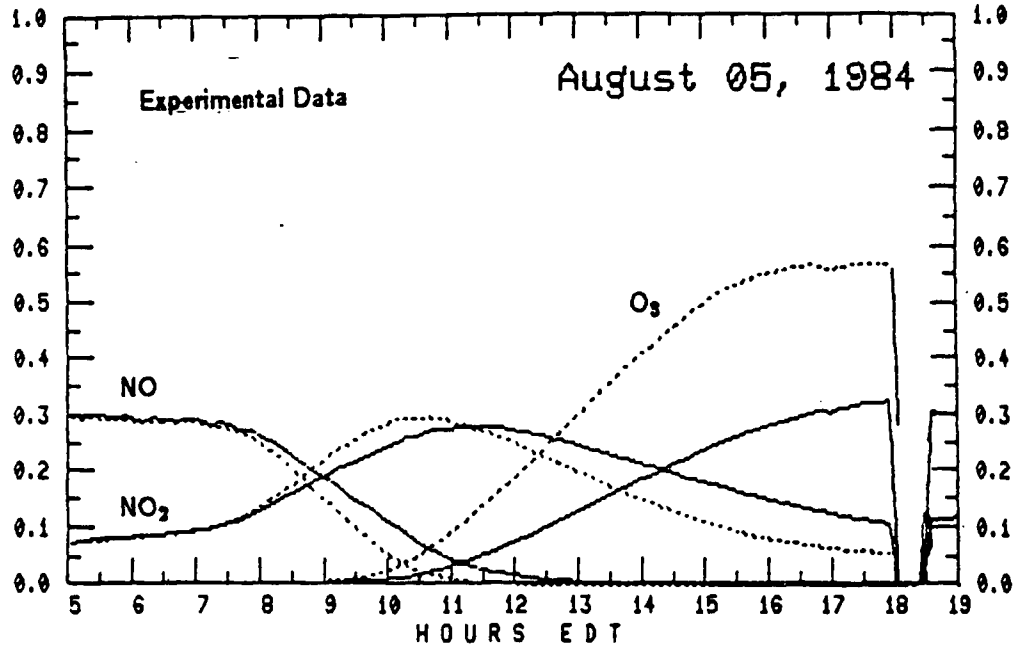

Figure 2a. NO, NO2, O3 data for August 5, 1984 dual smog chamber experiment. 1.19 ppmC (BLUE - dashed line) vs Ø.83 ppmC (RED - solid line) SYNAUTO; Ø.35 ppm NOx both sides.

