Chemical Consequences of Air Quality Standards and of Control Implementation Programs: Roles of Hydrocarbons, Oxides of Nitrogen, Oxides of Sulfur and Aged Smog in the Production of Photochemical Oxidant and Aerosol

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ABSTRACT

The environmental chamber facility established at the Statewide Air Pollution Research Center, University of California, Riverside, under a joint Air Resources Board--University of California (Project Clean Air) program has been employed in investigations:

To determine the relative rates of reaction of the hydroxyl (OH) radical with a large number of organic compounds including those representative of (a) combustion products, (b) solvent emissions, (c) natural emissions and (d) potential aerosol precursors.

To develop, in conjunction with the above experimental work, a new reactivity scale and classification of organic compounds based on their rates of reaction with the OH radical.

To provide data concerning the photochemically-promoted conversion of sulfur dioxide (SO_2) to sulfate aerosol.

Previously developed procedures for characterizing polluted ambient air parcels utilizing a diffusion model and available meteorological and air monitoring data have been further refined:

To determine the rates of dilution and diffusion for various pollutants in characteristic air parcels and to utilize this information to design chamber experiments simulating transport, new pollutant emissions and dilution phenomenon.

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EXECUTIVE SUMMARY

Despite two decades of intensive research concerning the photochemistry
of polluted atmospheres, and the concerted attention during the past ten
years of local, state and federal air pollution control agencies to the
problem of reducing photochemical oxidant in urban areas, substantial
uncertainty still remains as to the most cost-effective and societally
acceptable means of solving this major environmental problem. In order to
provide an experimental data base relating to the major unresolved issues of
photochemical smog formation, the SAPRC environmental chamber facility was
designed and constructed (1970-73) with support from the California Air
Resources Board. The facility was initially (1973-75) utilized in a study of
oxidant formation from hydrocarbon-oxides of nitrogen (HC-NO$_x$) mixtures irra-
diated under conditions simulating those found in the California South Coast
Air Basin. Using a twelve-hydrocarbon mixture as a surrogate for the ambient
pollutant mix, HC and NO$_x$ concentrations ranging from those found in present-
day polluted atmospheres down to those to be expected from the implementation
of emission control strategies aimed at meeting the State and Federal ambient
air quality standards were investigated. In conjunction with this program
evaluations of the accuracy or specificity of the analytical methods for two
major pollutants (ozone and oxides of nitrogen) were also carried out.

In response to some of the most recent developments in atmospheric
chemistry and pollution control, the original precursor-secondary pollutant
study has been extended or applied in the current year to

- determination of OH radical rate constants for a large number of
  organic compounds under simulated atmospheric conditions in an
  environmental chamber
- development of a new reactivity scale based on the reaction of
  organics with the OH radical
- a chamber study of the loss of SO$_2$ and formation of sulfate aerosol
  under simulated atmospheric conditions, and
- development of methods to more accurately simulate in smog chamber
  experiments the ambient conditions of transport, input of new emissions,
  and dilution.

OH Radical Rate Constants. The use of relative rates of reactions of
hydrocarbons determined in the SAPRC all-glass environmental chamber under

simulated atmospheric conditions was shown two years ago to be a reliable method for determining the OH rate constants for these compounds. The validation of the chamber method for OH radical rate constant determinations was based on: (a) the good to excellent agreement between rate constants determined using this method and those determined by elementary methods with the individual hydrocarbons (b) kinetic computer models of photochemical smog formation which uniformly indicate the OH radical to be the major reactive intermediate involved in consumption of hydrocarbons (other than alkenes which also react appreciably with ozone) and (c) support of the model predictions by the direct and indirect observation of OH radical concentrations in both ambient air and experimental systems at about the expected levels of 10^6 radicals cm^{-3}.

Utilizing the chamber method we have now determined OH rate constants for 32 additional organic compounds falling into four classes of potential importance in the production of photochemical air pollution (see Table 1) (i.e., combustion source organics, solvent components, naturally occurring hydrocarbons and potential aerosol precursors). The relative rates of disappearance which were obtained from the chamber experiments were converted to absolute rate constants using either n-butane or isobutene as a reference compound having a well established OH rate constant.

Some advantages of the chamber method include the ability to determine rates for several compounds in each series of experiments, the low purity requirements for the compounds studied (as long as interferences do not occur in the gas chromatographic analyses) and the ability to study compounds not amenable to elementary methods.

Reactivity Scale Based on Reaction with The OH Radical. We have proposed a hydrocarbon reactivity scale based on the primary chemical act of hydroxyl radical (OH) attack on organic species. As discussed above, the OH radical is the key reactive intermediate in photochemical air pollution. Moreover, a reactivity scale based on the depletion of hydrocarbons by reactions with OH has utility in assessing hydrocarbon chemical behavior in polluted ambient air, since only those compounds which participate at "significant" rates in atmospheric reactions are of consequence in the chemical transformations in ambient air.

Table 1. Rate Constants for Reaction of OH with Organic Compounds
Obtained Using the Chamber Method

Compound	Rate Constant 10^{-9} (ℓ mole^{-1} sec^{-1})	Reference
Combustion Sources		
Ethene	5.2 ± 1.0	a
Propene	17.5 ± 3.5	a
	14.9 ± 2.2	b
cis-2-Butene	39.2 ± 8.0	a
	37.9 ± 5.6	b
	32.9 ± 6.6	c
1,3-Butadiene	46.4 ± 9.3	a
2,3-Dimethylbutane	3.1 ± 0.5	f
Isopentane	2.0 ± 0.4	a
2-Methylpentane	3.2 ± 0.6	a
3-Methylpentane	4.3 ± 0.9	a
n-Hexane	3.8 ± 0.8	a
m-Xylene	12.9 ± 2.6	a
n-Propylbenzene	3.7 ± 0.8	a
Isopropylbenzene	3.7 ± 0.8	a
Ethylbenzene	4.8 ± 1.0	a
o-Ethyltoluene	8.2 ± 1.6	a
m-Ethyltoluene	11.7 ± 2.3	a
p-Ethyltoluene	7.8 ± 1.6	a
Solvent Components		
Methyl ethyl ketone	2.0 ± 0.6	b
Methyl isobutyl ketone	9.0 ± 3.0	b
Diisobutyl ketone	15 ± 5	b
Isopropyl alcohol	4.3 ± 1.3	d
Diethyl ether	5.6 ± 1.1	d
Di-n-propyl ether	10.4 ± 2.1	d
Tetrahydrofuran	8.8 ± 1.8	e
n-Propyl acetate	2.6 ± 0.5	e
sec-Butyl acetate	3.4 ± 0.7	e
Naturally Occurring Hydrocarbons		
α-Pinene	34.8 ± 5.2	b
β-Pinene	40.6 ± 6.1	b
d-Limonene	90.0 ± 13.5	b
Potential Aerosol Precursors		
2,2,3-Trimethylbutane	2.3 ± 0.5	f
1-Heptene	22 ± 5	f
Cyclohexene	47 ± 9	f
1-Methylcyclohexene	58 ± 12	f

[a] Lloyd, Darnall, Winer and Pitts, J. Phys. Chem., 80, 789 (1976).
[b] Winer, Lloyd, Darnall and Pitts, J. Phys. Chem., 80, 1635 (1976).
[c] Darnall, Winer, Lloyd and Pitts, unpublished results, 1976.
[d] Lloyd, Darnall, Winer and Pitts, Chem. Phys. Lett., 42, 205 (1976)
[e] Winer, Lloyd, Darnall and Pitts, Chem. Phys. Lett., submitted (1977).
[f] Darnall, Winer, Lloyd and Pitts, Chem. Phys. Lett., 44, 415 (1976).

For purposes of comparison with other reactivity scales, we have proposed a five-class scale which is based on order of magnitude differences in reactivity toward OH relative to that of methane (=1). Table 2 shows the five classes, the OH rate constant range appropriate to each class and the reactivity assignment for more than 110 compounds for which OH rate constants have been determined.

A comparison of this reactivity classification with the one based on ozone formation that was recently adopted by the ARB (which is very similar to the one under consideration by the EPA) shows them to be quite consistent with a few minor exceptions.

Advantages of the proposed OH reactivity scale include (a) its ready extension to additional compounds once their rate of reaction with OH is known, (b) its divisibility into as many classes as is desirable for the purposes of devising control priorities for organic emissions, and (c) the greater weight (than given previously) to alkanes and aromatics which over long irradiation periods will react to a significant extent. Disadvantages include (a) its limited applicability to compounds which undergo significant photodissociation in the atmosphere or which react at an appreciable rate with other atmospheric species, e.g., alkenes reacting with ozone, and (b) the uncertainties resulting from the lack of information concerning the identity and fates of subsequent products.

A Chamber Study of Sulfate Aerosol Formation. In polluted atmospheres, one of the major sources of sulfate aerosol appears to be the conversion of sulfur dioxide in conjunction with the nitrogen oxide-promoted photooxidation of organic compounds. In the South Coast Air Basin the sulfate burden has been increasing at a rate of about 10% per year. Although this may worsen if increased use of high sulfur fuels occurs, there is also the possibility of a counteracting effect resulting from decreased hydrocarbon and NO_x emission and therefore decreased conversion rates. To provide a quantitative experimental data base for a number of such future scenarios, we have extended our basic precursor-secondary pollutant program to include a study of SO_2 loss and aerosol formation.

The initial phase of this program has been completed. The feasibility of using the SAPRC all-glass environmental chamber has been established by study of the decay of SO_2 in pure air under both irradiated and non-irradiated

Table 2.   Proposed Reactivity Classification of Organics (and Selected Inorganics) Based on Reaction with the Hydroxyl Radical

Class I $(\leq 4.8 \times 10^7)^a$	Class II $(4.8 \times 10^7 - 4.8 \times 10^8)^a$	Class III $(4.8 \times 10^8 - 4.8 \times 10^9)^a$	Class IV $(4.8 \times 10^9 - 4.8 \times 10^{10})^a$	Class V $(\geq 4.8 \times 10^{10})^a$
Trifluoromethane	Trichloromethane	Neopentane	Ethylbenzene	2-Methyl-2-butene
1,1,2-Trichloro-1,2,2-trifluoroethane	Dichloromethane	Methanol	n-Octane	3-Carene
Tetrafluoromethane	Carbon monoxide	Methylacetylene	Diethyl ether	1-Methylcyclohexene
1,2-Dichloro-1,1,2,2-tetrafluoroethane	Ammonia	2,2,3,3-Tetramethylbutane	p-Xylene	β-Phellandrene
Chlorotrifluoromethane	Acetylene	Cyclobutane	p-Ethyltoluene	Carvomenthene
Dichlorodifluoromethane	1,2-Dichloroethane	Benzene	o-Ethyltoluene	d-Limonene
Fluorotrichloromethane	1,2-Dibromoethane	Isobutane	o-Xylene	2,3-Dimethyl-2-butene
1-Chloro-1,1-difluoroethane	Ethane	Propane	Tetrahydrofuran	Dihydromyrcene
Tetrachloromethane	1,1-Dichloroethane	n-Butane	Methyl isobutyl ketone	Myrcene
Difluoromethane	Chloroethane	Ethanol	p-Cymene	cis-Ocimene
Methane		Methyl ethyl ketone	Di-n-propyl ether	
2-Chloro-1,1,1-trifluoroethane		Isopentane	m-Ethyltoluene	
2-Chloro-1,1,1,2-tetrafluoroethane		1-Propanol	Methoxybenzene	
1,1,1-Trichloroethane		2,2,4-Trimethylpentane	Methylamine	
Fluoromethane		2,2,3-Trimethylbutane	m-Xylene	
Dichlorofluoromethane		n-Propyl acetate	1,2,3-Trimethylbenzene	
2,2-Dichloro-1,1,1-trifluoroethane		Allene	Diisobutyl ketone	
1,1-Difluoroethane		2,3-Dimethylbutane	Propene	
Chlorofluoromethane		Hydrogen sulfide	3,3-Dimethyl-1-butene	
Bromomethane		2-Methylpentane	1-Pentene	
Chloromethane		sec-Butyl acetate	1-Hexene	
Chlorodifluoromethane		Toluene	1,2,4-Trimethylbenzene	
		Cyclopentane	Methyl mercaptan	
		n-Propylbenzene	o-Cresol	
		Isopropylbenzene	1-Butene	
		n-Hexane	1-Heptene	
		n-Pentane	1,3,5-Trimethylbenzene	
		p-Menthane	Isobutene	
		1-Butanol	cis-2-Butene	
		Cyclohexane	2-Methyl-1-butene	
		2-Propanol	α-Pinene	
		4-Methyl-2-pentanol	cis-2-Pentene	
		3-Methylpentane	β-Pinene	
		Ethene	trans-2-Butene	
			Cyclohexene	
			1,3-Butadiene	
			Isoprene	

[a] Range of values (in liter mole^{-1} sec^{-1}) for the rate constant for reaction of the OH radical with the listed compounds.

conditions at various relative humidity levels. Decay rates in the presence of ozone, ozone + propene and SAPRC surrogate have also been determined. These results are summarized in Table 3.

A brief study of aerosol formation was conducted during one of the SO_2-ozone-propene experiments. Particle size distributions monitored as a function of time indicated (1) a rapid growth of small particles following the addition of propene to a SO_2-ozone mixture and (2) the increase in larger-sized particles was accompanied by a decrease in the smaller-sized particles.

An experiment to investigate the behavior of a test aerosol (spray-dried potassium sulfate) in the all-glass chamber indicated (a) that to obtain at least semiquantitative data on aerosol yield, the system should be seeded and (b) that measurement of b_{scat} in chamber experiments will not give a reliable indication of visibility reduction potential because the chamber wall losses leave the aerosol severely depleted in the high light scattering region (0.2-1.0 μm).

Air Parcel Transport Simulation. To provide a basis for designing realistic chamber experiments simulating air parcel transport effects during a full day irradiation, we have developed procedures for determining the rates of dilution and diffusion for the various pollutants in an air parcel. Thus for a given trajectory which was determined by interpolation of ground level meteorological data, the ambient air quality was determined by a similar interpolation procedure using the air quality data. Based on the results for the CO concentration history, a diffusion model was generated to allow for the transport of pollutants in the vertical direction. Both dilution and fresh pollutant injection rates required to approximate air parcel histories were then determined.

Recently, the choice of dilution rates of approximately 10% per hour by workers operating the large outdoor smog chambers in North Carolina (and by workers in a number of previous chamber studies explicitly employing dilution) has been challenged by Shair[1,2] as being too low. Our initial data suggest that the situation is complex and that both groups of workers are correct to some extent. For example, based on NO_x, the peak dilution we have calculated is approximately 50%-- far above those considered by previous chamber workers. However, for an

Table 3. Rate of SO$_2$ Loss in All-Glass Chamber under a Variety of Conditions (using FC-12 as Inert Tracer for Determination of Dilution Rate)

AGC Run No.	RH Range (%)	Amount of Water (torr)	Temp. Range (°C)	Light Intensity	Estimated Net[a] SO$_2$ Loss Rate (% hr^{-1})
216	1–2.5	0.6–1.0	32.6–33.7	0%	0.4
217[b]	11–24.5	5.1–10.3	34.4–36.6	100%	3
218[c]	40–49	15.5–18.9	33.2–33.8	0%	0.4
218[d]	31–55.5	14.0–22.2	33.0–36.0	100%	5
219[e]	81.5–71.5	30.1–26.9	32.6–34.2	0%	5
220[f]	41–40	15.2–15.3	32.7–32.8	0%	30
220[g]	40–38.5	14.9–14.5	32.8–33.1	0%	0.2
221[h]	44–38.5	16.4–13.9	32.7–33.2	0%	1[i]
222[j]	46.3–32.5	15.9–12.7	34.3–30.5	0%	2
222[k]	32.5–26.0	13.2–12.0	33.8–36.6	100%	4

[a] Total rate of SO$_2$ disappearance minus dilution rate (as determined from monitoring of FC-12).
[b] Continuation of 216 at 100% light intensity; additional SO$_2$ injected; approx. 0.5 ppm ozone present in this experiment.
[c] Flash lamp in Teco 43 replaced; instrument zeroed and spanned using MSA filter and calculated SO$_2$ in chamber, respectively.
[d] Ozone increased to ~0.3 ppm in first 6 hours of irradiation and remained at about that value.
[e] Lamp bases in Teco 43 replaced; zeroed and spanned as in b.
[f] 1 ppm propene and 0.6 ppm ozone present; average rate for first 30 min of reaction.
[g] 0.40 ppm propene and 0.20 ppm ozone present; average rate after 1.75 hr of reaction.
[h] 0.57 ppm ozone added.
[i] Value for time after ozone was added.
[j] Surrogate (~1700 ppbC) and NO$_x$ (0.3 ppm calc.) present initially.
[k] Surrogate (~1100 ppbC) and NO$_x$ (~0.5 ppm) present at beginning of irradiation.

air parcel beginning at ground level, the average dilution rate over the entire trajectory, again based on NO_x, was 16%; and if one uses only that portion of the trajectory from 6:00 in the morning till 1:00 in the afternoon, the average dilution rate is 21%. The dilution rates based on hydrocarbon are considerably lower than the above values for NO_x. Thus, the results of this analysis for hydrocarbon appear to be more in line with the lower dilution values used in previous chamber studies.

