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Photochemical Reactivity of Perchloroethylene

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PHOTOCHEMICAL REACTIVITY OF PERCHLOROETHYLENE

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FOREWORD

Man and his environment must be protected from the adverse effects of photochemical and other pollutants arising from atmospheric reactions of organic and inorganic emissions. Efforts to protect the environment require a focus that recognizes all aspects of the pollution generating process--emission, dispersion, transformation, and fate of man-made and natural pollutants. The Environmental Sciences Research Laboratory contributes to this multifaceted focus through programs engaged in

- studies of environmental processes and effects of atmospheric pollutants, and
- development of the research methodology needed to conduct such studies and to characterize heretofore unidentified or uncharacterized pollutants.

Perchloroethylene is an important commercial product suspected of contributing significantly to the problem of photochemical ozone and other oxidants in some urban atmospheres. The equivocal nature of the evidence implicating perchloroethylene in such problems and the socioeconomic importance of this chemical provided the justification and impetus for this research effort.

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ABSTRACT

Perchloroethylene (PCE), a solvent used in dry cleaning, has been suspected of contributing significantly to photochemical ozone/oxidant (O_3/O_x) problems in urban atmospheres. Past evidence, however, was neither complete nor consistent. To interpret more conclusively the past evidence, and further understand PCE's role in the O_3/O_x problem, a smog chamber testing program was conducted. The program's objectives were: (a) to explain the mechanism of the PCE reaction in smog chamber atmospheres, and (b) to extrapolate the smog chamber findings regarding PCE reactivity to the real atmosphere. Results showed that (a) in smog chambers, PCE reacts and forms O_3/O_x following a Cl-instigated photooxidation mechanism rather than the OH-initiated mechanism accepted in current smog chemistry, and (b) in the real atmosphere neither the Cl-instigated nor the OH-instigated photooxidations of PCE can generate substantial concentrations of O_3/O_x. In fact, PCE contributes less to the ambient O_3/O_x problem than equal concentrations of ethane.

CONTENTS

Foreword iii
Abstract iv
Figures vi
Tables vii
Acknowledgments viii

1. Introduction 1
2. The Concept of Reactivity 5
3. Analysis and Interpretation of Existing Evidence on Perchloroethylene Reactivity 7

Laboratory Data on O_3/O_x Yield and Consumption Rate Reactivities 7

Atmospheric Data on Consumption Rate Reactivity 15

Analysis and Intrepretation of All Existing PCE Evidence 15

4. Experimental Procedures and Results of New Perchloroethylene Reactivity Study 23

5. Discussion 39

References 47

Appendix Description of Experimental Apparatus and Procedures 51

The FTIR Spectrometer and Smog Chamber 51

The Bag Chamber Facility 53

Analytical Methods 54

References 61

FIGURES

Number		Page
1	Near-UV spectra of radiation within various smog chambers...	25
2	Chromatograms from GC-FID and GC-ECD analyses of PCE.....	26
3	Effect of Cl_2 on photooxidation of PCE (FTIR Chamber).....	35
4	UV absorption spectrum of liquid perchloroethylene.....	41
A-1	Schematic of long path infrared photochemical reaction chamber system.....	52
A-2	Chromatogram of GC-FID analysis of PCE.....	57
A-3	Chromatogram of GC-ECD analysis of PCE.....	60
A-4	PCE calibration curve for GC-ECD analysis.....	62

TABLES

Number		Page
1	Volatile Organic Compounds of Negligible Photochemical Reactivity That Should Be Exempt From Regulation Under State Implementation Plans (4)	3
2	Volatile Organic Compounds of "Low" Photochemical Reactivity (4)	3
3	Experimental Systems Used and Results from PCE Reactivity Studies	8
4	Reported Laboratory Studies and Results on PCE Reactivity	16
5	Comparison of Consumption Rates Observed in Smog Chambers with Consumption Rates Computed from k_{OH} Data for Hydrocarbons and Halocarbons	19
6	Rate Constants for PCE Reactions with Reactive Species	21
7	Initial Conditions and Results of Smog Chamber Tests	27
A-1	PCE-FID Analysis Parameters	56
A-2	Precision of GC/FID Analysis of PCE Calibration Mixtures	58
A-3	PCE-ECD Analysis Parameters	59

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SECTION 1

INTRODUCTION

Since its inception in 1970, the approach adopted by the Environmental Protection Agency (EPA) to reducing photochemical ozone (O_3) and other oxidants (O_x) has been based on unilateral control of the volatile organic compound (VOC) precursors. However, since the individual VOCs differ widely in O_3- or O_x-forming potential, EPA accepted the concept of discriminate control of organic emissions, and produced from time to time lists of VOCs that could be exempted from control by virtue of their negligibly low photochemical reactivity. More precisely, in developing State Implementation Plan (SIP) control strategies to attain the national ambient air quality standard for O_3, the EPA policy has been to identify those VOCs for which conclusive evidence supported exemption from control, and to assume all other VOCs reactive and, hence, non-exempt. However, this policy has also been continually open to revision as new evidence develops that might justify reclassifying the reactivity of specific VOCs.

Perchloroethylene (PCE), a VOC used as a solvent and emitted in significant amounts from dry-cleaning operations, was first thought to be unreactive and was exempted from control. Thus, it was included among the unreactive VOCs identified by EPA and listed in Appendix B of EPA's Requirements for Preparation, Adoption, and Submittal of Implementation Plans (1). The Los Angeles Rule 66 (2) also exempted PCE from control as being unreactive. Those early judgments were based on the 1960s Los Angeles Air Pollution Control District (LAAPCD) smog chamber study of solvent reactivities (3). In that study, irradiation of PCE and nitrogen oxides (NO_x) mixtures in a 1200 cu. ft. glass-aluminum smog chamber did not produce more oxidant than irradiation of the background air alone. That study, however, was one of the earliest efforts using smog chamber methodology, and, although responsive to the need at that time, is now considered one of the least sensitive. For example, irradiation of background air alone in that chamber resulted in as much as 0.2 ppm of total oxidant; such a high level of background reactivity makes it difficult to measure the reactivities of little but not insignificantly reactive organics.

In the years following the LAAPCD studies and the Appendix B and Rule 66 promulgations, there were several other PCE reactivity studies, which were

undertaken for several reasons. First, many researchers recognized that the LAAPCD data needed verification. Also, it was found that under conditions of long-range pollutant transport, investigated in the 1970's, some "unreactive" organic compounds can produce significant amounts of O_3. Finally, the discovery that halocarbons cause stratospheric ozone depletion increased interest in the atmospheric chemistry of PCE and other halocarbons with respect to their lifetimes in the troposphere. Thus, it became important to know the rate at which PCE (and other halocarbons) react and are consumed in the troposphere, and the reaction products and their impact on tropospheric and stratospheric air quality.

After the "Appendix B" guideline, the next PCE regulatory judgment EPA made was that described in EPA's Recommended Policy on Control of Volatile Organic Compounds in 1977 (4). That policy divided VOCs into three classes based on three criteria: photochemical reactivity, role in stratospheric O_3 depletion, and direct health effects. The first class, shown in Table 1, includes those VOCs which by virtue of their negligible reactivity could be exempted from regulation under ozone SIPs. The second class, shown in Table 2, includes those VOCs which have low photochemical reactivity and must be included in the ozone SIP inventories but their control has lower priority than that of the more reactive compounds. The third class, encompassing all VOCs other than those in Tables 1 and 2, includes those VOCs the control of which has relatively high priority. The PCE was judged to have photochemical reactivity comparable to those of the Table-2 VOCs but was not included in Table 2 because of its reported health effects. Note, however, that even in the absence of the health effects criterion, the EPA judgment in 1977 would still have been that PCE's photochemical reactivity is not sufficiently low to justify total exemption from control.

EPA's 1977 judgment on PCE reactivity was based mainly on findings from a 1974-75 EPA smog chamber study (5), the results of which were also supported by an independent 1974 Rutgers University smog chamber study (6). Three other reported studies, by SRI (7), Dow Chemical (8,9), and EPA (10), produced results that agreed with the EPA policy on PCE in some respects, disagreed in others, or were not comparable. More recently, there have been additional studies reported, some directly addressed to PCE's O_3-forming reactivity and some

TABLE 1. VOLATILE ORGANIC COMPOUNDS OF NEGLIGIBLE PHOTOCHEMICAL REACTIVITY THAT SHOULD BE EXEMP FROM REGULATION UNDER STATE IMPLEMENTATION PLANS (4)

Methane
Ethane
1,1,1-Trichloroethane (Methyl Chloroform)[1]
Trichlorotrifluoroethane (Freon 113)[1]
Methylene Chloride[1]
Trichlorofluoromethane[1]
Dichlorodifluoromethane[1]
Chlorodifluoromethane[1]
Trifluoromethane[1]
Chloropentafluoromethane[1]
Trichlorotrifluoroethane[1]
Dichlorotetrafluoromethane[1]

[1]According to more recent EPA notices in the Federal Register (Vol. 44, pp. 32042-43, June 4, 1979, and Vol. 45, pp. 48941-42, July 22, 1980), these compounds are of continuing concern to EPA over possible environmental effects and may be subject to future controls.

TABLE 2. VOLATILE ORGANIC COMPOUNDS OF "LOW" PHOTOCHEMICAL REACTIVITY (4)

Propane
Acetone
Methyl Ethyl Ketone
Methanol
Isopropanol
Methyl Benzoate
Tertiary Alkyl Alcohols
Methyl Acetate
Phenyl Acetate
Ethyl Amines
Acetylene
N,N-dmethyl formamide

to various mechanisms of PCE photooxidation. The new evidence appeared to be, again, partly in agreement and partly in disagreement with the 1977 EPA judgment on PCE reactivity. However, it became also apparent that most of the conflicting evidence could be reconciled, and this led us to reexamine the question of PCE reactivity in the light of the reconciled evidence. We concluded that more experimental testing was needed to more completely reconcile conflicting evidence and to support a more definitive and reliable judgment regarding the reactivity of PCE.

In this report we describe our latest experimental study. We also reanalyze and reinterpret all evidence now available on the atmospheric chemistry of PCE, and offer a new judgment of PCE's photochemical reactivity with respect to the ambient oxidant problem. To facilitate understanding of the rationale behind the objectives and design of our new study, and the reanalysis and interpretation of the experimental evidence, we discuss first the concept of reactivity, the past data and other relevant literature on PCE reactivity, and the current specific issues and information gaps.

SECTION 2

THE CONCEPT OF REACTIVITY

Definitions, significance, and applications of the VOC reactivity concept in air pollution problems have been discussed in detail elsewhere (11). The reactivity aspect of primary interest in this report is the ability of the VOC to participate in atmospheric reactions and form O_3/O_x. The prevalent method for measuring such reactivity has been the smog chamber method, by which the test VOC is exposed in a smog chamber to reactant mixture and radiation conditions similar to those in real urban atmospheres, and the yield in O_3/O_x is measured directly.

In the past nearly three decades there have been numerous smog chamber studies of VOC reactivity, and O_3/O_x-yield reactivity data are now available for a large number of VOCs (11). There are problems, however, in using the existing data base for this particular reactivity index. One conceptual problem is that the O_3/O_x reactivity is not a single-value molecular property. To explain, the smog chamber method of measurement does not give a single result; it gives results that vary depending, for example, on the reactant concentration conditions used in the chamber. Thus, the O_3/O_x yield reactivities of VOCs are not uniquely defined, absolutely or relative to each other, and this confuses the application of the reactivity concept in control. Another problem with the concept of O_3/O_x yield is that this measure of reactivity cannot be used for VOCs of small but significant reactivity, because smog chambers manifest levels of background reactivity comparable to those of such VOCs.

These problems with the O_3/O_x yield reactivity index have had two consequences. They forced researchers and regulators (a) to turn to simple, two-class reactivity classification schemes ("reactive", "unreactive") in preference to individual VOC reactivity ranking schemes, and (b) to consider other less direct but more usable reactivity indices. The reactivity indices considered and used here are the "O_3/O_x yield" reactivity and the "VOC consumption rate" reactivity. The O_3/O_x yield reactivity data are more reliable for reactive VOCs and are used to classify those organics. The classification of low-reactivity VOCs, for which the smog chamber measurements of O_3/O_x yield are

generally unreliable is based mainly on "VOC consumption rate" reactivity data, explained below.

The VOC consumption rate is the rate at which the VOC reacts when exposed to atmospheric conditions, and can be measured during the same smog chamber test used to measure the O_3/O_x yield reactivity. Its significance lies mainly in the fact that a VOC cannot produce O_3/O_x unless it participates--and, hence, is consumed--in the atmospheric reaction. The VOC consumption rate, therefore, offers the most reliable basis for recognizing the totally unreactive VOCs. Thus, VOCs whose consumption rates are negligibly small are classified as unreactive. By extension, it was also assumed, at first, that VOCs manifesting significant consumption rates in smog chambers are reactive. This latter assumption, however, has been questioned by some recent studies (5), and, as discussed later, by this study also.

SECTION 3

ANALYSIS AND INTERPRETATION OF EXISTING EVIDENCE ON PERCHLOROETHYLENE REACTIVITY

Existing evidence considered here consists mainly of data on the O_3/O_x yield and PCE consumption rate reactivities obtained in the laboratory. Since crude measures of consumption rate reactivity can also be derived from ambient concentration and emission rate data, these will also be included in this analysis. Each piece of reactivity data is critiqued to the extent allowed by the reported information, and labeled as of supporting a "negligibly reactive" or "reactive" classification for PCE. "Negligibly reactive" is defined here as equal or less reactive than ethane, the latter organic taken by the authors to be a "boundary" species separating the reactive VOCs from the unreactive ones. Results from attempts to reconcile conflicting data and to derive an overall reactivity rating for PCE relative to that of ethane are given later in this chapter.