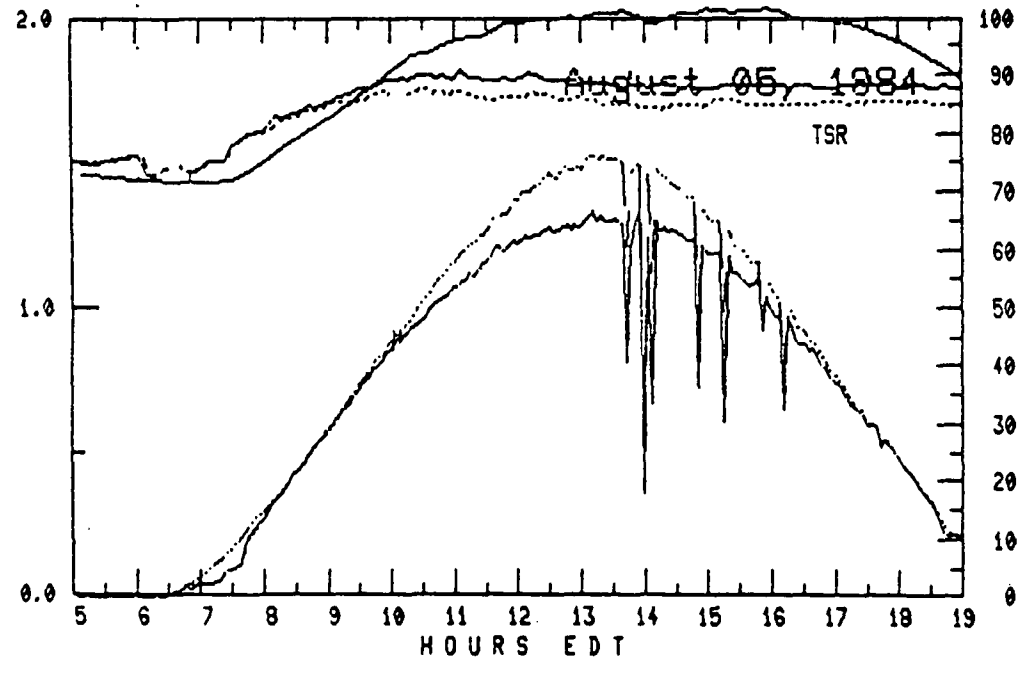

Figure 2b. Total Solar Radiation (solid line), Ultraviolet Radiation (dashed line), Dewpoint (both sides), and Temperature data for August 5, 1984 dual smog chamber experiment.

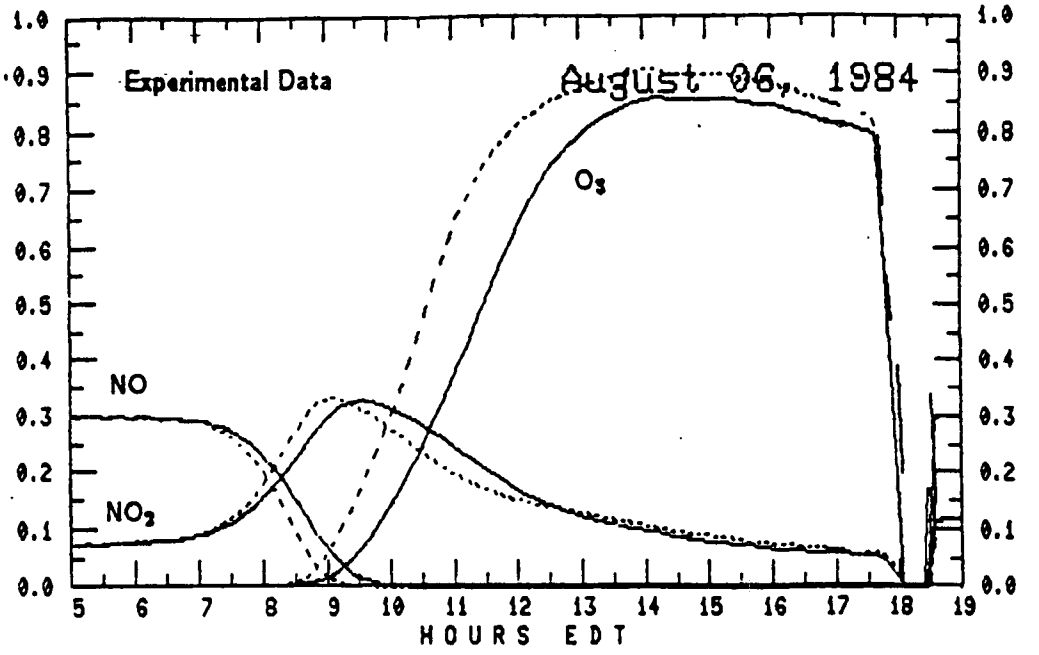

Figure 3a. NO, NO2, O3 data for August 6, 1984 dual smog chamber experiment. 3.12 ppmC (BLUE - dashed line) vs 2.16 ppmC (RED - solid line) SYNAUTO; Ø.35 ppm NOx both sides.