The fact that dilution rates based on NO_x are considerably larger than those based on hydrocarbon is a crucial observation and results from the fact that the concentration of hydrocarbons is far in excess of the concentration of NO_x. Consequently, less volume need be removed from the chamber to achieve the mass fluxes that occur. Obviously, this situation presents a problem in determining an appropriate simulation in actual chamber experiments and work is continuing to determine what dilution volume is required to maintain an appropriate hydrocarbon-to-NO_x ratio, a possibly more realistic control parameter.

ACKNOWLEDGMENTS

ALL OZONE AND OXIDANT DATA REPORTED IN THIS
STUDY WERE OBTAINED WITH INSTRUMENTS CALIBRATED
BY THE UB ABSORPTION METHOD ADOPTED BY THE
CALIBORNIA AIR RESOURCES BOARD, JUNE 1975.

I. INTRODUCTION

Events taking place in the area of control of photochemical air pollution, particularly in California, at the time the work presented here was proposed demonstrated anew the critical importance of approaching the air pollution problem on the strength of a valid technical, medical and socio-economic data base. Developments which illustrated this included (1) the strong public and legislative reaction to the Air Resources Board (ARB) NO_x retrofit program for 1966-1970 light duty vehicles in the South Coast Air Basin (SCAB), (2) the occurrence of discrepancies as large as factors of four in estimates of reactive hydrocarbons emitted in the SCAB by control agencies using differing reactivity scales,[3] (3) the conversion of power plants in the SCAB from natural gas to fuel oil and the increasing use of high sulfur fuels, and (4) the proposals for relaxation of the implementation of all automobile emission standards as a trade off for improved fuel economy to help combat dependence on foreign oil.

In the face of these developments, some of which threaten to substantially slow the momentum of the early 1970's toward achieving significantly lower pollutant burdens, the following facts concerning air quality in the California South Coast Air Basin must be recognized:

- Pasadena exceeded the Federal air quality standard for oxidant of 0.08 ppm for 1 hour on 197 days in 1976.

- The state and Federal ambient air quality standards for nitrogen dioxide (NO_2) continue to be violated at many locations in the SCAB as widespread as Long Beach, Pasadena and Pomona.

- Atmospheric particulate nitrate which, according to a recent preliminary EPA study,[4] may be associated with adverse health effects at levels estimated to be less than 10 micrograms per cubic meter, has been found at very high levels (about 70 micrograms per cubic meter, 24-hr average at one location) in the eastern portion of the Basin during the summer of 1975.

- Similarly, atmospheric particulate sulfate, which has been shown[5] to be associated with adverse health effects at levels of 8-10 micrograms per cubic meter (24-hr average) has been observed at

levels as high as 20.4 micrograms per cubic meter (24-hr average)
in West Covina.

In view of these developments and the apparent narrowing of control
strategy options, the SAPRC environmental chamber laboratory has conducted
a program designed to obtain quantitative data on chemical and physical
transformations in polluted urban atmospheres of direct applicability to
air pollution control strategies. In the current year research efforts
were made in the following areas: (a) determination of OH radical rate
constants under simulated atmospheric conditions in an environmental
chamber for a large number of organic compounds, including those from
combustion and other anthropogenic sources, as well as from natural sources,
(b) development of a new reactivity scale based on the reaction of organics
with the OH radical (c) a chamber study of the loss of SO_2 and formation
of sulfate aerosol under simulated atmospheric conditions, and (d) develop-
ment of methods to more accurately simulate in smog chamber experiments
the ambient conditions of transport, input of new emissions, and dilution.

II. FACILITIES AND METHODS

A. Chamber Facility and Analytical Methods

The experiments in this study were carried out in a 6400-liter
(226 ft^3), all-glass (Pyrex) chamber [6,7] which has a surface-to-volume
ratio of 3.4 m^{-1} (1.04^{-1}). The dimensions of the glass chamber are 8' x
8' x 4' (i.e., a flat box). Photolyzing radiation is provided by two
externally mounted, diametrically opposed banks of forty Sylvania 40-W
BL (black light) lamps, which are backed by arrays of Alzak-coated
reflectors. The supporting analytical facilities employed in the glass
chamber studies are shown schematically in Figure 1 and are described
in detail below. The on-line computer data acquisition system which was
installed in November 1974 and became fully operational in April, 1975,
has been used throughout this program.

The current physical and chemical measurement methods and the range,
precision, and accuracy of measurement of each of these parameters are
given in Table 4. The details of the analytical and data processing pro-
cedures are described below for each species or variable monitored. The
data obtained are computer processed and presented in tabular form for
each run and have not been corrected for losses due to sampling from
the chamber.

OZONE (O$_3$) was monitored by ultraviolet absorption analyzers (Dasibi-
1003 or AH-1003). Until January 1976, these instruments were calibrated
against 2% neutral buffered potassium iodide.[8] Since it has been demon-
strated[9,10] that at ~50% RH this calibration procedure yields ozone
values which are too high by a factor of ~1.25, all ozone data obtained
prior to January 1976 have been corrected by a factor of 0.8. In January
1976 the instruments were respanned using UV absorption method adopted by
the ARB in June, 1973.

NITROGEN OXIDES (NO, NO$_2$, and NO$_x$) were monitored by chemiluminescent
detection (TECO 14B). The NO$_2$ and NO$_x$ modes of this and similar chemi-
luminescent NO-NO$_x$ analyzers have been shown to respond quantitatively to
other nitrogen-containing compounds, such as peroxyacetyl nitrate (PAN)
and organic nitrates and nitrites.[11,12] All NO$_2$ and NO$_x$ data reported

3
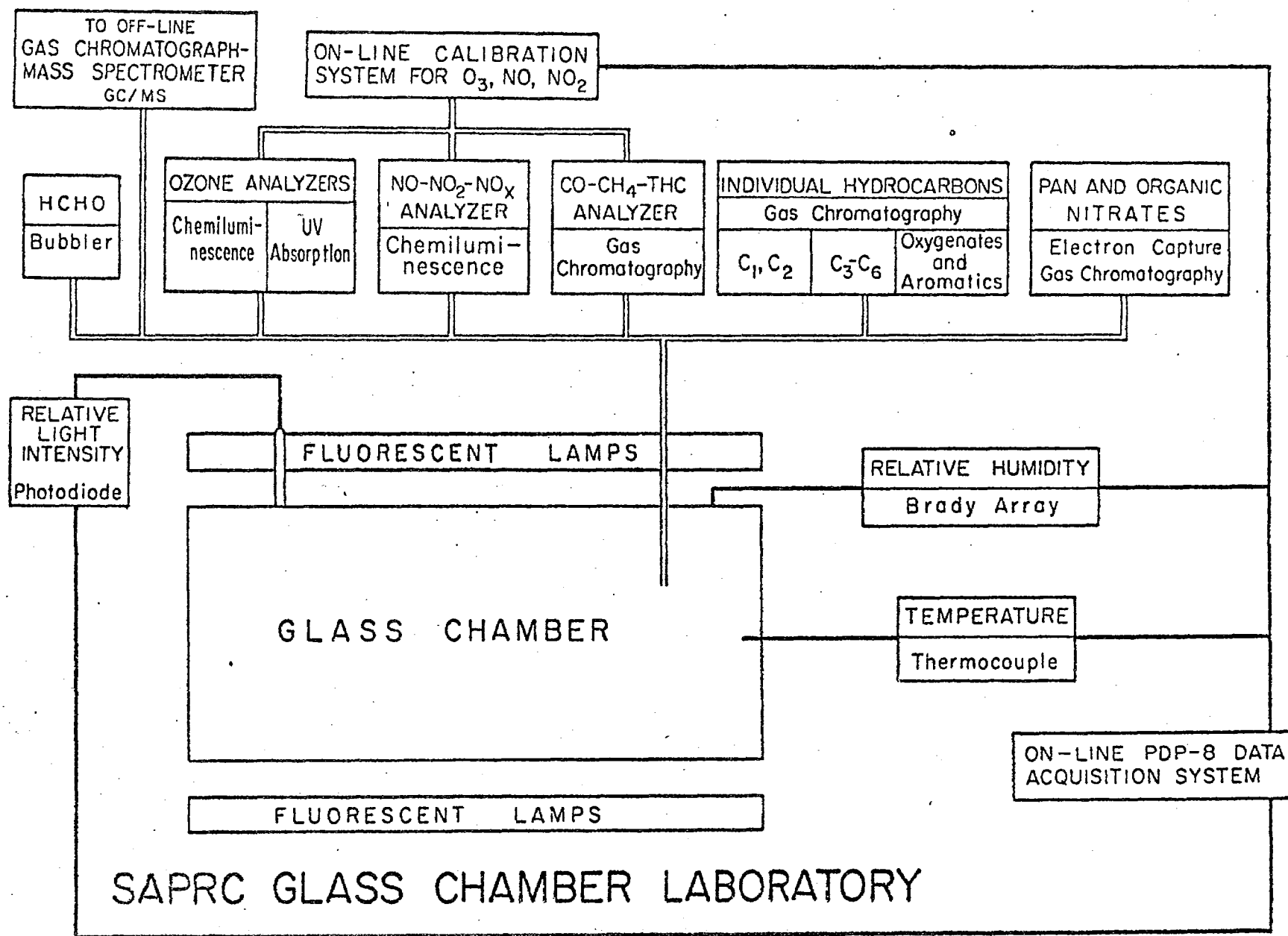
Figure 1.   Schematic Drawing of Glass Chamber Facility.

Table 4. Chemical and Physical Parameters Measured in Glass Chamber Studies

Parameter	Range	Method	Sampling Rate	Precision	Accuracy
Ozone	0-20 ppm	UV Absorption Analyzer	570 ml/min	$\pm$ 0.005 ppm	$\pm$ 5%
NO	0-10 ppm	Chemiluminescent Analyzer	895 ml/min	$\pm$ 2% F.S.	$\pm$ 5%
NO_2	0-10 ppm			By difference	By difference
NO_x	0-10 ppm			$\pm$ 2% F.S.	$\pm$ 5%
SO_2	0-5 ppm	Pulsed Fluorescence	1000 ml/min	$\pm$ 0.005 ppb	$\pm$ 5%
PAN	>1 ppb	GC		$\pm$ 0.5 ppb	$\pm$ 10%
Formaldehyde	>10 ppb[a]	Chromotropic Acid	1 ℓ/min (30 min samples)	$\pm$ 5%	$\pm$ 10%
Individual HCs	0.5-1 ppb	GC		$\pm$ 15%	Limited by calibration standard
	1-2 ppb	GC		$\pm$ 10%	(typically $\pm$ 5%) and/or by
	>2 ppb	GC		$\pm$ 2%	sampling techniques
CO	0-10 ppm	GC	100 ml/min	$\pm$ 2% F.S.	$\pm$ 10%
Temperature	$15°$ to $40°C$	Thermometer		$\pm$ $0.02°C$	$\pm$ $0.5°C$
		Thermocouple		$\pm$ $0.1°F$	$\pm$ $2°F$
Light Intensity	0-1 Solar Constant	NO_2 Actinometry		$\pm$ 5%	b
	Relative	Photodiode			
Relative Humidity	0-100%	Brady Array		$\pm$ 1% RH	$\pm$ 5%

[a]Determined by practical values of sampling time and flow rate   [b]See discussion on page 9.

here have been corrected by subtraction of measured or interpolated PAN concentrations.

SULFUR DIOXIDE (SO_2) was monitored by the pulsed fluorescence method (Teco 43). Approximate calibrations were obtained using chamber samples. A more precise calibration was carried out using a Monitor Labs model 8500 permeation type calibrator.

CARBON MONOXIDE (CO) was monitored by gas chromatography (Beckman-6800). The instrument was calibrated daily with a standard gas sample.

PEROXYACETYL NITRATE (PAN) was monitored by gas chromatography with electron capture detection (GC-ECD).[13,14] Samples were taken in a 100-ml precision bore syringe and transferred to the GC sampling system as quickly as possible. Peak heights were read from the strip chart and converted to concentration units using a calibration function which was determined periodically.

FORMALDEHYDE (HCHO) was monitored using the chromotropic acid method.[15] Air from the chamber was drawn through a bubbler at the rate of 1 ℓ min^{-1} and the total volume per sample was determined using a timer-controlled shutoff system. Generally, a 30-min. sample was taken. The concentration was recorded at the mid point of this time interval, except for the initial value, which was taken in the 30 minutes prior to lights on, and the final sample, which was taken in the 30 minutes prior to lights off. Absorbances were read on a Bausch and Lomb Spectronic 20, and calculations of the HCHO concentration from the absorbance and volume of air samples (HCHO vol) were made from the following equation:

$$HCHO \ (ppm) = \frac{HCHO \ (\mu g) \ X \ 2.037}{HCHO \ (vol)}$$

where HCHO (μg) is taken from the least squares fit of the experimentally determined calibration function of HCHO (μg) vs. absorbance.

The SAMPLE TEMPERATURE was read from either a Doric Thermocouple indicator (°F), using a thermocouple suspended in the chamber (TS2), or from a 19-35°C (0.01 degree/division) thermometer hung free inside the chamber close to the end window, but not in the direct light path (TS1).

RELATIVE HUMIDITY (RH) was measured using a Brady array (Thunder Scientific). The response in volts (V) was converted to percent RH, using

the calibration function supplied by the manufacturer.

HYDROCARBONS (HC) were monitored by gas chromatography with flame ionization detection (GC-FID), using the columns and methods developed by Stephens and Burleson.[16,17] Methane and C_2 HC's were analyzed using a 5' Poropak N Column, C_3-C_6 HC's using a 36' 2,4-dimethyl sulfolane column, and aromatics and oxygenates using a special three-part column. Oxygenates were also monitored using a 10' Carbowax 600 column. Each GC was calibrated frequently using specially prepared samples.[16] Computer processing of the data includes calculation of the concentration in ppbC for each data point.

B.   Experimental Procedures

General. Following each experiment in this program, the glass chamber was flushed with dry air provided by an air purification system[18] (see Figure 2) for about 2 hours at a flow of ~12 cfm. The chamber was then flushed with humidified pure air for about one hour just prior to the start of a run to achieve the desired initial RH. The temperature of the chamber prior to turning on the lamps was adjusted to the operating temperature anticipated during the irradiation by means of infrared lamps. During all flushing procedures, the two sonic pumps were in operation to provide maximum release of materials from the chamber walls.

The matrix air used during the flushing procedure and for the final fill for the experiment generally contained less than a total 60 ppbC of all hydrocarbons except methane, which was typically at a concentration between 550-850 ppb.[18] After completion of filling, analysis of the matrix air prior to injections showed somewhat higher hydrocarbon values due to off-gassing from the chamber walls, but generally these values were less than 200 ppbC nonmethane hydrocarbon.

Following flushing, starting materials were injected by using 100-ml precision bore syringes or micropipettes, and rapid mixing was obtained by brief (~5 minutes) use of the sonic pumps. During the run, the sample temperature was controlled at 32 ± 2°C by means of a variable air flow past the chamber walls.