LABORATORY DATA ON O_3/O_X YIELD AND CONSUMPTION RATE REACTIVITIES

Formal and informal reports on O_3/O_x yield and consumption rate reactivities of PCE, including some specifics on smog chamber system and conditions used, are listed in Table 3.

The Schuck and Doyle data (12) were obtained by irradiating 3 ppmv PCE and 1 ppmv NO_x in a 520-ft^3 chamber. Resultant stable O_3 concentration was 0.05 ppm, greater than the concentration produced by trichloroethylene or methane. Observed rate of PCE consumption was comparable to those for C_7-C_8 paraffins and, hence, higher than that for ethane, assuming the same smog chemistry to be applicable to PCE and to C_7-C_8 paraffins. These data support negligible O_3/O_x-yield reactivity and appreciable consumption rate reactivity for PCE but are suspect because they show trichloroethylene to be less reactive than PCE, a result that is inconsistent with all other studies of the two chloroethylenes.

The Brummelle, et al., data (3) were obtained by irradiating 6.34 ppm of PCE and 1.85 ppm NO_x in a 1,200-ft^3 aluminum-glass chamber. The data support negligible O_3/O_x yield reactivity and appreciable consumption rate reactivity

TABLE 3. EXPERMENTAL SYSTEMS USED AND RESULTS FROM PCE REACTIVITY STUDIES

Study reference	Chamber and radiation system design	Reactant concentrations, ppm (v/v) for organic, ppm for NO_x	Avg. rate of PCE reactions %/h	Max. O_3/O_x conc., ppm	Comments
Schuck and Doyle (1959) (15)	520-ft^3 glass-lined chamber with 24 400-watt H-1 mercury arcs and 78 blacklight lamps inside the chamber. Light intensity in near-UV approximately equal to full sunlight.	PCE/NO_x: 3/1	5.4	0.05	-PCE rate was comparable to those for C_7-C_8 paraffins. O_3/O_3 yields for methane and trichloroethylene were 0.
Brummelle et al. (1966) (3)	1180-ft^3 aluminum-glass chamber, with 12 GE H-400-E mercury vapor lamps and stainless steel reflectors, positioned outside the chamber behind Pyrex glass panes, and 48 GE-F-40-T-12-BL blacklight lamps placed inside the chamber. Radiation intensity approximately equal to full noonday sunlight in Los Angeles. Chamber temperature close to 100°F.	PCE/NO_x: 6.34/1.85	6.4 (estimated from total organic measurements by IR)	0	-Inadvertent chamber dilution was 6.3%/h. -Background O_3/O_x formation as high as 0.21 ppm with 0.75 ppm background NO_x concentration.
Wilson (1971) (7)	268-ft^3 aluminum-Pyrex glass chamber with all inside surfaces Teflon-coated. 72 F72T12/D/VHO daylight, 30 F40B bluelight, 28 F40BL blacklight, and 50 F40 sunlamps were used external to the chamber. Radiation intensity was 60% to 80% of noonday sunlight in Los Angeles. Chamber was operated at ~95°F.	PCE/NO_x: 8/1 : 8/1	4.0 5.0	0.11 0.08	-Inadvertent chamber dilution was 3-4%/h.

(Continued)

TABLE 3 (Continued).

Study reference	Chamber and radiation system design	Reactant concentrations, ppm (v/v) for organic, ppm for NO_x	Avg. rate of PCE reactions %/h	Max. O_3/O_x conc., ppm	Comments
Kopczynski (1971) (16)	335-ft^3 aluminum chamber with Tedlar windows, and with 24 sunlamps, 36 blue lamps and 88 blacklight lamps positioned externally to the chamber. Radiation intensity was equivalent to k_D = 0.4 min. Chamber was operated at 90°F.	PCE/NO_x: 2/1	5-6	0	
Lillian et al. (1975) (6), and Appleby (1976) (17)	200-lit Teflon bag irradiated with 12 GE F40 BLB, 6 GE F40 BL and 6 Westinghouse FS40 sunlamps. Radiation intensity equivalent to k_D = 0.39 min^{-1}. Chamber was operated at 95°F.	PCE/NO_x: 0.85/0.5	4.0 during first 2 h and 12.5 over entire 8-h run	0.50	-Radiation in the 2800-3000Å range was about 10 times that of natural sunlight.
		PCE/NO_x: 0.8/0	6.2 during first 2 h and 25.0 over entire 4-h run	0.01	-All runs showed an induction period of 1-4 h.
Gay et al. (1976) (10)	690-lit borosilicate glass chamber serving as absorption cell of FTIR spectrophotometer. 96 GE F40 BLB blacklight lamps external to chamber. Radiation intensity equivalent to k_D = 0.6 min^{-1}. Chamber was operated at 86°F.	PCE/NO_x: 5/1.8	2.3-7.0	0.07	-The chamber is the same as the one used in present study but with different radiation system.

(Continued)

TABLE 3 (Continued).

Study reference	Chamber and radiation system design	Reactant concentrations, ppm (v/v) for organic, ppm for NO_x	Avg. rate of PCE reactions %/h	Max. O_3/O_x Conc., ppm	Comments
Dilling et al. (1975) (8) and Dilling et al. (1976) (9)	9.6-lit Pyrex glass chamber irradiated with 2 GE 275-W reflector sunlamps with wavelength cutoff of 2900Å. Radiation intensity equivalent to ~2.6 times that of sunlight on summer day in Freeport, Texas. Chamber was operated at 81°F.	PCE/NO_x: 50/12	~20	0	
		: 10/5	4-6	No data	
		: 40/20	~7	No data	
		: 100/50	~13	No data	
Dimitriades and Joshi (1977) (5)	400-lit Teflon-Pyrex chamber irradiated with 22 GE-F40 BLB blacklight and 7 Westinghouse SF-40 sunlamps. Radiation intensity was equivalent to k_D = 0.34 min^{-1}. Chamber was operated at 86°F.	PCE/NO_x: 4/0.2 (9 tests)	5-45 during first 1 h and 20-55 over entire run	0.5-1.2	-There was an induction period of 0.5-1.0 h.
Yanagihara et al. (1977) (18) and Japan Environmental Agency (1975) (19)	70-ft^3 Pyrex chamber irradiated externally with 96 lamps including FL40A, FLR40SBL-A and FLR40SE-A types with output energy peaks at 4,200Å, 3,650Å, and 3,100Å, respectively. Radiation intensity equivalent to k_D = 0.33 min^{-1}. Chamber was operated at 86°F.	PCE/NO_x: 2/1	No data	0	
Gay (1977) (20)	690-lit borosilicate glass chamber used and described here by these authors. Irradiated by 72 BLB 40 blacklight and 24 FS40 sunlamps. Radiation intensity equivalent to k_D = 0.66 min^{-1}. Chamber operated at 86°F.	PCE/NO_x: 4/0.2	5-8	0.4	

(Continued)

TABLE 3 (Continued).

Study reference	Chamber and radiation system design	Reactant concentrations, ppm (v/v) for organic, ppm for NO_x	Avg. rate of PCE reactions %/h	Max. O_3/O_x conc., ppm	Comments
Kaiserman and Corse (1981) (22)	400-ft^3 aluminum chamber with Teflon windows, irradiated by 112 GE F96T8-BL blacklight and 18 Westinghouse FS20 sunlamps. Radiation intensity equivalent to k_D = 0.4 min^{-1}. Chamber operated at 90-104°F (rising T during irradiation test).	PCE/NO_x: 4/0.2	9.5	0.4	
Sickles et al. (1980) (22)	Four 1000-ft^3 Teflon chambers and several 250-lit Teflon bags, irradiated by natural sunlight in September-November at Research Triangle Park, North Carolina.	PCE/NO_x: 4/0.2	Low but significantly greater than zero	0.4-0.5	-Irradiation of purified air resulted in 0.06-0.07 ppm O_3. Irradiation of ambient air resulted in 0.23-0.29 ppm O_3. Irradiation of ambient air with 0.07 ppm NO_x resulted in 0.01-0.06 ppm O_3.

for PCE, but they are suspect because of excessively high chamber background reactivity problems, and because of poor analytical methods.

The Wilson data (7), informally reported, were obtained by irradiating 8 ppm of PCE and 1 ppm NO_x in a 268-ft^3 Teflon-coated aluminum-Pyrex chamber. Resultant O_3/O_x yields were 0.08-0.11 ppm, suggesting a borderline level of O_3/O_x yield reactivity for PCE. Consumption rates were 4 to 5%/h, which are only slightly higher than the dilution rate (3%/h) in the smog chamber. These rates are lower than those observed for butane and toluene (i.e., ~8%/h) (13)--organics which, according to current smog chemistry, are more reactive than ethane (11). These reactivities, however, may be somewhat low because the chamber's radiation in the 3000-4000Å wavelength region--which is the most energetic part of the surface sunlight spectrum--was, according to the investigators, some 15% less than the estimated natural radiation in Los Angeles (13). Overall these data, although questionable, are judged to suggest borderline levels of reactivity.

The Kopczynski data (14), informally reported, were obtained in a single smog chamber experiment in which 2 ppmv PCE and 1 ppmv NO_x were irradiated in a 335-ft^3 aluminum-Tedlar chamber. After 5.4 hours of irradiation, no O_3 was observed, a result that supports negligible O_3/O_x yield reactivity for PCE. Consumption rate was 5 to 6%/h, which is comparable to that for n-butane (measured in the same chamber), a VOC known to be reactive. These data are limited in amount and for that reason alone are questionable.

The Lillian et al. (6) and Appleby (15) data were obtained in a series of experiments, in which 0.8 ppm PCE was irradiated in 200-liter Teflon bags in the presence and in the absence of 0.5 ppm NO_x and of a hydrocarbon. Data from several experiments showed a pattern of slow PCE disappearance in the first three hours of irradiation when the O_3 concentration was low, and fast disappearance later in the experiment, after O_3 concentration reached a peak. The O_3/O_x yields varied but were always high (> 0.5 ppm), supporting high PCE reactivity. Irradiation of 0.8 ppm PCE alone in air (containing about 0.004 ppm of NO_x impurity) resulted in only 0.01 ppm of O_3, suggesting no background reactivity problems. Such high O_3/O_x yields and PCE consumption rates, however, strongly disagree with the previous studies.

The early data by Gay et al. (10) were obtained in a single experiment in which 5 ppm PCE and 1.8 ppm NO_x were irradiated (with blacklight fluorescent lamps) in the 690-liter FTIR chamber used in the present study. After 2.3 h, 0.1 ppm of O_3 formed, and there was a PCE loss equal to 2.3%/h. These data, assuming to be significant, support a negligible O_3/O_x yield reactivity and a possibly significant consumption rate reactivity, but are suspect because they are limited in amount.

The Dilling et al. data (8) on O_3/O_x yield reactivity were obtained by irradiating 50 ppmv PCE and 12-13 ppmv NO_x in a 10-liter Pyrex cylinder; PCE consumption rates (9) were measured in tests with 10 ppm PCE and 5 ppm NO_x. In all tests, the radiation intensity was, according to the authors, approximately 2.6 times higher than that of natural sunlight. The oxidant measurements made represented the sum of O_3 and NO_2 as well as of all other oxidants causing response to the KI method; specific O_3 yield data were not obtained in that study. Despite this limitation, it could be deduced from the oxidant measurements that the O_3 yields were low, supporting negligible PCE reactivity. The time for 50% PCE disappearance was 14.2 hours when all initial NO_x was NO, and 8.3 hours when all initial NO_x was NO_2. These consumption rates were roughly 3 to 3.5 times slower than those for trichloroethylene, but only 2 times slower than that for toluene, a reactive VOC. Assuming that PCE and toluene obey the same smog chemistry, these data again suggest a generally low level of consumption rate reactivity, but probably not below that of ethane. They are judged, therefore, to support a reactive nature for PCE. Because the apparatus and conditions used in that study are drastically different from the other studies and highly unrealistic, those data cannot be quantitatively compared with the other studies, and do not have absolute validity.

The Dimitriades and Joshi data (5) were obtained by irradiating 4 ppmv PCE and 0.2 ppmv NO_x in a 400-liter Pyrex-Teflon reactor. Resultant O_3 yields were around 0.5 ppm, corrected for 0.03 ppm background reactivity. The consumption rate data displayed a pattern similar to the one displayed by the Lillian et al. (6), and Appleby (15) data. That is, PCE disappeared slowly at

first, and extremely fast after O_3 had reached a peak. These data clearly support a reactive nature for PCE with respect to both O_3/O_x yield and consumption rate, but are suspect because of apparent inconsistencies with current smog chemistry. Thus, the reactivities of some organics that have been studied in that chamber, including methane and propane, were greater than those estimated on the basis of current smog chemistry (16,17).

The Yanagihara et al. data (18,19) were obtained by irradiating 4 ppmv PCE and 2 ppmv NO_x in a 70-ft^3 Pyrex smog chamber. Resultant O_3 yields were comparable to background O_3 reactivity, supporting, therefore, negligible reactivity for PCE.

Newer data by Gay (20) and Kaiserman and Corse (21) were obtained using two smog chambers: the 690-liter FTIR chamber used and described in our current study, and a 400-ft^3 aluminum-Teflon chamber (21). Since those tests were to check the reproducibility of the Dimitriades and Joshi results, these researchers used the same reactant concentration conditions as those used by Dimitriades and Joshi: 4 ppmv PCE and 0.2 ppmv NO_x. Resultant O_3/O_x yields were within 0.2-0.4 ppm for both chambers, supporting high PCE reactivity. Observed consumption rates in the two chambers were 5 to 8%/h and 9.5%/h, respectively, supporting a low reactivity level but still higher than that of ethane. These newer data, therefore, support high PCE reactivity with respect to both O_3/O_x yield and consumption rate.