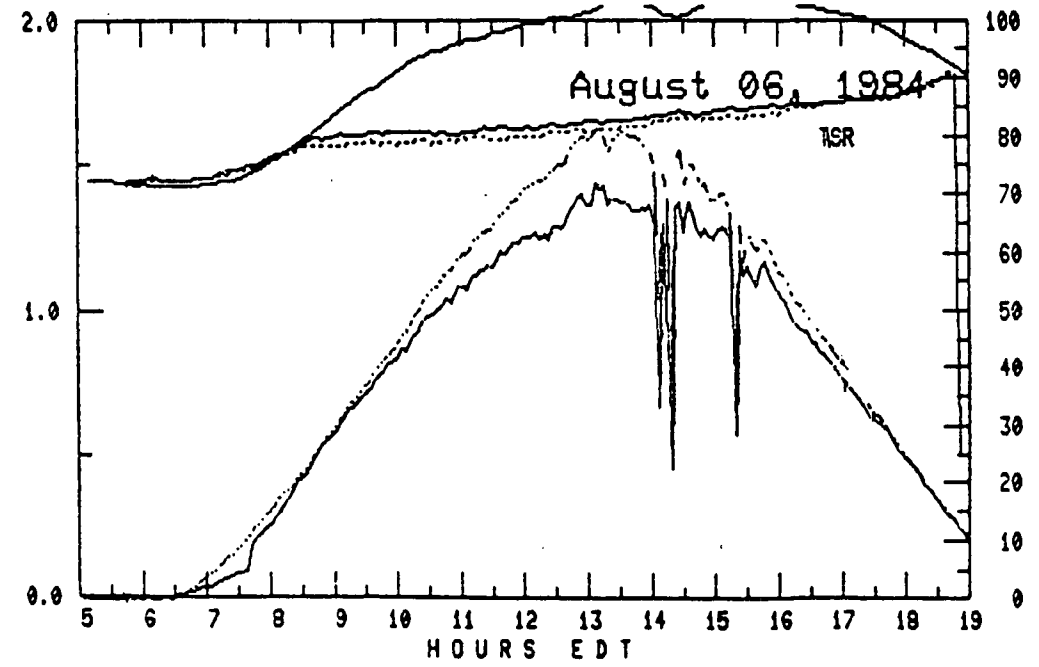

Figure 3b. Total Solar Radiation (solid line), Ultraviolet Radiation (dashed line), Dewpoint (both sides), and Temperature data for August 6, 1984 dual smog chamber experiment.

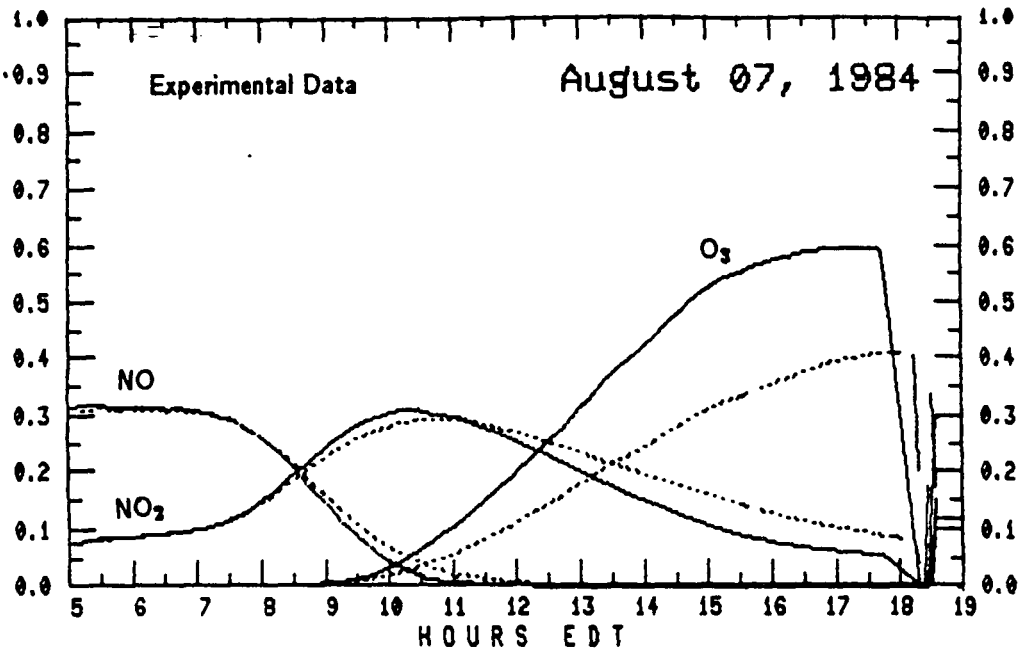

Figure 4a. NO, NO2, O3 data for August 7, 1984 dual smog chamber experiment. Synthetic MeOH exhaust substitution into SYNAUTO. 1.19 ppmC (RED - solid line) vs Ø.76 ppmC (BLUE - dashed line) SYNAUTO with Ø.3 ppm MeOH, Ø.ØØ3Ø ppm HCHO and Ø.ØØ3 ppm MeONO; Ø.35 ppm NOx both sides.