Light intensity (k_1) was periodically determined, using the method of Holmes et al.,[19] which employs the initial rate of NO_2 photolysis in
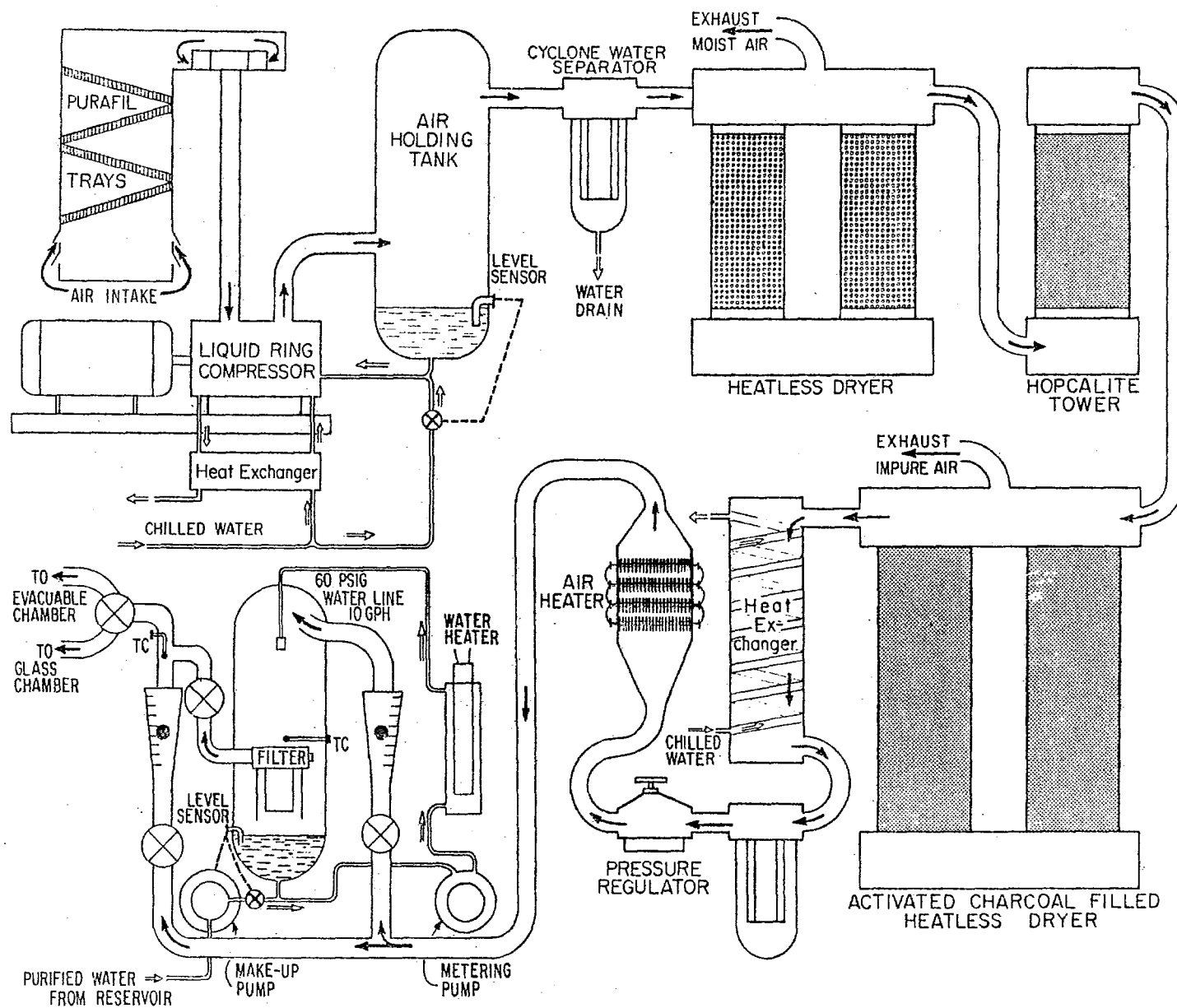
Figure 2. Air Purification System.

N_2 as a measure of absolute photon flux in the glass chamber in the actinic region (300-450 nm). However, some O_2 (of order tens of ppm or higher) will be present in the chamber which cannot be evacuated, but instead must be flushed repeatedly with N_2. Oxygen present in concentrations greater than approximately 10 ppm will lead to somewhat low values for k_1 as they were calculated in this study relative to the true k_1 which would be observed for the complete absence of O_2. Based on the purity of the nitrogen used (with respect to oxygen content) and a calculated efficiency for repetitive flushing of the chamber, it is estimated that the observed k_1 could be as much as 25% low with respect to the true k_1.

At full light intensity a k_1 of 0.41 min^{-1} was obtained and at 70% of maximum intensity, 0.26 min^{-1}.

Half-lives for ozone decay, measured at various times in this program under standard conditions of temperature, relative humidity, and light intensity, were $\geq$ 25 hours in the dark and 12 to 15 hours with irradiation. These half-lives are significantly longer than those reported for other chambers with comparable dimensions, surface to volume ratios, and light intensities and result in correspondingly smaller perturbations on ozone rates of formation and maximum ozone concentrations in the glass chamber experiments.

OH Rate Determinations. A variety of special surrogate mixtures were used in which the liquid components of the original surrogate (2-methyl-2-butene, 2,3-dimethylbutane, toluene and m-xylene) were replaced with the desired quantities of the new compounds to be studied. Isobutene was also added in some cases for use as a reference compound. A gaseous surrogate mixture containing no n-butane was used in the determination of rate of disappearance of methyl ethyl ketone. Hydrocarbons were injected into the chamber from previously prepared mixtures: the liquid hydrocarbons were prepared as a gaseous mixture in a nitrogen-filled 20-ℓ Pyrex bottle or as a liquid mixture, and the gaseous hydrocarbons were contained in an LPO bottle pressurized with nitrogen.

Experiments were carried out at either 70% or 100% of the maximum possible light intensity. Corrections for losses due to sampling were made based on the measured sampling rates of all instruments.

Sulfur Dioxide Decay Experiments. Temperature control for the

experiments carried out without irradiation was accomplished by incremental adjustments of six infrared lamps positioned on three sides of the chamber. During the day the temperature was generally maintained at 33 ± 1°C and at 33 ± 2°C overnight. For experiments with irradiation, the temperature was maintained by adjustment of the rate of flow of cooled air between the lamp banks and the chamber walls. The amount of cooling of the air was also varied to provide slight temperature adjustment. However, for experiments carried out at the full irradiation intensity, the lowest chamber temperature which can be maintained with maximum cooling and air flow is about 33°C. At these temperatures the maximum relative humidity which can be employed without condensation in the sample lines and/or instruments (which are at room temperature) is about 50% RH.

To accurately determine very low SO_2 rates during chamber experiments, a precise knowledge of the dilution (due to sampling and chamber leaks) rate is necessary. In an attempt to obtain this information, difluoro-dichloromethane (FC-12), a chemically inert compound, was added and its disappearance was monitored accurately by gas chromatography (gc). This method is limited, however, by the discovery that isobutane has the same gc retention time under the conditions used as does FC-12. Since isobutane is one of the major ambient hydrocarbons, on days of moderate air pollution the loss of FC-12 could be counteracted by diffusion of ambient isobutane into the chamber. Thus, the observed dilution rates may be low due to interference by isobutane.

III. DEVELOPMENT OF A REACTIVITY SCALE AND CLASSIFICATION FOR ORGANICS
BASED ON THEIR RATES OF REACTION WITH THE HYDROXYL RADICAL

A. Relative Rates of Reaction of Organic Compounds with the Hydroxyl
Radical

The use of the relative rates of reaction of hydrocarbons determined
under simulated atmospheric conditions using the SAPRC all-glass environ-
mental chamber has been previously validated as a method of determining
rate constants for reaction of hydrocarbons with the hydroxyl radical
(OH).[20,21] We have now extended the application of this chamber method
to the determination of OH rate constants for more than 30 additional
compounds.[22-26] The assumption that reaction with the OH radical is by
far the dominant reaction pathway for consumption of hydrocarbons during
the first 2-3 hours of irradiation in these experiments (conducted at 1 atm
pressure in air) has been comfirmed by the good agreement observed between
OH rate constants measured by the chamber method and those determined in
elementary rate studies of the individual hydrocarbon. This agreement
between relative and absolute rate determinations is illustrated in
Figure 3. The extent to which this assumption is valid is also supported
by the results of computer modeling calculations[27] (shown in Figure 4)
for an HC-NO$_x$ system of total hydrocarbon concentration identical to that
used in one of these studies.[22] In the computer simulation, a propene
and n-butane mixture was used as a surrogate for the complex hydrocarbon
mixture employed in the chamber experiment, and the rate of attack on
propene by OH, O_3, $O(^3P)$, and HO_2 was calculated. The relative and total
concentrations of propene and n-butane were chosen such that the overall
hydrocarbon reactivity towards the OH radical would equal that predicted
for the complex mixture. It is clear from Figure 4 that although OH is
the major attacking species in these experiments, the O_3 contribution
to the disappearance rates of the alkenes increases with the time of
irradiation. In contrast, the rates of reaction of O_3 with alkanes and
aromatics are many orders of magnitude slower,[28-32] and no correction for
their reaction with ozone was necessary. During the initial hours of
irradiation other species such as NO_3[33] and HO_2[34] may contribute slightly
to hydrocarbon disappearance rates, especially for alkenes, but since

The chart plots RELATIVE RATES OF HYDROCARBON DISAPPEARANCE IN CHAMBER EXPERIMENTS (y-axis, 0 to 25) versus PUBLISHED RATE CONSTANTS (ℓ mol^{-1} sec^{-1} $\times$ 10^{-9}) (x-axis, 1 to 40).

1. n-Butane
2. Isopentane
3. Toluene
4. 2-Methylpentane
5. n-Hexane
6. Ethene
7. 3-Methylpentane
8. p-Xylene
9. o-Xylene
10. m-Xylene
11. m-Xylene

12. 1,2,3-Trimethylbenzene
13. Propene
14. 1,2,4-Trimethylbenzene
15. 1,3,5-Trimethylbenzene
16. cis-2-Butene

Figure 3. Comparison of Relative Rates of Hydrocarbon Disappearance Determined by the Chamber Method with Selected Published Rate Constants for Reaction of Those Hydrocarbons with OH Radicals.
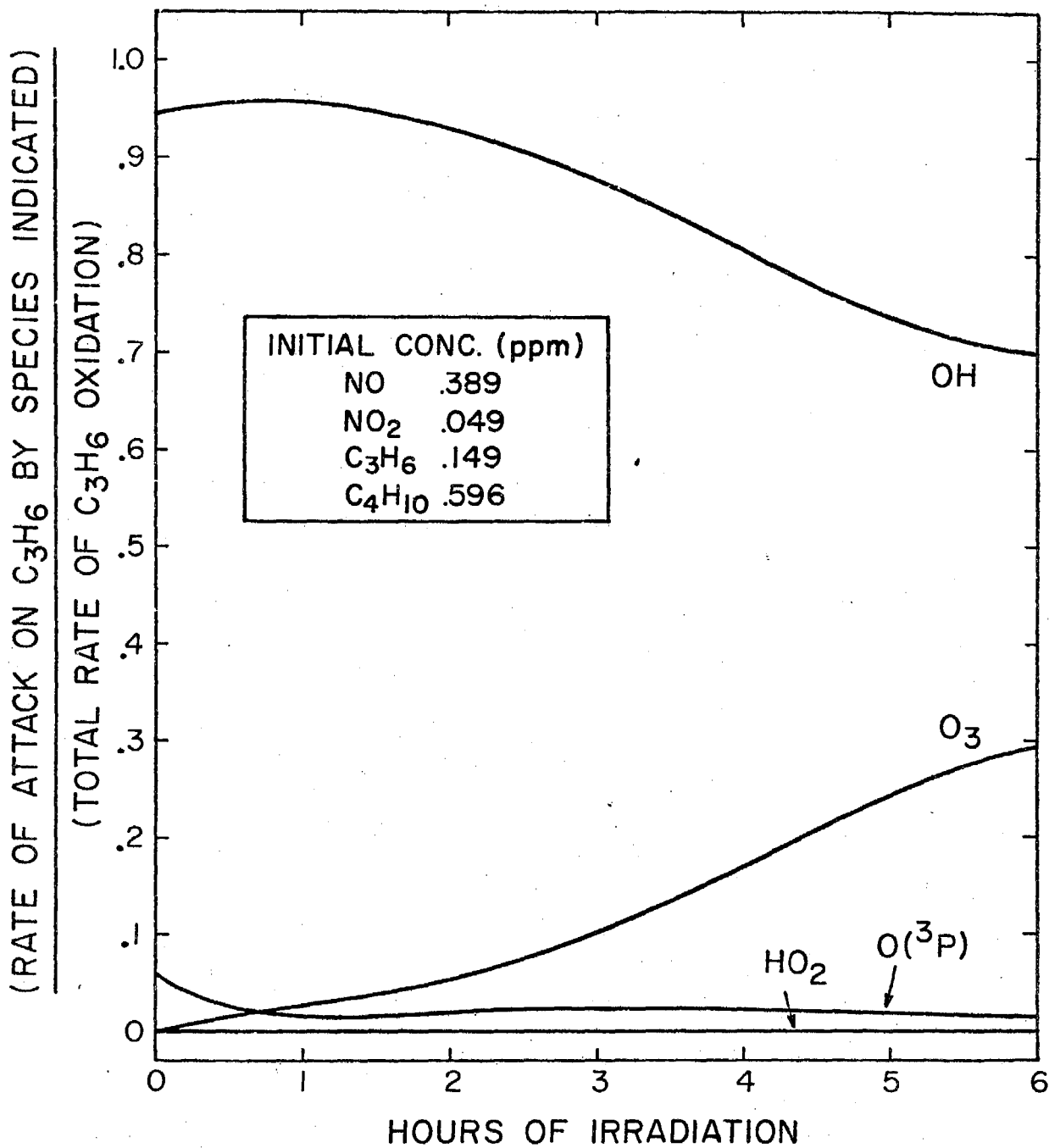
Figure 4. Predicted Relative Importance of Several Reactive Inter-
mediates during Photooxidation of a Propene-n-Butane
Mixture under Simulated Atmospheric Conditions.

their concentrations, and in some cases rate constants, are not known, correction is not possible.

Results. As had been proposed, four general types of compounds, based on their source or potential atmospheric significance, were studied: combustion source hydrocarbons, solvent components, naturally occurring hydrocarbons, and several compounds which are believed to be potential organic aerosol precursors (see Table 5). The relative rates of disappearance of some selected compounds are shown in Figures 5-7. Absolute rate constants were derived from the relative rates of disappearance using the literature values for the absolute OH rate constants for either n-butane[35-41] or isobutene[42] (1.8 x 10^9 and 3.05 x 10^{10} ℓ mole^{-1} sec^{-1}, respectively). The compounds by hydrocarbon class and the rate constants thus derived are given in Table 6.

Detailed discussions of the significance, both fundamental and applied, of these rate constant determinations as well as calculations of atmospheric half-lives and analyses of the role of these compounds in atmospheric chemistry have already been reported in the literature[22-26] and reprints are included in Appendix A.