Finally, the Sickles et al. data (22) were obtained using a battery of four 1000-ft^3 Teflon chambers and several 250-liter Teflon bags irradiated by natural sunlight. Reactant concentrations were 4 ppmv for PCE and 0.2 ppm and 0.067 ppm for NO_x, resulting in PCE-to-NO_x ratios of 20:1 and 60:1. Resultant O_3/O_x yields were 0.4-0.5 ppm, supporting high PCE reactivity. Repeated parallel irradiations of PCE and other organic compounds consistently resulted in higher O_3 yields for PCE relative to propane, for example, a result that leaves very little doubt about the high level of PCE reactivity manifested within these chamber atmospheres. Explicit data on PCE consumption were not reported by the investigators. However, they did report that the rate of PCE loss was significantly higher than the rate of disappearance of the co-reactant methane, and approximately equal to 2%/h. Based on this, the PCE consumption rate reactivity was judged to be comparable to (or greater than) that of ethane.

ATMOSPHERIC DATA ON CONSUMPTION RATE REACTIVITY

The main value of atmospheric data lies in the fact that they reflect "real world" behavior of pollutants. Their main shortcoming is that they can seldom be sufficiently abundant to allow accurate quantitative interpretations. Such data are used here to derive semi-quantitative measures of PCE consumption rate reactivity.

The data used in this analysis are those gathered and discussed by Singh and coworkers (23-25). A semi-quantitative estimate of PCE reactivity, based on 1977 data, can be derived as follows: The 1977 PCE emissions of 0.57×10^6 metric tons, assumed to be discharged all in the northern hemisphere (25), should create an ambient concentration of 40 ppt. Observed northern hemisphere concentration is 40 ppt (25), indicating an extremely low PCE consumption rate reactivity. Assuming the ambient PCE concentration to be constant [a reasonable assumption (23-25)] it follows that the annually added PCE concentration of 40 ppt is offset by atmospheric consumption the rate of which, obviously, is 100% per year or 0.02% per daylight hour. For comparison, the ethane removal rate, calculated from the ethane + OH rate constant $k_{OH} = 0.3 \times 10^{-12} cm^3$ molecule sec^{-1}, and the seasonally averaged tropospheric OH concentration of $3\text{-}4 \times 10^5$ molecules/cm^3 (25), is 0.03 to 0.04%/h. Thus, the atmospheric data appear to support an extremely low PCE reactivity, comparable to and perhaps lower than that of ethane.

ANALYSIS AND INTERPRETATION OF EXISTING PCE REACTIVITY DATA

Table 4 summarizes the existing laboratory and aerometric data from the 12 studies cited here. Six supported high or borderline O_3/O_x yield reactivity, six supported negligible O_3/O_x yield reactivity, and all of the studies supported high but widely varying consumption rate reactivities. The aerometric data supported negligible reactivity. Such a high level of inconsistency in experimental reactivity measurements is unusual, but not surprising in the case of PCE. The Rutgers University researchers also observed highly irreproducible results in repeated irradiations of PCE/NO_x systems (15). The same phenomenon was also observed by Dusoleil et al. in their studies of the kinetics of PCE photochlorination (26).

TABLE 4. REPORTED LABORATORY STUDIES AND RESULTS ON PCE REACTIVITY

Investigators	PCE Reactivity Found		Comments
	O_3/O_x yield	Consumption rate	
Shuck and Doyle (12)	Negligible	High	Results are suspect because of inconsistency with other, reliable evidence.
Brummelle et al. (3)	Negligible	High	Results are suspect because of excessive chamber background reactivity and poor analytical methods.
Wilson (7)	Borderline	Borderline	Uncertainties exist due to unrealistic radiation conditions.
Kopczynski (14)	Negligible	High	Uncertainties exist due to limited number of experiments.
Lillian et al. (6,15)	High	High	Questions raised by high results relative to other studies.
Gay et al. (10)	Negligible	High	Uncertainties exist due to limited number of experiments.
Dilling et al. (8,9)	Negligible	High	Reactant concentration and radiation conditions were considerably unrealistic.
Dimitriades & Joshi (5)	High	Very High	Some results are inconsistent with current smog chemistry.
Yanagihara et al. (18)	Negligible	No Data	
Gay (20)	High	High	
Kaiserman and Corse (21)	High	High	
Sickles et al. (16)	High	Borderline	Data quality could not be checked since explicit consumption rate data were not reported.

Use of low PCE-to-NO_x ratio conditions (i.e., around 2:1) in the smog chamber measurement at first appeared to be one possible reason for the low O_3/O_x yield reactivities found in six of the studies. But this explanation alone does not settle the issue, since the Rutgers University study also used low PCE-to-NO_x ratios but observed high O_3/O_x yield reactivities (6,15). For the same reason, the consumption rate reactivity variability also cannot be explained in terms of varying effects by the PCE-to-NO_x ratio factor alone.

In searching for clues to the causes of these inconsistencies, the smog chamber studies' results were compared with reactivities deduced from smog chemistry considerations. To explain, currently accepted smog chemistry (derived from atmospheric chemistry studies of hydrocarbons and aldehydes) explains VOC reactivity in terms of the VOC's ability to participate in a chemical process, a key step of which invariably is the initial reaction of the VOC with OH radicals (11). Reactions subsequent to the OH attack also have a role in the overall O_3-forming process, but, obviously, only if the initial reaction with OH occurs at a significant rate. Therefore, the value of the rate constant for the PCE + OH reaction can provide a useful first check on the reliability of the existing laboratory data, as explained next.

The rate constant, k_{OH}, of the PCE + OH reaction has been measured in several studies and found to be equal to 0.2×10^{-12} cm^3 $molecule^{-1}$ sec^{-1} (27). Assuming that ambient OH concentration during summer noon time in the Southern U.S. is 5×10^6 molecules per cm^3 (28) (reported values range within 2-8 X 10^6), the PCE consumption rate in ambient air due to reaction with OH is calculated to be

$$\frac{\Delta[PCE]}{[PCE]} \times 100 = k_{OH}[OH] \times 100 = 0.2 \times 10^{-12} \times 5 \times 10^6 \times 100 = 10^{-4}\%/sec =$$

$$0.36\%/h$$

Since the light intensities in all smog chamber studies cited here except Dilling et al. (8,9) are comparable to natural sunlight intensity, according to theory, the PCE consumption rates in the chambers should be roughly close to 0.36%/h, except for Dilling et al. The actual observed consumption rates, however, are

1-1 1/2 orders of magnitude higher, which means either that the smog chambers in the studies cited here did not perform consistent with smog chemistry predictions, or that current smog chemistry, for some reason, is not applicable in the PCE case. To further evaluate these two alternate explanations, consumption rates were computed from k_{OH} data for several VOCs (hydrocarbons and halocarbons), and compared with those observed in the smog chambers. Computation results and the comparison are shown in Table 5.

The Table 5 data show generally good agreement between observed and predicted consumption rate reactivities for hydrocarbons but extremely poor agreement for halocarbons. The halocarbon data disagreement is invariably in the direction of higher observed than computed reactivities, and seems to be highest for the polychlorinated ethylenes and lowest for the haloalkane. Therefore, the inconsistencies of the existing PCE reactivity data base cannot be attributed directly to smog chamber-related factors alone. The more logical conclusion is that current smog chemistry cannot be applied to polychlorinated ethylenes, or, more specifically, the reaction with OH is not the key step in the halocarbon consumption process. Some species, more potent than OH, must be responsible for the rapid PCE consumption in smog chambers. This raises, four questions:

1. What is the chemical species that causes rapid PCE reaction in smog chambers?
2. What is the chemistry of the process following that species attack? Does it result in O_3/O_x production?
3. Does this chemistry explain the inconsistencies among the various studies data (Table 4)?
4. Is this species and associated chemistry operative in the real atmosphere?

The first and second questions can be answered with reasonable certainty by referring to basic PCE chemistry studies. Based on studies on PCE reactions with such species as O_3, OH radicals, and O and Cl atoms, it has been established that the reaction with O_3 is too slow to account for the rapid PCE disappearance observed in smog chambers (10,15). In contrast, PCE reacts rapidly with Cl atoms, obeying a chain mechanism (29,30). The reactions with O atoms and OH radicals have lower rate constants than the reaction with Cl

TABLE 5. COMPARISON OF CONSUMPTION RATES OBSERVED IN SMOG CHAMBERS WITH CONSUMPTION RATES COMPUTED FROM k_{OH} DATA FOR HYDROCARBONS AND HALOCARBONS

Smog chamber data	Hydrocarbons consumption rate, %/h		Halocarbons consumption rate, %/h	
	Observed	Computed	Observed	Computed
Schuck and Doyle (12)				
Iso-octane	6	6.7		
Ethylene	9	9.0-18.0*		
Propylene	115	9-47*		
Xylene	64	34		
Trichloroethylene			17	4.1
PCE			5.4	0.4
Wilson (7)				
Trichloroethylene			~13	4.1
PCE			~5	0.4
Kopczynski (14)				
Butane	5-6	5.4		
PCE			~5	0.4
Lillian et al. (6,15)				
PCE			~70 (max)†	0.4
Trichloroethylene			~20 (max)†	4.1
Vinyl Chloride			~18	11.9
1,1,1-Trichloroethane			~0	0.03-0.05
Gay et al. (10)				
Ethylene	~15	9.0-18.0*		
Trichloroethylene			70 (max)†	4.1
PCE			~2.5, ~7	0.4
Dilling et al. (9)				
Toluene	14	7.2-10.8*		
Trichloroethylene			~30	4.1
PCE			~40	0.4
Dilling et al. (8)				
Toluene	~7	7.2-10.8*		
Ethylene	~15	9.0-18.0*		
Cyclohexene	50-150	122		
Trichloroethylene			14-17‡	4.1
PCE			3.5-6‡	0.4
Dimitriades and Joshi (5)				
Ethane	0.5	0.5		
Propane	2.0	1.4-3.6		
Butane	1.4	5.4		
PCE			13	0.4
Gay (20)				
Butane	3.3	5.4		
PCE			~4	0.4

* Range represents range of k_{OH}-values reported. Only the reaction with OH was considered.

† Observed maximum rate.

‡ Range represents results for varying NO_2/NO_x ratios in initial chamber mixture.

(Table 6) , but they may be releasing Cl atoms that could accelerate PCE consumption through autocatalysis.

Besides the evidence from the basic studies, some smog chamber data also suggest that Cl atoms have a major role in the rapid PCE reaction observed in smog chambers. For example, injection of small amounts of Cl_2 in irradiated PCE/NO_x/air systems caused a temporary but pronounced acceleration of PCE consumption (9). Also, presence of an effective Cl atom scavenger was observed to inhibit the PCE reaction (9,15). Finally, the pattern of PCE and O_3 disappearing rapidly in parallel, displayed in the Lillian-Appleby (6,15), Dimitriades-Joshi (5), Sickles et al. (22), and Joshi-Bufalini (32) studies, can be explained as caused by Cl atoms chain-reacting with and consuming both PCE and O_3, the latter chain reaction, with O_3, being as follows (33):

$$O_3 + Cl \rightarrow O_2 + ClO$$

$$ClO + O_3 \rightarrow 2O_2 + Cl$$

All these basic and smog chamber studies suggest that the PCE consumption observed in smog chambers is caused by a Cl-instigated chain photooxidation process, which, evidently, is also capable of generating O_3. Key reactions in this mechanism are the chain initiation steps resulting in Cl atoms. Whether these steps are photolyses of PCE and/or its reaction products, or are reactions following attack of OH or O atoms on PCE, it is not known, nor can it be speculated upon based on the studies reported todate. Also, the past studies did not investigate adequately the effects upon the generation and fate of the Cl atoms, of those experimental factors that differed from study to study (e.g., the radiation and chamber wall-related factors). In the absence of such evidence, the question whether the Cl-instigated photooxidation mechanism can explain past conflicting results cannot be answered. Finally, past evidence is lacking in that it does not permit extrapolation of the laboratory data on PCE reactivity to the "real atmosphere". Direct use of the laboratory data is not necessarily valid because such data are taken, by necessity, under conditions drastically different than those in ambient air. To validly extrapolate the laboratory data to the "real world", it is necessary that the PCE reactivity

TABLE 6. RATE CONSTANTS FOR PCE REACTIONS WITH REACTIVE SPECIES

Reaction	Bimolecular reaction rate Constant, $k(cm^3 molecule^{-1} sec^{-1})$	Reference
PCE + Cl → [PCE]·Cl	5.3×10^{-13}	31
PCE + $O(^3P)$ → [PCE]·O	0.8×10^{-13}	29
PCE + OH → [PCE]·OH	2×10^{-13}	27
PCE + O_3 → Product	"Negligible"	29

be defined as a function of the various conditions, especially, the reactant and co-reactant concentrations, radiation, and chamber wall-related conditions.

To summarize the discussion and conclusions thus far, the evidence reported todate on PCE reactivity is conflicting in that it supports both high reactivity and low reactivity for PCE. High reactivity is supported by some smog chamber data on O_3/O_x yield and by practically all smog chamber data on consumption rate. Negligible reactivity is supported by some smog chamber data on O_3/O_x yield, by the atmospheric data on consumption rate, and by the extremely low value of the k_{OH} for PCE. The major conflict between the high reactivity smog chamber data and the k_{OH}-related evidence is resolved by the finding that the k_{OH}-related evidence is irrelevant since in smog chamber PCE/NO_x photooxidation systems the key oxidizing species is Cl, not OH. The Cl-instigated photooxidation theory, however, in the lack of supporting specific data, does not explain the conflicting results of past studies. Furthermore, and more importantly, the evidence reported todate, cannot answer the question whether Cl-instigated photooxidation of PCE occurs in the real atmosphere significantly. It is these latter deficiencies in the existing evidence that led us to conduct a new study, and to reexamine the question of PCE reactivity in the light of our new experimental data.

