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Mr. W. R. Taylor
Diamond Shamrock Chemical Company
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Dear Mr. Taylor:

The Smog Reactivity of Vinyl Chloride Monomer

This letter will serve as Battelle's Columbus Laboratories report on the study conducted for Diamond Shamrock Chemical Company of the photochemical smog reactivity of vinyl chloride monomer (VCM). Photochemical smog reactivity can be stated in a number of ways, i.e., in terms of ozone formation, eye irritation, nitric oxide photo-oxidation, aerosol formation, etc. In the present study attention is focused on ozone formation, the principal photochemical smog manifestation from a regulatory point of view. Several other smog parameters have also been obtained and are discussed in this report, principally to present a more complete description of the reactivity of VCM.

Within the limited framework of the experiments carried out in this program the smog reactivity of VCM is not clearly defined. At the higher concentration studied it appears to be less reactive with respect to ozone production and eye irritation, while at the lower concentration studied it appears to be very definitely more reactive than toluene with respect to ozone production.

An absolute definition of smog reactivity does not exist; reactivities of VCM are therefore presented relative to smog profiles of toluene under similar chamber conditions. Profiles of smog-chamber runs with VCM and toluene are included with this report. Initial conditions and reactivity parameters are listed in Table 1. A run using diethylamine as a potential low reactivity hydrocarbon reactant was also carried out (Run 3) but was of questionable accuracy and has therefore been excluded from the overall analysis. Hydrocarbon values are reported as parts per million of carbon (ppmC). All other concentrations are reported as parts per million (ppm) on a volume basis.

All runs were carried out at 90 ± 2° F and at 40 ± 5 percent relative humidity. Illumination intensity as measured by NO_2 photodecomposition was $k_d = 0.45\ min^{-1}$, slightly greater than noon-day sunlight intensity. Total hydrocarbon was determined by flame ionization, NO and NO_2 continuous Saltzman techniques, ozone by chemiluminescence, total aldehyde by the sodium bisulfite procedure, and aerosol by broad band integrated nephelometry. Eye irritation measurements were made by two seven-member eye panels. The overall average eye irritation index for the two panels is reported for the fifth hour of irradiation. The eye irritation index is defined as $\frac{10(360-t)}{360}$ = index; where t is the arithmetic mean time, in seconds, for panel response. On this basis zero is the lowest possible irritation index value and ten the highest. Eye irritation data are obviously subjective data. In general an index of seven or more is fairly irritating while an index of five or less is mild-to-non-irritating.

Vinyl Chloride Monomer

The initial VCM experiment, Run 1 in Table 1, was carried out at the relatively high hydrocarbon loading of 4 ppm (by volume) VCM. The HC/NO_x ratio was approximately 2. This experiment should be compared with Run 4 which consists of toluene under the same volume loading and HC/NO_x conditions.

Overall, the VCM run was slower than the toluene experiment. The time to NO_2 maximum was about an hour slower for the VCM run. Ozone peaked at 0.24 ppm in the toluene run and was only 0.04 ppm although still increasing after six hours in the VCM experiment. Total aldehyde levels at the fifth hour of irradiation were similar for both toluene and VCM. Aerosol values as measured by light scattering were much higher in the toluene run. Eye irritation was also higher for the toluene experiment.

Comparing now VCM (Runs 2 and 6) and toluene (Run 5) at a lower hydrocarbon loading and higher HC/NO_x, we see in Table 1 that the time to NO_2 maximum is now similar for VCM and toluene and that VCM yields an ozone maximum which is considerably higher than that from toluene (Run 5). Once again toluene resulted in much higher aerosol yields than VCM. Eye irritation and total aldehyde values for the duplicate VCM experiments were scattered and bracketed the toluene values for these smog manifestations.

Aerosol reactivity is often reported in terms of light scattering. There was no evidence of any marked aerosol production in these studies for VCM.