B. Development of a Reactivity Scale and Reactivity Classification Based on the Reaction of Organics with OH

The important role of OH in photochemical smog formation is now well established[43-50] on the basis of both experimental and computer modeling studies, and OH has been directly observed[51-53] in both the laboratory and in ambient air. This awareness has led to a dramatic increase during the past several years in the number of compounds for which OH rate constants have been measured. In addition to the extensive elementary rate determinations carried out in this laboratory[35,54-62] and elsewhere, we have, as described above and previously,[21] measured rate constants for 40 compounds using the chamber method. This technique has also been employed recently by Niki and coworkers.[63]

From the successful correlation of OH rate constants with the rates of hydrocarbon disappearance observed in chamber simulations at the SAPRC[20,22-26,62] and Ford Motor Co.[63] laboratories, we conclude that, to a good approximation, this correlation can be extrapolated to the atmosphere

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Table 5. Rate Constants for Reaction of OH with Organic Compounds
Obtained Using the Chamber Method

Compound	Rate Constant 10^{-9} (ℓ mole^{-1} sec^{-1})	Reference
Combustion Sources		
Ethene	5.2 ± 1.0	a
Propene	17.5 ± 3.5	a
	14.9 ± 2.2	b
cis-2-Butene	39.2 ± 8.0	a
	37.9 ± 5.6	b
	32.9 ± 6.6	c
1,3-Butadiene	46.4 ± 9.3	a
2,3-Dimethylbutane	3.1 ± 0.5	f
Isopentane	2.0 ± 0.4	a
2-Methylpentane	3.2 ± 0.6	a
3-Methylpentane	4.3 ± 0.9	a
n-Hexane	3.8 ± 0.8	a
m-Xylene	12.9 ± 2.6	a
n-Propylbenzene	3.7 ± 0.8	a
Isopropylbenzene	3.7 ± 0.8	a
Ethylbenzene	4.8 ± 1.0	a
o-Ethyltoluene	8.2 ± 1.6	a
m-Ethyltoluene	11.7 ± 2.3	a
p-Ethyltoluene	7.8 ± 1.6	a
Solvent Components		
Methyl ethyl ketone	2.0 ± 0.6	b
Methyl isobutyl ketone	9.0 ± 3.0	b
Diisobutyl ketone	15 ± 5	b
Isopropyl alcohol	4.3 ± 1.3	d
Diethyl ether	5.6 ± 1.1	d
Di-n-propyl ether	10.4 ± 2.1	d
Tetrahydrofuran	8.8 ± 1.8	e
n-Propyl acetate	2.6 ± 0.5	e
sec-Butyl acetate	3.4 ± 0.7	e
Naturally Occurring Hydrocarbons		
α-Pinene	34.8 ± 5.2	b
β-Pinene	40.6 ± 6.1	b
d-Limonene	90.0 ± 13.5	b
Potential Aerosol Precursors		
2,2,3-Trimethylbutane	2.3 ± 0.5	f
1-Heptene	22 ± 5	f
Cyclohexene	47 ± 9	f
1-Methylcyclohexene	58 ± 12	f

[a]Lloyd, Darnall, Winer and Pitts, J. Phys. Chem., 80, 789 (1976).
[b]Winer, Lloyd, Darnall and Pitts, J. Phys. Chem., 80, 1635 (1976).
[c]Darnall, Winer, Lloyd and Pitts, unpublished results, 1976.
[d]Lloyd, Darnall, Winer and Pitts, Chem. Phys. Lett., 42, 205 (1976)
[e]Winer, Lloyd, Darnall and Pitts, Chem. Phys. Lett., submitted (1977).
[f]Darnall, Winer, Lloyd and Pitts, Chem. Phys. Lett., 44, 415 (1976).

Figure 5. Concentrations of Selected Organic Compounds during Irradiation of a HC-NO$_x$ mixture in Air at 305 $\pm$ 2 K (Propene and 1,3-Butadiene Concentrations Have Been Corrected for Reaction with Ozone).

16
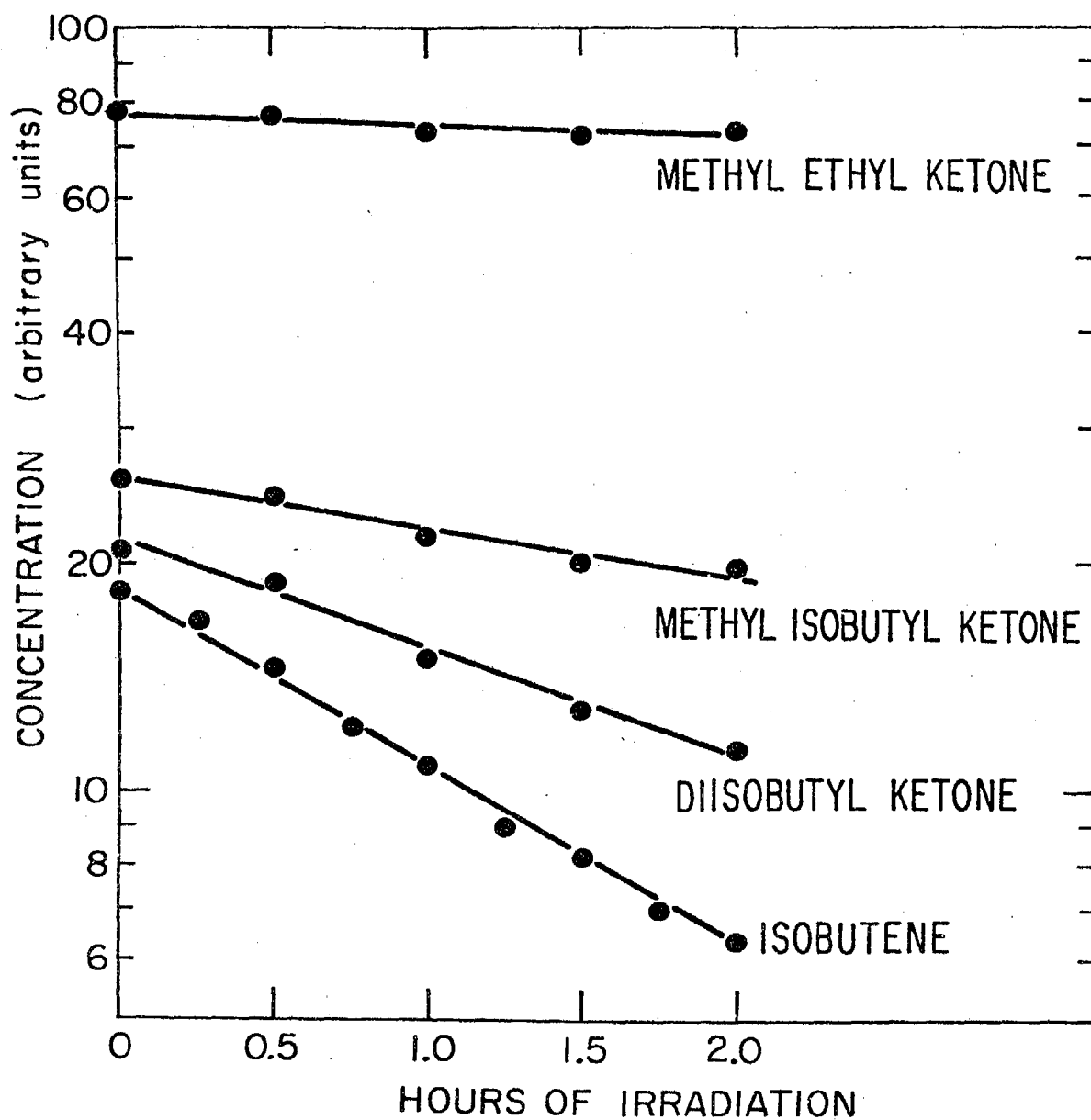
Figure 6. Concentrations of Ketones and Isobutene during Irradiation of a HC-NO$_x$ Mixture in Air at 305 $\pm$ 2 K.
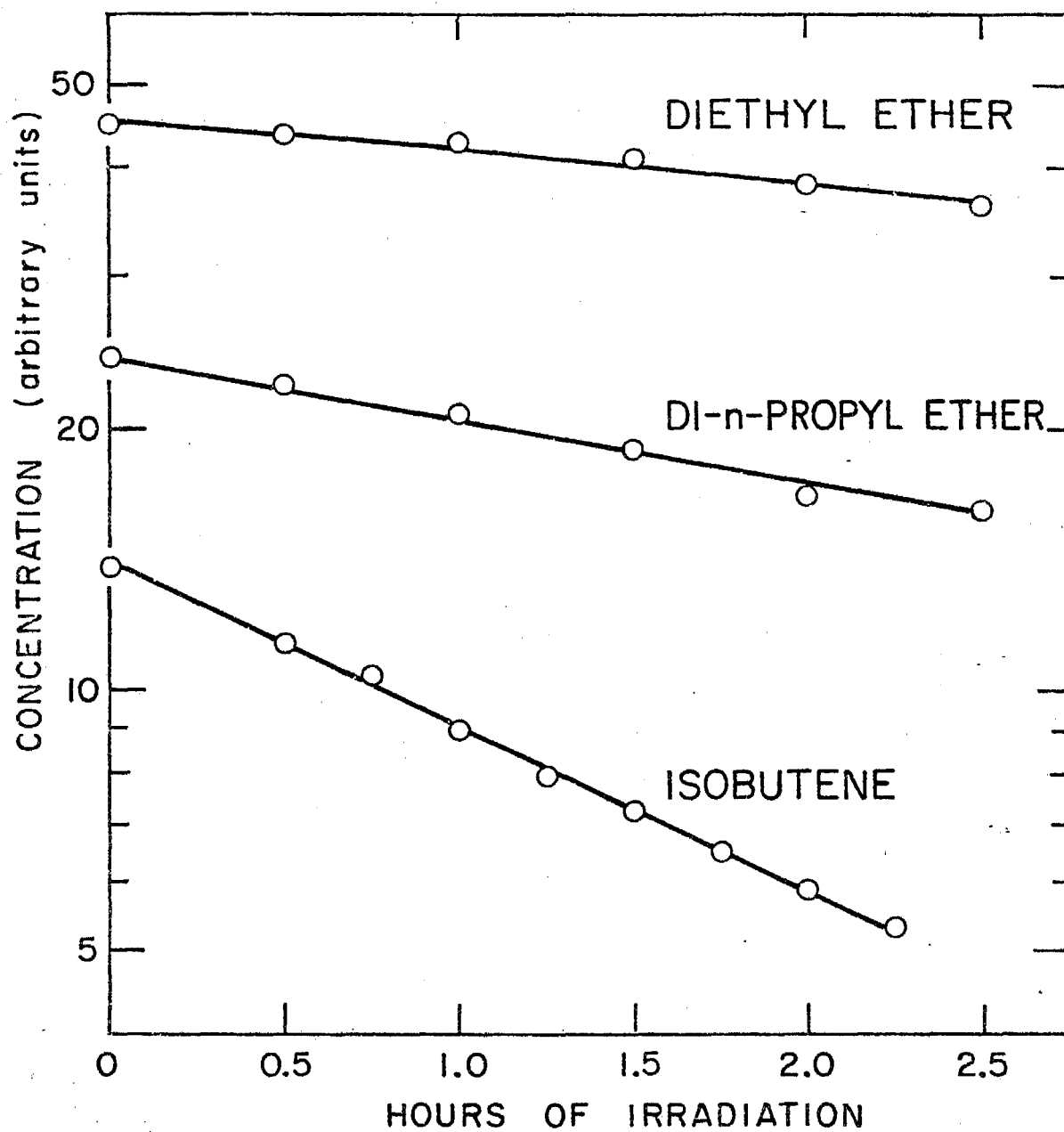
Figure 7. Concentrations of Ethers and Isobutene during Irradiation of a HC-NO$_x$ Mixture in Air at 305 $\pm$ 2 K.

Table 6.   Rate Constants for Reaction of OH with Organic Compounds
            Obtained Using the Chamber Method

Compound	Rate Constant 10^{-9} (ℓ mole^{-1} sec^{-1})	Reference
Alkenes		
Ethene	5.2 ± 1.0	a
Propene	17.5 ± 3.5	a
	14.9 ± 2.2	b
cis-2-Butene	39.2 ± 8.0	a
	37.9 ± 5.6	b
	32.9 ± 6.6	c
1,3-Butadiene	46.4 ± 9.3	a
1-Heptene	22 ± 5	d
Cyclohexene	47 ± 9	d
1-Methylcyclohexene	58 ± 12	d
α-Pinene	34.8 ± 5.2	b
β-Pinene	40.6 ± 6.1	b
d-Limonene	90.0 ± 13.5	b
Alkanes		
2,3-Dimethylbutane	3.1 ± 0.5	d
Isopentane	2.0 ± 0.4	a
2-Methylpentane	3.2 ± 0.6	a
3-Methylpentane	4.3 ± 0.9	a
n-Hexane	3.8 ± 0.8	a
2,2,3-Trimethylbutane	2.3 ± 0.5	d
Aromatic Hydrocarbons		
m-Hylene	12.9 ± 2.6	a
n-Propylbenzene	3.7 ± 0.8	a
Isopropylbenzene	3.7 ± 0.8	a
Ethylbenzene	4.8 ± 1.0	a
o-Ethyltoluene	8.2 ± 1.6	a
m-Ethyltoluene	11.7 ± 2.3	a
p-Ethyltoluene	7.8 ± 1.6	a
Oxygenated Compounds		
Methyl ethyl detone	2.0 ± 0.6	b
Methyl isobutyl ketone	9.0 ± 3.0	b
Diisobutyl ketone	15 ± 5	b
Isopropyl alcohol	4.3 ± 1.3	e
Diethyl ether	5.6 ± 1.1	e
Di-n-propyl ether	10.4 ± 2.1	e
Tetrahydrofuran	8.8 ± 1.8	f
n-Propyl acetate	2.6 ± 0.5	f
sec-Butyl acetate	3.4 ± 0.7	f

[a] Lloyd, Darnall, Winer and Pitts, J. Phys. Chem., 80, 789 (1976).
[b] Winer, Lloyd, Darnall and Pitts, J. Phys. Chem., 80, 1635 (1976).
[c] Darnall, Winer, Lloyd and Pitts, unpublished results, 1976.
[d] Lloyd, Darnall, Winer and Pitts, Chem. Phys. Lett., 42, 205 (1976).
[e] Winer, Lloyd, Darnall and Pitts, Chem. Phys. Lett., submitted (1977).
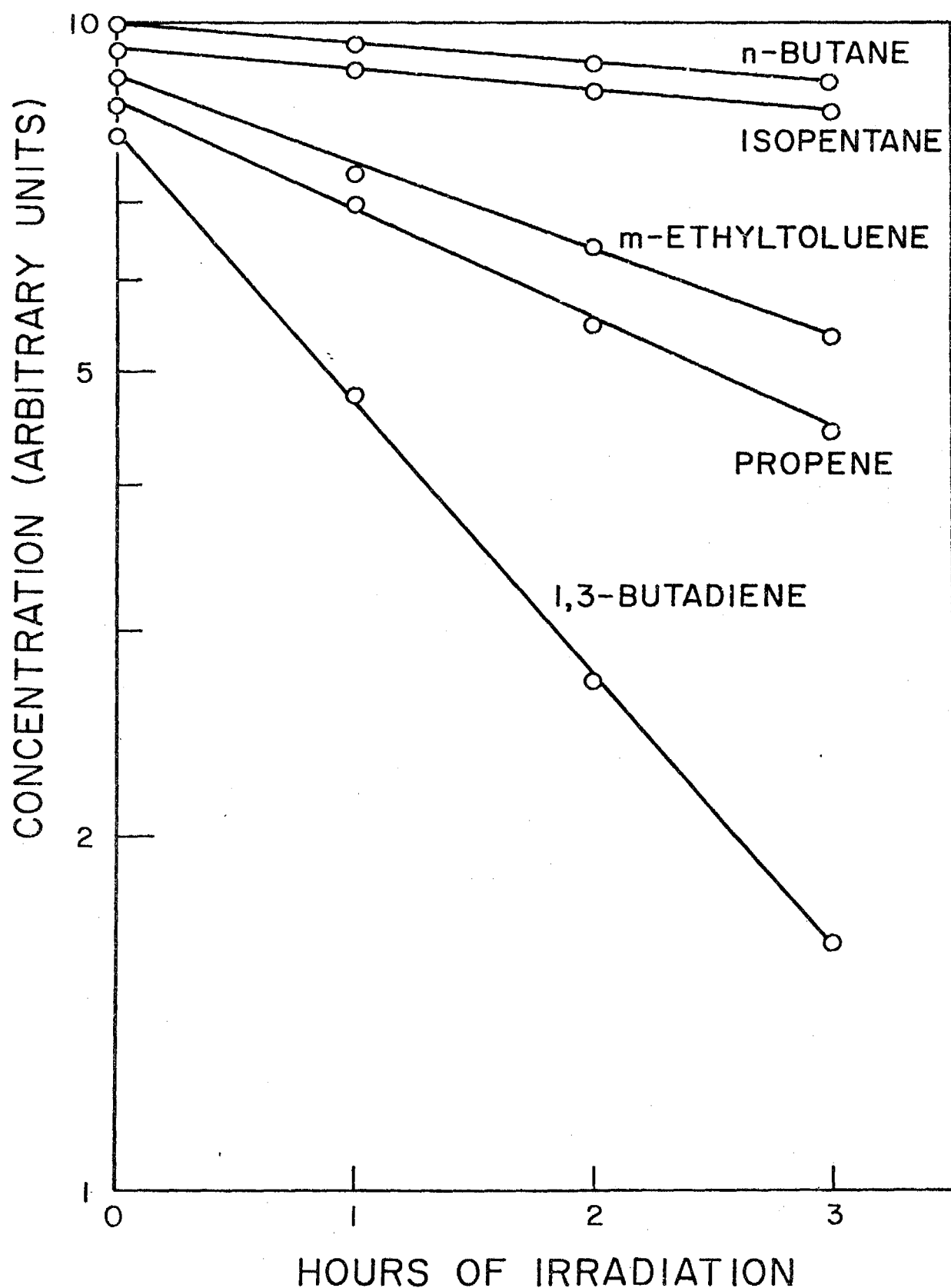[f] Darnall, Winer, Lloyd and Pitts, Chem. Phys. Lett., 44, 415 (1976).