SECTION 4

EXPERIMENTAL PROCEDURES AND RESULTS OF NEW PERCHLOROETHYLENE REACTIVITY STUDY

The analysis of existing evidence on PCE reactivity indicated that this experimental effort's objectives should be (a) to confirm that in the smog chamber measurements of PCE reactivity the operative chemistry in PCE degradation is Cl- rather than OH-instigated photochemistry, (b) to understand such Cl chemistry well enough to reconcile some seemingly conflicting evidence, and (c) to extrapolate the laboratory findings on PCE reactivity to the real atmosphere.

To achieve the first objective, tests were conducted in which PCE was reacted with Cl atoms, and tests in which PCE was reacted both in the presence and the absence of Cl scavengers. Also, direct photolysis of PCE and of some of its photooxidation products was investigated to determine the source of the Cl atoms that instigate the rapid disappearance of PCE observed in some smog chambers. To achieve the other objectives, smog chamber irradiation tests were conducted to determine the effects on PCE consumption of the following factors: initial PCE concentration, presence/concentration of organic co-reactant, radiation spectrum, chamber wall material, and chamber use before the test.

The irradiation tests used as smog chambers the absorption cell of a long path Fourier Transform Infrared Spectrophotometer (FTIR) and several bags made of Teflon. The FTIR cell and associated IR-measurement instrumentation and procedures have been described in detail elsewhere (10). Briefly, the FTIR chamber is a 690-liter borosilicate segmented glass tube surrounded by banks of fluorescent lamps (consisting of 24 FS 40 sunlamps and 72 BLB 40 blacklight lamps). Total radiation intensity inside the FTIR chamber, measured through irradiation of NO_2-N_2 mixtures, was found to be equivalent to a first order NO_2 disappearance rate constant, k_D, equal to 0.66 min^{-1} (11). The bag chambers were 60-liter to 360-liter bags made of 2-mil fluorinated ethylene-propylene (FEP) Type A Teflon film. For irradiation, one or two bags were suspended inside an 0.8 m X 1.4 m x 1.1 m aluminum box fitted with 22 BLB 40 blacklight lamps and 4 FS 40 sunlamps evenly distributed along two opposite

sides. The radiation intensity inside a bag was equivalent to $k_D = 0.45\ min^{-1}$. More details on the aluminum box chamber and operating procedures can be found elsewhere (35). The near-UV spectra of the radiation inside the various smog chambers used, from the blacklight lamps alone and from all lamps are shown in Figure 1. The smog chambers were operated at either 25 ± 2°C (bags) or 30 ± 2°C (FTIR).

Measurements of PCE and of other reactants or products in the FTIR chamber were made by infrared spectrophotometry (10). Measurements in the Teflon bag chambers were made by gas chromatography (GC) coupled with either flame ionization detection (FID) or electron capture detection (ECD). The GC system included a 6-ft X 1/8-inch O.D. stainless steel column packed with 10% SF-96 on 60/80 mesh Chromosorb W-AW, and operated at 100°C. Carrier gas was helium, for the GC/FID measurements, or 5%-methane-in-argon, for the GC/ECD measurements. Typical chromatograms are shown in Figure 2. Results from repeated measurements upon several calibration mixtures during a 2-1/2-month period showed a precision equivalent to a coefficient of variation of 23% (see Appendix).

The PCE reagent was of research grade quality. It was freshly redistilled, discarding the fractions outside the 119°-119.5°C boiling range. All other reagents were purchased in their purest form commercially available and were used without further purification.

A more detailed description of the apparatus and experimental procedures and the statistical evaluation of the analytical methods used can be found in the Appendix.

Thirty-seven smog chamber tests were conducted. Table 7 shows the initial conditions used and results for the various FTIR and Teflon bag tests in chronological order. A reasonable amount of test replication was applied to ascertain the significance of the observed effects.

Evidence of the role Cl chemistry plays in PCE smog chamber testing was provided by tests 4, 5, 6, and 8, in which PCE was irradiated in the FTIR chamber in the presence and the absence of Cl_2. The test procedure was to irradiate PCE alone for 2-3 h, inject a small amount of Cl_2, and continue irradiation again for 2-3 h. The injected Cl_2, as expected, photolyzed to Cl atoms. Results from all four tests consistently showed that the injected Cl_2

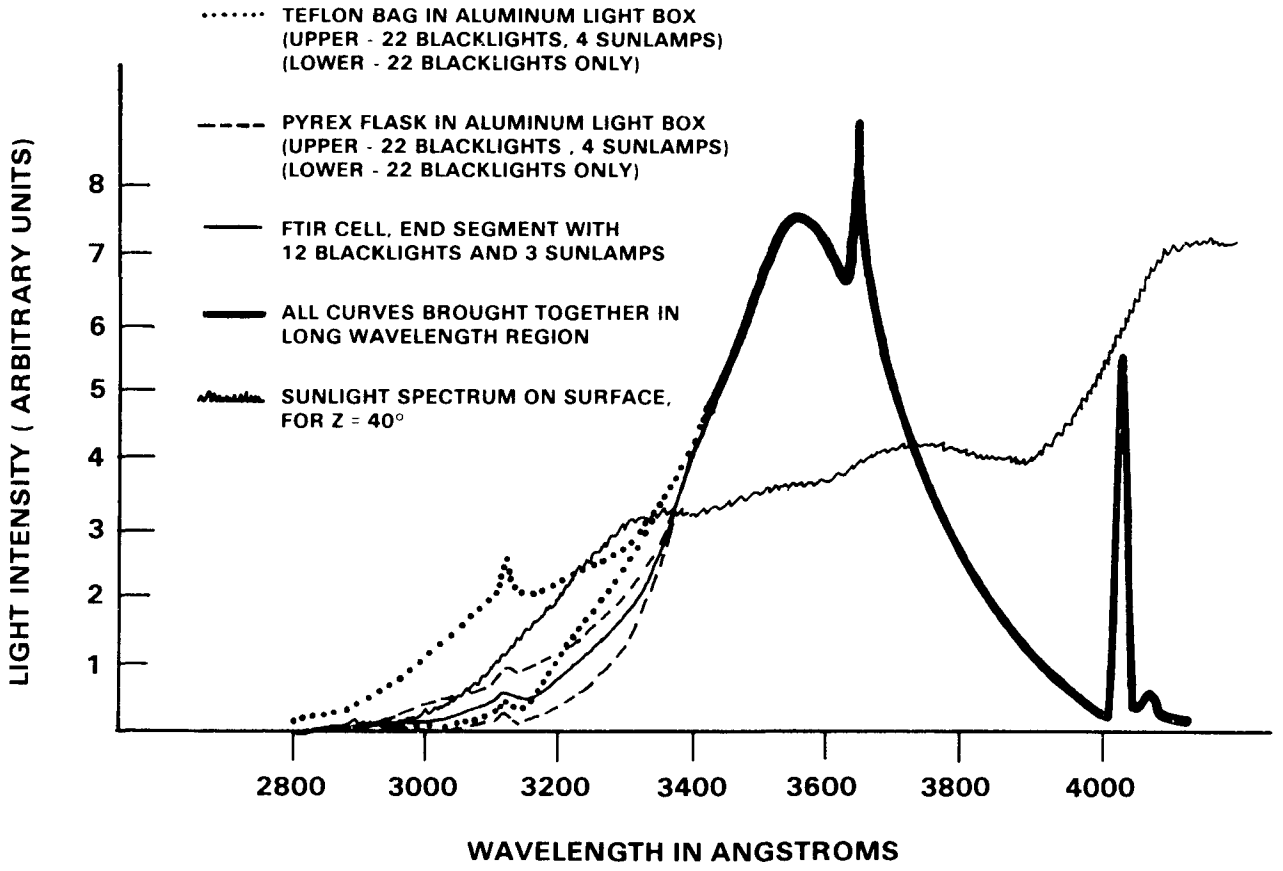

Figure 1. Near-UV spectra of radiation within various smog chambers.

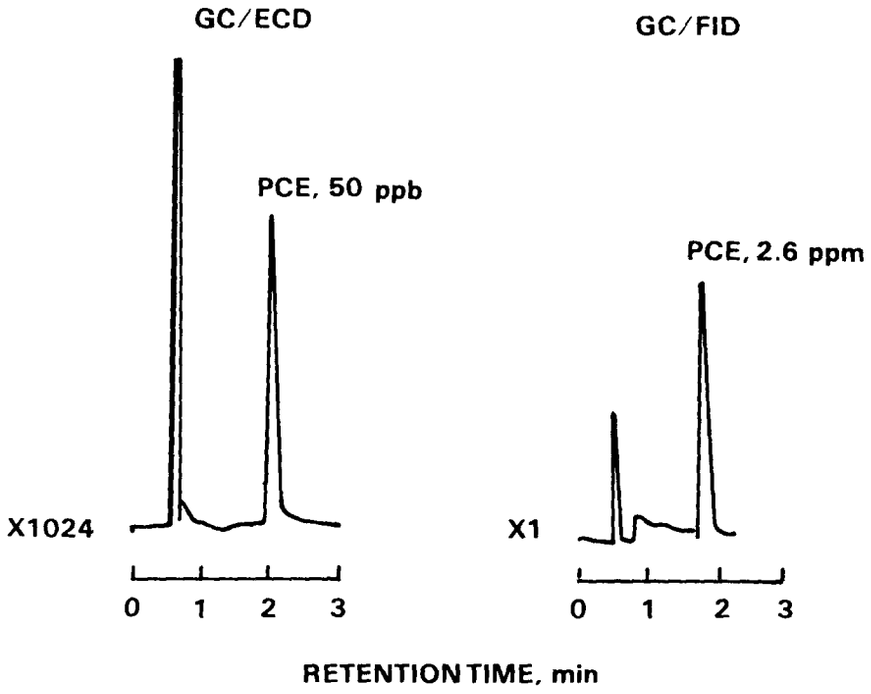

Figure 2. Chromatograms from GC-FID and GC-ECD analyses of PCE.

TABLE 7. INITIAL CONDITIONS AND RESULTS OF SMOG CHAMBER TESTS

Test No.	Date	Test Conditions: Chamber/Radiation	Test Conditions: Reactant Mixture (in zero tank air)	Test Results: Average Rate of PCE Reaction %/h	Test Results: Average Rate of PCE Reaction: Irradiation Period	Test Results: Comments
1	2/25/82	FTIR chamber All lamps on	2 ppm PCE 0.5 ppm NO_2	13.8 9.3	First h First 5 h	-O_3 built up to 0.28 ppm.
2	2/25/82	FTIR chamber All lamps on	2.5 ppm Trichloroethylene 0.5 ppm NO_2			-Trichloroethylene disappeared at the rate of ~25%/h. -O_3 built up to 0.5 ppm.
3	3/1/82	FTIR chamber All lamps on	2 ppm PCE 2 ppm Trichloroethylene 0.5 ppm NO_2	4.0 3.8	First h First 5 h	-Trichloroethylene disappeared at the rate of 30%/h in the first 1 h, and 24.3%/h in the first 5 h. -O_3 built up to 0.21 ppm.
4	3/2/82	FTIR chamber All lamps on	9.2 ppm PCE } Initially 0.5 ppm NO_2 } Add 100 ppb Cl_2 after 4-h irradiation	10.3 4.8 64.0	First h First 4 h First h following Cl_2 injection	-O_3 built up to 0.2 ppm in first 4 h.
5	5/11/82	FTIR chamber All lamps on	2.6 ppm PCE } Initially 0.5 ppm NO_2 } Add 100 ppb Cl_2 after 2-h irradiation	8.1 8.1 21.5	First h First 2 h First h following Cl_2 injection	
6	5/18/82	FTIR chamber All lamps on	2.7 ppm PCE initially. Add 10 ppb Cl_2 after 3.5-h irradiation	13.6 4.7 57.0 14.0	First h First 3.5 h First h following Cl_2 injection First 3 h following Cl_2 injection	

(Continued)

TABLE 7 (Continued).

Test No.	Date	Test Conditions: Chamber/Radiation	Test Conditions: Reactant Mixture (in zero tank air)	Test Results: Average Rate of PCE Reaction %/h	Test Results: Average Rate of PCE Reaction: Irradiation Period	Test Results: Comments
7	5/22/82	FTIR chamber All lamps on	2.8 ppm PCE 0.3 ppm Trichloroacetyl chloride	6.4 6.2	First h First 6 h	-Unusually large amounts of scatter in FTIR measurements of PCE. -Trichloroacetyl chloride disappeared at the rate of ~3%/h.
8	5/26/82	FTIR chamber All lamps on	2.5 ppm PCE } Initially 20% R.H. } Add 50 ppb Cl_2 after 4.5-h irradiation	8.3 5.6 13.7 4.5	First h First 4 h First h following Cl_2 injection First 3 h following Cl_2 injection	
9	6/7/82	FTIR chamber Irradiate with all lamps on for 2 h, let stand in dark for 16 h, irradiate for 3 h, add 300 ppb Cl_2, irradiate for 3 h	1.0 ppm Trichloroacetyl chloride	10.3* 4.1* 11.4* 14.7*	First 2 h of irradiation Dark period (16 h) First 3 h following dark period First 3 h following Cl_2 injection	-Only product observed prior to Cl_2 injection was CO at 0.02 ppm; phosgene was not observed. -Traces of phosgene were observed following Cl_2 injection and irradiation.
10	6/9/82	FTIR chamber All lamps on	2.1 ppm PCE 20 ppb Trichloroacetyl chloride	5.0 5.0	First h First 6 h	-Phosgene built up to ~0.1 ppm.
11	6/21/82	FTIR chamber All lamps off for 3.5 hours, Irradiate with all lamps for 1 hour following dark period	1.6 ppm PCE } 2.9 ppm O_3 } Initially 10.0 ppm CH_4 } Add 200 ppb Cl_2 after 3.5-h standing in dark	1.4 61.0	First 3.5 h First h of irradiation following Cl_2 injection	-O_3 disappeared at the rate of ~0.5%/h during the dark period.