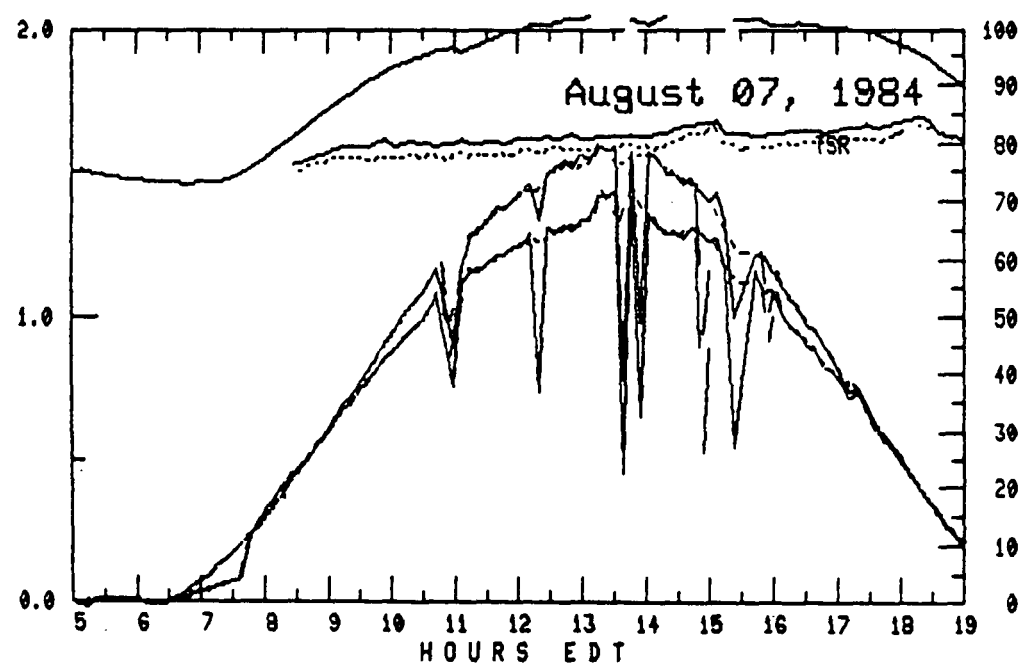

Figure 4b. Total Solar Radiation (solid line), Ultraviolet Radiation (dashed line), Dewpoint (both sides), and Temperature data for August 7, 1984 dual smog chamber experiment.

