

EXECUTIVE SUMMARY

FORMATION AND FATE OF TOXIC CHEMICALS
IN CALIFORNIA'S ATMOSPHERE

Final Report

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A. Introduction and Statement of the Problem

1. The Lifetimes and Fates of Toxic Chlorinated Olefins in the Atmosphere

While we now have a reasonable understanding of the chemistry of hydrocarbons associated with the formation of photochemical air pollution, little is known about the mechanisms, products and, in many cases, lifetimes associated with the atmospheric degradation pathways of many other classes of organics containing O, S, N or halogen atoms (Atkinson et al. 1979). These compounds are presently emitted into the atmosphere through manufacturing processes, fuel usage, and solvent evaporation, as well as from chemical waste sites.

Since many of these organics are, or may be, toxic, there is a growing concern in the U.S., and in California in particular, over the health effects of such chemicals. However, in order to develop accurate risk/assessment evaluations for these volatile organics, a much more detailed knowledge of their atmospheric lifetimes and fates is required than presently exists.

The study of all such organics would be a monumental and prohibitively expensive experimental task; therefore we decided to study carefully selected representative members of the various classes of organic compounds relevant to the needs of California. These include the carcinogen vinyl chloride and certain widely used halogenated solvents, as well as the ubiquitous insecticide fumigant 1,3-dichloropropene. The experimental results derived from these chamber studies will provide a data base from which the lifetimes, products and mechanisms for other homologues or analogues can be estimated with reasonable reliability, thus minimizing time-consuming and expensive experimental research.

2. Reaction Products and Rates of Formation for Representative Aromatic and Aliphatic Hydrocarbons in Fuels for Gasoline and Diesel Engines

Today the mechanisms of formation of O₃, PAN and certain other secondary pollutants (i.e., formaldehyde, HCHO) are reasonably well understood for approximately a dozen paraffinic, olefinic and aromatic hydrocarbons. However, there are two specific areas that are important in the

overall chemistry of these simple HC/NO_x systems for which additional experimental data are required. These are (a) the mechanisms and products of the photooxidations of aromatic hydrocarbon-NO_x-air systems and (b) the efficiencies of formation of alkyl nitrates from NO_x-air photooxidations of the higher alkanes. These two research areas are especially relevant to California's air pollution problems since aromatic hydrocarbons constitute a large fraction of unleaded gasoline, and the higher alkanes (>C₆) are major constituents of diesel fuels.

During our previous ARB program (Contract No. Al-030-32) we initiated studies of both of these systems, and our results proved to be both fundamentally interesting and useful to atmospheric scientists employing models of photochemical air pollution for development of control strategies. In the present program we completed our studies in these two areas and our detailed results are presented in this report.

B. Objectives

The specific objectives of this program were:

- To investigate the atmospheric chemistry of the two 1,3-dichloropropene isomers. These are widely used as agricultural insecticides in California under a variety of trade names.

- To investigate the atmospheric chemistry of three toxic chloroethylenes, vinyl chloride (an industrially used carcinogen) and tri- and tetrachloroethylene (widely used solvents which are suspected carcinogens).

- To determine the oxygenated products formed from the NO_x-air photooxidations of the aromatic hydrocarbons toluene and m- and p-xylene, important constituents of unleaded gasoline.

- To determine the yields of alkyl nitrates formed directly from the reaction of alkyl peroxy radicals with NO at room temperature and atmospheric pressure, a process previously shown to be important for the long chain alkane constituents of gasoline and diesel fuels.

C. Approach

The research carried out in this program was made possible by the unique experimental facilities available at the Statewide Air Pollution Research Center (SAPRC), funded by previous CARB programs as well as by

the National Science Foundation, U. S. Environmental Protection Agency and other agencies. In particular, for the majority of these investigations the SAPRC 5800-2 evacuable thermostatted environmental chamber was used in conjunction with our 25 KW arc solar simulator. Rate constant determinations and monitoring of the disappearance of reactants and the appearance of products were carried out by in situ long pathlength Fourier transform infrared (FT-IR) spectroscopy or by use of an in situ differential optical absorption spectrometer (DOAS) in the UV-visible spectral region (or both). In addition to these spectroscopic techniques, appropriate gas chromatograph methods were employed as needed.

Detailed information concerning these and other experimental methods used are provided in Sections II-V of our report.