(Continued)

TABLE 7 (Continued).

Test No.	Date	Test Conditions: Chamber/Radiation	Test Conditions: Reactant Mixture (in zero tank air)	Test Results: Average Rate of PCE Reaction %/h	Test Results: Average Rate of PCE Reaction: Irradiation Period	Test Results: Comments
12	4/16/82	360-lit Teflon Bag #1 All lamps on	2.5 ppm PCE 40-60% R.H.	~110	First 0.9 h	-There was an induction period of ~30 min following which PCE disappeared rapidly and completely. -O_3 built up to ~2 ppb.
13	4/19/82	360-lit Teflon Bag #1 All lamps on	3 ppm PCE 40-60% R.H.	~110	First 0.9 h	-Induction period of ~20 min. -O_3 built up to ~2.5 ppb.
14	4/20/82	360-lit Teflon Bag #1 All lamps on	2.6 ppm PCE 92 ppm n-butane 40-60% R.H.	0.3	First 16.6 h	-O_3 built up to 13 ppb.
15	4/21/82	360-lit Teflon Bag #1 All blacklights on All sunlamps off	2.6 ppm PCE 40-60% R.H.	0.4	First 15 h	-O_3 built up to 17 ppb.
16	4/26-27/82	360-lit Teflon Bag #1 All blacklights on All sunlamps off	2.5 ppm PCE 40-60% R.H.	2.5	First 21 h	-O_3 built up to 37 ppb.
17	4/27-28/82	360-lit Teflon Bag #1 All blacklights on All sunlamps off	2.5 ppm PCE 40-60% R.H.	6.5	First 20 h	-O_3 built up to 16 ppb.
18	4/28-29/82	360-lit Teflon Bag #1 All lamps off	2.8 ppm PCE 40-60% R.H.	0.4	First 20 h	

(Continued)

TABLE 7 (Continued).

Test No.	Date	Test Conditions: Chamber/Radiation	Test Conditions: Reactant Mixture (in zero tank air)	Test Results: Average Rate of PCE Reaction %/h	Test Results: Irradiation Period	Test Results: Comments
19	4/29-5/1/82	360-lit Teflon Bag #1	Bag #1: 2.5 ppm PCE	-11.0	First 18 h in Bag #1	-Induction period of 6 h in Bag #1.
		280-lit Teflon Bag # 2 (new unused bag).	Bag #2: 2.4 ppm PCE 40-60% R.H.	0.8	First 17 h in Bag #2	-No induction period in Bag #2.
		Following an 18-h dual bag irradiation test, the contents of Bag #2 were transferred to emptied Bag #1 and were reirradiated. All blacklights on All sunlamps off		4.5	First 22 h following transfer of Bag #2 contents into emptied Bag #1	
20	5/17-18/82	280-lit Teflon Bag #5 (new unused bag). All lamps off	0.7 ppb PCE 40-60% R.H.	-0.2	First 20 h	
21	5/18-19/82	280-lit Teflon Bag #3	Bag #3: 0.7 ppb PCE	-1.1	First 20 h in Bag #3	
		280-lit Teflon Bag #5	Bag #5: 0.6 ppb PCE 40-60% R.H.	-1.3	First 20 hours in Bag #5	
		Dual bag irradiation with all lamps on for 20 h. Add HC in Bag #3 and continue irradiation	Following 20-h irradiation add 0.25 ppmC propylene and 0.75 ppmC n-butane to Bag #3 and continue irradiation	-0.5	First 22 h following propylene/butane injection in Bag #3	
22	5/20-21/82	280-lit Teflon Bag #5 All lamps on	55 ppb PCE 40-60% R.H.	-1.5	First 21 h	

(Continued)

TABLE 7 (Continued).

Test No.	Date	Test Conditions: Chamber/Radiation	Test Conditions: Reactant Mixture (in zero tank air)	Test Results: Average Rate of PCE Reaction %/h	Test Results: Irradiation Period	Test Results: Comments
23	6/8-9/82	280-lit Teflon Bag #5 All lamps on	2.6 ppm PCE 1000 ppm n-butane 40-60% R.H.	0.4	First 24 h	
24	6/9-10/82	280-lit Bag #4 280-lit Bag #5 (dual bag irradiation) All lamps on	2.6 ppm PCE 1000 ppm n-butane 40-60% R.H. } in Bag #4	0.7	First 16 h in Bag #4	
			2.6 ppm PCE 1000 ppm n-butane 40-60% R.H. } in Bag #5	0.3	First 16 h in Bag #5	
25	6/10-11/82	280-lit Bag #4 280-lit Bag #5 (dual bag irradiation All lamps on	2.2 ppm PCE 10,000 ppm n-butane } in Bag #4	2.4	First 17 h in Bag #4	
			2.3 ppm PCE 10,000 ppm n-butane } in Bag #5 40-60% R.H.	0.4	First 17 h in Bag #5	
26	6/16-17/82	280-lit Bag #6 280-lit Bag #7 (dual bag irradiation) All lamps on	2.6 ppm PCE 10 ppm n-butane } in Bag #6	0.4	First 20 h in Bag #6	
			2.6 ppm PCE 10 ppm n-butane } in Bag #7 40-60% R.H.	0.5	First 20 h in Bag #7	
27	6/17-18/82	280-lit Bag #7 All lamps on	2.6 ppm PCE 1 ppm n-butane 40-60% R.H.	0.6	First 22 h in Bag #7	
28	6/21-22/82	280-lit Bag #7 All lamps on	2.6 ppm PCE 1 ppm n-butane 40-60% R.H. } in Bag #7	0.4	First 18 h	
29	6/23-24/82	60-lit Bag #10 60-lit Bag #11 placed inside Pyrex flask (dual bag irradiation) All lamps on	2.6 ppm PCE in Bag #10 2.6 ppm PCE in Bag #11 40-60% R.H.	~110	First 1.1 h in Bag #10	-Induction period of ~0.6 h in Bag #10.
				4	First 21 h in Bag #11	

(Continued)

TABLE 7 (Continued).

Test No.	Date	Test Conditions: Chamber/Radiation	Test Conditions: Reactant Mixture (in zero tank air)	Test Results: Average Rate of PCE Reaction %/h	Test Results: Average Rate of PCE Reaction: Irradiation Period	Test Results: Comments
30	6/25/82	60-lit Bag #10 60-lit Bag #11 placed inside Pyrex flask (dual bag irradiation) All lamps on	2.3 ppm PCE in Bag #11 2.8 ppm PCE in Bag #10 40-60% R.H.	~110 10.6	First 0.9 h in Bag #10 First 5 h in Bag #11	
31	6/28/82	60-lit Bag #12 60-lit Bag #13 (dual bag irradiation outdoors)	2.5 ppm PCE in Bag #12 2.5 ppm PCE in Bag #13 40-60% R.H.	3.0 3.0	First 4 h in Bag #12 First 4 h in Bag #13	-Partly cloudy skies. Bags were placed on aluminum foil. -No induction period.
32	6/29/82	100-lit Bag #12 100-lit Bag #13 (dual bag irradiation outdoors)	2.8 ppm PCE in Bag #12 2.4 ppm PCE in Bag #13 40-60% R.H.	4.7 2.0	First 4.5 h in Bag #12 First 4.5 h in Bag #13	-Partly cloudy skies. -No induction period.
33	6/30/82	100-lit Bag #12 100-lit Bag #13 (dual bag irradiation outdoors)	2.4 ppm PCE in Bag #12 2.3 ppm PCE in Bag #13 40-60% R.H.	2.9 3.5	First 5 h in Bag #12 First 5 h in Bag #13	-Clear skies.
34	7/7-8/82	60-lit Bag #14 placed inside Pyrex flask 60-lit Bag #15 (dual bag irradiation) All lamps on	2.6 ppm PCE in Bag #14 2.6 ppm PCE in Bag #15 40-60% R.H.	1.0 50.0	First 17 h in Bag #14 First 2 h in Bag #15	-Induction period of ~1 hr in Bag #15.

(Continued)

TABLE 7 (Continued).

Test No.	Date	Test Conditions: Chamber/Radiation	Test Conditions: Reactant Mixture (in zero tank air)	Test Results: Average Rate of PCE Reaction %/h	Test Results: Average Rate of PCE Reaction: Irradiation Period	Comments
35	7/8-9/82	60-lit Bag #14 60-lit Bag #15 placed inside Pyrex flask (dual bag irradiation) All lamps on	2.7 ppm PCE in Bag #14 2.8 ppm PCE in Bag #15 40-60% R.H.	20.0 4.0	First 2.5 h in Bag #14 First 18 h in Bag #15	
36	8/12/82	280-lit Bag #18 280-lit Bag #19 All lamps on	50 ppb PCE in Bag #18 50 ppb PCE in Bag #19	0.5 0.5	First 23 h in Bag #18 First 23 h in Bag #19	
37	8/13/82	280-lit Bag #18 280-lit Bag #19 All lamps on	50 ppb PCE, 5 ppb TCAC in Bag #18 50 ppb PCE, 5 ppb TCAC in Bag #19	0.5 0.3	First 11 h in Bag #18 First 11 h in Bag #19	

* Data are for trichloroacetyl chloride reaction

accelerated the PCE reaction by factors of 1.6 to 6.0. This effect is graphically illustrated in Figure 3.

Additional evidence on the role of Cl chemistry was provided by the FTIR tests 1, 3, 4, 5, 6, 8, and 11 and Teflon bag tests 12, 13, 14, and 23-30, in which PCE was irradiated in the presence and the absence of another organic compound capable of scavenging Cl atoms. The scavenger organic compounds used were trichloroethylene (FTIR tests) and n-butane (Teflon bag tests). Results from the FTIR tests showed that trichloroethylene, present at a concentration equal to that of PCE, inhibited the PCE reaction by approximately a factor of 2. The Teflon bag test results showed that n-butane, at concentrations as low as four times that of PCE, reduced the PCE reaction rate from about 100%/h to about 4%/h.

To determine whether direct PCE photolysis is the source of Cl atoms in smog-chamber-irradiated PCE/air systems, Teflon bag tests 18, 20, 23, 24, and 25 were conducted, in which PCE was irradiated alone or in the presence of high n-butane concentrations (1000-10,000 ppm). The rationale for these tests was that in the presence of high concentrations of a radical scavenger (butane) the only cause of PCE disappearance would be direct photolysis. Results suggested that PCE may indeed be photolyzing, albeit at an extremely low rate. Specifically, in tests 23, 24, and 25, (in which PCE was irradiated in the presence of butane) PCE disappeared at 0.4, 0.7, 0.3, 2.4, and 0.4%/h, whereas in tests 18 and 20 (in which the PCE mixtures were allowed to stand in the dark) the PCE disappearance rates were 0.4 and 0.2%/h. At the 70% probability level, the dark and irradiated rates (and their confidence intervals) are calculated to be 0.3 (±0.3)%/h and 0.84 (±1.1)%/h, respectively. This is interpreted to mean that, if PCE photolyzes, its photolysis rate cannot exceed approximately 1.9%/h.

The appearance of an induction period in tests 12, 13, 29, and 34, in which the PCE reacted rapidly, suggested that a PCE reaction product may be a source of Cl atoms and thus exert an autocatalysis-type effect on the PCE reaction. To explore this possibility, we conducted FTIR tests 7 and 10, in which PCE was irradiated before and after injecting trichloroacetyl chloride (TCAC). TCAC was selected because of evidence that it is a PCE photooxidation product (10), and because it was considered the most likely reaction product

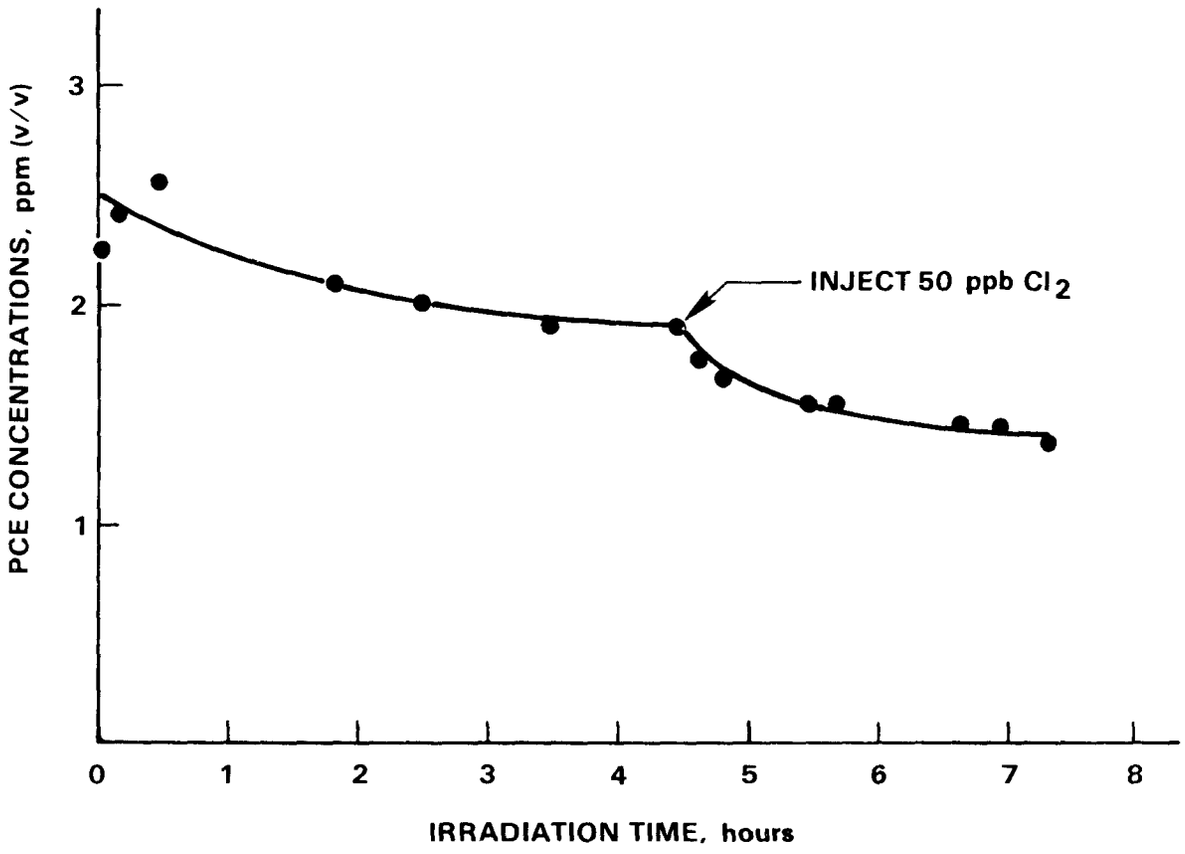

Figure 3. Effect of Cl_2 on photooxidation of PCE (FTIR Chamber).

that could be photolyzed by solar radiation. Although the reaction system in the FTIR system receives a smaller amount of short wavelength radiation (2800-3300Å) than in the bag chambers (see Figure 1), the FTIR chamber walls still transmit enough such radiation for the purposes of these tests. Similar tests were also conducted using Teflon bags (tests 36 and 37). Results showed no perceptible effect of TCAC on the PCE reaction. Also, consistent with this finding was the result of test 9, in which TCAC disappeared rather slowly (10.3%/h) when irradiated in the FTIR chamber. These tests showed that photolysis of TCAC could not be a significant source of Cl atoms in smog chamber photooxidation of PCE.