TABLE 1. REACTIVITY EXPERIMENTS

Run No.	1	2	4	5	6
	Vinyl Chloride	Vinyl Chloride	Toluene	Toluene	Chloride
Hydrocarbon, ppmC					
Background	4.6	2.4	2.7	2.1	2.7
Injection	7.9	2.2	27.5	7.2	2.2
HC/NO_x, $\frac{ppm\ V/V}{ppm\ V/V}$	2.0	3.6	2.0	2.7	3.5
NO, ppm	1.80	0.31	1.80	0.38	0.32
NO_2, ppm	0.20	0.00	0.20	0.00	0.00
NO_2,max, ppm	0.69	0.16	0.60	0.20	0.20
NO_2 t-max, min.	246	65	180	62	50
O_3 max, ppm	0.04	0.34	0.24	0.13	0.21
O_3 t-max, min.	>360	265	340	105	95
Relative O_3*	0.17	2.6	1.0	1.0	1.6
Eye Irritation Index	5.8	7.6	7.9	6.7	5.7
Aerosol, Δb-scat, $10^6 m^{-1}$	0.0	0.0	52.0	49.8	0.2
Total Aldehyde, ppm t=300 min.	1.22	0.59	1.12	0.82	0.96

* Relative O_3 = O_3 max/O_3 max (Toluene)

Summary

The photochemical smog reactivity of VCM as observed in these experiments is qualitatively summarized in the following tabulation. The reactivity of VCM is somewhat in question in that low ozone and eye irritation reactivity is observed at the high concentration loading, and high reactivity is observed at the low concentration loading.

We appreciate the opportunity to work with Diamond Shamrock on this study. Please call me if you would like further amplification on the results presented here.

Very truly yours,

Arthur Levy

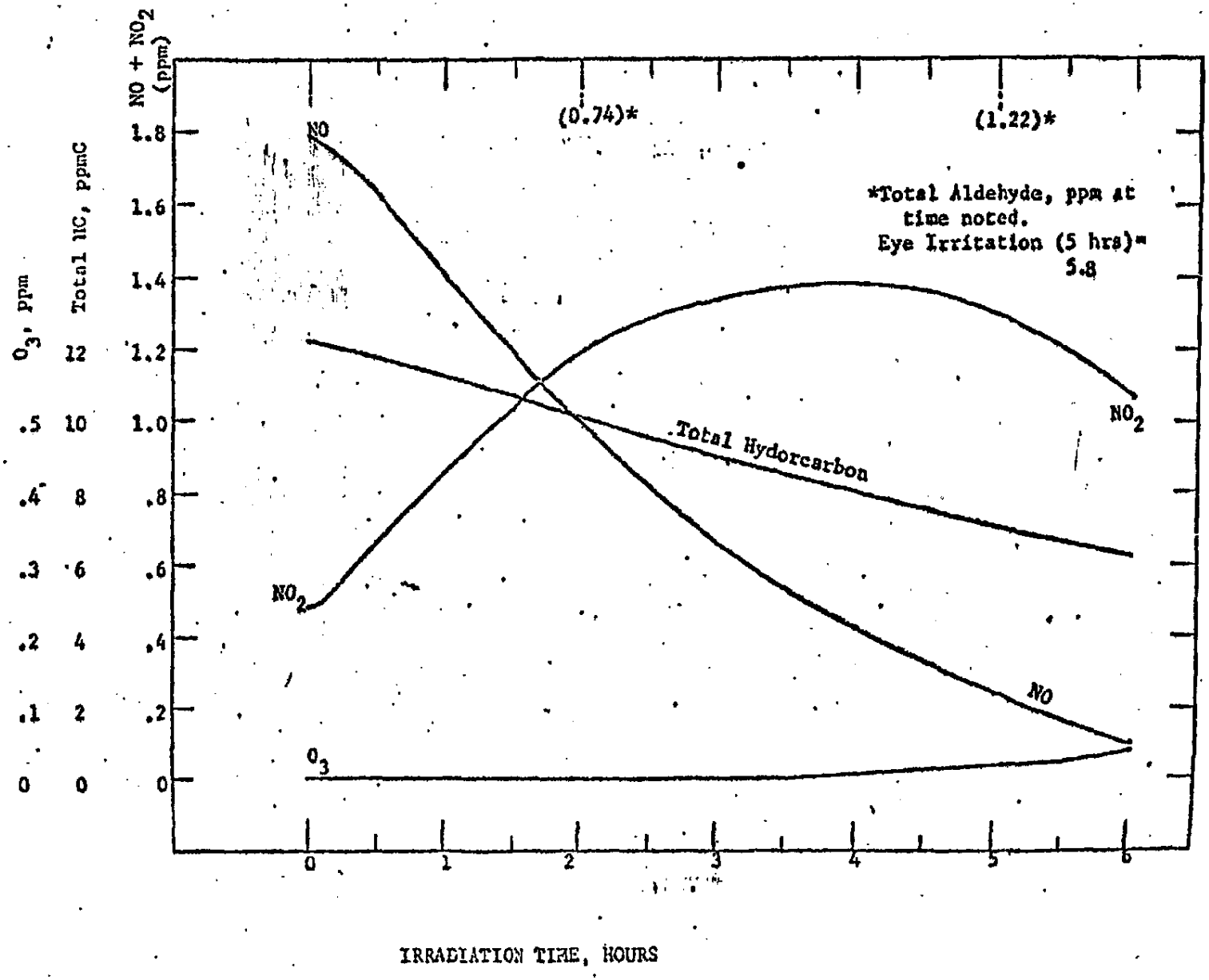
Arthur Levy,
Senior Research Leader
Atmospheric Chemistry and Combustion
Systems Section

