



Project Summary

The Primary Photochemical Processes of Acrolein

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Pollutants are removed from the atmosphere by a number of processes: reaction with OH and O₃, dry and wet deposition, photodissociation by solar radiation, or biodegradation. This summary discusses the photodissociation processes of acrolein. Quantum yields of acrolein loss are given. The dominant reactions in the lower troposphere are the formation of C₂H₄ and CO. Also produced are CH₂CHCHO, H, CH₂CH, and HCO radicals, but at lower quantum yields. Since the OH attack on acrolein is quite large (1.9 x 10⁻¹¹ cm³ molec⁻¹ s⁻¹), ambient levels of OH (~ 10⁶ molec cm⁻³) will remove acrolein very rapidly, usually in ~ 15 h. Thus, the major loss mechanism for acrolein in the troposphere is OH attack, and the photodissociation process is of negligible importance.

This Project Summary was developed by EPA's Atmospheric 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 atmospheric concentration of hazardous pollutants is determined by a number of factors: the release rate of these pollutants, their rate of generation if produced *in situ* (e.g., formaldehyde), their rate of photodissociation by sunlight, rates of OH and O₃ reaction, rates of dilution and dispersion, and rate of biological degradation.

This summary presents the results of a quantitative investigation of the mecha-

nism of and quantum yields for the tropospheric photooxidation of acrolein, the simplest unsaturated aldehyde and a potent lachrymator.

Acrolein has been observed at concentrations as high as 13 ppb (v/v) in the atmosphere and is often observed at about 15% of the formaldehyde concentration. When present in polluted atmospheres, acrolein reacts quickly in the presence of NO_x to produce ozone and formaldehyde.

Experiments with acrolein were designed to simulate closely the conditions encountered in the troposphere. Small concentrations of acrolein were photooxidized by light at a wavelength of 313 nm at 25°C in the presence of synthetic air.

Experimental

The experimental apparatus for studying the mechanism and quantum yields for acrolein photooxidation were (1) a vacuum line, (2) a reaction cell, (3) a light source, and (4) a sampling apparatus consisting of a gas chromatograph and a mass spectrometer. The vacuum line was a multifunctional gas-handling system consisting of a storage facility, a measurement facility to monitor precise volumes of gas, a distillation flask, and a calibration/mixing system. With this system, very precise and pure concentrations of acrolein could be prepared. The reaction cell is coupled to the vacuum line and is designed to create a photochemical system. The internal optical path of the cell is 155.8 cm and it has Suprasil end windows. A narrow-band interference filter was used with the cell; this enabled light at 313 nm to be transmitted. The

light source was a high-pressure mercury arc (Osram HBO 500 w/2).

A Varian gas chromatograph equipped with flame ionization and thermal conductivity detectors was employed to monitor both the acrolein and the reaction products (CH₄, CO₂, C₂H₄, HCHO, HOH, CH₃OH, CH₃CHO, and HCOCHO). The mass spectrometer (CEC model 21-104) was used to confirm the identity of compounds identified by the gas chromatographic analyses and to quantify the hydrogen product.

Results and Discussion

Because the primary objective of this study was to determine the primary and secondary decomposition paths of acrolein in the troposphere, experiments were conducted to determine the rate of photodecomposition with increasing atmospheric pressure. Table 1 shows the data obtained when acrolein (20 to 800 torr) was irradiated at 25°C with 313 nm wavelength light isolated by a Jarrell-Ash grating monochromator (runs 1M - 6M) or narrow band filter (runs 7F - 11F). All runs were conducted with acrolein at a pressure of approximately 0.355 torr with 20% O₂ and 80% N₂.

A complete list of product quantum yields for all runs (1M - 11F) is provided in Table 2. From these data, the following observations were made:

- (1) The dominant products are CO and C₂H₄. The identified quantified products are listed in the following order according to the amount produced.
CO > C₂H₄ > HCHO (≈ H₂) > HCOCHO > CO₂ > CH₃OH (≈ CH₄)
Traces of acetaldehyde, acetylene, and acetic acid were also observed.
- (2) Much C₂H₄ was formed, in spite of high O₂ levels; this suggests that C₂H₄ is eliminated (as is CO) by a primary dissociative pathway. The other products, HCHO and HCOCHO in particular, are secondary O₂-associated products; their production involves CH₂CH and CH₃CH free radicals.
- (3) The small quantum yield of acrolein loss suggests that the deactivation of excited acrolein is very efficient; this also suggests that energy is transferred very quickly to oxygen followed by intersystem crossing of the singlet to triplet state.
- (4) The quantum yield of acrolein loss and product formation decreases with increasing air.

- (5) The presence of CH₄ as a product is indicative of the primary formation of the ethylidene (CH₃CH) radical, which oxidation would preface the reaction CH₃COOH* → CO₂ + CH₄. However, the CO₂/CH₄ ratio is greater than unity.
- (6) The CO/C₂H₄ quantum yield ratio increases with increasing pressure from approximately 1.0 at 20 torr to ~ 3.0 at 700 torr and above.
- (7) Both C₂H₄/CO₂ and CO/CO₂ ratios decreased with increasing concentrations of air. The C₂H₄/CO₂ ratio showed an exponential decrease; the CO/CO₂ ratio was linear. The production of CO was apparently the result of a secondary process.