In an effort to reconcile some conflicting data on PCE reactivity, studies were included of some experimental factors that were known or suspected to have significant effects on the PCE reaction and to differ in the various investigations. Most important among these factors were judged to be: radiation, chamber wall, and initial reactant concentration.

Radiation intensity did vary somewhat with investigation but this variation did not seem to correlate with the variation of the PCE reactivity measurement results. Therefore, this factor was judged to have little relevance to this study's objectives. Radiation spectrum also varied with investigation, especially within the 2800-3300Å wavelength region, and there was no reason to discard this factor as irrelevant. Therefore, several tests were conducted in which the radiation spectrum was varied either by changing the lamp composition or by using glass to filter out selected wavelengths. Specifically, the amount of 2800-3300Å radiation was disproportionately reduced either by shutting off the sunlamps or by placing the reactor bag inside a Pyrex flask. The effects of these modifications on the wavelength spectrum are shown in Figure 1. Teflon bag tests 12, 13, 15, 16, 17, 19, 29, 30, 34, and 35 specifically studied this factor. Results showed the PCE reaction to be extremely sensitive to radiation within the 2800-3300Å wavelength range. With all lamps on and without the glass screen, PCE reacted at rates from 110%/h (four tests) to 20%/h (one test). But with the sunlamps off or when the bag was placed inside the Pyrex flask the PCE reaction rate was from 0.4 to 11.0%/h. While a part of this effect is undoubtedly due to the total light intensity loss caused by the glass screen or by shutting off the sunlamps, this loss is obviously far

too small (see Figure 1) to account for the drastic reduction in the PCE reaction rate. Based on these results, and on the differences in radiation intensity and radiation spectrum between the FTIR chamber and the Teflon bag (see respective k_D values and Figure 1), we concluded that the lower PCE rates observed in the FTIR chamber are mainly due to lower 2800-3300Å radiation intensity.

The smog chamber wall could have two distinct effects on the PCE reaction: one related to the radiation transmitted by the window material, and one related to the scavenging of radicals (especially of Cl atoms) by the inside wall surface. As discussed above, the radiation transmission was found in this study to be a strong factor, suggesting that using sunlamps in smog chambers and Teflon film as window material should cause relatively higher PCE reactivity measurement results. There is an abundance of evidence published on the radical scavenging role of walls. In fact, evidence has been reported for the specific case of Cl atom scavenging by Teflon surfaces. Specifically, NASA investigators reported that the strong inhibitive effect of Cl atoms on O_3 formation from O_2 photolysis was considerably reduced when the Teflon surface of their reactor was exposed to prolonged $CFCl_3$ photolysis reaction (36). The investigators attributed this effect to a reduction in the Cl-scavenging ability of the Teflon walls, caused by excessive deposition of $CFCl_3$ reaction products. Tests 15, 16, 17, and 19 in this study also suggested such an effect. Specifically, when Teflon bag #1 was used four times in succession to irradiate 2.5-2.6 ppm PCE (with the blacklight lamps only) for several hours, the PCE loss rate appeared to increase with bag usage, from 0.4 to 11.0%/h. Considering that bag #1 had been used (and perhaps already been conditioned) before these four tests, and that some of the rate value variation is due to error, these results may or may not reflect a significant surface effect.

Of the initial reactant concentration factors in photochemical reactivity studies, those relevant here are the organic reactant concentration, the NO_x concentration, and the interaction of these two factors or the organic-to-NO_x ratio. In the case of PCE, the data from this study indicated that the NO_x does not appreciably influence the PCE reaction rate. Thus, the reaction rates in the absence of NO_x (tests 6 and 8) are well within the range of values obtained in the presence of NO_x (tests 1, 4, and 5). Teflon bag tests

12, 13, 21, 22, 29, 30, 34, and 35, provide evidence on the effect of PCE concentration. Irradiation of 2.5-3.0 ppm PCE resulted in PCE rates of 20 to 110%/h, whereas for initial PCE concentrations of 0.6-55 ppb, the rates were 0.5 to 1.5%/h. These results show that the initial PCE concentration is a strong factor, and that variation of this factor should be reflected in the various PCE studies' results.

The final objective in this experimental effort was to obtain evidence that would permit extrapolation of the laboratory data on PCE reactivity to the "real atmosphere". As already discussed, such evidence is on the effects on PCE reactivity of radiation intensity and spectrum, co-reactant organic compounds, and PCE concentration. Data on the co-reactant, PCE concentration, and some radiation factors were described above. There were also additional data on the radiation factor obtained in this study, from parallel tests in which PCE-air mixtures were irradiated with the laboratory radiation system and with natural sunlight. Results from the natural sunlight irradiation tests (tests 31, 32 and 33) showed the PCE rates to be 2 to 5%/h. These rates are considerably lower than those observed in the artificial sunlight tests (tests 12, 13, 29, 30, and 35), and comparable to those observed when the 2800-3300Å component was reduced (i.e., tests 15, 16, 17, 29, 30, 34, and 35). This means that use of Teflon film smog chambers and of radiation with a strong near-UV component would tend to cause unrealistically high PCE reactivity results.

SECTION 5

DISCUSSION

The evidence obtained in this and the previous studies on the effects upon PCE reactivity of the initial reactant concentrations, Cl_2, and organic co-reactants, is consistent with a Cl-instigated chain photooxidation mechanism analogous to the OH-initiated mechanism accepted in current smog chemistry:

$$CCl_2 = CCl_2 + Cl \rightarrow CCl_3CCl_2$$

$$CCl_3CCl_2 + O_2 \rightarrow CCl_3CCl_2O_2$$

$$CCl_3CCl_2O_2 + NO \rightarrow CCl_3CCl_2O + NO_2 \xrightarrow{h\nu} NO + O \xrightarrow{O_2} O_3$$

$$CCl_3CCl_2O \rightarrow CCl_3C(O)Cl + Cl$$

$$\rightarrow COCl_2 + CCl_3 \xrightarrow{O_2} COCl_2 + ClO$$

In the absence of NO, main reaction products should be $CCl_3CCl(O)$ and $COCl_2$. In the presence of moderate concentrations of NO, O_3 also should form through photolysis of NO_2, as well as PAN-type products arising from the CCl_3CO radical through reactions similar to those in smog chemistry for hydrocarbons/aldehydes. Finally, as with all VOC/NO_x systems, excess NO should suppress production of O_3, PAN and other oxidants.

Conceivable sources of Cl atoms in the irradiated PCE/NO_x system are several, for example:

$$OH + CCl_2 = CCl_2 \rightarrow\rightarrow Cl \ (\text{or} \rightarrow Cl_2 \overset{h\nu}{\rightarrow} 2Cl) \qquad \text{or}$$

$$O(^3P) + CCl_2 = CCl_2 \rightarrow\rightarrow Cl \ (\text{or } Cl_2 \overset{h\nu}{\rightarrow} 2Cl) \qquad \text{or}$$

$$CCl_2 = CCl_2 \xrightarrow{h\nu} Cl + CCl_2 = CCl$$

Additionally, photolysis of the $CCl_3CCl(O)$ product could produce Cl atoms, which would tend to cause an "autocatalysis"-type acceleration of PCE consumption.

The rate constants for the PCE reactions with $O(^3P)$ and OH are, respectively, 0.8×10^{-13} cm^3 $molecule^{-1}$ sec^{-1} (29) and 2×10^{-13} cm^3 $molecule^{-1}$ sec^{-1} (27), whereas the concentrations of $O(^3P)$ and OH in photochemical VOC/NO_x systems are roughly 10^{-8} ppm and 10^{-7} ppm, respectively (37). These data show that the reaction of PCE with $O(^3P)$ may be relatively less important. Furthermore, Appleby found that PCE disappeared rapidly when irradiated in a Teflon bag in mixture with pure N_2 (15). This finding, <u>if indeed valid</u>, would suggest that neither $O(^3P)$ nor OH are necessarily the main instigators of the Cl-releasing process. It is conceivable, however, that some atmospheric O_2 permeated the Teflon bag, in which case OH could not be ruled out as an instigator. We concluded from tests 7, 10, 36, and 37 of the current study that photolysis of $CCl_3CCl(O)$ also should be ruled out as a source of Cl atoms. These findings and the results of tests 18, 20, 23, 24, and 25 of this study tend to support direct photolysis of PCE as the most likely--although weak--source of Cl atoms in smog chamber irradiated PCE/air or PCE/NO_x/air systems. Consistent with this deduction is the absorption spectrum in Figure 4, showing that liquid PCE--and conceivably gaseous PCE also--absorbs at wavelengths near 3000Å (38). Other sources, e.g., reaction with OH, are not likely but cannot be completely ruled out either.

The next question of interest is whether Cl-instigated PCE photooxidation explains the wide diversity of PCE reactivity results in the various studies.

With respect to the consumption rate reactivity, the present study and two others (5,6) resulted in the highest values, ranging from 20 to 110%/h, whereas all the other studies except Dilling et al. (9) resulted in values of 2.3 to 9.5%/h. Factors our current study identified as having strong effects on the PCE consumption rate are the radiation intensity within the 2800-3300Å wavelength region, the presence of organic co-reactants, and the PCE concentration. Since widely diverse data were obtained for comparable PCE concentrations, and there were no organic co-reactants except the background

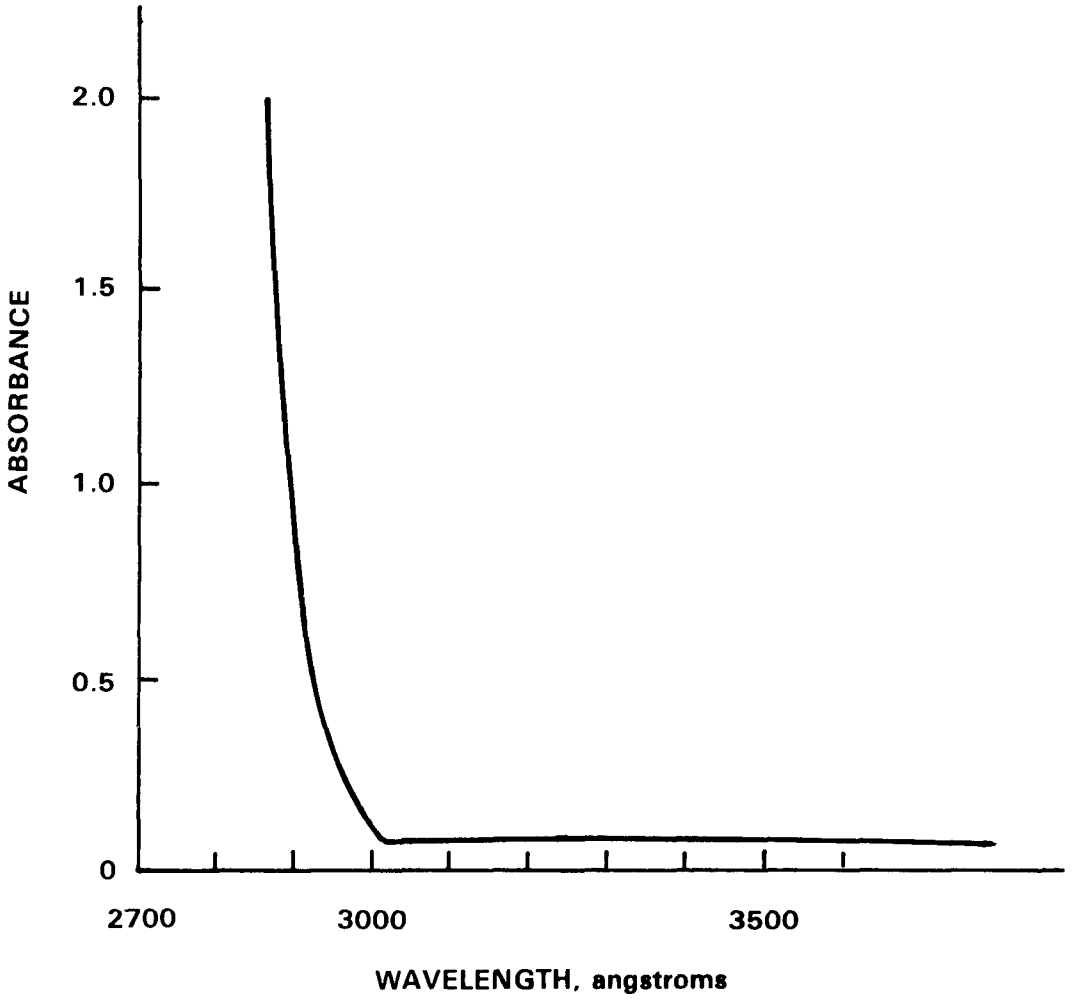

Figure 4. UV absorption spectrum of liquid perchloroethylene.

contaminants (see Table 3), the radiation factor could conceivably explain the diversity. PCE investigators have not reported complete quantitative data on this radiation factor but the little qualitative information available is usually consistent with this explanation. Thus, of the chambers reporting low consumption rate data, the ones of Brummelle et al. (3), Wilson (7), Kopczynski (16), Gay et al. (10), Yanagihara et al. (18), and the FTIR chamber of the present study used as window material either glass or Tedlar film both of which are less transparent to 2800-3300Å radiation than Teflon (39), the window material used in our smog chamber and the Lillian et al. (6) studies. Sickles et al. (22), who also reported low consumption rate results, used Teflon chambers but they also used natural sunlight radiation which, relative to the radiation used in the present study, was found to cause lower consumption rates (tests 31, 32, and 33 versus tests 12, 13, 15-17, 29, 30, 34, and 35). The Dimitriades/Joshi chamber (5), associated with high consumption rate data, was made of glass but because of its relatively small volume and cylindrical shape, the 2800-3300Å radiation generated by the chamber's six sunlamps was more intense than in all the larger chambers except the FTIR chamber of this study.

