



## Project Summary

# Photochemical Reactivity of Perchloroethylene

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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 to understand further the role of PCE in the  $O_3/O_x$  problem, a smog chamber testing program was conducted. The program's objectives were (a) to generate additional evidence on 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 ethane.

*This Project Summary was developed by EPA's Environmental Sciences Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).*

### Introduction

The approach adopted by the U.S. 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 from time to time produced lists of VOCs that could be exempted from control by virtue of their negligibly low photochemical reactivity.

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. That early judgment was based on Los Angeles Air Pollution Control District (LAAPCD) smog chamber studies of solvent reactivities in the 1960s, which are now considered to be in error. In the years following the LAAPCD studies, there were several other PCE reactivity studies upon which EPA judged that PCE's photochemical reactivity is not sufficiently low to justify total exemption from control.

EPA's latest judgment on PCE reactivity was based mainly on findings from EPA and EPA-sponsored studies in the mid-1970s. Other studies during that period 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, some directly addressed to PCE's  $O_3$ -forming reactivity and some to various mechanisms of PCE photooxidation. The new evidence appeared again to partly agree and partly disagree with the latest EPA judgment on PCE reactivity. However, it became also apparent that most of the conflicting evidence could be reconciled, which led

to reexamining the question of PCE reactivity in the light of the reconciled evidence. We concluded that more experimental testing was needed to completely reconcile conflicting evidence and to support a more definitive and reliable judgment regarding the reactivity of PCE.

This report describes 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 an understanding of the rationale behind the objectives and design of our new study, and the reanalysis and interpretation of the experimental evidence, we discuss the concept of reactivity, the past data and other relevant literature on PCE reactivity, and the current specific issues and information gaps.

### The Concept of Reactivity

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, in 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 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. There are problems, however, in using the existing data base for this particular reactivity index. These problems forced researchers and regulators to (a) turn to simple, two-class reactivity classification schemes ("reactive," "unreactive") in preference to individual VOC reactivity ranking schemes, and (b) consider other less direct but more usable reactivity indices. The reactivity index used here in addition to the " $O_3/O_x$  yield" was the "VOC consumption rate" reactivity. The significance of the latter index 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, and, as discussed later, by this study also.

### 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 were included in this analysis. Each piece of reactivity data was critiqued to the extent allowed by the reported information, and labeled as supporting a "negligibly reactive" or "reactive" classification for PCE. "Negligibly reactive" was 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).

Existing data on  $O_3/O_x$  yield and consumption rate reactivities were extracted from 13 formal and informal reports on laboratory studies. Estimates of consumption rate reactivity of PCE were also derived from PCE emission and aerometric data.

Examination of those data revealed considerable inconsistencies. Thus, of the 13 studies, 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.

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. 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. Such a value is known, and based on that

and on the OH concentration in the atmosphere, the rate of PCE consumption in ambient air was computed to be 0.36%/h. Such a rate is 1 to 1½ orders of magnitude lower than the rates observed in smog chambers, which means either that the performance of the smog chambers was not 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. Results showed 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. 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?
4. Is this species and associated chemistry operative in the real atmosphere?

With respect to the first and second questions, past basic and smog chamber studies suggested that the PCE consumption observed in smog chambers is caused by a Cl-instigated chain photooxidation process which, apparently, is also capable of generating  $O_3$ . The evidence available, however, on the origin of the Cl atoms in such systems, and on the effects of experimental factors on the PCE reaction with Cl, was lacking. In the absence of such evidence, the support of the Cl-instigated mechanism was weak, and the question of whether this mechanism can explain the inconsistent results of past

studies could not be answered. Furthermore, there was no evidence that the Cl-instigated photooxidation mechanism, presumably operative in smog chamber systems, is necessarily operative in the real atmosphere also. These deficiencies of the past evidence led these investigators to conduct a new PCE study, and to reexamine the question of PCE reactivity in the light of the new experimental evidence.

## 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 to (a) confirm that in the smog chamber measurements of PCE reactivity the operative chemistry in PCE degradation is Cl- rather than OH-instigated photochemistry, (b) understand such Cl chemistry well enough to reconcile some seemingly conflicting evidence, and (c) 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 the absorption cell of a long path Fourier Transform Infrared Spectrophotometer (FTIR) and several bags made of Teflon as smog chambers. Irradiation in both cases was provided by fluorescent lamps simulating natural sunlight.

Thirty-seven smog chamber tests were conducted. Results showed that injection of Cl<sub>2</sub> accelerated strongly the PCE reaction, and that presence of a Cl-scavenging co-reactant inhibited the PCE reaction drastically. These results indicated that PCE consumption was instigated by Cl atoms. To identify the sources of Cl atoms, tests were conducted to determine whether PCE or its reaction products

photolyze to Cl atoms. Results suggested that direct photolysis of PCE is the most likely source of Cl atoms, although other sources (e.g., the PCE + OH reaction) could not be completely ruled out.