AL:mb

Duplicate

Enc.

Run No. 1 VCM 4 ppm (v/v)



QUALITATIVE COMPARISON WITH TOLUENE

	VCM	
	4 ppm (^{v}/v), HC/NO 2/1	2 ppm (^{v}/v), HC/NO 3/1
O_3 Max	--	++
O_3 Dosage	--	++
Eye Irritation	-	0
-dNO/dt	-	0
NO_2 Max	++	0
NO_2 Dosage	++	0/-

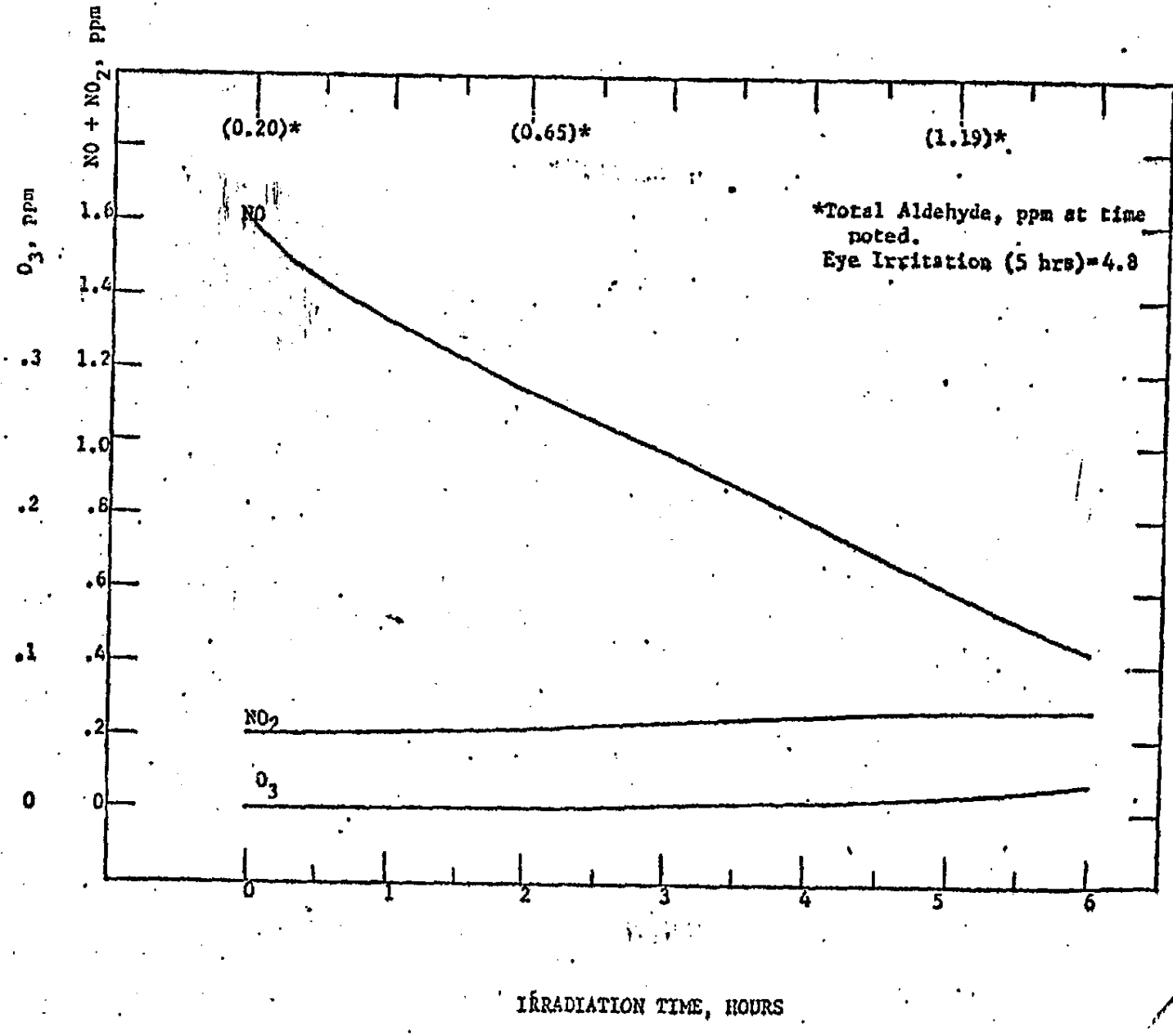
++, -- Much greater, much less than toluene