Differences in 2800-3300Å radiation apparently do not explain the difference in consumption rate results observed between the Dimitriades and Joshi chamber and (5) the FTIR chamber of this study. Thus, considering these two chambers' diameters, the numbers of sunlamps used, and the fact that the chambers are made of the same material, the 2800-3300Å radiation intensity should be higher in the FTIR chamber. Yet the PCE consumption rates observed for comparable initial PCE concentrations were higher for the Dimitriades and Joshi chamber by a factor of approximately 2. The disagreement in this case may be related to chamber wall effects. Thus, the pattern of PCE disappearance in the Dimitriades and Joshi chamber (rapid acceleration of the reaction following an induction period) is consistent with little or no scavenging of Cl atoms by the chamber walls. In contrast, the uniform PCE disappearance observed in the FTIR chamber and the tendency for the effect of injected Cl_2 to diminish with time (see Figure 3) are consistent with strong Cl scavenging by the chamber walls. Therefore, a difference in the walls' Cl-scavenging ability (evidently due to different usage histories) most likely caused the disagreement in PCE consumption rate results between the two chambers.

Finally, no attempts were made to reconcile the reactivity data obtained by Schuck and Doyle (12) and by Dilling et al, (9) with those of the other studies. The effects of the Schuck and Doyle chamber's unorthodox design (lamps were inside the chamber) and of the unrealistic radiation and reactant concentration conditions used by Dilling et al. are not well enough understood to permit meaningful comparisons with the other studies.

With respect to the O_3/O_x yield reactivity, the proposed Cl-photooxidation mechanism dictates that such reactivity should be influenced by the same factors that influence the consumption rate reactivity and, additionally, by the PCE-to-NO_x ratio factor. This means that of the reported studies, those that resulted in the highest consumption rate reactivity data, and those that used optimum PCE-to-NO_x ratio conditions in the smog chamber tests, should also have resulted in the highest O_3/O_x yield reactivity data. This is indeed the case, as the data in Tables 3 and 7 show. Thus, the highest O_3/O_x yield reactivity data were obtained by Lillian et al. (6), Dimitriades and Joshi (5), Sickles et al. (22), Gay (20), and the present study. Of these, Lillian et al., Dimitriades and Joshi, and the present study also gave high consumption rate reactivity results. Gay, Sickles et al. and some tests of this study used a PCE-to-NO_x ratio of 20, which is much more conducive to O_3/O_x formation (22) than the ratios of 2-8 or >100 used in the other studies.

To summarize the discussion and conclusions thus far, the evidence obtained in this study is consistent with the deduction derived from past studies that in smog chamber testing of PCE, current smog chemistry, with the OH attack as its key reaction step, is not operative; instead, a Cl-instigated chain photo-oxidation chemistry is operative. Furthermore, in the light of this new evidence, the Cl-instigated photooxidation mechanism seems to provide reasonable explanations of the reactivity differences observed in the various smog chambers. The most significant feature, however, of this mechanism is that, relative to the OH-initiated mechanism of current smog chemistry, it results in substantially higher levels of PCE reactivity. This raises then the final and most important question, which is whether the Cl-instigated photooxidation chemistry observed in smog chambers can also produce O_3 in the real atmosphere.

Analysis of atmospheric data indicated a negligibly reactive nature for PCE which suggests that the Cl chemistry is not effective in the real atmosphere.

But such data are usually too limited to support reliable conclusions. One must rely, therefore, on existing laboratory evidence and theoretical deductions. The relevant laboratory evidence is the smog chamber data on the effects of various factors on PCE consumption in irradiated PCE/NO_x systems. These factors, their effects, and their implications regarding the question in hand are discussed below.

First, the PCE concentration factor was found in our present study to have a strong co-directional effect on PCE consumption rate. Thus, the PCE consumption rates for initial PCE concentrations of 2.5-3.0 ppm were 20 to 110%/h (tests 12, 13, 34, and 35), whereas for initial PCE concentrations of 0.6-55 ppb, the rates were 0.5 to 1.5%/h (tests 21, 22 and 36). That is, reducing initial PCE concentration by 2 to 3 orders of magnitude reduced the normalized PCE consumption rate by about 2 orders of magnitude. Extrapolation of these results to the real atmosphere, where the PCE concentration is only a few ppt, can be made only very roughly. Since the normalized PCE consumption rate is a function of PCE concentration, it follows that the order of the PCE consumption reaction with respect to the PCE reactant must be greater than 1. Lacking detailed mechanism and complete kinetic data, the assumption is made that the kinetic rate equation is $R = k[PCE]^n$ (where $n > 1$) and the normalized rate (R', %/h) equation is

$$R' \equiv \frac{R}{[PCE]} \times 100 = k[PCE]^{n-1}.$$

Using these authors' data (tests 12, 13, 21, 22, 29, 30, and 34-36), k and n are estimated to be 31.6 and 1.77, respectively. From these results it follows that for the ambient hemispheric PCE concentration of 40 ppt (25), the PCE consumption rate should be 0.01%/h. In urban atmospheres, where the PCE concentration can reach 1-7 ppb (23), the PCE consumption rate can be as high as 1.75%/h. For comparison, the atmospheric reaction rate of ethane, based on its reaction with OH ($k_{OH} = 0.3 \times 10^{-12} cm^3$ molecules sec^{-1}, $[OH] = 3\text{-}5 \times 10^5$ molecules/cm^3) is 0.03 to 0.04%/h. Similar results are also derived from the Dilling et al. data (9). Dilling et al. reported that reduction of the initial PCE concentration in their smog chamber from 100 ppm to 10 ppm caused the normalized PCE consumption rate to be reduced by a factor of 2.9, down to

a half-life of 11.2 h. Again using again the rate equation $R = k[PCE]^n$ (where $n > 1$), and the Dilling et al. data, k and n are calculated to be 33.1 and 1.47, respectively, values that lead to a PCE consumption rate in the real atmosphere from 0 004%/h (hemispheric average) to 0.7%/h (urban maximum). The highest rates are higher than those of the ethane reaction with OH in the real atmosphere or of the PCE reaction with OH (Table 5). Therefore, based on the effect of the PCE concentration factor alone, the PCE consumption rate reactivity, and by inference the O_3/O_x yield reactivity also, could be significant in the real atmosphere.

Co-reactant VOCs capable of competing with PCE for Cl atoms were found in our present study and by others (9,15,40) to inhibit the PCE reaction in smog chambers extremely strongly (see, for example, results from tests 12-14, and 23-30 of our study). This finding is consistent with available kinetic data showing the rate constant for the Cl + PCE reaction ($5.3 \times 10^{-13} cm^3$ molecule^{-1} sec^{-1}), to be 2 to 3 orders of magnitude lower than those for the reactions of Cl with non-methane hydrocarbons (31). Another role of the co-reactants, also resulting in inhibition of the PCE reaction, could be to scavenge the radicals (e.g. OH) that instigate the Cl-releasing process. Applying these results to the real atmosphere, where PCE is invariably accompanied by hydrocarbons at concentrations several hundred times its own, the PCE reaction with Cl should proceed at a rate 4 to 5 orders of magnitude lower than the rates of the non-methane hydrocarbon reactions with Cl. Since the ambient hydrocarbons are known to have lifetimes of hours or longer (41), and their disappearance is due mainly to their reaction with OH rather than with Cl, the PCE reaction with Cl in the real atmosphere seems too slow to have any significance. Therefore, based on the effect of the co-reactant factor, the PCE reactivity in the real atmosphere should be negligible.

In conclusion, although the laboratory evidence currently available is not absolutely consistent and complete, it does permit collective interpretation of the diverse smog chamber data available and extrapolation of such data and findings to the real atmosphere. Furthermore, notwithstanding its limitations, the evidence clearly points to the conclusion that Cl-instigated photooxidation of PCE cannot occur in the real atmosphere at a high enough rate for substantial O_3/O_x production. The main bases of this conclusion is that in ordinary urban

atmospheres, Cl atoms are effectively scavenged by the unavoidably present hydrocarbon pollutants. In rural atmospheres, it is, additionally, the extremely low concentrations at which PCE typically occurs. Thus, contrary to the smog chamber data, and to the viewpoint held thus far within EPA, PCE is now judged to contribute less to the ambient photochemical O_3/O_x problem than equal concentrations of ethane.

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APPENDIX

DESCRIPTION OF EXPERIMENTAL APPARATUS AND PROCEDURES

The experimental apparatus used in this study included (a) a long path Fourier Transform Infrared Spectrometer (FTIR), the absorption cell of which was used as a smog chamber, (b) an aluminum box inside which plastic film bags could be irradiated by artificial sunlight, (c) an air purification system, and (d) analytical equipment. The experimental apparatus and procedures are described below, except where such information has been reported elsewhere.

THE FTIR SPECTROMETER AND SMOG CHAMBER

Construction design and optics-related information on the FTIR spectrometer and smog chamber have been given elsewhere (1). Figure A-1 shows a schematic of the system. The infrared absorption coefficients of reactants and products were determined in most cases for conditions similar to those of the irradiation experiments. Thus, known small amounts of gaseous samples were injected in the absorption cell, diluted to the concentration level desired with zero grade air, and spectra were taken at 23°C and 1 atmosphere (760 torr) using 0.5 or 1 wave number spectral resolution and 360 meters optical path length. PCE was measured from its infrared absorption bands at 780, 805, and 918 cm^{-1}, trichloroethylene at 848 and 940 cm^{-1}, and trichloroacetyl chloride at 745 and 1250 cm^{-1}.

The requisite concentrations of the reactant vapors were obtained for irradiation by diluting torr amounts of the chemical compound in a glass manifold and glass gas handling system. The dilution system consisted of a multiport manifold and a 12.4-l dilution flask. Two MKS Baratron pressure gauges were used to measure accurately pressure in the 0-10 and 0-1000 torr ranges. Once the appropriate reactant concentration was established in the dilution flask, the flask contents were transferred to the partially evacuated long path infrared cell via the glass manifold to injection ports located in the five spacers separating the cylindrical sections of the cell.

Linde zero grade compressed tank air containing less than 0.1 ppmC total organic impurities was used as a diluent gas in the FTIR chamber experiments. Filling the 690-liter chamber with tank air resulted in a low water vapor

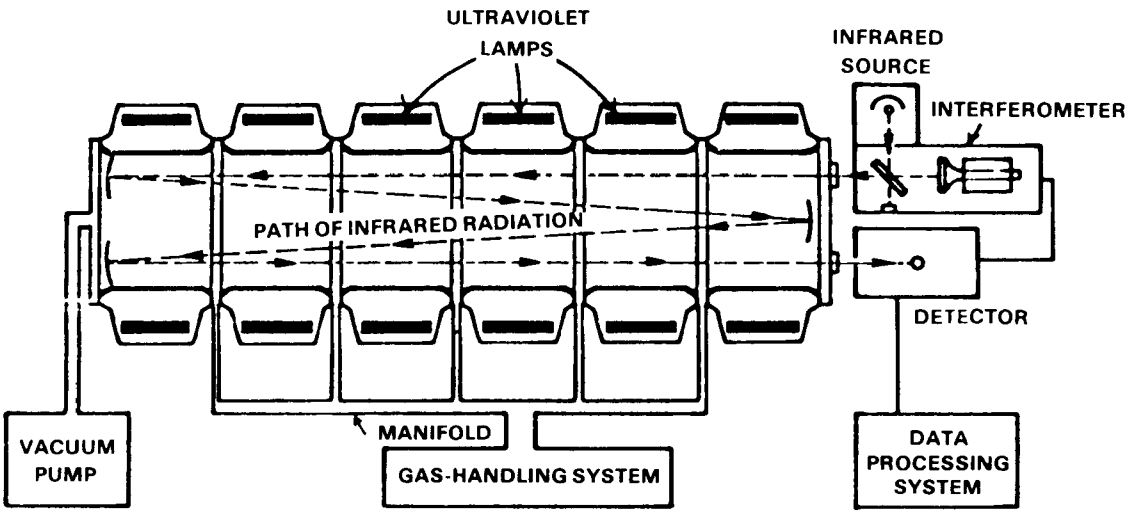

Figure A-1. Schematic of long path infrared photochemical reaction chamber system.

content (approximately 100 ppm H_2O). To increase the water vapor content for those experiments requiring higher relative humidity the tank air was bubbled through 30 ml of distilled water, using a course frit bubbler.