(a) for alkenes in ambient air parcels during the early morning hours when ozone levels are generally quite low (≤ 0.05 ppm), and (b) for alkanes, aromatics, and most of the other classes of compounds discussed here at essentially all times and locations. The latter assumption, namely that an OH rate constant is a good "reactivity index" for alkanes, aromatics, halocarbons, etc. throughout an irradiation day (or multiple irradiation days) rests upon the fact that the rates of reaction of these classes of organics with species such as ozone, $O(^3P)$ atoms and the hydroperoxyl radical HO_2 are substantially slower than with OH.[28-30,64,65] For example, even at the highest ozone concentrations experienced in ambient atmospheres, O_3 will not contribute significantly to the consumption of alkanes and aromatics. This is in contrast to the case for alkenes which, although the rate constants for reaction of O_3 are not particularly large,[31,32,65] are depleted rapidly by reaction with ozone at the average concentrations commonly encountered in polluted ambient air (~0.1 to 0.2 ppm).

Proposed Reactivity Scale and Classification. In view of the above, and the very recent availability of a large number of OH rate constants, we have proposed[66,67] a hydrocarbon reactivity scale based on the primary chemical act of hydroxyl radical (OH) attack on organic species. We have done so on two bases. First, as discussed above, the OH radical is a key reactive intermediate in photochemical air pollution. Second, a reactivity scale based on the depletion of hydrocarbons by reactions with OH has utility in assessing hydrocarbon chemical behavior in polluted ambient air, since only those compounds which participate at "significant" rates in atmospheric reactions are of consequence in the chemical transformations in ambient air, including, of course, the production of photochemical oxidant. Thus, our working premise has been that the relative reactivity of organics towards OH is generally a useful and directly measurable index of their potential importance in the production of secondary pollutants. As we have previously pointed out,[68] our proposed reactivity classification would not be valid if specific reactivity criteria unrelated in varying degrees to oxidant formation (for example, aerosol formation and associated visibility effects, mutagenic activity, etc.) are of concern.

Although a reactivity scale based on OH rate constants can, in principle, be divided into a large number of classes (see below), it is

convenient, particularly for purposes of comparison with other scales, to use a five-class scale which is based on order of magnitude differences in reactivities of organics toward OH relative to methane (=1). This scale is shown in Table 7, which also gives the range of half-lives of compounds appearing in each class assuming depletion solely due to reaction with the OH radical at a concentration of 10^7 radicals cm^{-3}.

Table 7. Reactivity Scale for Organics Based on Rate of Consumption Due to Reaction with the Hydroxyl Radical

Class	Half-Life[a] (days)	Reactivity Relative to Methane (=1)
I	≥10	≤10
II	1 – 10	10 – 100
III	0.1 – 1	100 – 1000
IV	0.01 – 0.1	1000 – 10,000
V	≤0.01	≥10,000

[a] $t_{1/2}$ = 0.0693/k_{OH}[OH]. [OH] is assumed to be 10^7 radicals cm^{-3}.

We have attempted to present a reactivity classification which is exhaustive with respect to the reported room temperature literature for OH rate constant determinations (as well as recent, as yet unpublished, measurements in this laboratory). Thus, we have compiled a reactivity classification consisting of more than 110 compounds assigned into the 5 classes of our proposed reactivity scale.[69] Table 8 gives the rate constant (with its source)*, the reactivity (relative to methane = 1)

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* The rate constant data given in Table 8 are not to be construed as critically evaluated or recommended values. In general, absolute rate determinations were used when available, and average values are often given.

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Table 8. Rate Constants for Reaction of Organics (and Selected Inorganics) with the Hydroxyl Radical and the Corresponding Reactivity Classification

Compound	$k_{OH + Cpd}^a$ (ℓ mol^{-1}s^{-1}) x 10^{-9}	Reference	Reactivity Relative to Methane = 1	Proposed Class
Alkanes				
Methane	0.0048	b-f	1	I
Ethane	0.17	c,f,g	35	II
Propane	1.3	f,h	270	III
n-Butane	1.8	c,h-m	375	III
Isobutane	1.3	c,n	270	III
Cyclobutane	0.72	h	150	III
n-Pentane	3.9	n	810	III
Isopentane	2.0	o	420	III
Cyclopentane	3.7	p	765	III
Neopentane	0.49	c	100	III
n-Hexane	3.6	n,o,q	750	III
Cyclohexane	4.2	c,h,n	875	III
2-Methylpentane	3.2	o	665	III
3-Methylpentane	4.3	o	900	III
2,3-Dimethylbutane	3.1	r	645	III
2,2,3-Trimethylbutane	2.3	r	480	III
2,2,4-Trimethylpentane	2.3	c	480	III
n-Octane	5.1	c	1060	IV
2,2,3,3-Tetramethylbutane	0.67	c	140	III
Alkenes				
Ethene	4.7	s	985	III
Propene	15.1	t	3145	IV
1-Butene	21.3	t	4440	IV
Isobutene	30.5	t	6355	IV
cis-2-Butene	32.3	t	6730	IV
trans-2-Butene	42.1	t	8770	IV
1-Pentene	18	n	3750	IV
cis-2-Pentene	39	n	8125	IV
2-Methyl-1-butene	35	n	7290	IV
2-Methyl-2-butene	48	u	10,000	V
1-Hexene	19	n	3960	IV
Cyclohexene	43	r,n	8960	IV
2,3-Dimethyl-2-butene	92	l	19,170	V
3,3-Dimethyl-1-butene	17	n	3540	IV
1-Methylcyclohexene	58	r	12,080	V
1-Heptene	22	r	4585	IV
Di-Alkenes				
Allene	2.7	v	560	III
1,3-Butadiene	46.4	o	9670	IV
Isoprene	47	w	9790	IV

(continued)

Table 8.   (Continued)

Compound	$k_{OH + Cpd}^a$ (ℓ mol^{-1}s^{-1}) x 10^{-9}	Reference	Reactivity Relative to Methane = 1	Proposed Class
Alkynes				
Acetylene	0.099	x	21	II
Methylacetylene	0.57	v	120	III
Aromatic Hydrocarbons				
Benzene	0.85	y,z	180	III
Toluene	3.6	y,z	750	III
n-Propylbenzene	3.7	o	770	III
Isopropylbenzene	3.7	o	770	III
Ethylbenzene	4.8	o	1000	IV
p-Xylene	7.4	y,aa	1540	IV
o-Xylene	8.4	y,aa	1750	IV
m-Xylene	14.1	y,aa	2940	IV
p-Ethyltoluene	7.8	o	1625	IV
o-Ethyltoluene	8.2	o	1710	IV
m-Ethyltoluene	11.7	o	2440	IV
p-Cymene	9.2	w	1920	IV
1,2,3-Trimethylbenzene	14.9	y,aa	3100	IV
1,2,4-Trimethylbenzene	20	y,aa	4170	IV
1,3,5-Trimethylbenzene	29.7	y,aa	6190	IV
Ketones				
Methyl ethyl ketone	2.0	w	420	III
Methyl isobutyl ketone	9.0	w	1875	IV
Diisobutyl ketone	15	w	3125	IV
Alcohols				
Methanol	0.57	q	120	III
Ethanol	1.8	q	375	III
n-Propyl alcohol	2.3	q	480	III
Isopropyl alcohol	4.3	bb	895	III
n-Butanol	4.1	q	855	III
4-Methyl-2-pentanol	4.3	cc	895	III
Ethers				
Diethyl ether	5.6	bb	1170	IV
Di-n-propyl ether	10.4	bb	2170	IV
Tetrahydrofuran	8.8	dd	1830	IV
Esters				
n-Propyl acetate	2.7	dd	560	III
sec-Butyl acetate	3.4	dd	710	III

Table 8. (Continued)

Compound	$k_{OH + Cpd}^a$ (ℓ mol^{-1}s^{-1}) x 10^{-9}	Reference	Reactivity Relative to Methane = 1	Proposed Class
Natural Hydrocarbons				
α-Pinene	35	w	7290	IV
β-Pinene	41	w	8540	IV
p-Menthane	4	w	830	III
3-Carene	52	w	10,830	V
β-Phellandrene	70	w	14,580	V
Carvomenthene	76	w	15,830	V
d-Limonene	90	w	18,750	V
Dihydromyrcene	101	w	21,040	V
Myrcene	137	w	28,540	V
cis-Ocimene	192	w	40,000	V
Halocarbons				
Fluoromethane	0.0096	d	2	I
Chloromethane	0.025	d,ee,ff	5	I
Bromomethane	0.023	d,ff	5	I
Difluoromethane	0.0047	d	1	I
Chlorofluoromethane	0.022	d	5	I
Dichloromethane	0.084	d,ee,ff	18	II
Trifluoromethane	0.00012	d	0.025	I
Chlorodifluoromethane	0.025	d,gg	5	I
Dichlorofluoromethane	0.016	d,ee	3	I
Trichloromethane	0.065	d,ff	14	II
Tetrafluoromethane	<0.00024	d	<0.05	I
Chlorotrifluoromethane	<0.00042	d	<0.09	I
Dichlorodifluoromethane	<0.0006	d,gg	<0.13	I
Fluorotrichloromethane	<0.0006	d,gg	<0.13	I
Tetrachloromethane	<0.0024	d	<0.5	I
Chloroethane	0.235	g	49	II
1,2-Dichloroethane	0.132	g	28	II
1,2-Dibromoethane	0.15	g	31	II
1,1-Difluoroethane	0.019	g	4	I
1,1-Dichloroethane	0.16	g	33	II
1-Chloro-1,1-difluoroethane	0.0017	g	0.35	I
1,1,1-Trichloroethane	0.0090	g	2	I
1,1,1-Trifluoro-2-chloroethane	0.0063	g	1	I
1,1,1,2-Tetrafluoro-2-chloroethane	0.0075	g	2	I
1,1,1-Trifluoro-2,2-dichloroethane	0.0171	g	4	I
1,1,2,2-Tetrafluoro-1,2-dichloroethane	<0.0003	g	<0.06	I
1,1,2-Trifluoro-1,2,2-trichloroethane	<0.0002	g	<0.04	I

(continued)

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Table 8. (Continued)

Compound	$k^a_{OH + Cpd}$ (ℓ mol^{-1}s^{-1}) x 10^{-9}	Reference	Reactivity Relative to Methane = 1	Proposed Class
Nitrogen–Containing Compounds				
Ammonia	0.0988	hh	22	II
Methylamine	13.2	ii	2750	IV
Sulfur–Containing Compounds				
Hydrogen sulfide	3.16	hh	660	III
Methyl mercaptan	20.4	ii	4250	IV
Miscellaneous				
Carbon monoxide	0.084	jj	18	II
Methoxybenzene	11.8	ii	2460	IV
o–Cresol	20.5	ii	4280	IV

[a] "At room temperature" (i.e., within range 292–305 K).

[b] D. D. Davis, S. Fischer, and R. Schiff, J. Chem. Phys., **61**, 2213 (1974).

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and proposed classification for each compound, with the compounds arranged by chemical class. In view of the growing attention being given to nitrogen- and sulfur-containing compounds in the polluted troposphere we have included ammonia, methylamine, hydrogen sulfide, and methyl mercaptan in our classification (as well as carbon monoxide as a matter of interest). For convenience, we also present, in Table 9, the compounds appearing in each of the 5 classes of the SAPRC reactivity scale in order of increasing reactivity within each class.

Comparison with Other Reactivity Classification. In our proposed reactivity classification Class I contains methane and most halocarbons. The remaining half-dozen halocarbons appear in Class II along with carbon monoxide, ammonia, acetylene, and ethane. Almost all alkanes appear in Class III, while alkenes other than ethene appear in Classes IV or V. Aromatics and oxygenates appear in Classes III or IV and the natural hydrocarbons (not specifically identified in previous reactivity classifications) are of high reactivity and appear in Classes IV and V. Clearly our proposed classification emphasizes that most compounds react in polluted atmospheres and Classes I and II contain the relatively few compounds which have half-lives greater than 10 days and 24 hours, respectively. This result parallels the conclusion by Altshuller and Bufalini in their 1971 review article that "almost every hydrocarbon except methane can produce some oxidant when photooxidized in the presence of high enough ratios of hydrocarbons to oxides of nitrogen."

Although our proposed reactivity scale and classification is based solely on consumption rates of organics, Altshuller and Bufalini[70] have shown that this measure of reactivity is similar to one based on nitric oxide oxidation rates. They showed that the ranking of reactivities of hydrocarbons from the nitric oxide photooxidation studies of Altshuller and Cohen[71] and Glasson and Tuesday[64] was essentially the same as that obtained from the studies of hydrocarbon consumption carried out by Schuck and Doyle,[72] Stephens and Scott,[73] and Tuesday.[74] The ranking of reactivities for the aromatic hydrocarbons in our classification is very similar to that obtained by Altshuller et al.[75] and by Kopczynski.[76,77] We have previously[66,67] shown that our classification is in general agreement with that proposed by Dimitriades in 1974[78] and noted where significant

Table 9. Proposed Reactivity Classification of Organics (and Selected Inorganics) Based on Reaction with the Hydroxyl Radical

Class I $(\leq 4.8 \times 10^7)^a$	Class II $(4.8 \times 10^7 - 4.8 \times 10^8)^a$	Class III $(4.8 \times 10^8 - 4.8 \times 10^9)^a$	Class IV $(4.8 \times 10^9 - 4.8 \times 10^{10})^a$	Class V $(\geq 4.8 \times 10^{10})^a$
Trifluoromethane	Trichloromethane	Neopentane	Ethylbenzene	2-Methyl-2-butene
1,1,2-Trichloro-1,2,2-trifluoroethane	Dichloromethane	Methanol	n-Octane	3-Carene
Tetrafluoromethane	Carbon monoxide	Methylacetylene	Diethyl ether	1-Methylcyclohexene
1,2-Dichloro-1,1,2,2-tetrafluoroethane	Ammonia	2,2,3,3-Tetramethylbutane	p-Xylene	β-Phellandrene
Chlorotrifluoromethane	Acetylene	Cyclobutane	p-Ethyltoluene	Carvomenthene
Dichlorodifluoromethane	1,2-Dichloroethane	Benzene	o-Ethyltoluene	d-Limonene
Fluorotrichloromethane	1,2-Dibromoethane	Isobutane	o-Xylene	2,3-Dimethyl-2-butene
1-Chloro-1,1-difluoroethane	Ethane	Propane	Tetrahydrofuran	Dihydromyrcene
Tetrachloromethane	1,1-Dichloroethane	n-Butane	Methyl isobutyl ketone	Myrcene
Difluoromethane	Chloroethane	Ethanol	p-Cymene	cis-Ocimene
Methane		Methyl ethyl ketone	Di-n-propyl ether	
2-Chloro-1,1,1-trifluoroethane		Isopentane	m-Ethyltoluene	
2-Chloro-1,1,1,2-tetrafluoroethane		1-Propanol	Methoxybenzene	
1,1,1-Trichloroethane		2,2,4-Trimethylpentane	Methylamine	
Fluoromethane		2,2,3-Trimethylbutane	m-Xylene	
Dichlorofluoromethane		n-Propyl acetate	1,2,3-Trimethylbenzene	
2,2-Dichloro-1,1,1-trifluoroethane		Allene	Diisobutyl ketone	
1,1-Difluoroethane		2,3-Dimethylbutane	Propene	
Chlorofluoromethane		Hydrogen sulfide	3,3-Dimethyl-1-butene	
Bromomethane		2-Methylpentane	1-Pentene	
Chloromethane		sec-Butyl acetate	1-Hexene	
Chlorodifluoromethane		Toluene	1,2,4-Trimethylbenzene	
		Cyclopentane	Methyl mercaptan	
		n-Propylbenzene	o-Cresol	
		Isopropylbenzene	1-Butene	
		n-Hexane	1-Heptene	
		n-Pentane	1,3,5-Trimethylbenzene	
		p-Menthane	Isobutene	
		1-Butanol	cis-2-Butene	
		Cyclohexane	2-Methyl-1-butene	
		2-Propanol	α-Pinene	
		4-Methyl-2-pentanol	cis-2-Pentene	
		3-Methylpentane	β-Pinene	
		Ethene	trans-2-Butene	
			Cyclohexene	
			1,3-Butadiene	
			Isoprene	

^{a}Range of values (in liter mole^{-1} sec^{-1}) for the rate constant for reaction of the OH radical with the listed compounds.