+, - Greater, less

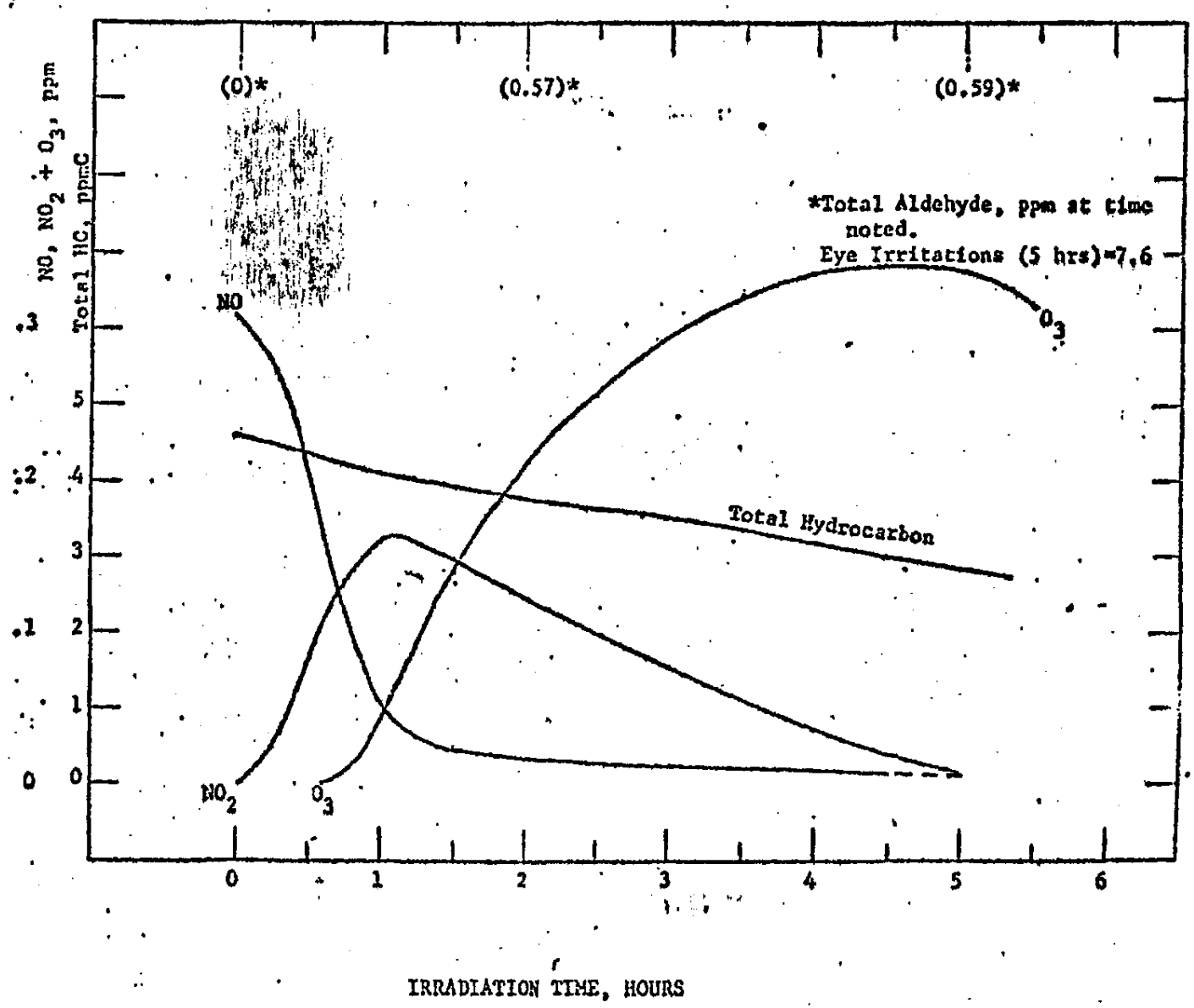
0 Unchanged

0/+, 0/- Possibly greater, possibly less