The PCE used in these experiments was research grade Eastman tetrachloroethylene freshly purified by redistillation from which only the middle fraction, in the 119-119.5°C range, was used. The trichloroethylene used was ACS-certified research grade and was used without further purification. The trichloroacetyl chloride was Kodak research grade and was also used without further purification. Gases such as nitrogen dioxide (NO_2), nitric oxide (NO), and chlorine (Cl_2) were of high purity research grade, obtained in lecture bottles and used without any further purification.

THE BAG CHAMBER FACILITY

Irradiation of PCE/air blends in Teflon bags was carried out in an air-conditioned aluminum box 0.78 m wide, 1.35 m long, and 1.12 m high. Two banks of 40-watt ultraviolet fluorescent lamps, evenly distributed along two lengths inside the chamber, provided the necessary irradiation. In these experiments 22 General Electric F40 BLB filtered blacklamps with energy maxima at 3660Å and four Westinghouse GS40 sunlamps with energy maxima at 3160Å were used to simulate lower atmospheric solar radiation between 2900 and 3800Å. The light intensity was measured by irradiating NO_2 in N_2 (2). Resultant first order rate constant, k_d, for NO_2 disappearance was 0.45 min^{-1}, representing total NO_2 disappearance due to photolysis and secondary reaction of O atoms with NO_2. Since the photolysis rate constant, k_1, is 0.64 k_d (3), k_1 for this irradiation system is 0.29 min^{-1}. The air-conditioned irradiation box maintained a temperature of 25°C (± 2°C) around the bags during irradiation. In this study one or two bags were suspended in the chamber. Air samples for analytical instruments were withdrawn via FEP Teflon tubing. When two bags were irradiated simultaneously, sampling was alternated between the bags using a microprocessor-controlled (Chrontrol, Lindburgh Enterprises) three-way Teflon solenoid valve (Model DV3 122A1, The Fluorocarbon Company).

The bags were made of DuPont Type A (heat sealable) 2-mil FEP Teflon film heat-sealed with a thermal impulse heat sealer (Vertrod Corporation, Brooklyn, NY). FEP Teflon was chosen for its chemical inertness, flexibility, and

transparency to near-UV radiation. Before use the bags were flushed with clean air several times and evacuated, filled with clean air and placed in the irradiation box for twenty-four hours, and finally evacuated.

A laboratory purification system supplied clean air for preparing reaction mixtures. This system consisted of a Thomas Teflon-lined diaphragm pump (Model 917CA18TFE), which draws air from the laboratory roof and pressurizes it into a 1.8 liter stainless steel sphere that serves as a ballast. From there the air is forced through a bowl moisture trap and pressure gauge, and through a catalytic combustor consisting of a 13/16" i.d. X 14" stainless steel pipe packed with rhodium-on-aluminum pellet catalyst (Engelhard) held at 600°C in a Lindbergh tube furnace. After combustion to remove hydrocarbons the air stream is cooled by passing through 12 ft. of 1/4" o.d. stainless steel tubing submerged in water at 20°C, and further purified by passing through three Wilkerson (Model X03-02-600) filters. These three filters are filled with silica gel (for moisture control), Purafil (Borg Warner) odor-oxidant (for NO and NO_2 removal), and activated charcoal (for hydrocarbon removal), respectively. The chemically filtered air finally passes through a particle filter to remove particles larger than 0.2 micron (Matheson Model 6184P4). A Brooks needle valve and Rotameter (Model 1355CB1C1AAA) control and monitor the flow. All system tubing connections are either Teflon or stainless steel.

Contaminants in the air supplied by this system are: NO_x < 2 ppb, O_3 < 0.5 ppb, CO ≤ 0.1 ppm, CH_4 0.7 ppm, and total nonmethane vapor organics 50 ppbC (mostly ethane and propane). Water vapor within the bags is generally near ambient levels due to rapid permeation of ambient moisture through the Teflon film.

ANALYTICAL METHODS

As previously discussed, the FTIR spectrometer made almost all necessary measurements of the FTIR smog chamber program. Analytical needs of the Teflon bag program were limited to measuring PCE and butane and are discussed here.

Gas chromatography with flame ionization detection (GC-FID) was the PCE analysis method for all irradiation tests in which initial PCE concentration was 2-3 ppm; the same method was also used for the butane measurements. For

the irradiation tests in which the initial PCE concentration was below 100 ppb, gas chromatography with electron capture detection was preferred.

The gas chromatograph was positioned on a bench one meter from the irradiation chamber. Sample was drawn from the irradiation bags through the GC gas sampling valve using the laboratory's vacuum line or a pump. The sample flow was turned off seven seconds before each GC injection to allow the sampling loop pressure to come to atmospheric pressure, thereby eliminating a source of measurement variability. An electronic timer was programmed to turn on and off the sample flow, injection valve, and peak area integrator at the desired time intervals. When dual bag irradiations were conducted, a Teflon 3-way solenoid valve was used to control the sampling. The GC analysis parameters are listed in Table A-1 and Figure A-2 shows a typical chromatogram.

For quality assurance, tests were conducted to determine the linearity of detector response and the precision and reproducibility of the method. To test the response-linearity of the GC-FID method, samples were prepared using a 1000-ml syringe to dilute a sample of PCE four times. Resultant PCE concentrations in the samples ranged from 12 to 0.3 ppm. Results gave a linear regression correlation coefficient $r^2 = 0.998$, which was interpreted to mean that the FID response to PCE was linear.

The initial reactant mixtures prepared for irradiation were also used as calibration standards. These mixtures were prepared by syringe injection of known amounts of liquid PCE into Teflon bags filled with known volumes of air. Data from repeated GC/FID measurements upon several such mixtures are listed in Table A-2. These data were statistically treated by an Analysis-Of-Variance method to determine standard deviations (S) associated (a) with sampling and GC/FID measurements upon a single calibration mixture (S_s), (b) with preparation of calibration mixtures (S_c) and (c) with day-to-day variation in instrument response (S_i). Resultant standard deviations, expressed in terms of Coefficients of Variation (CV ≡ S X 100/mean) are included in Table A-2.

The GC-ECD method was the same as the GC-FID method, except that a tritium-scandium electron capture detector was used in lieu of FID, and 5%-methane-in-argon was used as carrier instead of He. The GC-ECD analysis parameters are listed in Table A-3. Figure A-3 shows a typical chromatogram.

TABLE A-1. PCE-FID ANALYSIS PARAMETERS

Gas Chromatograph	Perkin Elmer Model 900
Integrator	Hewlett-Packard Model 3390A
Gas Sampling Valve	Seiscor (Tulsa, Oklahoma)
Detector	Flame Ionization
Column	6-ft X 1/8-inch o.d. ss packed with 10% SF-96 on 60/80 mesh Chromosorb W-AW
Temperatures	
Column	100°C
Detector	250°C
Sample Valve	Room Temperature, 24°C
Carrier Gas	Helium
Flow Rates	
Carrier	25 ml/min
Detector Air	536 ml/min
Detector Hydrogen	39 ml/min
Sample	160 ml/min
Sample Size	2 and 4 ml loops used
Detector Voltage	1 volt, 0.1 volt
Chart Speed	0.9 cm/min
Total Cycle Time	5 min

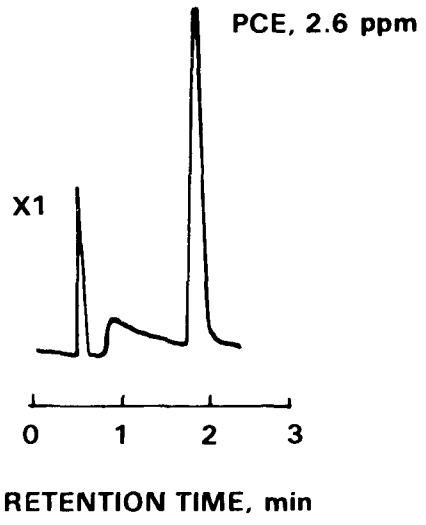

Figure A-2. Chromatogram of GC-FID analysis of PCE.

TABLE A-2. PRECISION OF GC/FID ANALYSIS OF PCE CALIBRATION MIXTURES

Date	GC/FID Data for 4-cc Samples (Arbitrary Units) Calibration Mixture #1 (2.592 ppm PCE)							Calibration Mixture #2 (2.592 ppm PCE)					
4/20	3103	3121	3113										
4/21	3208	3251	3221	3189									
4/26	3085	3266	3310										
4/27	3005	3030	3022										
5/11	3009	3083	3095					2991	2991	2903			
5/12	3204	3231	3213					3189	3198	3192	3167		
6/8	2921	2968	2955	2966				2862	2934	2857	2874		
6/9	2904	2906						2968	2940				
	GC/FID Data for 2-cc Samples (Arbitrary Units)												
6/16	1299	1302	1314	1314	1302	1332		1317	1323	1336			
6/17	1342	1326	1343	1333	1343			1305	1297	1285	1293	1281	1296
6/21	1274	1286	1292	1299	1353	1311	1306						
6/24	1301	1313						1277	1266				
6/29	1036	1039	1073	1062	1042			1220	1206	1239	1241	1198	
6/30	1232	1244	1237	1241	1224			1264	1267	1241	1240	1267	
7/6	1168	1192	1203					1258	1207	1192			
7/7	1151	1146						1251	1232				
7/8	1227	1243						1237	1229				
7/9	1274	1292						1298	1312				

Analysis of Variance

	CV_s [a]	CV_c [b]	CV_i [c]
Data for 4-cc, Mix #1	3%	-	6%
Data for 4-cc, Mix #1, #2	2%	4%	12%
Data for 2-cc, Mix #1, #2	1%	11%	23%

a/ Coefficient of variation associated with sampling and GC/FID measurements upon a single calibration mixture.

b/ Coefficient of variation associated with preparation of calibration mixture.

c/ Coefficient of variation associated with day-to-day variation in calibration mixture preparation and instrument response.

TABLE A-3. PCE-ECD ANALYSIS PARAMETERS

Gas Chromatograph	Perkin Elmer Model 900
Integrator	Hewlett-Packard Model 3390A
Gas Sampling Valve	Seiscor 6-port
Detector	Electron Capture, Analog Technology Corporation, Model 140
Column	6-ft X 1/8-inch o.d. ss packed with 10% SF-96 on 60/80 mesh Chromosorb W-AW
Carrier Gas	5% methane in argon
Temperatures	
Column	100°C
Detector	160°C
Sample Valve	Room Temperature, 24°C
Flow Rates	
Carrier	25 ml/min
Sample	160 ml/min
Sample Size	0.63 ml
Detector Voltage	1 mv
Chart Speed	0.9 cm/min
Total Cycle Time	5 min

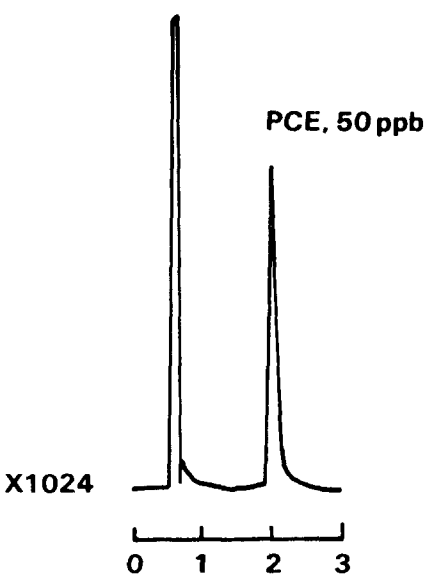

Figure A-3. Chromatogram of GC-ECD analysis of PCE.

For calibration of the GC-ECD system, standard PCE mixtures were prepared using a 163-ml exponential dilution flask. First, 4 μl of PCE was injected into a 1000-ml heated glass bulb. Then 0.25 ml of the glass bulb contents was injected into the dilution flask. The outlet of the flask was connected to the GC gas sampling valve, and tank air was used as the diluent gas. A sample from the exponential dilution flask was analyzed every five minutes. The response-versus-concentration curve (Figure A-4) was not linear, but it did fit a power curve function with a regression correlation coefficient R^2 of 0.994. The precision of the method was determined from 14 repetitive analyses of a 267-ppb PCE/air sample. The relative standard deviation was 2.3% and the 95% confidence interval was ±4.8%. The method's reproducibility was estimated from the calibration input variables (syringe error, volume error, and flow rate error) to be ±18% (95% confidence interval).

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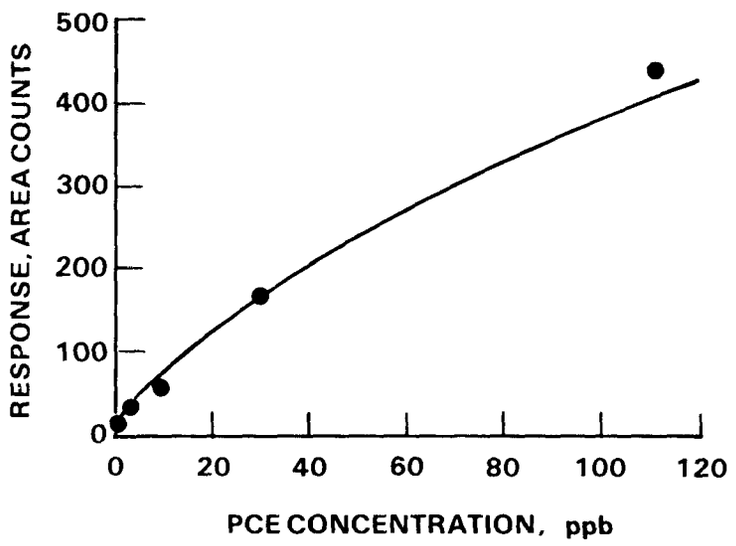

Figure A-4. PCE calibration curve for GC-ECD analysis.

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