



## Project Summary

# Atmospheric Chemistry of Several Toxic Compounds

Edward Edney, Steven Mitchell, and Joseph Bufalini

**The hydroxyl radical initiated gas phase oxidation of several toxic compounds in nitrous acid, oxides of nitrogen, in air mixtures were investigated. The chemical species studied were: formaldehyde, acrylonitrile, vinylidene chloride, trichloroethylene, allyl chloride, acetaldehyde, and acrolein. Propylene and ethylene were also studied for comparative purposes. Experimental protocols were established for measuring hydroxyl rate constants. Product studies were also conducted. The results and their atmospheric implications are discussed.**

*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

Large amounts of toxic chemicals are emitted into the atmosphere. Because of their possible carcinogenic/mutagenic properties, these chemicals are of concern to man's ecosystem. EPA's Environmental Sciences Research Laboratory is addressing the problem of hazardous chemicals by conducting research programs to investigate the emissions rates, ambient concentration levels, and atmospheric fate of these species. This report examines the atmospheric lifetimes of several hazardous pollutants and determines their degradation pathways.

The atmospheric lifetimes of gaseous pollutants are usually determined by their photolysis i.e., the stability to solar radiation, reactions with ozone, reactions with hydroxyl radicals, and reactions with other

free radicals such as RO, NO<sub>3</sub>, HO<sub>2</sub>, etc. Photolysis is usually unimportant unless the molecules absorb energy in the solar radiation region (2900 Å - 8000 Å). The organic compounds that photodissociate most readily are the carbonyls and the nitrites. For non-alkenes, the O<sub>3</sub> reaction is too slow to be important. Other free radicals (RO, NO<sub>3</sub>, etc.) are usually not present in very high concentrations or they react too slowly with organics to make these reactions important. For most hazardous chemicals, therefore, the main degradation pathway is reaction with OH radicals. An examination of such reactions is the subject of this paper.

In this study, the OH reaction rate constants for some selected organic compounds were measured. Reaction products from OH-organic compounds reactions in the presence of NO<sub>x</sub> were also studied. The hazardous chemicals studied were: vinylidene chloride, trichloroethylene, formaldehyde, acetaldehyde, acrylonitrile, acrolein, and allyl chloride. In addition, propylene was studied in order to obtain the photolysis rate for HONO while ethylene was studied to test the technique employed. The choice of the particular toxic compounds investigated in this study was based on two factors: their high volume production and their suspected carcinogenic/mutagenic activities.

### Procedure

All experiments were performed in a 700 liter cell. This cell consisted of 6 cylinders each 1.5 m in length and 0.31 m in diameter. Each end of the cell contained eight mirrors with multiple reflection optics. This system gave a 216 m path length for the experiments.

Each cylinder section of the cell was surrounded by a bank of 16 40 W ultra-

violet fluorescent lamps. Twelve lamps were blacklights with an energy maximum of 365 nm while four were sunlamps with an intensity maximum at 310 nm. The photolysis constant for NO<sub>2</sub> in nitrogen was 0.60 min<sup>-1</sup>.

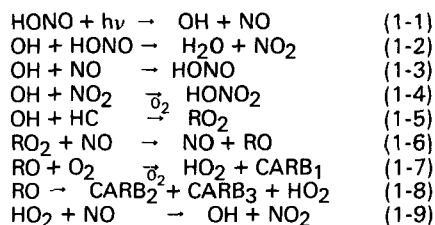
A Digilab FTIR spectrometer coupled to a computer controlled scanning Michelson interferometer was used for the detection system. Mercury-cadmium-telluride and indium-antimonide were the two signal detectors employed. The spectra were taken at 1.0 cm<sup>-1</sup> resolution.

HONO was used as the OH radical source. When HONO is exposed to radiation between 3000-4000 Å, it decomposes to produce OH and NO. The HONO was prepared by adding a solution of sulfuric acid to sodium nitrite. The gaseous HONO was flushed into the cell with nitrogen gas.

The organic material was introduced into the cell by liquid syringes or by a gas dilution system. Formaldehyde was produced by slowly heating paraformaldehyde in a mixing bulb and then using the gas dilution system.

## Data Analyses

The reaction mechanism for the photolysis of HONO in the presence of an organic compound and NO<sub>x</sub> in air can be expressed as:



If steady state approximations are made for OH, HO<sub>2</sub>, and RO<sub>2</sub> radicals, we obtain the following result for the steady state concentration of OH radicals:

$$[\text{OH}] = \frac{k_1 [\text{HONO}]}{k_2 [\text{HONO}] + k_3 [\text{NO}] + k_4 [\text{NO}_2]} \quad (1-4)$$

The OH concentration is independent of the HC concentration. The reason for this is that the OH radical destroyed by the HC is regenerated when the HO<sub>2</sub> radical is converted back to OH by reaction (1-9).

The time derivative for the reaction of the organic compound with OH radicals is given by:

$$(d/dt)[\text{HC}(t)] = -k_5 [\text{OH}(t)] [\text{HC}(t)] \quad (1-5)$$

and if we assume that the OH concentration is constant, then

$$\frac{[\text{HC}(t)]}{[\text{HC}(0)]} = \exp(-k_5 [\text{OH}] t) \quad (1-6)$$

This equation was used to determine all the OH rate constants reported in this study.

Although the first order dissociation constant for NO<sub>2</sub> was measured, the dissociation constant for HONO (reaction 1-1) in our system was not determined. In order to derive this value, propylene was employed as the reference compound.