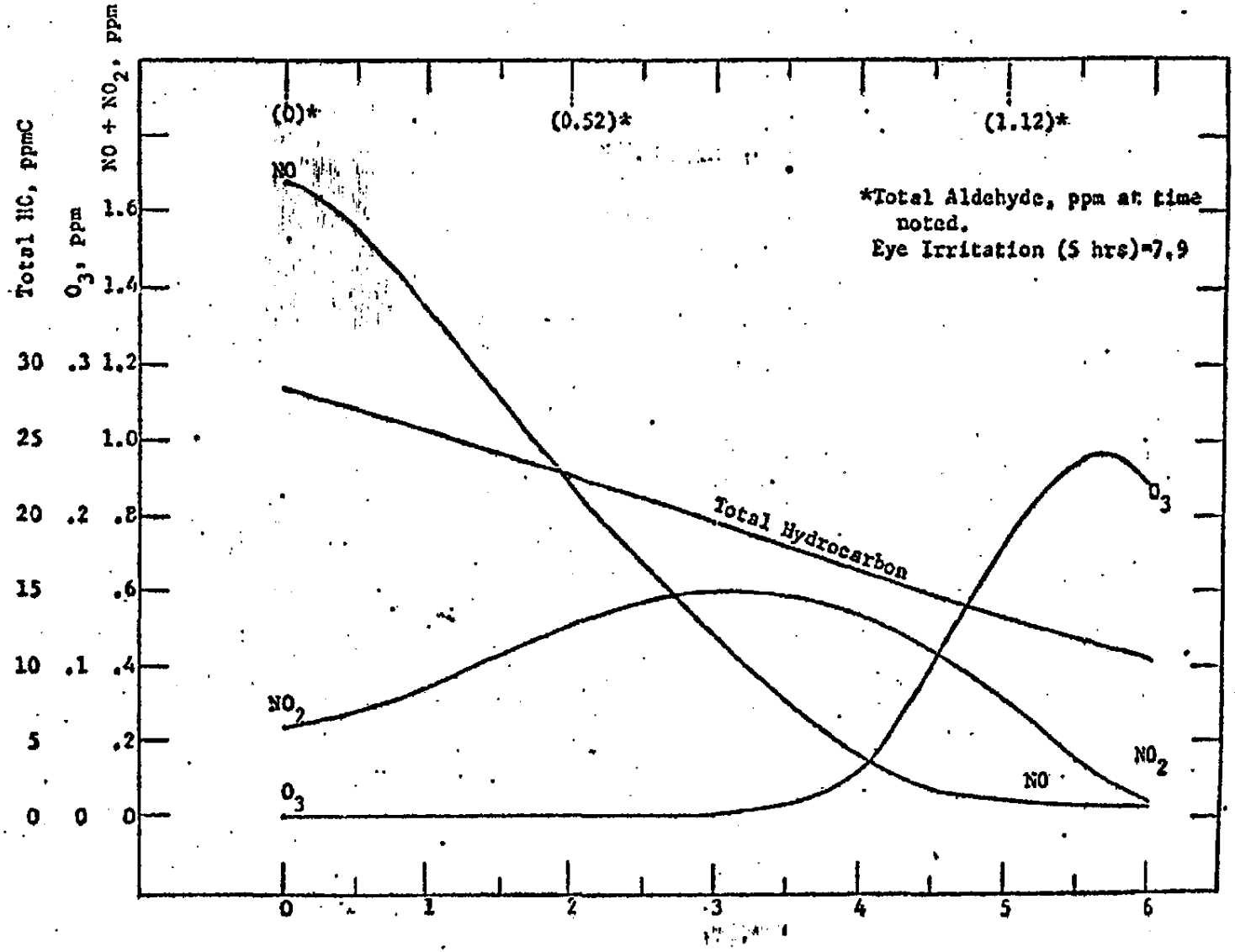
Run No. 3 Diethylamine (approximate loading 4 ppm (V/v)