The quantum yields of acrolein loss observed in this study can be represented as a function of the concentration of air [M], expressed as molecules per cubic centimeter. The mathematical expression of this is

$$1/(\Phi_A - 0.00400) = 0.086 + 1.613 \times 10^{-17} [M]$$

This expression shows that a marked increase in photolytic rate will occur with increasing altitude, i.e., lower pressures of air [M].

Table 1. Summary of Photolysis Conditions

Run #	I _A Quanta	Filling Temp °C	Total Pressure torr	λ _{max} = 3130 Å			Total Number Density molec cm ⁻³	Total Run Time min
				Mole Fraction of Acrolein	Mole Fraction of Nitrogen	Mole Fraction of Oxygen		
1M	2.1911 x 10 ¹⁹	22.75	658.29	5.3840 x 10 ⁻⁴	0.79983	0.19963	2.1483 x 10 ¹⁹	2341
2M	1.8694 x 10 ¹⁹	24.60	79.221	4.4795 x 10 ⁻³	0.80071	0.19436	2.5689 x 10 ¹⁸	2100
3M	2.6468 x 10 ¹⁹	23.42	524.67	6.7797 x 10 ⁻⁴	0.80759	0.19173	1.7084 x 10 ¹⁹	2610
4M	1.2858 x 10 ¹⁹	22.80	25.540	1.3886 x 10 ⁻²	0.79737	0.18874	8.3333 x 10 ¹⁷	1200
5M	1.1724 x 10 ¹⁹	22.35	790.85	4.4792 x 10 ⁻⁴	0.79958	0.19997	2.5843 x 10 ¹⁹	1621
6M	1.1363 x 10 ¹⁹	24.25	359.46	9.8466 x 10 ⁻⁴	0.79907	0.19995	1.1671 x 10 ¹⁹	1620
7F	1.3261 x 10 ²⁰	24.08	25.607	1.3914 x 10 ⁻²	0.78564	0.19905	8.3192 x 10 ¹⁷	1620
8F	1.6889 x 10 ²⁰	25.80	359.96	9.8656 x 10 ⁻⁴	0.80947	0.18954	1.1627 x 10 ¹⁹	2770
9F	1.5464 x 10 ²⁰	24.34	110.43	3.20415 x 10 ⁻³	0.79741	0.19906	3.6243 x 10 ¹⁸	2351
10F	1.9265 x 10 ²⁰	23.28	231.79	1.53407 x 10 ⁻³	0.79838	0.20008	7.5506 x 10 ¹⁸	2340
11F	1.8918 x 10 ²⁰	25.42	47.523	7.44088 x 10 ⁻³	0.81311	0.17870	1.5370 x 10 ¹⁸	2359

Table 2. Summary of Quantum Yields

Run	Total Pressure	*CH ₂ =CHCHO	*C ₂ H ₄	*CO ₂	*CO	*CH ₃ OH	*HCHO	*HCOCHO	*CH ₄	*H ₂
1M	658.29	0.00693	0.00181	0.00179	0.00533	0.000341	0.000533	—	—	—
2M	79.221	0.0334	0.0121	0.00349	0.0244	0.00137	0.00583	—	—	—
3M	524.67	0.00734	0.00193	0.00175	0.00589	0.000388	0.000610	—	—	—
4M	25.540	0.0834	0.0523	0.0106	0.0714	0.00317	0.0149	—	—	—
5M	790.85	0.00649	0.00177	0.0019	—	0.00036	0.00041	—	—	—
6M	359.46	0.00909	0.00234	0.00171	0.00785	0.000477	0.000897	—	—	—
7F	25.607	0.0786	0.0521	0.0101	0.0674	0.00418	0.0141	0.00561	0.0001909	0.00891
8F	359.96	0.00882	0.00244	0.00167	0.00823	0.000438	0.00100	0.00238	—	—
9F	110.43	0.0257	0.00838	0.00273	0.0188	0.000625	0.00447	0.00200	0.0004522	0.00628
10F	231.79	0.0137	0.00346	0.00197	0.0102	0.000628	0.00126	0.00211	0.0010300	—
11F	47.523	0.0681	0.0230	0.00566	0.0420	0.00376	0.00788	0.00306	0.0001300	—

The data obtained from this study show that at a solar zenith angle of 40° , the photodissociation lifetime of acrolein in the troposphere will be approximately 5 days. For comparison, at the same zenith angle lifetimes for acetone, acetaldehyde, and formaldehyde were calculated to be 14.8 days, 5.3 days, and 5.9 h, respectively. If photodissociation were the only removal process for acrolein, a reasonably long residence time would be expected and emissions would cause regional problems. However, the rate constant for the OH-acrolein reaction is quite high ($k = 1.9 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$). Therefore, at an atmospheric OH level of $10^6 \text{ molec cm}^{-3}$, the lifetime of acrolein will be only 14.6 h. Thus, the major loss mechanism for acrolein is the reaction with OH radicals, and the photochemical destruction mechanism is relatively unimportant in the troposphere.

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Joseph J. Bufalini is the EPA Project Officer (see below).

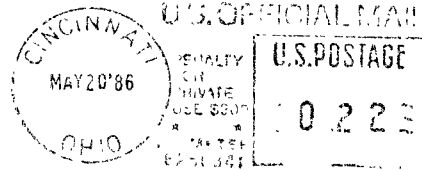
The complete report, entitled "The Primary Photochemical Processes of Acrolein," (Order No. PB 86-145 802/AS; Cost: \$16.95, subject to change) will be available only from:

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