Equations 1-4 and 1-6 can be combined since  $k_3 = k_4 = 1.7 k_2$ . Then, the rate of disappearance for propylene can be written as:

$$-\frac{1}{t} \ln \frac{[\text{HC}(t)]}{[\text{HC}(0)]} = k_5$$

$$\frac{k_1}{k_2} \frac{[\text{HONO}]}{[\text{HONO}] + 1.7 [\text{NO} + \text{NO}_2]} \quad (1-10)$$

A value for the  $k_1/k_2$  ratio is found by substituting in the observed concentrations for the propylene experiment. Once the  $k_1/k_2$  ratio is found, then a general relationship can be developed:

$$k = 5.47 \times 10^{-9} \frac{\alpha \text{ cm}^3}{\beta \text{ molecule}}$$

$$\text{where } \alpha = -\frac{1}{t} \ln \frac{[\text{HC}(t)]}{[\text{HC}(0)]}$$

$$\text{and } \beta = \frac{[\text{HONO}]_0}{[\text{HONO}] + 1.7 ([\text{NO}]_0 + [\text{NO}_2]_0)}$$

## Results

Propylene was used as the reference compound in order to obtain the photolysis constant for HONO. Therefore, no OH rate constant was obtained for this compound. Products observed with the photooxidation of propylene with HONO and NO in air were acetaldehyde, formaldehyde, and nitric acid. Ozone and PAN were not observed since these experiments were conducted over short irradiation times with NO still present at the termination of the experiments. Most of the carbon was accounted for with the two aldehydes. However, there were residual absorbances in the spectra suggesting the presence of some other compound or compounds. Perhaps some propylene glycol 1,2-dinitrate was present but we did not have any reference spectra for this compound. The  $\Delta\text{NO}/\Delta\text{propylene}$  ratio was observed to be 2.17.

To make certain that the technique employed in this study was satisfactory, ethylene was also tested. The products observed with this hydrocarbon were for-

maldehyde, carbon monoxide and nitric acid. The  $\Delta\text{NO}/\Delta\text{ethylene}$  ratio was 1.77 and an OH rate constant value of  $8.0 \times 10^{-12}$  cm<sup>3</sup>/sec was obtained.

The OH reaction of formaldehyde in the presence of NO<sub>x</sub> and air resulted in the formation of carbon monoxide and nitric acid. The  $\Delta\text{NO}/\Delta\text{formaldehyde}$  ratio was 1.03 and the OH-formaldehyde rate constant was  $14.1 \times 10^{-12}$  cm<sup>3</sup>/sec.

The OH initiated reaction with acrylonitrile resulted in formaldehyde, CO, and HNO<sub>3</sub> as products. Some unknown bands were also observed suggesting that a nitrile group was present. This was tentatively identified as formyl cyanide. HCN was also observed as a product. The  $\Delta\text{NO}/\Delta\text{acrylonitrile}$  ratio was 2.13 while the OH-acrylonitrile rate constant was  $3.2 \times 10^{-12}$  cm<sup>3</sup>/sec.

Vinylidene chloride reacted with OH and NO in air to produce chloroacetyl chloride, phosgene, formaldehyde, carbon monoxide and nitric acid. The number of NO oxidized per vinylidene chloride reacted was 1.68 and the OH-vinylidene chloride rate constant was determined to be  $12 \times 10^{-12}$  cm<sup>3</sup>/sec.

In the OH reaction with trichloroethylene, dichloroacetyl chloride, phosgene, formyl chloride, carbon monoxide and nitric acid were the observed products. The  $\Delta\text{NO}/\Delta\text{trichloroethylene}$  ratio was 2.25 and the OH rate constant was  $3.6 \times 10^{-12}$  cm<sup>3</sup>/sec.

The OH-allyl chloride rate constant was observed to be  $19.8 \times 10^{-12}$  cm<sup>3</sup>/sec and the  $\Delta\text{NO}/\Delta\text{allyl chloride}$  was 1.80. Formaldehyde and nitric acid were the only identifiable products although a number of unidentified absorption bands were observed.

In the OH reaction with acetaldehyde/NO<sub>x</sub>/air system, PAN, methyl nitrate, methyl nitrite, and nitric acid were observed. The  $\Delta\text{NO}/\Delta\text{acetaldehyde}$  ratio was 1.60 and the OH rate constant was  $27.7 \times 10^{-12}$  cm<sup>3</sup>/sec.

The last compound studied was acrolein. A peroxyxynitrate, glycoaldehyde, formaldehyde, carbon monoxide, and nitric acid were the observed products. The OH rate constant with this aldehyde was found to be  $34.3 \times 10^{-12}$  with a  $\Delta\text{NO}/\Delta\text{acrolein}$  value of 1.71.

## Discussion

The FTIR technique employed in these studies has been shown to yield both kinetic and product formation information. Products as well as reactants have been monitored with ease. The OH rate constant determinations were in reasonable agreement with the previously published values. The lifetimes of the compounds studied,

assuming an OH concentration of  $10^6 \text{ cm}^{-3}$  are shown below:

Atmospheric Lifetimes	
Compound	$\tau$ (h)
Propylene	7.7
Ethylene	2.6
Acetaldehyde	9.0
Formaldehyde	13.6
Acrylonitrile	60.3
Trichloroethylene	53.6
Vinylidene chloride	16.1
Allyl chloride	9.7
Acrolein	5.6

The lifetimes shown for the compounds studied are relatively short indicating that these pollutants will not build up in the troposphere. They will however be important on an urban and regional scale.

*The EPA authors Edward Edney, Steven Mitchell, and Joseph J. Bufalini (also the EPA Project Officer, see below) are with the Environmental Sciences Research Laboratory, Research Triangle Park, NC 27711.*

*The complete report, entitled "Atmospheric Chemistry of Several Toxic Compounds," (Order No. PB 83-146 340; Cost: \$13.00, subject to change) will be available only from:*

*National Technical Information Service  
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