Run No. 2 VCM 1.1 ppm (v/v)

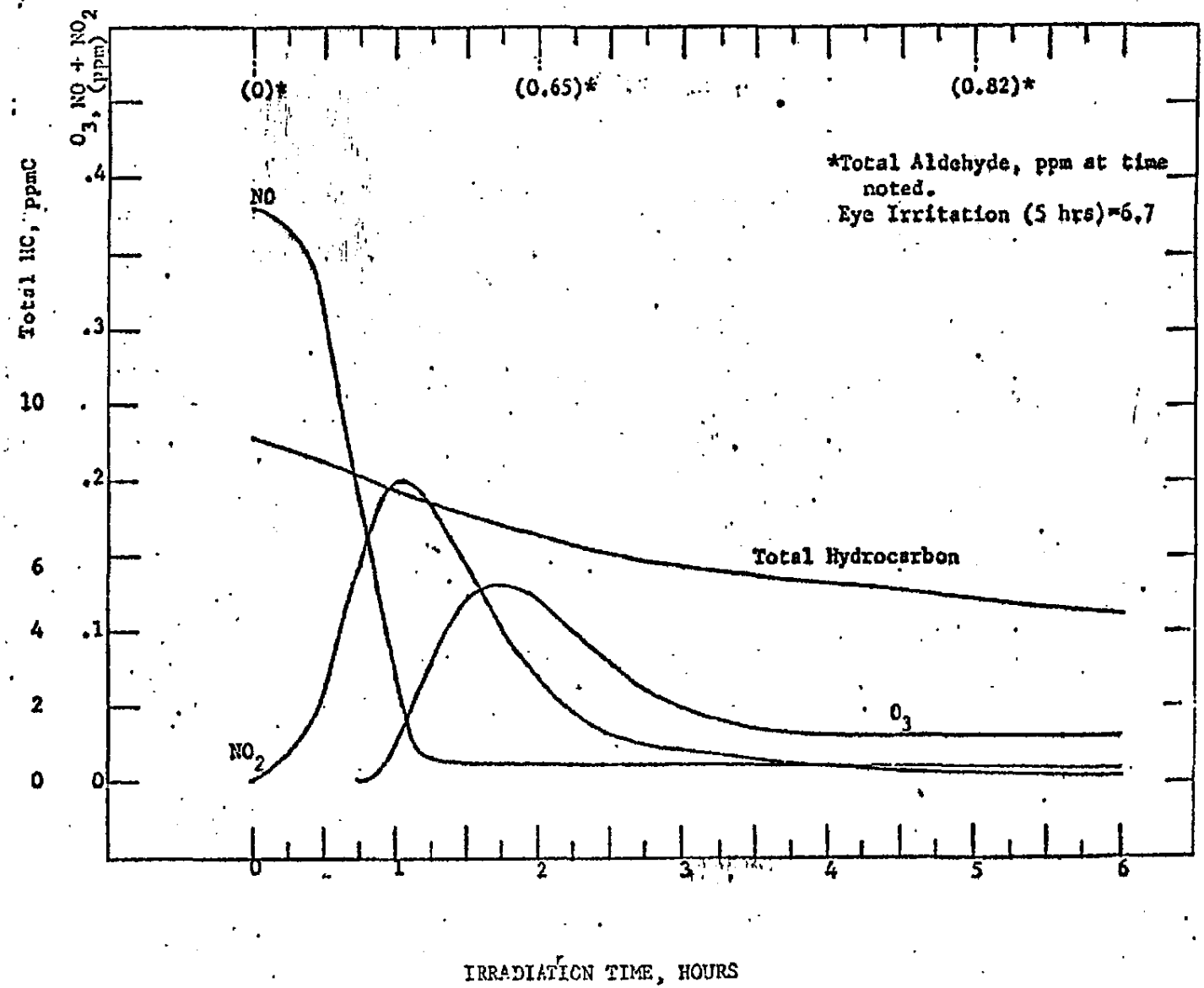


Run No. 4 Toluene 3.9 ppm (V/v)



IRRADIATION TIME, HOURS

Run No. 5 Toluene 1.8 ppm (V/v)



IRRADIATION TIME, HOURS

Run No. 6 VCM 1.1 ppm (V/v)