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differences existed. Several of these differences arose from the greater degree of differentiation in reactivity permitted by the OH reactivity criterion.

A three-class reactivity classification of organic compounds very recently adopted by the ARB[79] is shown in Table 10, and is similar to one now under consideration by the EPA.[80] As described by the ARB,[79,80] Class I includes low reactivity organic compounds, yielding little if any ozone under urban conditions. Class II consists of moderately reactive organic compounds which give an intermediate yield of ozone within the first day of solar irradiation, while Class III is limited to highly reactive organic compounds which give high yields of ozone within a few hours of irradiation.

In general, the ARB three-tiered classification is consistent with the reactivity classification presented here, based on OH rate constants, with only minor exceptions. For example, the ARB scale shows the primary and secondary C_{2+} alcohols to be highly reactive in Class III, while our scale shows them to be of moderate reactivity.

Advantages and Limitations of the OH Reactivity Classification. In contrast to previous reactivity scales, where it is commonly recognized that uncertainties in the number of classes into which the reactivity scales can be meaningfully divided,[78,80] OH reactivity as developed here could be divided into a large number of classes based on the fact that the accuracy of OH rate constant measurements is generally better than ±20%. Thus, one significant strength of this approach is the very high degree of resolution obtained in ranking compounds in order of their rate of reaction with OH. A second advantage of the present classification is that it can be readily extended to include additional organic (and inorganic) compounds once their rate of reaction with OH is known. Thus, it is not necessary to conduct a major new experimental program each time a significant number of new compounds become of interest (as has been felt necessary in the usual smog chamber approach, in order to obtain consistent data for all compounds of interest at a given time). Finally, our proposed classification gives greater weight than most previous classifications to the alkanes and aromatic hydrocarbons, which as discussed above, require a longer irradiation period but can, during downwind transport or stagnant air episodes, contribute significantly to ozone formation.

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Table 10. California Air Resources Board (ARB) Reactivity Classification or Organic Compounds[†]

Class I (Low Reactivity)	Class II (Moderate Reactivity)	Class III (High Reactivity)
C_1-C_2 Paraffins	Mono-tert-alkyl-benzenes	All other aromatic hydrocarbons
Acetylene	Cyclic ketones	
Benzene	Alkyl acetates	All olefinic hydrocarbons (including partially halogenated)
Benzaldehyde	2-Nitropropane	
Acetone	C_{3+} Paraffins	Aliphatic aldehydes
Methanol	Cycloparaffins	Branched alkyl ketones
Tert-alkyl alcohols	n-Alkyl ketones	Cellosolve acetate
Phenyl acetate	N-Methyl pyrrolidone	Unsaturated ketones
Methyl benzoate	N,N-Dimethyl acetamide	Primary & secondary C_{2+} alcohols
Ethyl amines	Alkyl phenols[*]	
Dimethyl formamide	Methyl phthalates[**]	Diacetone alcohol
Perhalogenated Hydrocarbons		Ethers
Partially halogenated paraffins		Cellosolves
		Glycols[*]
Phthalic anhydride[**]		C_{2+} alkyl phthalates[**]
Phthalic acids[**]		Other esters[**]
Acetonitrile[*]		Alcohol amines[**]
Acetic acid		C_{3+} Organic acids + di acid[**]
Aromatic amines		C_{3+} di acid anhydrides[**]
Hydroxyl amines		Formin[**] (Hexa methylene-tetramine)
Naphthalene[*]		Terpenic hydrocarbons
Chlorobenzenes[*]		Olefin oxides[**]
Nitrobenzenes[*]		
Phenol[*]		

[†] This reactivity classification is identical to that suggested by the EPA in August, 1975[79,80] except that the ARB has moved propane from Class I to Class II. [*]Reactivity data are either non-existent or inconclusive, but conclusive data from similar compounds are available; therefore, rating is uncertain but reasonable. [**]Reactivity data are uncertain.

These strengths notwithstanding, several caveats should be borne in mind in applying the proposed OH reactivity scale. First of all, it is not strictly applicable to compounds which undergo significant photodissociation in the atmosphere (e.g., aliphatic aldehydes) or which react in the atmosphere at significant rates with species other than OH (e.g., the alkenes with O_3). In such cases, the compound will be more reactive than predicted from a scale based on consumption due solely to OH attack. It is interesting to note, however, that with respect to the reaction of ozone with alkenes, this limitation is not as serious as it would appear to be based only on the relative rates of consumption of alkenes by ozone and OH, respectively. This follows from the fact that recently Niki and coworkers[81] have shown that O_3-alkene reactions do not lead predominantly to radical products, and hence this additional alkene consumption pathway will contribute significantly less "additional reactivity" (over that obtained for OH reaction alone) than if it led to radical chain propagation.

A second, and perhaps more significant, limitation in the application of our reactivity classification concerns the inherent problem arising from uncertainties in the identity and fates of subsequent products.[78] For example, two compounds which have the same rate constant for reaction with OH may not necessarily have the same oxidant-producing potential in undergoing further photooxidation. As another example, we have recently reported that alkoxy radicals of the higher alkenes ($\geq C_4$) undergo internal isomerization[82] and also that reaction of alkylperoxy radicals ($\geq C_4$) with NO leads to the formation of alkyl nitrates ($RONO_2$) rather than to $RO + NO_2$.[83] Thus, estimates of ozone formation (or other secondary smog manifestations) for the higher alkanes which are based solely on their rates of reaction with OH are likely to be somewhat high since nitrate formation is effectively radical terminating.

IV. A CHAMBER STUDY OF SULFATE AEROSOL FORMATION

A.   Introduction

The formation of inorganic aerosols containing sulfate and nitrate
anions is a well established feature of photochemical air pollution.
Recent work has reemphasized the overriding importance of these anions
for the phenomenon of visibility reduction.[84-86] It is also becoming
apparent that inhaled sulfate and nitrate aerosols have appreciable
effects on the health of exposed populations,[4,87-89] a more serious
although until recently less well-known effect than visibility reduction.

The ultimate fate of emitted sulfur compounds is conversion to
sulfate and eventual transfer to the oceans on a worldwide basis. Con-
version processes are active throughout the atmosphere[90] but proceed at
an accelerated rate in a polluted urban atmosphere. Accumulation of
sulfate is due to two factors, a higher precursor emission rate than
the worldwide average, primarily due to the combustion of sulfur-containing
fossil fuels, and the promotion of conversion processes by the presence of
other anthropogenic primary or secondary pollutants. One major promoted
conversion process is the entrainment of anthropogenic sulfur compounds,
mostly sulfur dioxide, into the reactions accompanying the nitrogen oxides-
promoted photooxidation of organics (mostly hydrocarbons).

In recent years the sulfate burden in the SCAB has been increasing
at a rate of about 10% per year.[5] The inorganic aerosol problem is there-
fore not under control and promises to become significantly worse in the
future, especially if aggravated by nondiscriminatory use of higher sulfur-
content fuels as a result of fuel shortages.

The major uncertainties in the above projections are the effects of
current and future control programs on the conversion processes. As hydro-
carbon emissions are reduced, the atmospheric photochemical activity will
presumably decrease, but whether this will reduce conversion rates proportion-
ately remains to be seen. Thus, it is possible that the rates will be
reduced only sufficiently to transfer most of the aerosol problem to peripheral
areas.

On considering questions of this sort, it is evident that quantitative
data are needed to assess the directions to be taken to control formation

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of inorganic aerosol in urban and downwind atmospheres. In addition, the control of anthropogenic inorganic particulates, particularly the stable sulfates, may have worldwide implications with regard to inadvertent climate modification through changes in albedo and by furnishing an excess of water droplet nuclei.

The initial phase of the program to study the formation of sulfate aerosol from SO_2 has been largely completed. The major goals of this portion of the program were to establish the experimental techniques necessary to quantitatively study the loss of SO_2 under simulated atmospheric conditions in the SAPRC all-glass chamber, to characterize the effect of various parameters on SO_2 lifetime and to determine the suitability of using added seed aerosol to facilitate the characterization of aerosol formed from SO_2.

B.   Results and Discussion

Rates of Disappearance of SO_2. In order to characterize the behavior of SO_2 in the all-glass chamber, a number of control experiments have been carried out. Three types of experiments have been completed: (a) SO_2 disappearance as a function of irradiation intensity and relative humidity, (b) effect of alkene and ozone and of ozone alone on SO_2 lifetime, and (c) loss of SO_2 in the presence of the SAPRC surrogate for ambient pollutants.

The results of experiments to determine the net SO_2 disappearance rate (i.e., corrected for dilution) under the above conditions are given in Table 11. Detailed data sheets for these experiments are presented in Appendix B. Appendix C contains plots of ln SO_2 versus time showing least squares fits to the experimental data and the total disappearance rates.

As expected[91] the consumption of SO_2 is greatly accelerated in the presence of ozone and propene. The initial (averaged over first half hour) net loss of SO_2 is ~30% hr^{-1}, but this falls off rapidly to ~0.2% hr^{-1} for 1.75 to 5 hours. The decay of SO_2 in the presence of ozone alone was about ~1% hr^{-1}. The disappearance of SO_2 in the presence of surrogate and NO_x is similar to that observed in pure air at the same humidity during irradiation (see Table 11).

Aerosol Formation. During the latter part of Run 218 at 100% light intensity, propene (and additional SO_2) was added to the reaction mixture

Table 11. Rate of SO$_2$ Loss in All-Glass Chamber under a Variety of Conditions (using FC-12 as Inert Tracer for Determination of Dilution Rate)

AGC Run No.	RH Range (%)	Amount of Water (torr)	Temp. Range (°C)	Light Intensity	Estimated Net[a] SO$_2$ Loss Rate (% hr^{-1})
216	1-2.5	0.6-1.0	32.6-33.7	0%	0.4
217[b]	11-24.5	5.1-10.3	34.4-36.6	100%	3
218[c]	40-49	15.5-18.9	33.2-33.8	0%	0.4
218[d]	31-55.5	14.0-22.2	33.0-36.0	100%	5
219[e]	81.5-71.5	30.1-26.9	32.6-34.2	0%	5
220[f]	41-40	15.2-15.3	32.7-32.8	0%	30
220[g]	40-38.5	14.9-14.5	32.8-33.1	0%	0.2
221[h]	44-38.5	16.4-13.9	32.7-33.2	0%	1[i]
222[j]	46.3-32.5	15.9-12.7	34.3-30.5	0%	2
222[k]	32.5-26.0	13.2-12.0	33.8-36.6	100%	4

[a] Total rate of SO$_2$ disappearance minus dilution rate (as determined from monitoring of FC-12).
[b] Continuation of 216 at 100% light intensity; additional SO$_2$ injected; approx. 0.5 ppm ozone present in this experiment.
[c] Flash lamp in Teco 43 replaced; instrument zeroed and spanned using MSA filter and calculated SO$_2$ in chamber, respectively.
[d] Ozone increased to ~0.3 ppm in first 6 hours of irradiation and remained at about that value.
[e] Lamp bases in Teco 43 replaced; zeroed and spanned as in b.
[f] 1 ppm propene and 0.6 ppm ozone present; average rate for first 30 min of reaction.
[g] 0.40 ppm propene and 0.20 ppm ozone present; average rate after 1.75 hr of reaction.
[h] 0.57 ppm ozone added.
[i] Value for time after ozone was added.
[j] Surrogate (~1700 ppbC) and NO$_x$ (0.3 ppm calc.) present initially.
[k] Surrogate (~1100 ppbC) and NO$_x$ (~0.5 ppm) present at beginning of irradiation.

Table 12. Aerosol Measurements Using the Whitby and Climet Analyzers during Propene-Ozone-SO_2 Experiment (AGC-218)

Size (μm)	Concentration (particles cm^{-3})											
	Initial[a]	1440hrs	1450hrs	1505hrs	1515hrs	1525hrs	1535hrs	1545hrs	1555hrs	1605hrs	1615hrs	1625hrs
Whitby												
.0075	---	---	---	---	---	---	---	---	---	---	---	---
.0133	---	2.3×10^3	1.75×10^4	4.17×10^2	---	---	---	---	---	---	---	---
.0237	1.17×10^3	1.72×10^5	1.62×10^5	9.52×10^4	8.85×10^4	6.90×10^4	4.34×10^4	8.35×10^3	2.71×10^4	1.57×10^4	1.25×10^4	1.22×10^4
.0422	1.74×10^2	7.83×10^2	2.60×10^4	4.09×10^4	2.96×10^4	3.30×10^4	3.65×10^4	4.35×10^4	3.83×10^4	3.44×10^4	2.76×10^4	2.05×10^4
.0750	1.54×10^3	1.69×10^3	5.95×10^3	1.54×10^3	2.10×10^4	2.08×10^4	2.26×10^4	2.21×10^4	2.28×10^4	2.46×10^4	2.62×10^4	2.95×10^4
.133	5.7×10^3	5.59×10^3	5.49×10^3	6.10×10^3	6.53×10^3	7.21×10^3	7.56×10^3	7.66×10^3	8.19×10^3	8.10×10^3	8.15×10^3	7.93×10^3
.237	3.75×10^3	3.51×10^3	3.46×10^3	3.33×10^3	3.37×10^3	3.35×10^3	3.27×10^3	3.38×10^3	3.36×10^3	3.39×10^3	3.30×10^3	3.27×10^3
.422	6.47×10^2	5.40×10^2	5.74×10^2	4.87×10^2	4.87×10^2	4.67×10^2	4.93×10^2	4.80×10^2	4.46×10^2	4.54×10^2	4.67×10^2	4.74×10^2
.750	8.42×10	8.73×10	7.02×10	5.26×10	6.32×10	5.97×10	4.91×10	5.96×10	7.37×10	4.9×10	6.32×10	5.97×10
	Initial[a]	1442hrs	1452hrs	1502hrs	1510hrs	1520hrs	1530hrs	1540hrs	1550hrs	1600hrs	1620hrs	1638hrs
Climet												
>.3[b]	5.0×10	5.7×10	6.28×10	6.78×10	6.78×10	7.24×10	7.52×10	7.83×10	8.35×10	9.15×10	9.11×10	8.95×10
>.5[b]	2.3×10^{-1}	2.5×10^{-1}	3.24×10^{-1}	3.24×10^{-1}	3.53×10^{-1}	1.83×10^{-1}	2.97×10^{-1}	3.68×10^{-1}	3.81×10^{-1}	3.11×10^{-1}	3.53×10^{-1}	3.30×10^{-1}
>1	4.5×10^{-2}											
>3	1.0×10^{-3}											

[a] Prior to injection at 1424 of SO_2 and propene.

[b] Dilution system used, 100 to 1.

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which contained ~0.3 ppm ozone. Particle size distributions were monitored with both a TSI Electrical Aerosol Analyzer (Whitby) and a Climet Optical Particle Analyzer. Background readings were taken prior to the injection of SO_2. The data obtained with both instruments are given in Table 12. Subsequent work with the Climet has indicated difficulties in calibration and this probably is the source of the variation in results obtained with the two instruments in this study. However, the relative values obtained do show that (1) there was a rapid growth of small particles following the injection of propene in the presence of SO_2 and ozone, and (2) the growth of these particles to larger sizes was accompanied by the decrease of smaller sized particles.

Added Seed Aerosol. A series of calculations were carried out in order to design the most effective experiments for characterizing aerosol stability in the all-glass chamber (AGC). These calculations suggested that the chamber should be seeded with approximately 10^4 cm^{-3} of 0.1 μm diameter particles, a mass loading of about 40 μg m^{-3}. It was calculated that such a seed cloud should have a life expectancy of approximately 100 hours in the 6400-liter all-glass chamber.

Based on these results, spray-dried K_2SO_4 doped with 10 mole percent of $KHSO_4$ was used as a test aerosol. This material was intended to play the part of an innocuous surrogate for generated aerosol, organic or inorganic. It was found that the most stable size is in the 0.1 to 0.2 μm diameter range which has an irradiated chamber life expectancy of 30 hours or more (17% or less loss to the walls after 6 hours). Lifetimes estimated from the data decrease rapidly outside of the stable size range, reaching 12 hours at both 0.04 μm and 0.3 μm. An expectancy of 12 hours corresponds to 40% wall loss in 6 hours. These estimates are thought to be conservative estimates representing lower limits on the actual life expectancy.