D. Summary of Results and Conclusions

The principal findings obtained in this investigation and the conclusions which may be drawn from them are as follows:

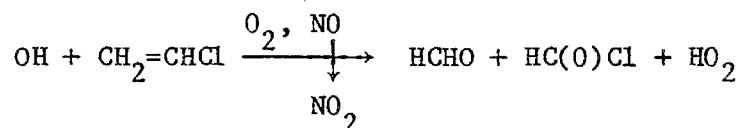
- The rate constants for the reactions of OH radicals with cis- and trans-1,3-dichloropropene were determined to be 0.77 and $1.31 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, respectively. The analogous rate constants for reaction of these isomers with ozone were determined to be (1.5 ± 0.5) and $(6.7 \pm 0.8) \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$, respectively. Based on appropriately chosen ambient concentrations for O_3 and OH radicals the corresponding atmospheric half-lives with respect to reaction with ozone are 12 days and 52 days and with respect to reaction with OH radicals 7 hr and 12 hr for the trans- and cis-forms of 1,3-dichloropropene, respectively.

These experiments also indicated that the only significant loss process for 1,2-dichloropropane in the atmosphere would be reaction with OH radicals, for which a half-life of ≥ 13 days is estimated for a 24-hr average OH radical concentration of $1 \times 10^6 \text{ cm}^{-3}$. This result is of interest since 1,2-dichloropropane, along with the cis- and trans-1,3-dichloropropenes, is an important component of the fumigant formulations D-D and Telone.

In evaluating the possible harmful effects of 1,3-dichloropropene, it would be prudent as well to consider the potential health risks associated with the products of the 1,3-dichloropropene reaction with OH radicals, namely formyl chloride (HCCl) and chloroacetaldehyde (ClCH_2CHO). Whereas

formyl chloride is known to eventually decompose and hydrolyze to CO, HCl, and HCOOH, the other toxic product chloroacetylaldehyde may actually persist appreciably longer in the environment. Of course the levels of these products may be low enough so as to not constitute a threat, except possibly in specific occupational settings.

Our observed unit yield of formyl chloride from vinyl chloride implies a corresponding unit yield of formaldehyde, and shows that the reaction of OH radicals with vinyl chloride proceeds via essentially 100% cleavage of the double bond:



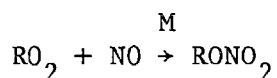
However, for trichloroethylene, the yields of formyl chloride and phosgene, though essentially identical, are only ~20-25%. Hence it is evident that the reaction of OH radicals with trichloroethylene leads, ~75-80% of the time, to products other than these cleavage products observed. An analogous situation occurs in the case of tetrachloroethylene, where the observed ~53% yield of COCl₂ shows that the above discussed reaction scheme leaving to cleavage of the double bond occurs only ~25% of the time, with other unidentified products being formed in the majority of the reaction.

- The yields of the ring cleavage products, the α-dicarbonyl compounds glyoxal and methylglyoxal, from attack of OH radicals on the aromatic hydrocarbons toluene and m- and p-xylene, were determined at room temperature and atmospheric pressure. Our yields of these α-dicarbonyls are much lower than those which have been used in previous chemical computer models for the atmospheric degradation of these aromatic hydrocarbons. In fact for toluene the identified reaction pathways subsequent to the initial OH radical reaction account for only ~50% of the overall reaction. Clearly the products and mechanisms of a major portion of the OH-aromatic reactions under atmospheric conditions are presently not identified. This has major implications for urban airshed models currently being used to develop control strategies for photochemical air pollution.

- The yields of alkyl nitrates were determined for the NO_x-air photooxidations of neopentane, cyclohexane, 2-methylbutane, 2-methyl-

tion of alkyl nitrates from the reactions of NO with alkyl peroxy radicals generated from these cyclic or branched alkanes at 298 ± 2 K and 735 torr total pressure. In addition, rate constants for the reaction of OH radicals with several of the alkyl nitrates formed in these systems were also determined.

Since the reaction



is a removal process for both NO_x and radicals, it has a marked effect in decreasing the photochemical reactivity of these longer chain alkanes. The data obtained in this work, together with our previous studies, now allow approximate a-priori predictions of the significance of this reaction for the alkanes emitted into the atmosphere from anthropogenic uses.

E. Recommendations for Future Research

- It is important to investigate the atmospheric transformations and loss processes of other "model" organic compounds representative of various classes of airborne toxic organics. These model compounds should be chosen to contain functional groups or chemical structures which are found in a wide range of airborne volatile industrial and agricultural chemicals.

- Specific values are needed for the rate constants for the reactions of these model compounds with ozone and with OH and NO_3 radicals so that their atmospheric lifetimes can be calculated. In addition, the products resulting from such reactions must be characterized.

- These combined kinetic and product data for appropriate model compounds should be used to develop a-priori predictive techniques for assessing, in a time- and cost-effective manner, the atmospheric lifetimes and fates of many airborne toxic chemicals currently in use.

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