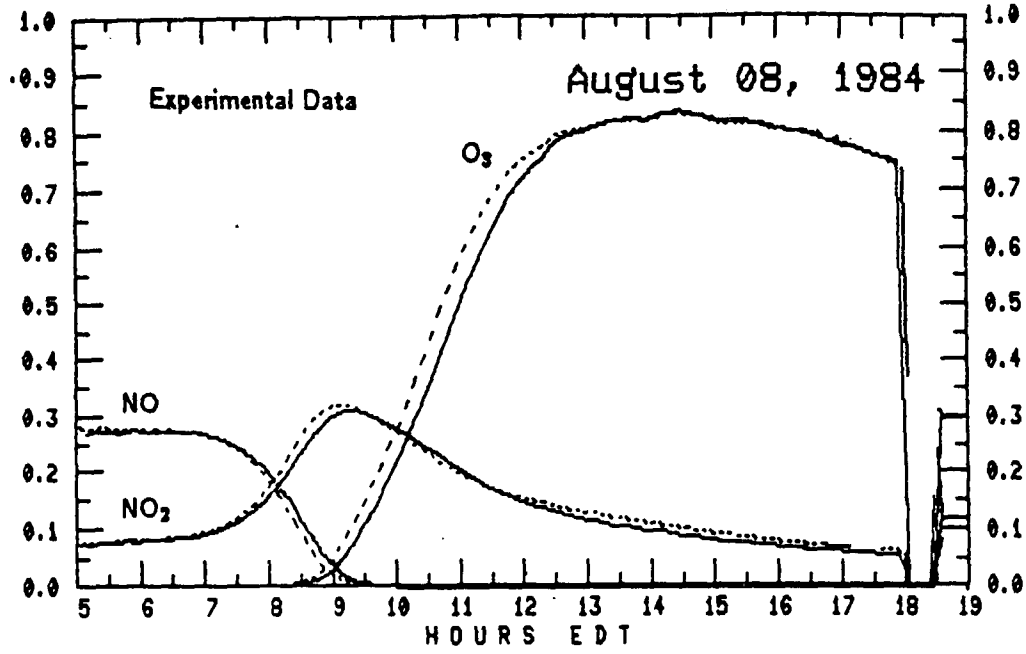

Figure 5a. NO, NO2, O3 data for August 8, 1984 dual smog chamber experiment. Synthetic MeOH exhaust substitution into SYNAUTO. 3.34 ppmC (BLUE - dashed line) vs 2.23 ppmC (RED - solid line) SYNAUTO with Ø.79 ppm MeOH, Ø.2 ppm HCHO and Ø.Ø1 ppm MeONO; Ø.35 ppm NOx both sides.

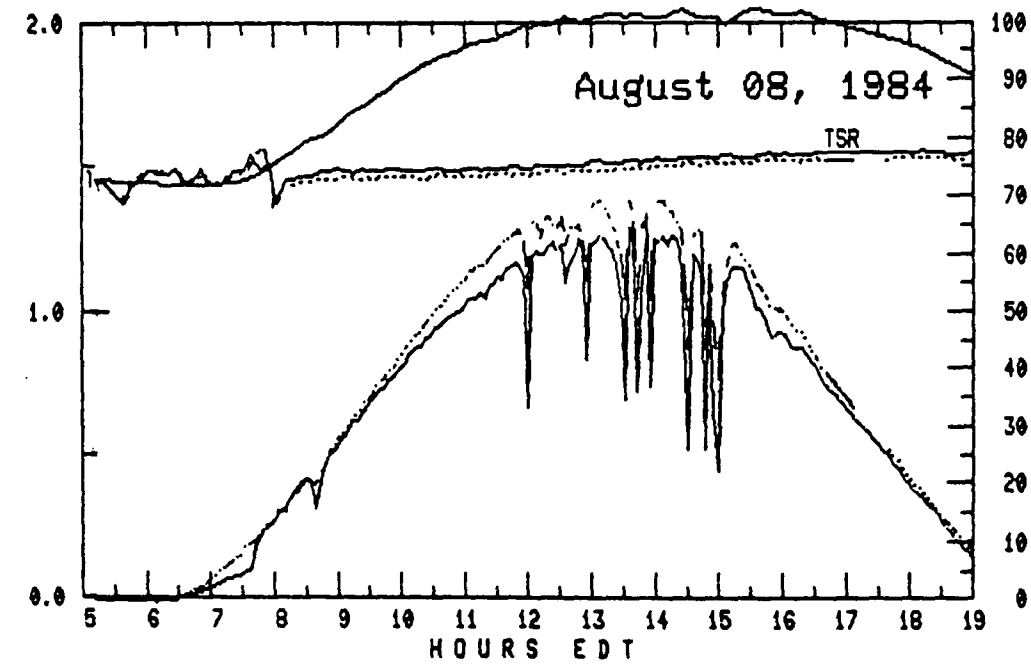

Figure 5b. Total Solar Radiation (solid line), Ultraviolet Radiation (dashed line), Dewpoint (both sides), and Temperature data for August 8, 1984 dual smog chamber experiment.