These findings have the following implications:

- Any experiment involving aerosols, either inorganic or organic, should be seeded if semi-quantitative results on the material yield are desired. The seed particles should be somewhat less than or equal to 0.1 μm in size. Otherwise wall losses can diminish the apparent yield, sometimes to negligibility.

- Measurements of gross light scattering properties like b_{scat} have

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no meaning with regard to mass concentration or visibility reduction potential. The particle size distribution resulting from the appearance of aerosol material will be severely deficient in the high light scattering region (0.2 to 1.0 μm). This will be the case for either seeded or unseeded mixtures because of the accumulated wall losses beyond 0.2 μm. In the case of properly seeded mixtures, comparatively few particles will grow into the light scattering region in any case.

Most of the uncertainty about the estimates originates from the limitations of the TSI 3030 (Whitby mobility analyzer). The particle number concentration cannot be reduced to values where the effects of the second order processes of coagulation are neglibible during several hours without encountering the sensitivity limits of the TSI 3030. Consequently, the observed decay had to be corrected for coagulation as well as for the exchange rate. For some particle sizes the correction was about equal to the overall decay rate. In addition, methods of estimating coagulation rate constants are subject to considerable uncertainty, especially when the sizes are comparable to the mean free path for air molecules (0.065 μm). The detailed methods of calculation will be presented in our final report.

Consideration of the coagulation rate constants calculated suggests a strategy for obtaining better estimates of wall loss as a function of particle size. The rates imply that coagulation can be dramatically reduced if a monodispersive aerosol is used to test the chamber. Our data suggest that tests with particle sizes around 0.05 μm and 0.45 μm would more definitely determine the loss curve. A test at the larger size would allow use of an optical particle counter to check the TSI 3030 data.

A nearly monodisperisve aerosol of size 0.05 μm can be derived from the output of the spray dryer. Figure 8 shows three size distributions of spray-dried aerosols in the AGC according to the TSI 3030. These distributions were measured early in the aerosol's history in order to get as close as possible to the aerosol seen at the spray dryer's output. There is a trend towards larger sizes as the K_2SO_4 concentration is increased. The 7% solution has a good yield near 0.05 μm. Larger sizes can be removed at the cost of considerable loss at 0.05 μm by using a nucleopore filter. Smaller sizes could be removed by either a diffusion battery or by allowing some coagulation in a plastic bag before filtering.
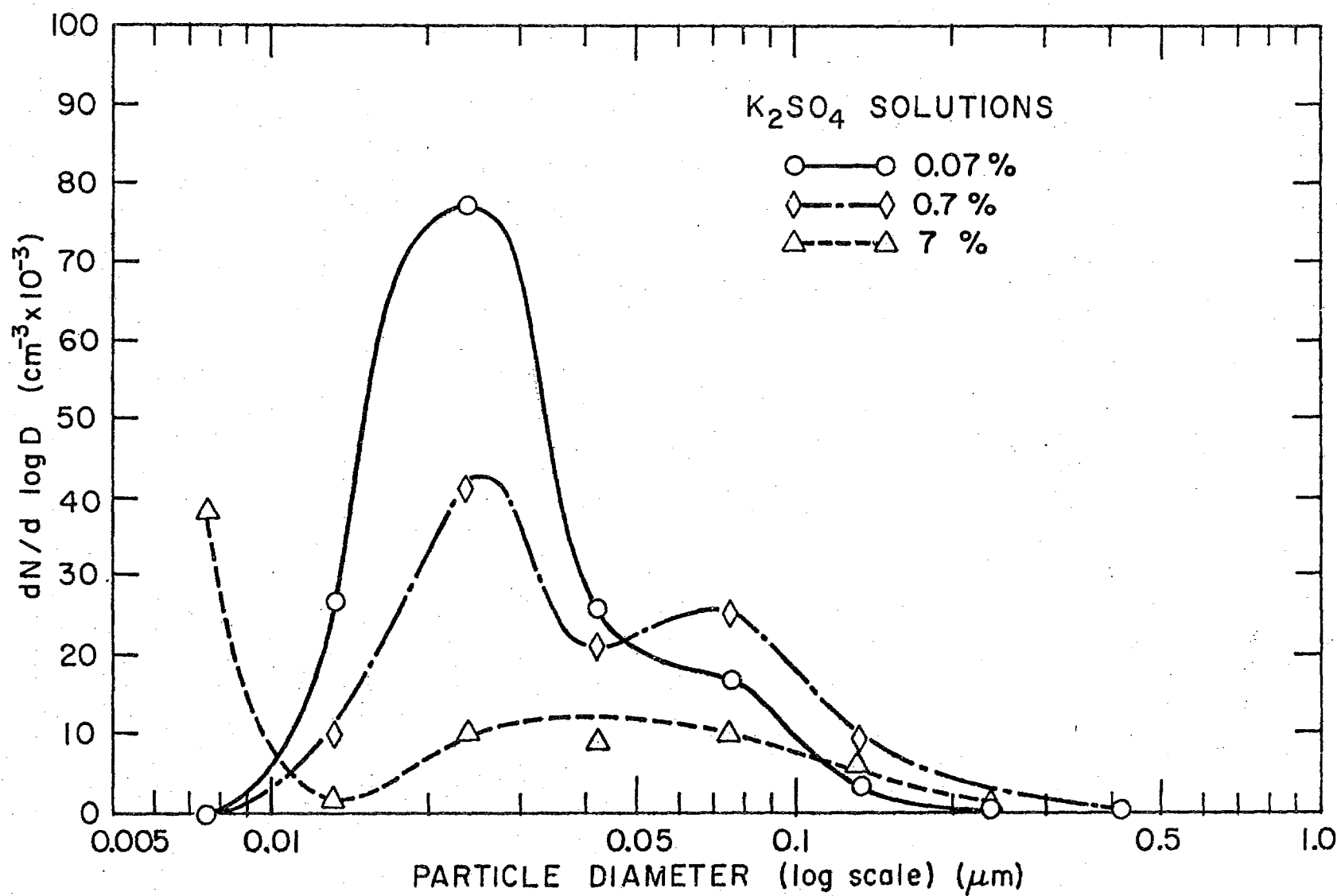
Figure 8. Size Distributions (Whitby) of Spray-Dried Potassium Sulfate Solutions in SAPRC All-Glass Chamber.

V. FURTHER DEVELOPMENT OF AN AIR PARCEL TRANSPORT SIMULATION METHODOLOGY

The purpose of this study was to provide a basis for designing realistic chamber experiments simulating air parcel transport effects during a full day irradiation. In our final report[92] to ARB Contract No. 4-214, we described in some detail a methodology for determining the primary pollutant concentration profiles in an air parcel as it is transported and gave specific results for an air trajectory which terminated in Pasadena at 1300 Pacific Daylight Time on July 25, 1973. During our current work we have developed procedures for determining the rate of dilution and diffusion for the various pollutants in that air parcel and we describe these here.

As discussed in the previous report[92] for a given trajectory which is determined by interpolation of ground level meteorological data, the ambient air quality is determined by a similar interpolation procedure using the air monitoring data. Based on the results for the CO concentration history, a diffusion model is generated to allow for the transport of pollutants in the vertical direction. The emissions inventory used in the estimate is that adopted by the General Research Corporation (GRC) from one developed by Systems Applications, Inc.[93] and the diffusion model is a portion of the GRC DIFKIN model.[94] Given these tools, both dilution and fresh pollutant injection rates required in a chamber experiment in order to approximate an air parcel history can then be determined by the following procedure.

The results of the GRC Diffusion program are the concentration profiles in the vertical direction as a function of time of day along the given trajectory of interest. These are based on the diffusion coefficient profiles estimates which yield reasonable CO ground level concentrations as compared with the CO ambient air quality data for that particular day. In order to determine the dilution/diffusion rates for the various pollutants, an air mass has to be defined. In the following example, two air masses were studied—one extended from ground level up to 108 meters, while the other started at 27 meters above ground level and extended up to 135 meters. Note in both cases that the depth of the air parcel was 108 meters. The mass rate of diffusion

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transport of the various pollutants was determined from the concentration profile and the diffusion coefficients assumed. The mass flux across the boundary is given by the follow equation:

$$\dot{m} = -D \frac{dc}{dz}$$

where $\dot{m}$ = mass flux rate, D = turbulent diffusion coefficient, c = local concentration, and z = vertical space variable. From this equation the mass flux by diffusion of the pollutants was determined both in and out of the air parcel. In the case where one of the boundaries of the air parcel was the ground level, the source flux was used for the mass flux into the air parcel. In addition to determining the fluxes, the average concentration of pollutants within the parcel was determined by numerically integrating under the concentration profile.

These dynamic processes in the atmosphere must now be related to the chamber operation. We define VDIL as the volume of chamber material which must be removed from the chamber each hour in order to accomplish the efflux of a given pollutant as determined for the air parcel. This amount is computed by the following formula:

$$VDIL = 6400 \left(\frac{\dot{m}_o}{H \; C_{AVG}} \right)$$

where $\dot{m}_o$ = mass flux out of parcel, H = height of parcel and C_{AVG} = average concentration in parcel. We define VIN as that volume of pure pollutant which then must be added back with the clean air make-up to maintain the chamber conditions. This essentially is the rate of influx predicted from the transport model.

Figures 9 through 12 show the time variation of VDIL and VIN for the two air parcels considered above (i.e., 0-108 m and 27-135 m) for NO_x and for hydrocarbon. It is interesting to note that there is a large variation in these quantities as a function of time of day as one would intuitively expect. The two contributing factors for this large variation are variations in the emissions inventory as a function of time of day

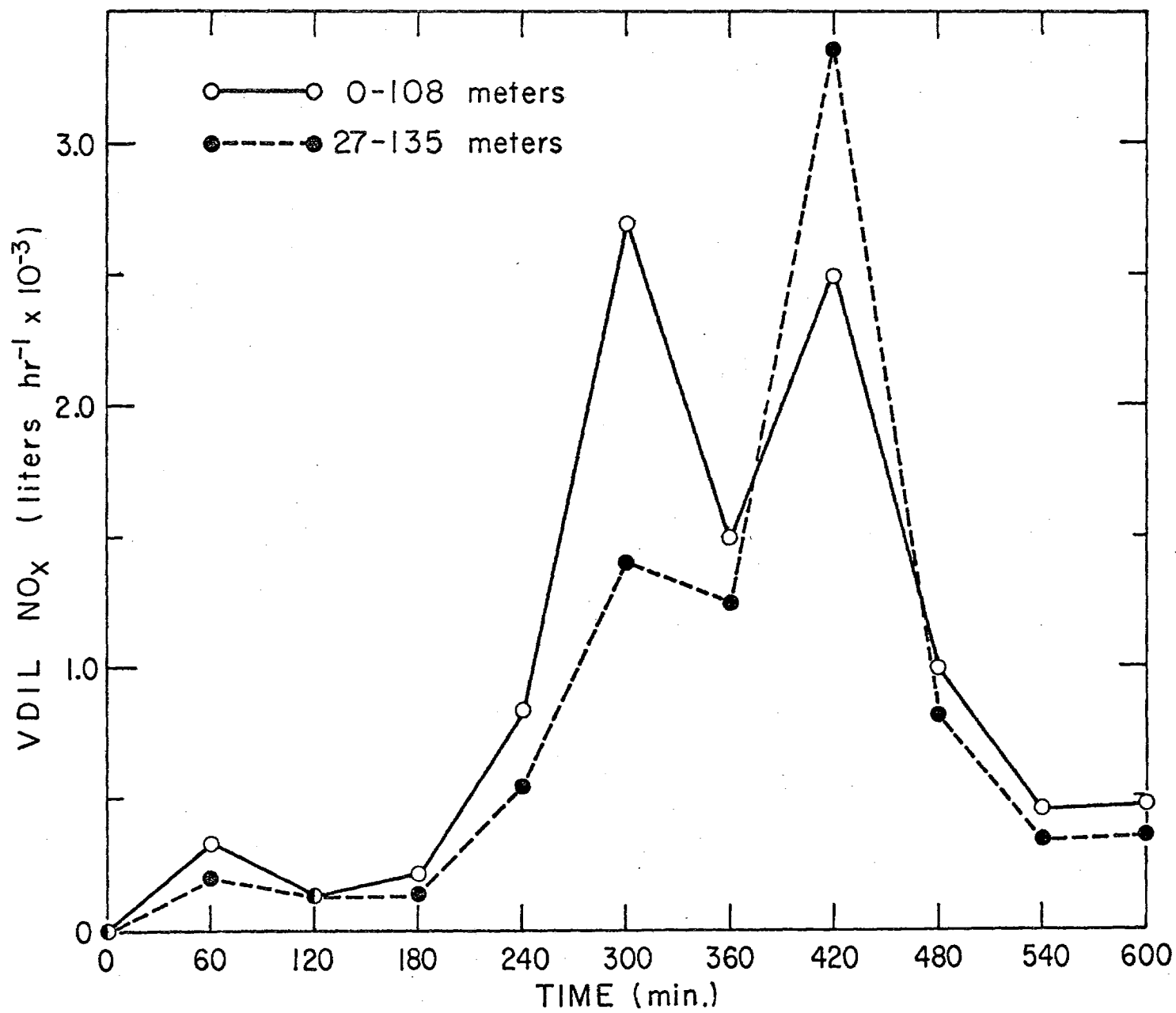Figure 9. Volume of Chamber Sample to be Removed Each Hour (VDIL) for Simulation of NO_x Concentration in Ambient Air Parcels.