In an effort to reconcile some inconsistencies in the data from past studies, tests were included to study 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 such factors were: radiation spectrum, chamber wall, and initial reactant concentration. Of these factors, radiation spectrum probably varied the most with investigation, especially within the 2800-3300Å wavelength region. Several tests, therefore, were conducted in which this factor was varied either by changing the lamp composition or by using glass to screen out selected wavelengths. Results showed that the PCE reaction was extremely sensitive to radiation within the 2800-3300Å wavelength range.

Two smog chamber wall factors were investigated: one related to the radiation transmitted by the window material, and the other related to the scavenging of radicals—especially of Cl atoms—by the inside wall surface. As already discussed, the radiation transmission factor in this study was a strong one. In regards to the radical scavenging role of walls, tests in this study were merely suggestive of such an effect.

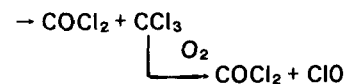
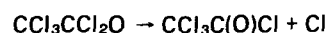
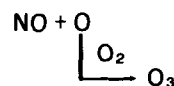
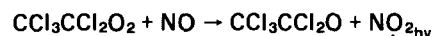
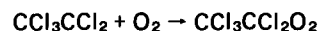
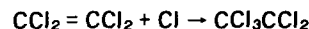
Of the initial reactant concentration factors in photochemical reactivity studies, those relevant here are the concentration of the organic reactant, the concentration of NO<sub>x</sub>, and the interaction of these two factors or the organic-to-NO<sub>x</sub> ratio. In the case of PCE, the data from this study indicated that the NO<sub>x</sub> does not influence the PCE reaction rate appreciably. The PCE concentration, however, was found to have a strong effect.

The final objective in this experimental effort was to obtain evidence that would permit extrapolation of the laboratory findings on PCE reactivity to the real atmosphere. The requisite evidence considered the effects of various reactant and radiation conditions on PCE reactivity, especially the radiation intensity and spectrum, the presence of co-reactant organics, and the PCE concentration. Data on the co-reactant, PCE concentration, and radiation factors have been obtained in this study, including data from tests in which PCE-air mixtures were irradiated in parallel, with the laboratory radiation system and with

natural sunlight. Results from the latter, natural sunlight irradiation tests showed the PCE rates to be lower than those observed in the artificial sunlight tests when all lamps were on, and comparable to those observed when the 2800-3300Å component was reduced. Thus, reactivity data taken with Teflon film smog chambers and near-UV-rich radiation would tend to be erroneously high.

## Discussion

The evidence obtained in this and the previous studies on the effects of the initial reactant concentrations, Cl<sub>2</sub>, and organic co-reactants upon PCE activity is consistent with a Cl-instigated chain photooxidation mechanism analogous to the OH-initiated mechanism accepted in current smog chemistry:



In the absence of NO, main reaction products should be CCl<sub>3</sub>CCl(O) and COCl<sub>2</sub>. In the presence of moderate concentrations of NO, O<sub>3</sub> also should form through photolysis of NO<sub>2</sub>, as well as PAN-type products arising from the CCl<sub>3</sub>CO radical through reactions similar to those in smog chemistry for hydrocarbons/aldehydes. Finally, as with all VOC/NO<sub>x</sub> systems, excess NO should suppress production of O<sub>3</sub>, PAN and other oxidants.

Of the various conceivable origins of Cl atoms, direct photolysis of PCE appears to be the one most consistent with existing data, although other sources (e.g., reaction of PCE with OH) cannot be completely ruled out. The above mechanism seems to provide reasonable explanations of the wide diversity of PCE reactivity results obtained in the various

studies. Thus, the higher consumption rate reactivity results observed in most studies are probably due to the higher intensities of 2800-3300Å radiation used in those studies. The high O<sub>3</sub>/O<sub>x</sub> yield reactivity results are probably due to the same factor and also to optimum PCE-to-NO<sub>x</sub> ratio conditions.

The final and most important question addressed was whether this Cl-instigated photooxidation chemistry observed in smog chambers is effective in producing O<sub>3</sub> in the real atmosphere also. An answer was provided by the evidence from this study related to the effects of the PCE concentration and organic co-reactant factors on PCE reactivity. Based on that

evidence, the presence of much higher concentrations of Cl-scavenging co-reactants in the real atmosphere would cause the PCE to have an extremely low reactivity, lower than that of ethane.

### Conclusions and Recommendations

Currently accepted smog chemistry, with OH attack as the key initial reaction step, does not explain the rapid disappearance of PCE observed in some smog chambers. A Cl-instigated photooxidation mechanism appears to be more consistent with the smog chamber data available. This should be verified through quantitative comparisons of existing smog cham-

ber data with mechanistic predictions using modeling techniques.

Based on the proposed Cl-instigated photooxidation mechanism, it is derived that in the real atmosphere the PCE consumption rate is extremely small because relatively high concentrations of Cl-scavenging organics are present in ambient air. In fact, the PCE consumption rate, and, hence, its O<sub>3</sub>/O<sub>x</sub> yield reactivity also, are estimated to be lower than those of ethane.

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*The complete report, entitled "Photochemical Reactivity of Perchloroethylene," (Order No. PB 83-163 014; Cost: \$8.50, subject to change) will be available only from:*

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