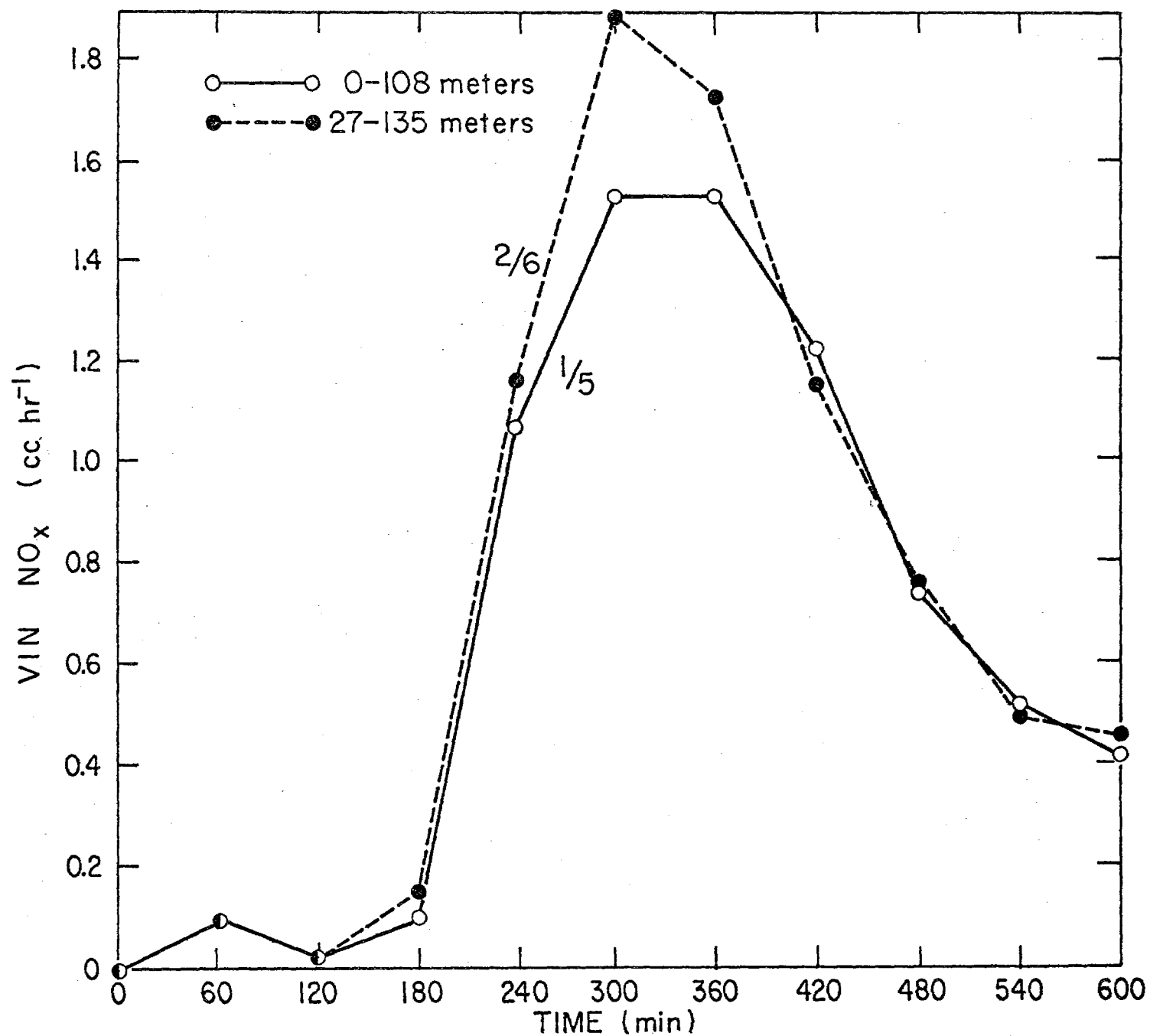Figure 10. Volume of Pure NO_x to be Added to Chamber Each Hour (VIN) for Simulation of NO_x Concentration in Ambient Air Parcels.
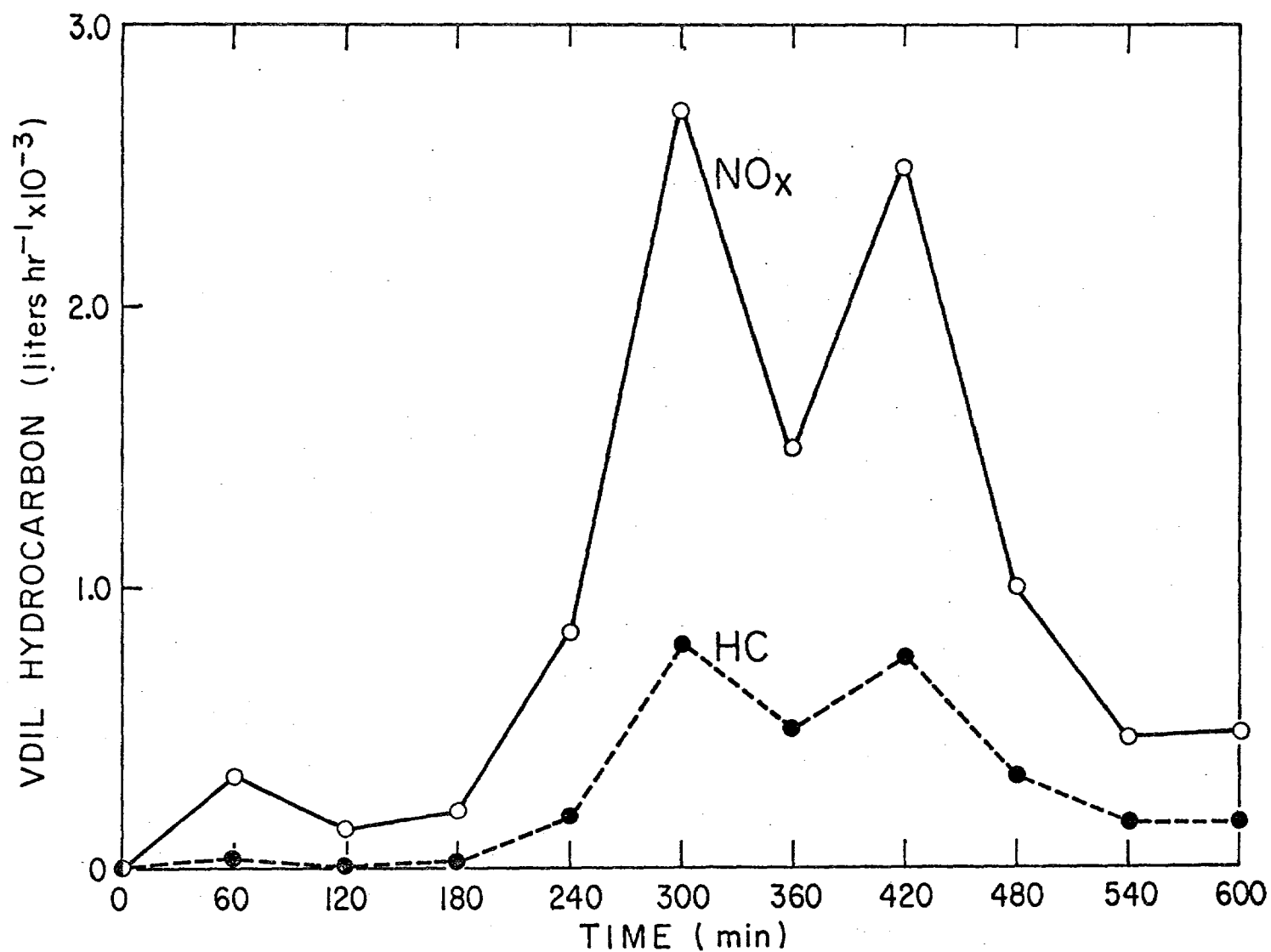
Figure 11. Volume of Chamber Sample to be Removed Each Hour (VDIL) for Simulation of Hydrocarbon Concentration in Ambient Air Parcels.
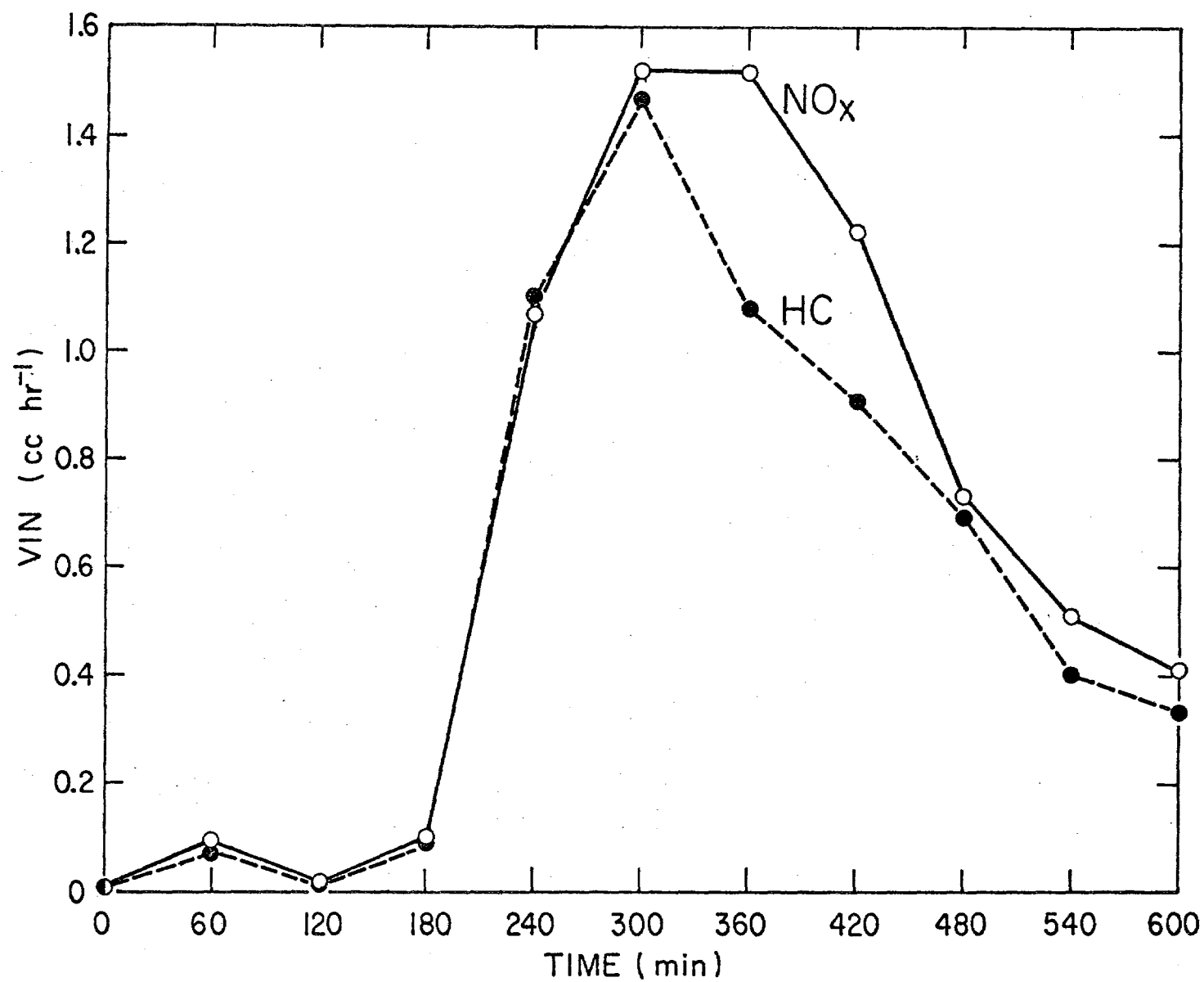
Figure 12. Volume of Pure Hydrocarbon to be Added to Chamber Each Hour (VIN) for Simulation of Hydrocarbon Concentration in Ambient Air Parcels.

and geographic location, and a changing of the diffusion coefficients as the air parcel warms up. Figure 13 shows the variation in the average concentration of the two pollutants as a function of time for the 0-108 m air parcel. It should be noted that for this trajectory there is a continuous increase in the average concentration. Thus, there are no dilution effects apparent. Clearly one would expect that a dilution effect for other trajectories which pass over low source regions later in the day would result.

Recently the choice of dilution rates of approximately 10% per hour by workers operating the large outdoor smog chambers in North Carolina (and by workers in a number of previous chamber studies explicitly employing dilution) has been challenged by Shair[1,2] as being too low. In essence, our initial data suggest that the situation is complex and that both groups of workers are correct to some extent. For example, based on NO_x, the peak dilution we have calculated is approximately 50%--far above those considered by previous chamber workers. However, for the air parcel beginning at ground level, the average dilution rate over the entire trajectory, again based on NO_x, was 16%; and if one uses only that portion of the trajectory from 6:00 in the morning till 1:00 in the afternoon, the average dilution rate is 21%. Clearly from Figure 11 the dilution rates based on hydrocarbon are considered lower than the above values for NO_x. Thus, the results of this analysis for hydrocarbon appear to be more in line with the lower dilution values used in previous chamber studies.

The fact that dilution rates based on NO_x are considerably larger than those based on hydrocarbon is a crucial observation and results from the fact that the concentration of hydrocarbons is far in excess of the concentration of NO_x. Consequently, less volume need be removed from the chamber to achieve the mass fluxes that occur. Obviously, this situation presents a problem in determining an appropriate simulation in actual chamber experiments and work is continuing to determine what VDIL is required to maintain an appropriate hydrocarbon-to-NO_x ratio, a possibly more realistic control parameter.
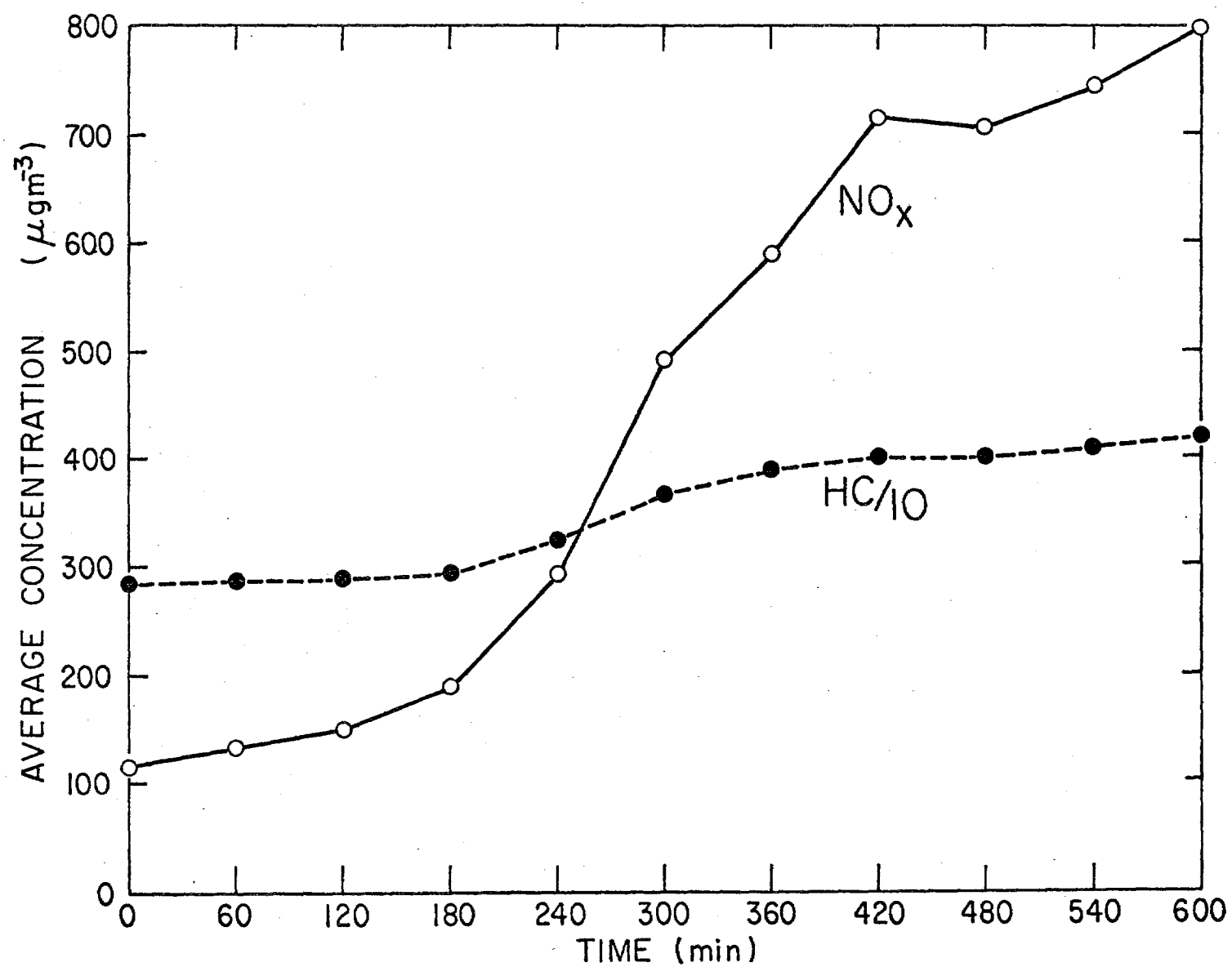
Figure 13. Hourly Average Concentrations of NO_x and Hydrocarbons for Ambient Air Parcel.

VI. AMBIENT AIR ANALYSIS

In April, 1976, the SAPRC was selected by the Environmental
Protection Agency to conduct a three-year study of trace pollutants in
ambient air using a 22-meter base path multiple reflection cell and
FT-IR spectrometer which together are capable of operating at total
pathlengths in excess of 2 km. This system, designed and initially
assembled by P. Hanst and coworkers at the RTP laboratories of EPA,
has now been established on the roof of Weber Hall East on the UCR
campus several hundred yards from the ARB mobile laboratory and Fawcett
Laboratory which houses the SAPRC environmental chamber facility.
Since the EPA long-path infrared (LPIR) spectrometer has an effective
pathlength which is a factor of 10-20 times that of the in-situ
multiple reflection cells in the SAPRC smog chambers, we have chosen
to concentrate our efforts in ambient air analysis by LPIR spectroscopy
on setting up and operating the 2-km FT-IR spectrometer. This system
is now successfully operating and spectra are being recorded routinely
(even during the only moderate smog episodes which have been character-
istic of this summer). Under SAPRC's policy of resource sharing, results
which are obtained using the 2-km FT-IR spectrometer will be considered
in the context of the aerosol and gas phase data which are being obtained
under our companion ARB contract for investigation of ambient aerosols.
Our goal remains to obtain the most complete heterogeneous and homo-
geneous mass balance for carbon and nitrogen-containing species
possible through the combined capabilities of the major instrumental
facilities which have now been assembled at SAPRC under the auspices of
the ARB, NSF-RANN and EPA,

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